

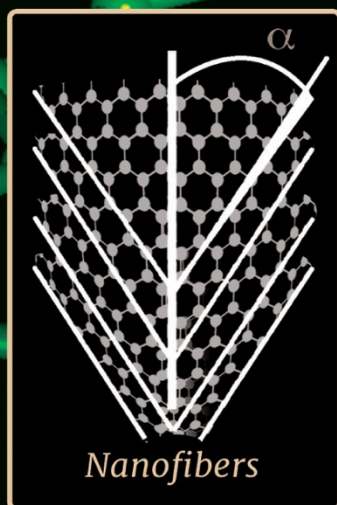
# CARBON NANOFIBERS

*Fundamentals  
and Applications*

*Edited By*

**MADHURI SHARON**

**MAHESHWAR SHARON**



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# Carbon Nanofibers

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The unique properties of nanomaterials encourage the belief that they can be applied in a wide range of fields, from medical applications to electronics, environmental sciences, information and communication, heavy industries like aerospace, refineries, automobile, consumer and sports good, etc.

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## **Fundamentals and Applications**

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and

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Dedicated to  
To Our Daughters  
Dr. Manisha Sharan  
&  
Dr. Chetna Sharon

*You make us incredibly fortunate and help us keep our greymatter  
alive and active*





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## Foreword

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Carbon is an inevitable part of nature and has amazed researchers with its special properties. Various forms of carbon, such as fullerenes, nanotubes, nanofibers, and now graphene, have changed the prospects of future applications. Professor Maheshwar Sharon and I have worked on carbon nanoforms, especially carbon fibers and tubes, for photovoltaic device applications. As there currently isn't a book that collects all the information related to carbon nanofibers, *Carbon Nanofibers:*

*Fundamentals and Applications* will help readers interested in carbon nanofibers understand everything about it. In this book the authors cover all aspects concerning the synthesis and applications of carbon nanofibers. I wish them all the best.

Masayoshi Umeno  
Emeritus Professor of Nagoya Institute of Technology  
Director, C's Techno Inc.,  
Nagoya Science Park, Nagoya, Japan



## Preface

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This book covers the fundamentals and applications of Carbon Nanofiber (CNF), especially the area in which our group is working.

With his first chapter on the fundamentals of CNF, Prof. Maheshwar Sharon, whom we all consider to be the Father of Carbon Nanotechnology in India, has left a trail for generations to come by promoting an understanding of CNF and kindling the spark hidden deep inside this subject.

The next chapter is my humble contribution in honoring the plant kingdom that has been a great source for producing the unique morphologies of CNF that makes it applicable to various areas. This chapter is followed by the role of catalysts and composites in promoting and enhancing the synthesis and application of CNF. We have realized that those who want to enter into the arena of carbon nanomaterials are often stuck with the characterization of CNF. Therefore, a very detailed chapter is devoted to its characterization. Following these five introductory chapters about CNF, the book encompasses its various applications such as its use as a possible superconductor, to adsorb and store hydrogen and as a microwave absorber. The application of CNF for environmental concerns is also touched upon by assessing its usefulness in dye and heavy metal removal from polluted water, its application in lithium-ion battery, solar cell, antenna, cosmetics, usefulness in regenerative medicine and in various aspects of agrotechnology.

My group has ensured that during the process of creating this book they contributed to the best of their ability. Our lengthy critical discussions on many aspects of scientific discoveries and inventions, especially in the field of understanding carbon nanofibers, has enthralled us with the thrilling research pertaining to various applications. I would like to pay my obeisance and gratitude to all those who have strived very hard to contribute to this book.

Dr. Madhuri Sharon  
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December 2020





# An Introduction to Carbon Nanofiber

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*The goal of education is not to increase the amount of knowledge but to create the possibilities for a child to invent and discover, to create men who are capable of doing new things.*

**Jean Piaget**

## 1.1 Introduction

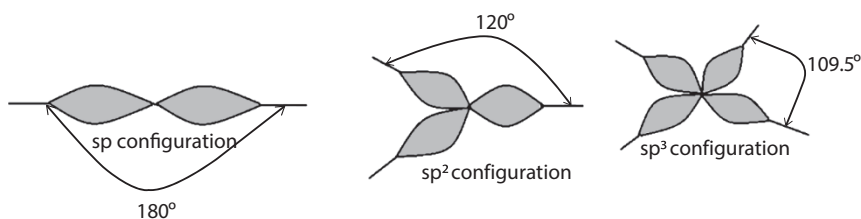
Carbon (Latin word: *carbo* “coal”) is a chemical element with symbol **C** belongs to group 14 of the periodic table. Its atomic number is 6 and has the electronic structure of  $1s^2 2s^2 2p^2$ . The valence of carbon will depend upon the arrangement of electrons in 2s and 2p orbitals. 2s orbitals are supposed to house maximum of 2 electrons and 2p can possess a maximum of 6 electrons. The energy of electrons in 2s and 2p orbitals is not much different from each other. Therefore, depending upon the condition of the electronic arrangement, carbon atom can show valence of 2 due to hybridization of  $2s^1 2p^1$  orbitals. The  $2s 2p$  orbital can also be hybridized as  $2s^1 2p^2$  showing a valence of 3. Likewise,  $2s 2p$  orbital can be hybridized to show  $2s^1 2p^3$  configuration making a carbon valence of 4. Carbon compound with  $2s^1 2p^1$ , i.e., with valence of 2, is rarely seen, and if some carbon compounds are made with such configuration, they are not stable. Most common compounds with configuration of  $2s^1 2p^2$  (like graphite) and  $2s^1 2p^3$  (like diamond) are found in nature. Angles between each carbon for  $2s^1 2p^1$ ,  $2s^1 2p^2$  and  $2s^1 2p^3$  are shown in Figure 1.1.

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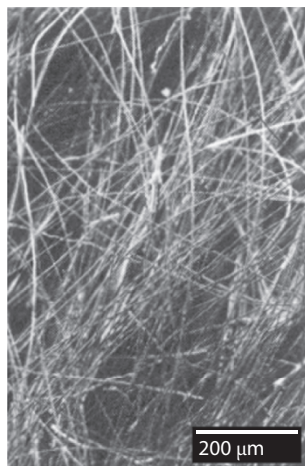
**Figure 1.1** The formation angle between the carbon for  $sp$ ,  $sp^2$  and  $sp^3$  configuration.

In this chapter we shall restrict our discussions to carbon with configuration of  $sp^2$  and  $sp^3$ . In addition, we shall also restrict our discussions especially regarding carbon fiber (discussed in detail in later on), though we may touch upon carbon nanotube.

It will not be the scope of this chapter to discuss diamond or graphite, mainly because information about these materials are available in almost all textbooks dealing with carbon. Our discussion will be confined to materials like carbon fiber, carbon nanofibers and to some extent carbon nanotubes for making a clear distinction between these materials.

### 1.1.1 History of Carbon Fiber

The development of carbon fibers dates back as early as the 18th century but its applications were only realized after 1960, making it possible to develop carbon fibers with high strength. Some landmarks in the development of carbon fibers are given here. In 1860, Joseph Swan first produced carbon

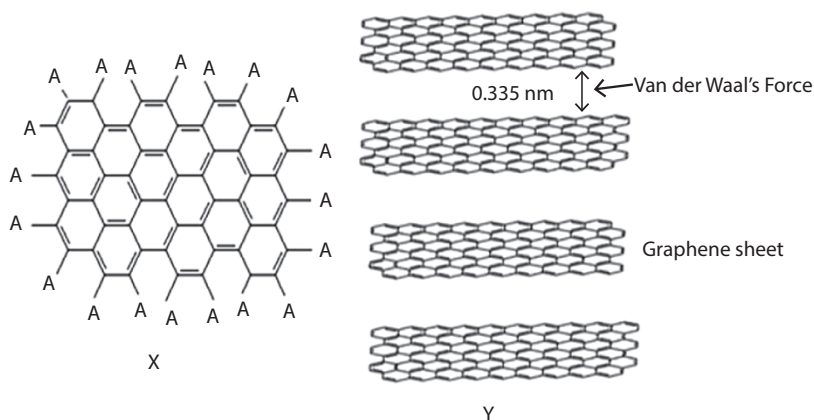


**Figure 1.2** SEM image of carbon fiber.

fibers. In 1879, Thomas Edison carbonized cotton threads or bamboo slivers to produce carbon fiber. He used it as wire filament which glows under electric current. Roger Bacon prepared carbon fiber containing about 20% carbon in 1958 by carbonizing rayon. The process of carbonizing rayon was later improved in 1960 by Richard Millington (US Patent No 3,294,489) [1] to get carbon fiber with almost 99% carbon. During the 1960s, a Japanese firm produced carbon fibers from a petroleum pitch which contained 85% carbon and had excellent flexural strength. After 1960, it seems various efforts were made to prepare carbon fibers (Figure 1.2) from different types of precursors to improve the quality of carbon fibers; for example, giving tensile strength 4,000 MPa and a modulus of 400 GPa to be used in aircraft.

### 1.1.2 What Is a Carbon Fiber?

Carbon fibers are classified symbolically as CF. These fibers are of size about 5–50  $\mu\text{m}$  in diameter and composed mostly of carbon atoms. They are also known as graphite fiber. Graphite is made of pure carbon arranged into big sheets of hexagonal aromatic rings (Figure 1.3X). The structure of carbon fibers is like the structure of graphite arranged in layers of long graphite sheets of length about 5–50  $\mu\text{m}$  and each layer of graphite is stacked together forming a ribbon-like structure. Depending upon the precursors used to synthesize carbon fibers and the manufacturing processes, each layer planes may be either turbostratic graphitic, or a hybrid structure. In graphitic crystalline regions, the layer planes are stacked parallel to each



**Figure 1.3** (X) A sheet of graphite showing free edges A, which are reactive and can be functionalized, (Y) shows four layers of graphene sheet separated by van der Waals forces. In graphite this separation distance between two consecutive layers is 0.335 nm.

other in a regular fashion. The atoms in each layer are covalently bonded through  $sp^2$  bonding while the interaction between each layer is relatively weak van der Waals forces. In a single graphitic crystal,  $d$ -spacing between two graphene layers ( $d_{002}$ ) is about 0.335 nm (Figure 1.3Y).

If carbon content in the fiber is 92 wt% then it is considered as *carbon fiber*. However, if carbon content is more than 99 wt% then the fiber is known as *graphite fiber*. This classification depends on the percentage content of carbon, process of synthesis and precursors; Carbon fibers can possess excellent tensile strength, low densities, high electrical conductivities, high temperature tolerance, low thermal expansion and chemical stabilities. High tensile strength and lightweight carbon fiber can be developed by making its composite with suitable polymers. Because of these properties, carbon fiber has found its place in aerospace, civil engineering, the military, and motorsports, along with other areas like sports.

***Classification of carbon fibers based on precursor used to make them:***

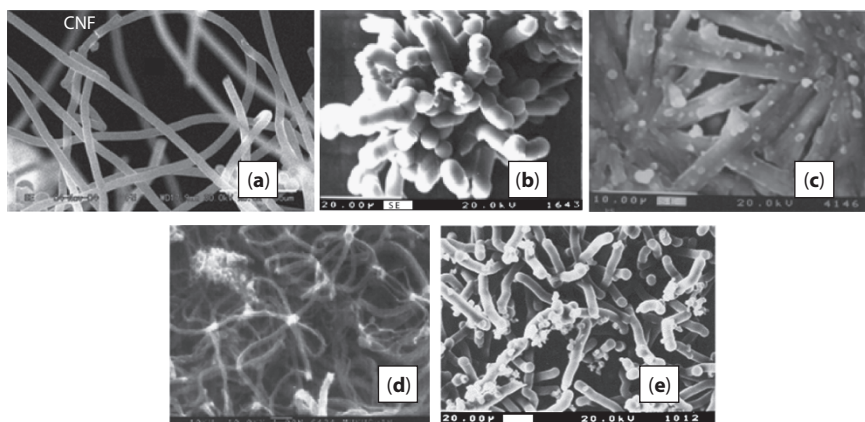
- PAN-based carbon fibers (90% of fibers made from this precursor)
- Pitch-based carbon fibers (about 10% or less are made from this precursor)
- Mesophase pitch-based carbon fibers
- Isotropic pitch-based carbon fibers
- Rayon-based carbon fibers (this also falls under the category of pitch-based (10% are made from this precursor)
- Gas-phase-grown carbon fibers

***Classification of carbon fibers based on heat treatment temperature:***

- **Type-I**, High-heat-treatment carbon fibers (HTT)  
Carbon fibers obtained after heat treatment at temperature above 2000 °C. These fibers are associated with high-modulus type fiber.
- **Type-II**, Intermediate-heat-treatment carbon fibers (IHT)  
Carbon fibers obtained after heat treatment at temperature around 1500 °C. These fibers are associated with high-strength type fiber.
- **Type-III**, Carbon fibers obtained with low-heat-treatment.  
Carbon fibers obtained with heat treatment at temperature around 1000 °C show low modulus and low strength.

### 1.1.3 Structures of Carbon Fibers

Some carbon fibers synthesized by the author [2, 3] and his research group from camphor under different but specific conditions are shown in Figure 1.4. These are grown by chemical vapor deposition technique. It is observed that though precursor was the same, i.e., camphor, by altering the nature and form of catalyst, carbon fibers of different morphologies are obtained. For this growth, nickel in different forms was used as a catalyst. Nickel plate, cleaned by acid followed by acetone, gave carbon fiber as shown in Figure 1.4a. When the top surface of nickel was oxidized and then cleaned, it gave carbon fiber as shown in Figure 1.4b. It grew from one point on the catalyst surface in a cauliflower-like shape. In another experiment, camphor was pyrolyzed without using any catalyst. Under this condition, plate type (cactus type) carbon fiber was obtained (Figure 1.4c). These fibers also contained some small beads attached to the fiber. In one experiment nickel powder of size 20 nm spread over nickel plate was used. Under this condition, branched carbon fiber as shown in Figure 1.4d was obtained, with Ni catalyst sitting at the center. Vapor-grown carbon fibers (VGCFs) (Figure 1.4e) were obtained by pyrolysis on the Ni coated quartz substrate. All these experiments were carried out under argon atmosphere at temperature 750 °C.



**Figure 1.4** SEM images of carbon fibers (CF) synthesized from camphor as precursors by pyrolyzing them at 700 °C in presence of argon under varying conditions: (a) Long tube-like CF over nickel plate, (b) cauliflower-like CF over oxidized nickel plate, (c) CF grown without using any catalyst, (d) branched carbon fibers obtained at temperature 750 °C, with Ni sitting at the center, and (e) VGCFs obtained by pyrolysis on the Ni coated quartz substrate (Source: Debabrata Pradhan, 2003) [4].

### 1.1.4 Synthesis of Carbon Fibers

The process of synthesis of carbon fibers is patented and each company has its own trade secret. It is difficult to provide a detailed and very accurate process. It is therefore only possible to discuss an overall process without providing the intricacies of the actual process. Hence, the synthesis process of the most popular carbon fibers prepared from polyacrylonitrile (PAN) precursor is discussed here.

#### 1.1.4.1 Carbon Fibers from PAN

Before carbon fibers are made from PAN, some pretreatments are made, like mixing Acrylonitrile powder with a suitable plastic (e.g., methyl acrylate, methyl methacrylate) and a catalyst to form a polyacrylonitrile plastic. This plastic is then spun to form the internal atomic structure of the fiber. These fibers are stabilized by heating them in air at about 200–300 °C for about 30–120 minutes. During this process some oxidation of carbon takes place, which helps to rearrange their atomic bonding pattern. These fibers are then carbonized at temperature 1000–3000 °C for several minutes in gas like argon (but in absence of any oxygen). By this process most of the non-carbon atoms and a few carbon atoms as well are lost in the form of gas like  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , water vapor  $\text{H}_2$ , etc. This process helps to form strongly bonded carbon atoms that are aligned parallel to the long axis of the fiber. Due to losing different types of material during the carbonizing process, the surface of the fiber is very rough. Hence, to obtain better bonding properties, surfaces are oxidized in a controlled manner by techniques like exposing them in oxygen environments or by performing some chemical treatments like dipping them into some oxidizing solutions like nitric acid. In order to protect the fibers from environmental oxidation, they are coated with epoxy, polyester, nylon, urethane, and others.

### 1.1.5 Properties of Carbon Fibers

It is difficult to give the properties of carbon fibers by quantity because that depends on how the fiber was made and what treatments were done to the fiber. Here we give properties qualitatively only. Specific strength of carbon fiber (which is the ratio of strength to weight) is very high. Strength of material is the ratio of the force per unit area applied to fiber at which it breaks to its density. Carbon fiber is very rigid, i.e., its Young's

modulus is high. In other words, it needs high force to deflect it. The fiber is chemically stable and resistant to corrosion. Carbon fiber is electrically conductive and is resistant to fatigue, especially its composites. Carbon fiber has good tensile strength, which means it can stand maximum stress while it is stretched or pulled. Carbon fibers are normally fire resistant/nonflammable in the absence of oxygen. They are a good thermal conductor. Carbon fibers have a unique property of low coefficient of thermal expansion. They are nonpoisonous, biologically inert and X-ray permeable. These properties are especially good for any medical applications.

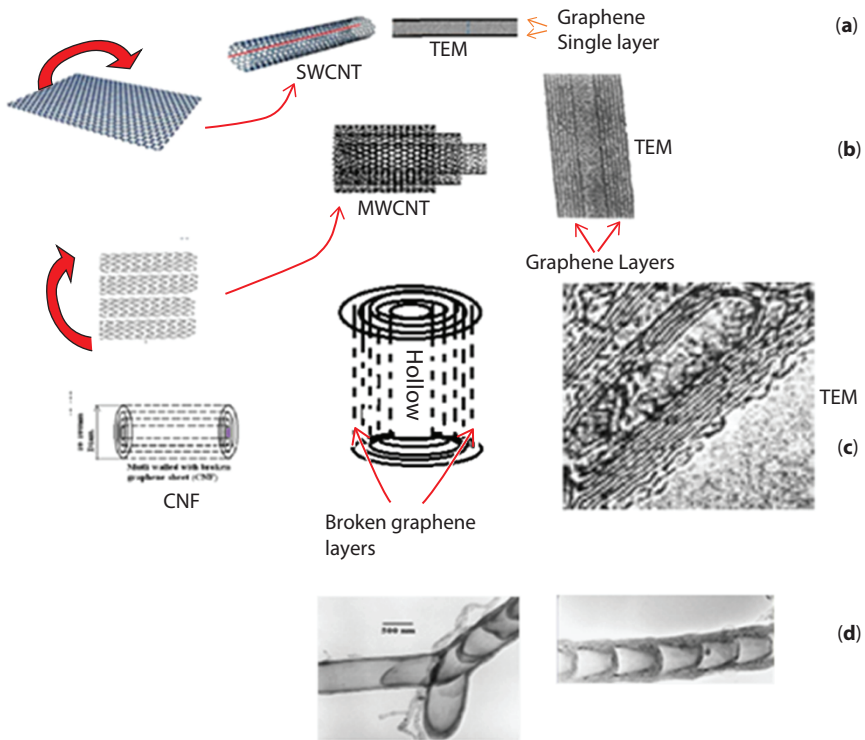
Some general properties of PAN-based fiber are given below, but these values may be different if PAN-based fibers are prepared under some specific condition. Hence, these data can be taken as approximate values.

- Density: 1750–1870 kg/m<sup>3</sup>
- Tensile strength: 0.9–6.37 kN/mm<sup>2</sup>
- Young's modulus: 40–588 kN/mm<sup>2</sup>
- Elongation: 0.7%–2.2%
- Filament diameter: 4.4–7.2  $\mu$ m
- Tensile strength of carbon fiber: 4127 MPa
- Carbon fiber reinforced epoxy (thermal conductivity): 24 W/(m.K)

## 1.2 Properties of Carbon Nanofiber and How It Differs from Carbon Nanotube

Intrinsically, there is not much difference between carbon nanofiber and carbon nanotube. When a single layer of graphene sheet is rolled into a cylinder (Figure 1.5a) it takes the shape of a single-walled carbon nanotube. When a multiple number of graphene sheets separated by a distance of 0.335 nm are rolled into a cylindrical shape it takes the shape of multi-walled carbon nanotubes (Figure 1.5b). However, when broken sheets of multiple graphene sheets are rolled into a cylinder it takes the shape of carbon nanofiber (Figure 1.5c). In other words, carbon nanofibers appear as cylindrical nanostructures with graphene layers organized as packed cones, cups or plates. The surface area of CNF is much larger compared to MWCNT of the same dimension, because the former has many broken graphene sheets which are not aligned as that of MWCNT (well-defined layer, as shown in the TEM image in Figure 1.5b).

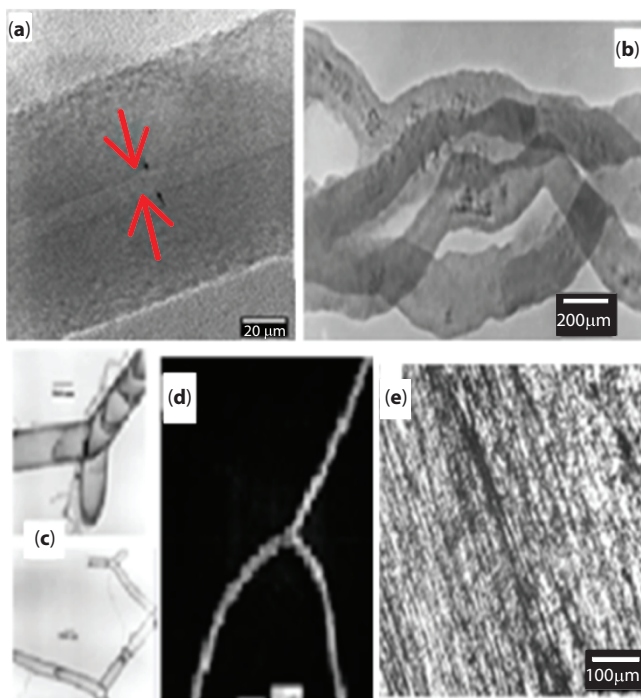




**Figure 1.5** Schematic illustration of (a) how single layer of graphene folds to make a single-wall carbon nanotube; (b) how multilayers of graphene fold together to form a multi-walled carbon nanotube; and (c) sketch of how broken graphene layers fold to form a carbon nanofiber, and TEM image of CNF with broken graphene layers, and (d) TEM image of packed cones, cups.

### 1.2.1 History of CNF

Carbon nanofibers (CNFs) were first reported by Hughes and Chambers in a patent in 1889 [5] while carrying out the synthesis of filamentous carbon. Pyrolysis of methane/hydrogen gaseous mixture yielded carbon nanofibers in the form of a filament growth. The first electron microscopy observations of hollow carbon nanofibers of 50 nm in diameter was reported in the early 1950s by the Soviet scientists Radushkevich and Lukyanovich. Then, in 1988 Morinobu Endo [6] at Shinshu University, Japan, reported carbon nanofibers with a diameter of 1  $\mu\text{m}$  and length of above 1 mm. In 1991, Yoshinori Ando [7] synthesized carbon nanomaterial by Arc process which was examined by Sumio Iijima while working

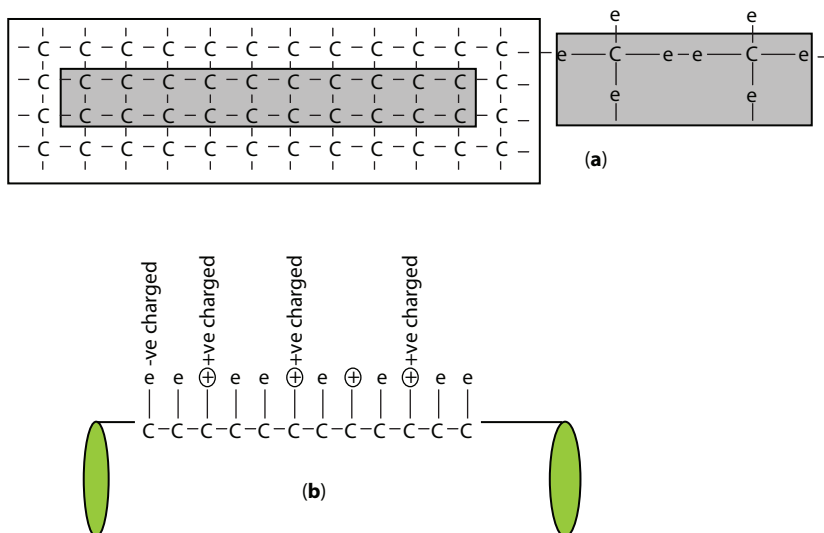


**Figure 1.6** (a) TEM image showing graphene layers of (b) entwined carbon nanofibers synthesized at 1100 °C in presence of Ni: Al catalyst and n-hexane; (c, d) TEM images of open-ended bent, V-shaped inner novel growth of carbon nanotubes at 1000 °C in presence of nickel particles; and (e) SEM micrograph image of straight VGCFs (Source: Debabrata Pradhan, 2003) [4].

at NEC as a new form of carbon nanotube. Pradhan synthesized carbon nanofibers by the pyrolysis of precursor camphor. Some of the peculiar shaped carbon nanofibers synthesized are shown in Figure 1.6.

### 1.2.2 Role of Surface States in Controlling the Properties of CNFs

Carbon nanofibers possess excellent mechanical properties, high electrical conductivity, electromagnetic shielding and high thermal conductivity. Carbon nanofibers have average diameters ranging from 125–150 nm depending upon the precursors and technique used to manufacture them and have lengths ranging from 50–100 μm. They can form composites with various types of polymers and can be easily functionalized due to the presence of unique surface states (Figure 1.7).



**Figure 1.7** Schematic illustration showing (a) the formation of bonds of carbon atoms present at different layers of carbon fiber's surface and missing of electrons from the top layer of carbon atoms; and (b) the effect of the missing electrons from the surface of top layer atoms, creating positive and negative charges which are responsible for making the carbon fibers reactive.

Each layer of carbon nanofiber or nanotubes, contains a set of carbon atoms arranged in one plane. In x-y direction, each carbon is attached with  $\sigma$ -bonds. Bottom layers of carbons (in z direction) are also arranged in the same fashion, such that each carbon shares its electron with bottom layers of carbon by either  $\sigma$ -bonds or  $\pi$ -bonds as the case may be (Figure 1.7a). However, electrons of carbon atoms present in the top layer are not satisfied with its electron due to the absence of any carbon atoms above its layer. These carbon atoms are dissatisfied with electrons. As a result, these carbon atoms would either behave as positively charged (lost its electron) or negatively charged (contains more than its normal electron). However, these distributions of charges would be such that overall the carbon tube will behave like a neutral particle. These unsatisfied carbon atoms are more reactive as compared to carbon atoms present in the layers below the top layer. These carbon atoms are said to possess active sites which are designated as a surface state. The presence of surface state depends upon the types of graphene layers present on the top layers of carbon tube. Its broken graphene layers will show a large number of surface states as well as surface areas. It is for this reason that carbon nanofibers are more reactive as compared to carbon nanotubes.

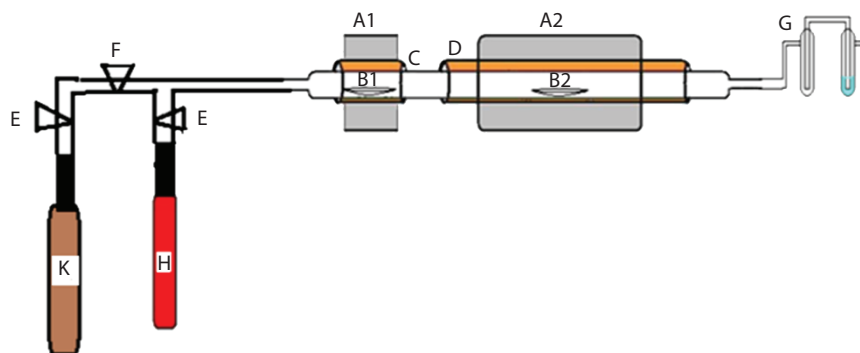
### 1.3 Synthesis of Carbon Nanofiber (CNF)

Catalytic chemical vapor deposition (CCVD) or simply CVD is the foremost commercial technique for the fabrication of CNF as well as CNT. This is a batch process. This technique also produces CMF known as vapor-grown carbon nanofiber (VGCNF). In this type of process, precursor near its boiling temperature is converted into gas-phase molecules and is transported by some carrier gas to decompose at high temperatures in the presence of a transition metal catalyst kept on a substrate. A subsequent growth of the fiber around the catalyst particles is achieved. The nanofiber diameter depends on the catalyst size. There can be different designs of a CVD unit.

#### 1.3.1 Chemical Vapor Deposition (CVD) Method

A typical CVD setup is shown in Figure 1.8. A long quartz tube (C) is inserted into two ceramic tubes (D). Electrical heating wire is wrapped over two ceramic tubes (D). These two ceramic tubes are arranged to maintain two different temperatures (A1 and A2). In the quartz tube (C) two quartz boats (B1 and B2) are kept. In boat B1 a known amount of precursor which is to be pyrolyzed is kept. In boat B2 catalyst powder is spread over the boat. Two gas cylinders (K and H) are connected to the long quartz tube (C) via two controllers (E) and flow meter (F). The outlet of tube C is connected to two bubblers (G). Temperature of A1 is maintained at a value which can boil the precursor kept in quartz boat B1, which is normally kept at around 400 °C. Temperature of furnace A2 is maintained at a suitable temperature where the precursor gas can be decomposed in the presence of the catalyst to get the CNF. Before setting the temperatures of two furnaces, inert gas like argon gas (H) is purged through the quartz tube (C) to remove the presence of oxygen. The temperature of furnace A2 is set to a required temperature (which could be in the range of 600–1000 °C). When the required temperature has attained the temperature of the furnace, A1 is set to boiling temperature of the precursor. During this process the flow of carrier gas is maintained which helps to carry the vapor of precursor to the furnace A2 for completing the process of pyrolysis. Undecomposed gas and carrier gas are allowed to escape to atmosphere through the bubblers (G). At the end of pyrolysis CNF is collected from the furnace (A2).

It is possible to control the length of carbon nanofibers by controlling the rate of gas flow in the quartz tube (C). In addition, direction of fiber growth can also be controlled by adjusting the direction of gas flow. If adjusted properly, the variable parameters of the process can yield CNF with submicrometer diameters and lengths of a few to 100  $\mu\text{m}$ .



**Figure 1.8** A sketch of a typical CVD unit. A1 and A2 are two furnaces operating at two different temperatures. B1 and B2 are two quartz boats used for keeping precursor and catalyst respectively. CNF is grown on the boat B2 as well as over the entire area covering the furnace A2, C is the quartz tube in which growth of CNF takes place, D is ceramic tube over which heating wire is wrapped to create required temperature, E and F are gas valves and flow meter to regulate flow rate of gas. G is a gas bubbler to prevent backflow of gas into the quartz tube and allow the escape of unreacted gas into the atmosphere, H is the gas cylinder containing the carrier gas and K is precursor gas like methane or acetylene.

### 1.3.2 Precursors for CNF

Precursor for synthesizing CNF can be several types of hydrocarbons such as natural oils like mustard oil, pure fatty acids (liquid or solid), camphor, terpene oil, acetylene, ethylene, methane, natural gas, benzene, etc. Introduction of carbon monoxide (CO) into the gas flow can increase the carbon yield, hence yields a greater amount of CNF. It is also possible to use plant seed materials like mustard seed, stem of any plant, plant leaves, bamboo, rice straw, bagasse, etc. It is also possible to use some gasses directly like methane, acetylene, etc. When using solid materials like plant leaves, there is no need to use the furnace (Figure 1.8A1). These precursors can be kept directly in the boat (Figure 1.8B2) along with any catalyst (if needed). If gases like methane are to be used as a precursor then there is also no need to use the furnace (Figure 1.8A1). Gas from the cylinder (Figure 1.8K) can be sent to the furnace (Figure 1.8A2) where suitable catalyst is kept in the boat. The precursor gas can either be directly fed into the unit or is mixed with carrier gas in the required proportion.

### 1.3.3 Use of Catalyst in the Synthesis of CNF

There are variations in the type of catalyst used for the synthesis of CNF. There are some catalysts which are solid like ferrocene, cobaltocene, etc.

These catalysts vaporize in the temperature range of 300 to 400 °C. Such catalysts are kept in a boat (Figure 1.8B1) in the furnace (Figure 1.8A1) along with the precursor like oil. The vapor of oil and the vapor of catalyst like ferrocene are carried with carrier gas to the furnace (Figure 1.8A2). Catalyst decomposes into its metal oxide and *in-situ* reaction takes place with the vapor of oil to produce CNF. These CNFs are collected in the boat (Figure 1.8B2).

Catalyst can be used either in the form of powder or as a thin film deposited on a substrate like quartz glass, alumina plate, or as a metal plate like nickel, iron metal, etc. Normally, after scratching a metal plate with diamond powder it is cleaned with water and dried with acetone, which is also used as a catalyst. Scratching the plate creates more roughness of the metal, which produces more surface states and surface area over which the reaction of vapor of precursor reacts more favorably with catalyst. The preferred size of catalyst particles should be in the range of 5–25 nm in diameter. Some examples of the role of different types of catalysts and their effect on the carbon nanomaterials produced are shown in Figure 1.4.

There is no hard and fast rule to suggest which type of catalyst will produce better CNF. Better CNF means the value of its diameter, length, surface area and surface states. Selection of catalyst and its type depends upon the type of precursor and size of catalyst powder, which can only be decided by carrying out some specific experiments. Powder or thin films of Fe/Ni, Ni, Co, Mn, Cu, V, Cr, Mo, Pd, MgO, and  $\text{Al}_2\text{O}_3$  are used as catalyst. But most popular catalysts are powder or thin film of organometallic compounds of iron or nickel or cobalt. Details of the use of different catalysts are presented in Chapter 3 of this book.

### 1.3.4 Selection of Variable Parameters for Growth of CNF

Variable parameters of pyrolysis under the CVD units are: precursor (oil, solid materials like plant materials, camphor, etc.), temperature (Figure 1.8A1 and A2), type and size of catalyst (usually nickel, iron and cobalt), carrier gas (argon, nitrogen, etc.), reactive gas (hydrogen), and duration of pyrolysis. Due to the large number of variables, it becomes very time-consuming to reach a suitable condition to obtain the desired type of CNF.

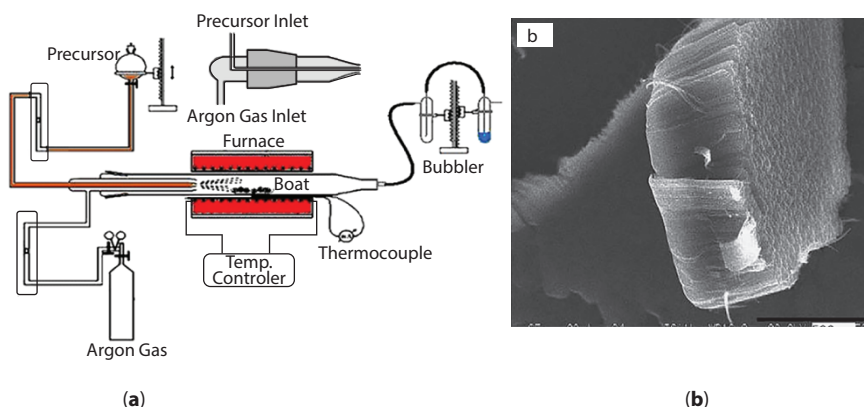
It is advisable that one should adopt the Taguchi method, which can provide information of effective variables to produce the required type of CNF [1–3]. For example, with 4 variables (requires 24 experiments) one needs to carry out only 9 sets of experiments; whereas, with 6 variables (requires 720 experiments) one needs to carry out only 16 sets of experiments.

### 1.3.5 Epitaxial Growth of Aligned CNF

Afre *et al.* [8] have developed a CVD with spray techniques (Figure 1.9A) to get epitaxial growth of aligned, continuous (Figure 1.9B), catalyst-free carbon nanofiber from vapor of turpentine oil. Aligned CNF possesses properties like high mechanical strength, high directional electrical conductivity, and high thermal conductivity. The main difference between the CVD unit described in Figure 1.8 and 1.9 is the inclusion of a spray facility so that solution containing precursor and the catalyst sprays its liquid in the furnace like a cloud of material.

### 1.3.6 Mechanism of CNF Synthesis

There are different mechanisms suggested to explain the role of catalyst but none of them can explain why CNFs are formed over the entire reaction tube in a larger amount than the amount of catalyst used for the purpose. The author of this chapter suggests that vapor of precursor at high temperature breaks down into lower very reactive carbon fragments and this decomposition is catalyzed by the catalyst. These reactive fragments move around the furnace (Figure 1.8A2) with the help of the carrier gas. Since these fragments are highly reactive, they recombine to give CNF. The process of recombination giving the product depends upon the variable conditions used for the synthesis of CNF. The nature of CNF formed thus depends upon variables like temperature, the flow rate of carrier gas, etc. It is for this reason one finds deposition of CNF not only in the boat (Figure 1.8B2) but



**Figure 1.9** (a) typical sketch of CVD unit with a spray system and (b) the aligned carbon nanofibers produced from this process using turpentine oil.



throughout the quartz tube (Figure 1.8C). Moreover, the amount of CNF formed are far in excess of the amount of catalyst used for the purpose.

## 1.4 Properties of CNF and Its Composites

Electrical conductivity in CNF/polymer composites depends upon the nature of the network and their alignment in the matrix. Therefore, for good electrical conductivity a good fiber dispersion and the continuation of the network of carbon nanofibers is necessary. Also, by controlling the loading amount of CNF in the composite different electrical resistivity values can be achieved. CNF/polymer composite can increase the tensile strength (gain of 50 to around 300%), compression strength (50–100%), Young's modulus (almost 100%), inter-laminar shear strength (with 1% CNF increases in the range of 20–50%), fracture toughness (with 1% CNF increases in the range of 30–50%), and vibration damping of the base polymer. These improvements depend upon the nature of polymer, extent of dispersion, etc. [9–15]. Thermal conductivity of CNF with 20 wt% epoxy resin has been observed to increase from 0.2 W/m-K to 2.8 W/m-K [15]. CNF composite with thermoplastic material is found to retard fire properties like delay in burning when exposed to flame and slow heat transmission [16, 17]. Polymeric composites with carbon nanofibers have shown substantially lower coefficients of thermal expansion as compared to graphite. Details of CNF and its composites are presented in Chapter 4 of this book.

## 1.5 Applications of CNF

Some of the applications of CNF are enumerated here:

- Scientists, after understanding the properties of carbon fibers, have started using this material in various engineering applications to reinforce concrete, replace steel with carbon fibers, as material for bridge work, etc. CNFs are being applied or are thought to apply for strengthening of structures with carbon fiber composites in precast concrete and plastic, and fiber-cement. The traditional method of strengthening the reinforcement of brick is by utilizing steel clamps, which provide strength but also become heavy and are prone to corrosion. CNFs are being thought of to use in



place of steel to get almost the same strength. Carbon fibers in precast concrete has also become popular since 2003. Carbon fiber grid reinforcement is applied in the wall panel face, which allows the use of less concrete, reducing weight and raw material.

- CNF composites with a conductive polymer, polypyrrole (PPy), in N,N-dimethylformamide (DMF) solvent increases its strength.
- The non-corrosive nature of carbon fibers prevents the rusting and staining which otherwise occur with steel reinforcing. Carbon fiber composites have low thermal conductivity, thus reducing the transfer of heat or cold from outside to inside. Carbon fiber composites used for building works provide the benefit from long-term energy savings. CNF is used in bridge construction because CNF-reinforced plastic provides reduction in bridge weight and economy of lifting equipment. Carbon fibers possess the property of repelling water, hence are used by mixing with grits and coal tar to give more life to the road.
- CNFs are used as additive for anode and cathode materials in energy conversion and storage systems because they possess properties like good chemical stability, thermal stability, and electrical conductivity, high specific surface area and good charge transport properties.
- CNF is used for the delivery of therapeutic drugs. It has been proposed that when a needle-shaped carbon nanofiber is loaded with therapeutic drugs and embedded into an elastic material (which can be inflated to form a balloon) and inserted next to the diseased site, the needle-shaped CNF penetrates the diseased cell and delivers the therapeutic drugs.
- Since CNF has large surface area and good electrochemical properties, it is observed that it increases the capacity of lithium battery more than graphite. CNF is used to improve overall energy capacity and cycling stability of anode material of lithium-ion battery. Because of its reversible electrochemical properties, it increases good charging/discharging cycles of lithium battery. Metal/CNF composites, like carbon/TiO<sub>2</sub>, Carbon/SnO<sub>2</sub>, etc., have been found to enhance the capacity of lithium-ion battery.

- CNF is used to develop gas mask sensor because it changes its color after absorbing chemical.
- Since the electrical conductivity in CNF is highest along its length, it can be used as electron field emitter if aligned CNF is grown along its length.
- Supercapacitors (electric double-layer capacitors) are gaining in popularity because they can provide high energy density and better power density than normal batteries. There has been increasing interest in the use of porous carbon nanofibers to develop supercapacitors because of their higher specific surface area ( $1200 \text{ m}^2/\text{g}$  or more). The electrode (e.g., CNF/ $\text{V}_2\text{O}_5$  composite) has given specific capacitance of  $150 \text{ F/g}$  and energy density of  $18.8 \text{ W h kg}^{-1}$  over a power density range of  $400\text{--}20,000 \text{ W kg}^{-1}$ . Number of operating cycles with CNF supercapacitor has also been found in the range of 2000 cycles.
- Because of their low-cost, dye-sensitized solar cells (DSSC) are being thought of to replace silicon solar cells. DSSC consists of a photoanode and a counter electrode separated by a redox electrolyte (iodide/triiodide). CNFs are highly stable against electrochemical corrosion in either alkaline or acidic media, hence are found to possess significant catalytic activity and power conversion efficiency in DSCs. This material is expected to replace expensive counter electrode made of noble metals like platinum.
- CNF can be used as catalyst due to its high specific surface area, high chemical resistance, outstanding electrical properties, and suitable mechanical properties. Because of good electrical properties, it is developed for high loaded active enzymes and for fast kinetics at electrode surface, especially for enzymatic cathodes in biofuel cell devices. Carbon of CNF acts both as catalyst and adsorbent for the catalytic oxidation of NO into  $\text{NO}_2$  or reduction of  $\text{NO}$  into  $\text{N}_2$ .
- In developing electrodes for fuel cell, it is essential to replace platinum with some other materials which are inexpensive. CNFs loaded with nickel, iron and nitrogen are found to be suitable material for use as an electrode in alkaline fuel cell.
- Microbial fuel cell (MFC) is a bio-electrochemical cell that uses microorganisms to utilize organic substrates at anodes to generate electricity. For this purpose, it is necessary to

develop biocompatible electrode materials with high surface area and long-term stability to support the maximum growth of bacteria and enhance electron transfer rate. CNFs are finding their use as anode in MFC [18].

- CNFs have generated interest in the area of sensors and biosensors because of their functionalization ability, electrochemical property, mechanical flexibility, and biocompatibility. They have exhibited a good response for developing glucose biosensor. Metal-loaded CNFs are gaining in popularity in developing biosensors. For example, palladium-loaded CNFs exhibit good electrochemical catalytic activities for determining dopamine (DA), uric acid (UA), and ascorbic acid (AA). These three chemicals can be determined simultaneously from their mixture because of their difference in overpotential [19].
- CNFs are used as good adsorbent material especially in the field of adsorption/separation because of their high specific surface area and high porosity. Removal of dissolved impurities, such as dyes and metals present in drinking and industrial water, is being tried using CNFs. There are several chapters devoted to different applications of CNF presented in this book.

## 1.6 Health Hazards of CNF

Though many studies are being conducted with CNFs, some studies have indicated that there are health hazards associated with CNFs especially due to their sizes [20, 21]. One of the hazards associated with CNF is that it is expected to cause respiratory damage such as pulmonary inflammation, granuloma, and fibrosis. These effects are observed with mice. There seem to be no studies available on its effect on human beings. However, it is proposed to wear some type of mask when working with CNF so that it is not inhaled. Sharon and his research team have observed that CNF of a particular band gap if spread over skin affected by cancer cells, and simultaneously exposed to visible light, can kill cancerous cells, suggesting that this material can be used in dermatology for killing the growth of cancer cells grown over skin. However, this experiment was done with mice only [22–25].

## 1.7 Summary

In this chapter an effort was made to discuss the various aspects of carbon fibers and carbon nanofibers, including their synthesis, properties and applications. An effort was also made to explain the basic differences between carbon fibers, carbon nanofibers and carbon nanotubes.

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# Biogenic Carbon Nanofibers

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*My relationship to plants becomes closer and closer.  
They make me quiet; I like to be in their company.*

**Peter Zumthor**

## 2.1 Introduction

With the advent of nanotechnology, the first question that arose was how to synthesize the desired nanoparticles, resulting in the evolution of many physical and chemical methods [1] to synthesize various nanomaterials. The curious nature of human beings has always directed them to look to nature for solutions to many questions. Primitive man exploited his gray matter to unlock the mystery of plants and the possibilities stored in them, be it for food, shelter, weapons, medicine, source of energy (fire), clothes, etc. With the increase in their intellectual capacities they used plants for developing vehicles, furniture, pulleys and the list goes on. The scenario is no different today; nanotechnologists have turned their attention to plants for solving puzzles to synthesize nanoparticles. Scientists have realized the perfection of nano-sized particles (DNA) apparent in their mega impact. Biological materials are highly organized from the molecular to the nanoscale, microscale and macroscale, often in a hierarchical manner with intricate nano-architecture that ultimately makes up a myriad of different functional elements. Nature uses commonly found materials. Properties of the materials surfaces result from a complex interplay between the surface structure and the morphology

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and physical and chemical properties. Many materials, surfaces and devices provide materials and fibers with high mechanical strength, biological self-assembly, antireflection properties, structural coloration, thermal insulation, self-healing and sensory aid mechanisms, which are just some of the examples found in nature that are of interest in fabricating nanoparticles. Carbon nanomaterials (CNMs) are on the verge of becoming an important material for various industrial applications. One of the hurdles in the production of CNMs is the cost of the raw material. There are two components in producing the CNM, the precursors and the technique of the synthesis. It is almost certain that chemical vapor deposition (CVD) technique would be most suitable for the production of large quantities of CNM. As a result, the CVD technique is being explored by many research groups for the synthesis of CNM. This book encompasses the various aspects of carbon nanofibers (CNF), one of them being their synthesis, and plants have provided a unique platform that offers their metabolites as well as organs as a base or precursor to fabricate CNF.

No doubt there are many chemical precursors, mostly hydrocarbons, that have been used for synthesis of CNF [2]; but most of them are chemicals derived from fossil fuels. Fossil fuels are destined for depletion in the very near future. Hence, as an alternative to fossil fuel-derived materials Sharon's group started looking at plant-derived materials as a precursor of carbon nanomaterials including CNF, because carbon is known to be a vital constituent of all living organisms.

Sharon's group was the first to begin developing carbon nanomaterials from both plant parts and plant metabolites over more than the last two decades from many plants [1–5]. The advantages of using plant materials are that they can be cultivated when desired, hence are regenerative material, and are low-cost material. Moreover, plant tissues are composed of oils, lipids, carbohydrates, proteins, cellulose, lignin, etc., which are a rich source of carbon.

Both CNTs and CNFs appear almost the same under SEM analysis. Both are like a hollow cylinder. The outer layer of CNT is made of unbroken graphene sheet whereas CNFs are made of broken graphene sheet. Biogenic CNF has been mostly synthesized by high temperature pyrolysis (Figure 2.13). The parameters that affect the synthesis process are the same as for the standard CVD process of CNM synthesis, i.e., temperature, duration of pyrolysis, carrier gas, catalyst and precursor (plant part or plant metabolite).

## 2.2 Plants as Source of Precursor for CNF Synthesis

Most of the plant parts that have been used as precursor for the synthesis of carbon nanomaterial have yielded CNF. Whereas, plant-derived products or

metabolites have produced different forms of carbon nanomaterials (CNM) such as single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), carbon nanobeads (CNB), etc. Almost all parts of plants (stem, roots, leaves, seeds, etc.), and many plant-derived products (camphor, juice, latex, oil pinene, resins, etc.) have been used as precursors of CNMs. Both plant parts and plant metabolites have wide availability, making it a suitable choice. Moreover, they are composed of many different hydrocarbons, a rich source of carbon. Synthesis of CNF from plant parts as well as plant derivatives is mostly done by the process of chemical vapor deposition (CVD) under pyrolytic conditions. The setup used for the CVD process is explained in detail in Chapter 1 of this book. The CVD method involves thermal decomposition of the carbon-containing material into carbon vapors. The carbon vapors are deposited on the catalyst, usually transition metals, leading to formation of various forms of carbon nanomaterials.

For preparing CNF from plant sources, the traditional CVD process is slightly modified. However, the various parameters which play a definitive role in the type of CNM being synthesized by the standard CVD process remain the same. The parameters are:

- (i) **Precursor:** Impact of precursor can be explained by the pyrolysis of bamboo, which forms CNM only in the range of 1200 to 1400 °C. This is because bamboo contains  $\text{CaSiO}_3$  which melts in this range. But at temperatures greater than or equal to 1500 °C, there is no CNT formation as the nature of  $\text{CaSiO}_3$  changes. There have been efforts to thermally (calcining) or chemically [6] pretreat plants prior to pyrolysis.
- (ii) **Pyrolysis Temperature:** Controls the yield and nature of CNMs; yield of CNM at higher temperature is significantly higher than at lower temperatures. This is because at higher temperature carbonaceous compounds are completely cracked into carbon. Moreover, reformation of graphene-like honeycomb structure of carbon arrangement into different forms on the CNM also depends on the CVD temperature. Moreover, when the algae *Euglena* was used as precursor [7] for CNM he found that the diameter distribution of MWCNTs increases with increasing temperature. The lower the temperature, the narrower the diameter distribution. At higher temperature the diffusion of carbon particles in the catalyst or vice versa is more facile.



Not only plant parts but also plant metabolites exhibit the cardinal role of temperature on the formation of CNM; for example, oil being pure hydrocarbons is accepted as suitable precursor for synthesis of CNM, also shows the impact of temperature during pyrolysis in the formation of CNM. While reaction at lower temperature does not lead to complete decomposition of oil into graphitic carbon synthesis, at higher temperature it dictates higher yield because the stability of the graphitic carbon is affected at higher temperatures, which narrows the temperature range at which CNTs are obtained in scalable amounts. Here precursor also plays an important role. The most dramatic effect of temperature on the quantity and quality of CNMs is shown in the study of Karthikeyan and Mahalingam [8], who have synthesized CNMs using pine oil, methyl ester of *Jatropha curcas* oil and methyl ester of *Pongamia pinnata* oil at comparatively lower temperatures of 550°, 650° and 750 °C. Their study shows a relatively low yield of CNTs at lower temperature of 550 °C, while at 650 °C the formation of well-defined MWCNTs is high as the decomposition of vapors into carbon over catalyst is more effective. Conversely, the studies show a rise in yield of amorphous carbon upon raising the temperature to 750°C. Hence, the intermediate temperature of 650 °C is found to be optimum for producing graphitic carbon. A similar impact can be exhibited during formation of CNE.

- (i) **Catalyst:** Transition metals serve as excellent catalysts for synthesis of CNMs as they enable catalytic decomposition of carbon source, form metallic carbides easily and enable diffusion or dissolution of carbon through bulk or through the surface of the metal, leading to precipitation of carbon nanomaterial. The phase diagram of carbon and the transition metals, namely iron, cobalt and nickel, indicate solubility. The growth of the CNM starts at the catalytic surface; hence, it is imperative that the size of the catalyst should be in the nanometer scale range, i.e., 1–100 nm. Koziol *et al.* [9] have proposed two mechanisms for catalyst-fueled growth of CNM by CVD method: (a) **Tip Growth Method**, which states that after decomposition of the carbon species, the carbon dissolves in the catalyst and diffuses through it and finally precipitates at the end to form carbon nanotubes. The catalyst is predicted to be always present at the top of the growing nanotube. (b) **Base Growth Model**, which involves bottom carbon diffusion through catalytic particle in which the catalyst

particle is proposed to be present at the base of the growing nanotube.

- (ii) The dissolution of the carbon at one part of the catalyst and subsequent precipitation at another part is aided by a temperature gradient which might develop due to the exothermic nature of the decomposition of hydrocarbons. The carbon diffusion parameter depends on the dimensions of the catalyst particles, nature of metal catalyst, temperature and hydrocarbons and gases involved in the process. It has also been proposed that when the substrate catalyst interaction is strong, CNT grows up with the catalyst particle rooted at its base. Conversely, when the substrate catalyst interaction is weak, the catalyst particle is lifted up by the growing nanotube. The driving force for carbon diffusion and subsequent CNM formation is the difference in solubility of carbon at the gas-catalyst interface and the catalyst-CNM interface, determined by the affinity for carbon formation in the gas phase and the thermodynamic properties of the CNM respectively. Qi *et al.* (2016) [10] have highlighted the effect of not only catalyst but their method of preparation, presence of catalyst support and catalyst promoters also.

Synthesis of CNM *without any external catalyst* has also been successfully done during biogenic synthesis of CNF because some precursor contains certain elements (K, Mg, Ca, Si, O, Fe, S, P) which aid in the formation of CNMs and the presence of an external catalyst is not required. These minerals aid in the growth of the nanoforms by adjusting pore size and modifying the pyrolytic process. Chen *et al.* (2009) [10] synthesized CNFs using activated carbon produced from agricultural waste by CVD. They reported that the activated carbons containing iron can be used directly to synthesize CNFs. This eliminates the need for the preparation of iron catalyst.

- (iii) **Carrier Gas:** Most common carrier gases used during the CVD method and pyrolysis are argon, nitrogen and hydrogen. The most important function of a carrier gas is to remove all traces of oxygen, which might oxidize the CNM produced, and to provide an inert atmosphere for the production of CNMs. Khorrami and Lotfi (2016) [12] conducted a study on the impact of carrier gas flow rates

on growth of CNTs over copper catalyst, in which a higher gas flow rate showed a decrease in the growth of CNTs from ethanol precursor. This study involved the deposition of a copper nanolayer on mirror polished Si wafer by sputtering technique. The results led to the conclusion that equilibrium is established between the flowing gas molecules and the adsorbed gas molecules on the catalyst nanolayer. With an increase in carrier gas flow rates most of the catalyst sites are occupied by the carrier gas molecules, hence unavailable for the precursor molecules. This leads to a drop in production of CNTs at higher carrier gas flow rates. Also, it has been observed that a better yield is obtained with hydrogen gas since it helps in the reduction of hydrocarbons present in the precursor.

### 2.2.1 Plant Parts

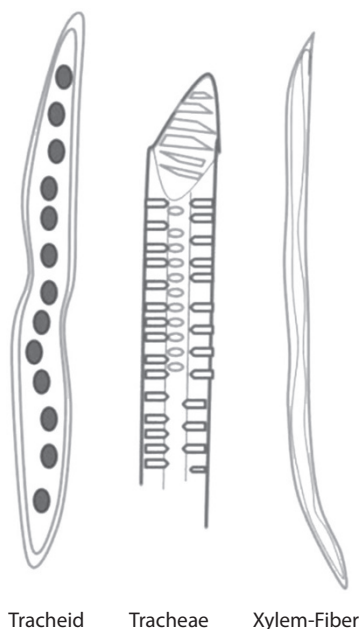
Plant materials that are rich in plant fibers have been the material of choice of many carbon nanotechnologists; for example, Paul (2012) [13] has worked on a number of plant species from Northeast India and others have tried sugar cane [14] (Romanovicz, 2013), cotton fiber [15] (Sharon *et al.*, 2011), rice straw [16] (Viswanathan *et al.*, 2014), corncob [17] (Shukla *et al.*, 2012), bamboo [18] (Zhu *et al.*, 2012), etc., as raw materials with promising results. The aquatic algae *Euglena* [19] has also been tried. The nature of precursor to a large extent determines the type of CNMs obtained. The advantage of using plant fibers is that its inherent anatomy helps in producing the unique morphology of CNF with channel-like structures which otherwise will be difficult to fabricate by other methods.

#### 2.2.1.1 Fibrous Plant Material Used for Synthesizing CNF

Plant stems, leaves and even seeds have fibrous tissues. There are three major plant fibers made up of tissues having thickened walls and complex permanent dead tissue. They are:

- (i) **Mature xylem tissues** composed of *tracheids*, *tracheae*, *fibers* (Figure 2.1), which translocates water and mineral in plants.

Walls of tracheids, tracheae and plant fibers of all types are composed of cellulose and lignin. *Cellulose*

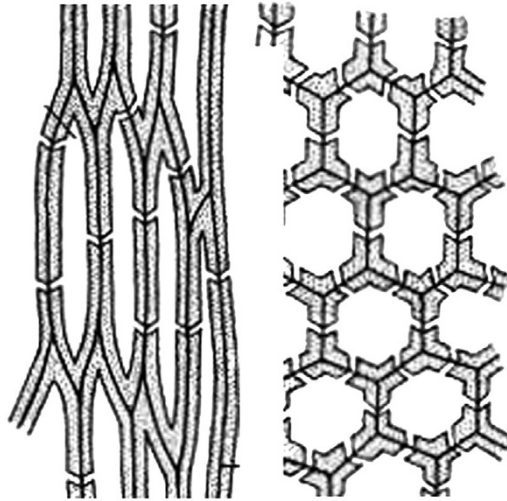


**Figure 2.1** Schematic diagram of Tracheid, Tracheae and Xylem fiber.

is a linear polysaccharide polymer composed of many  $\beta$ -glucose monosaccharide units, i.e., in cellulose the acetal linkage is mainly beta. Alpha glucose monomer unit is also found in the cellulose; *Lignin* is formed by the removal of hydroxyl groups from sugars, creating phenolic compounds and short-chain alcohol ligands. Lignin polymers are heavily crosslinked. The basic monomer of lignin is 4-alkylcatechol.

- (ii) **Sclerenchyma** are long narrow tapering tissues with thick side walls. It has great tensile strength and yet are elastic and gives mechanical support to plants. There are two types of sclerenchyma fibers and sclereids (Figure 2.2).
- (iii) **Phloem Fiber or Bast Fiber:** Tissues are composed of long cells with lignified cell walls. Flax and hemp are phloem fibers (Figure 2.3).

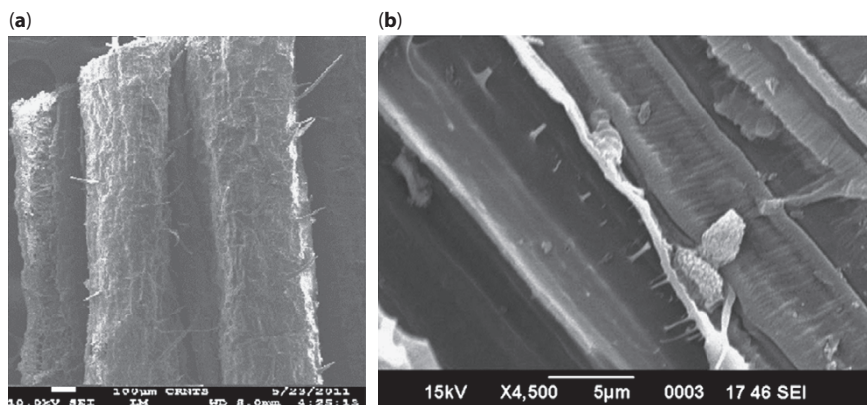
A look at the SEM images of plant fibers [20], sclerenchyma and xylem tissues (tracheids, tracheae) and CNF fabricated from them gives an existing correlation between the two (Figure 2.4).



**Figure 2.2** Schematic diagram of Sclerenchymatous fiber (left) in L.S. view and right in T.S. view.



**Figure 2.3** Schematic diagram of Phloem fiber.



**Figure 2.4** (a) Maize fiber and (b) maize fiber after pyrolysis as CNF.

### 2.2.1.2 Characterization of CNF Obtained by Pyrolysis of Plant Seeds

**SEM Images:** Morphological characterization of various plant materials (Figure 2.5) by many scientists have shown that CNFs derived from plants have channel-like structure, offering many sites for its use in adsorption/absorption of organic and inorganic materials, gases and liquids.

**XRD Characterizations:** Characteristic planes for each carbon material obtained by XRD analysis of carbon materials prepared by the pyrolysis of various precursors are shown in Figures 2.5, 2.6 and 2.7. For comparison, XRD of pure CNF [21] is shown in Figure 2.6. XRD analysis suggests that CNF shows peaks at  $26.4^\circ$ ,  $42^\circ$  and  $62^\circ$  for (002), (100) and (103) planes respectively. In addition, XRD spectrum exhibits few broad peaks with weak intensity, indicating low crystallinity of the CNF. The most intense peaks appear close to (002), (100) and (103) peaks for graphitized samples. CNFs can be assumed to be composed of a short-range order of graphitic structure, i.e., partially graphitized carbon. The broadened (100) and (103) peaks also reflect the disordered character of graphite sheets for the CNFs. Carbon obtained from fibrous plant materials shows the development of (002) plane with the exception of carbon obtained from bamboo, which shows very crystalline character (Figure 2.5).

**Micro-Raman Characterization:** Raman spectrum was taken over a broad frequency range using  $E_{\text{laser}} = 785 \text{ nm} = 1.58 \text{ eV}$  excitation. Each of the materials showed the presence of D-band and G-band. Their peak positions were not at the same position as one would get from pure graphite and diamond. Ratios of the intensity of G-band and D-band were

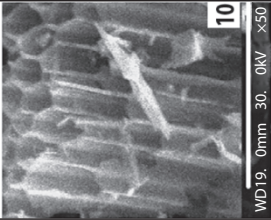
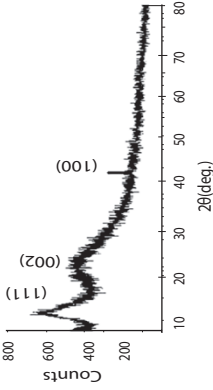
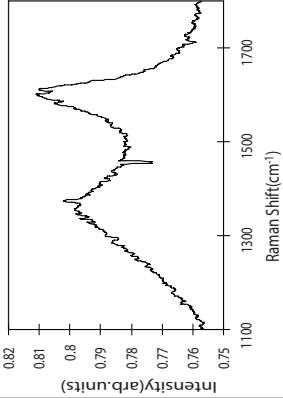
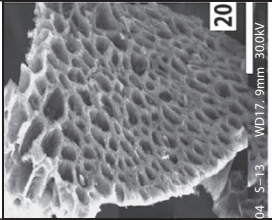
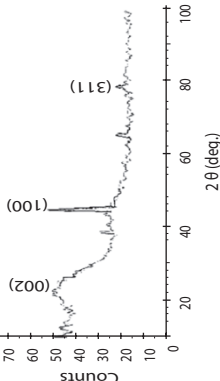
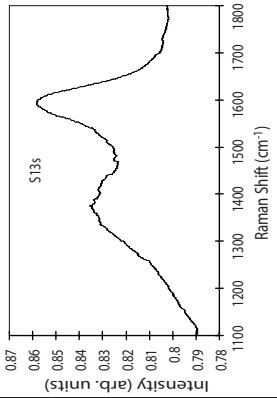
| SEM of CNF from<br>corresponding Plant                                                           | XRD                                                                                | $I_G$ Intensity                                                                   | $I_D$ Intensity | G-<br>Band $\text{cm}^{-1}$ | D-<br>Band $\text{cm}^{-1}$ |
|--------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------|-----------------------------|-----------------------------|
| <br>Baggage   |  |  | 0.81            | 1600                        | 1360                        |
| <br>Corn Stem |  |  | 0.86            | 1600                        | 1367                        |

Figure 2.5 Characterization of CNF obtained by pyrolysis of plant stems (Courtesy of Sunil Bhardwaj). (Continued)

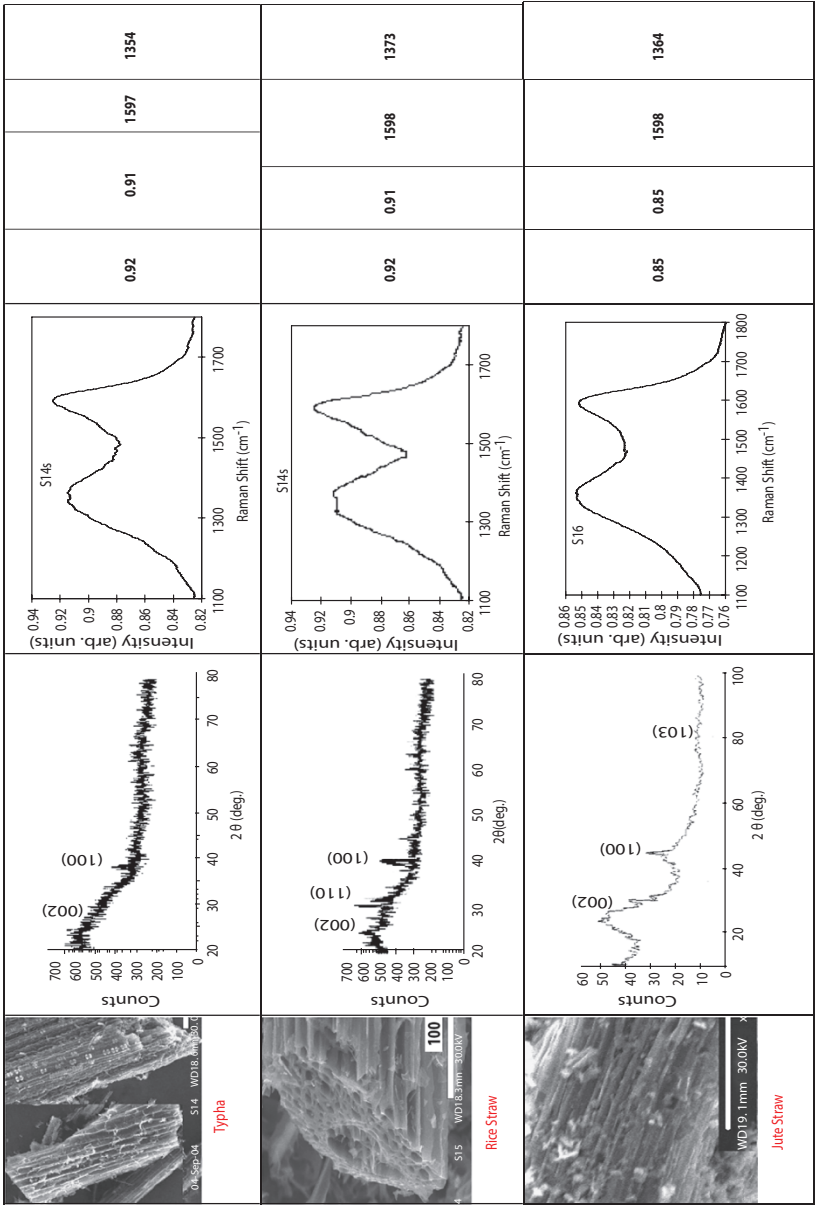


Figure 2.5 (Continued) Characterization of CNF obtained by pyrolysis of plant stems (Courtesy of Sunil Bhardwaj).



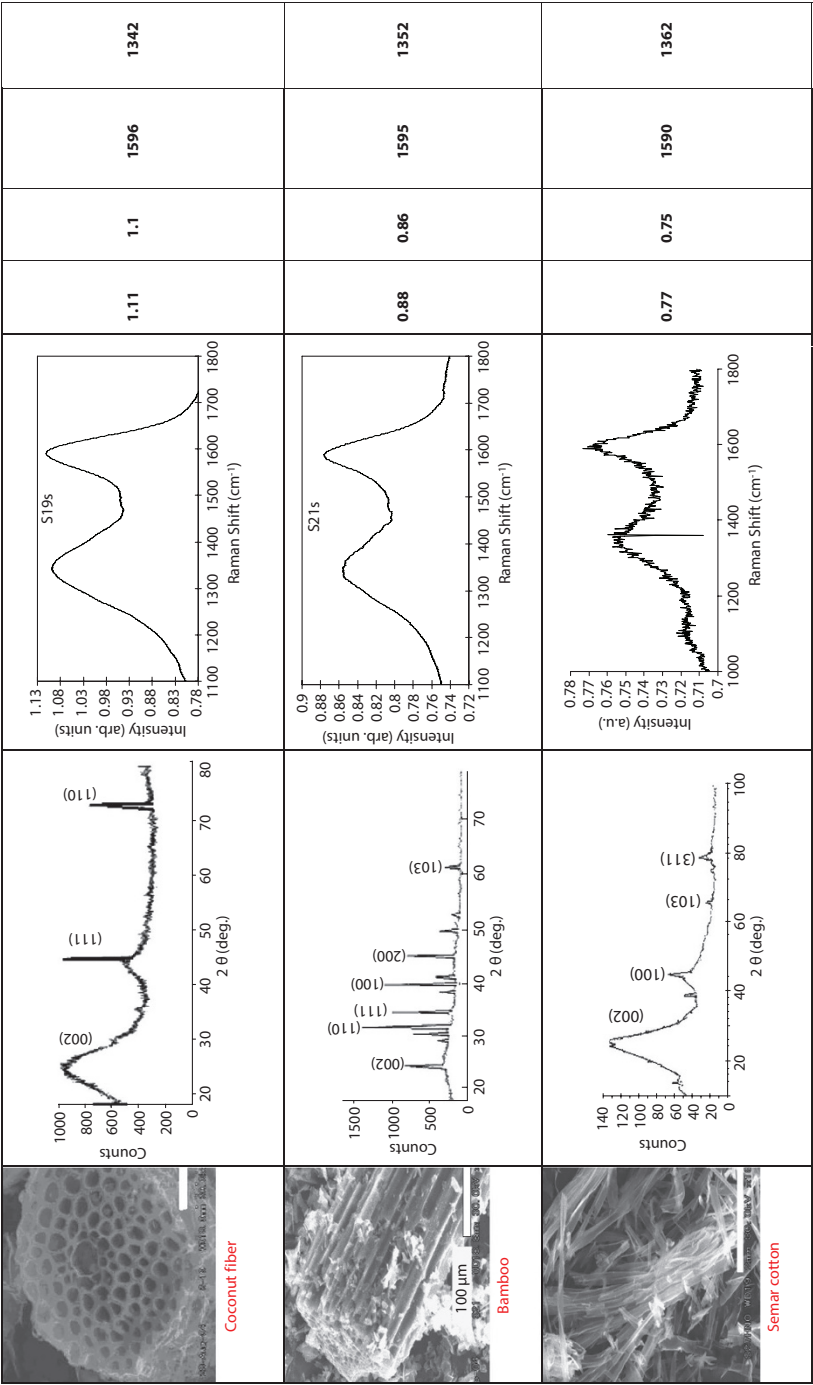
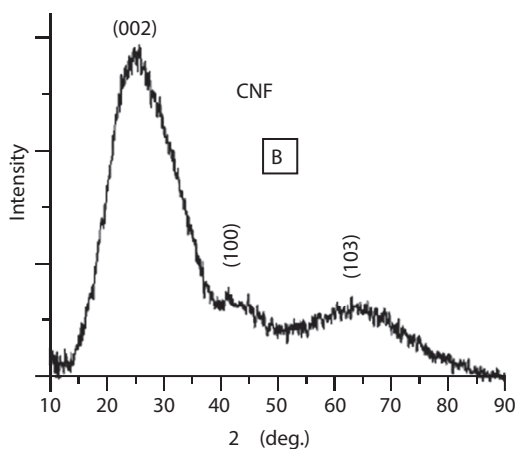


Figure 2.5 (Continued) Characterization of CNF obtained by pyrolysis of plant stems (Courtesy of Sunil Bhardwaj).



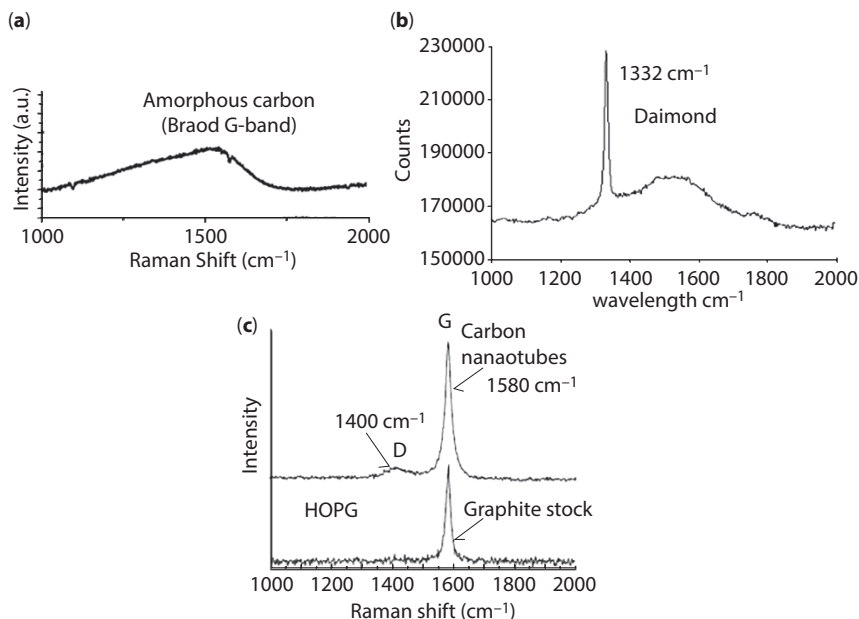
**Figure 2.6** XRD of CNF showing (002) plane of graphite (Hsieh *et al.*, 2003).

calculated from each graph obtained from each carbon material. Details of the Raman spectra and the position of D-band and G-band are shown in Figure 2.5.

For comparison, Raman spectra of amorphous carbon, diamond, graphite and CNT are shown in Figure 2.7. The Raman peaks at  $1580\text{ cm}^{-1}$  in both samples (i.e., CNT and graphite) are attributed to the tangential stretching G mode. The peak at  $1400\text{ cm}^{-1}$  is attributed to disorder-induced D mode which did not occur in the Raman spectrum of the graphite stock. The appearance of D band is due to the defect on the CNTs or the amorphous carbon in the product, which shows the graphitization degree of the product.

The characterizations justified the use of plant material as a unique source of graphitic carbon that can have many applications.

It can be concluded that the CNF synthesized by pyrolysis from fibers of Corn straw (*Zea mays*), Rice straw (*Oryza sativa*), Jute straw (*Corchorus capsularis*), Bamboo (*Bombax bambusa*), Bagasse (*Saccharum officinarum*), Cotton (*Bombax malabaricum*), and Coconut (*Cocos nucifera*) exhibit micro-sized channels like morphology of fibers with nano-size pores. Moreover, such CNFs show a lot of similarity with the original anatomy of the plant fibers used as precursor. Carbon waxy contents like tyloses and pits present on fiber tracheids that were seen in the inherent anatomy disappear after pyrolysis and only the carbon skeleton remained [5]. XRD spectra of all the CNFs shown in Figure 2.5 show development of a (002) plane, except CNF obtained from bamboo (which shows crystalline character). Raman studies of all carbon materials showed the presence



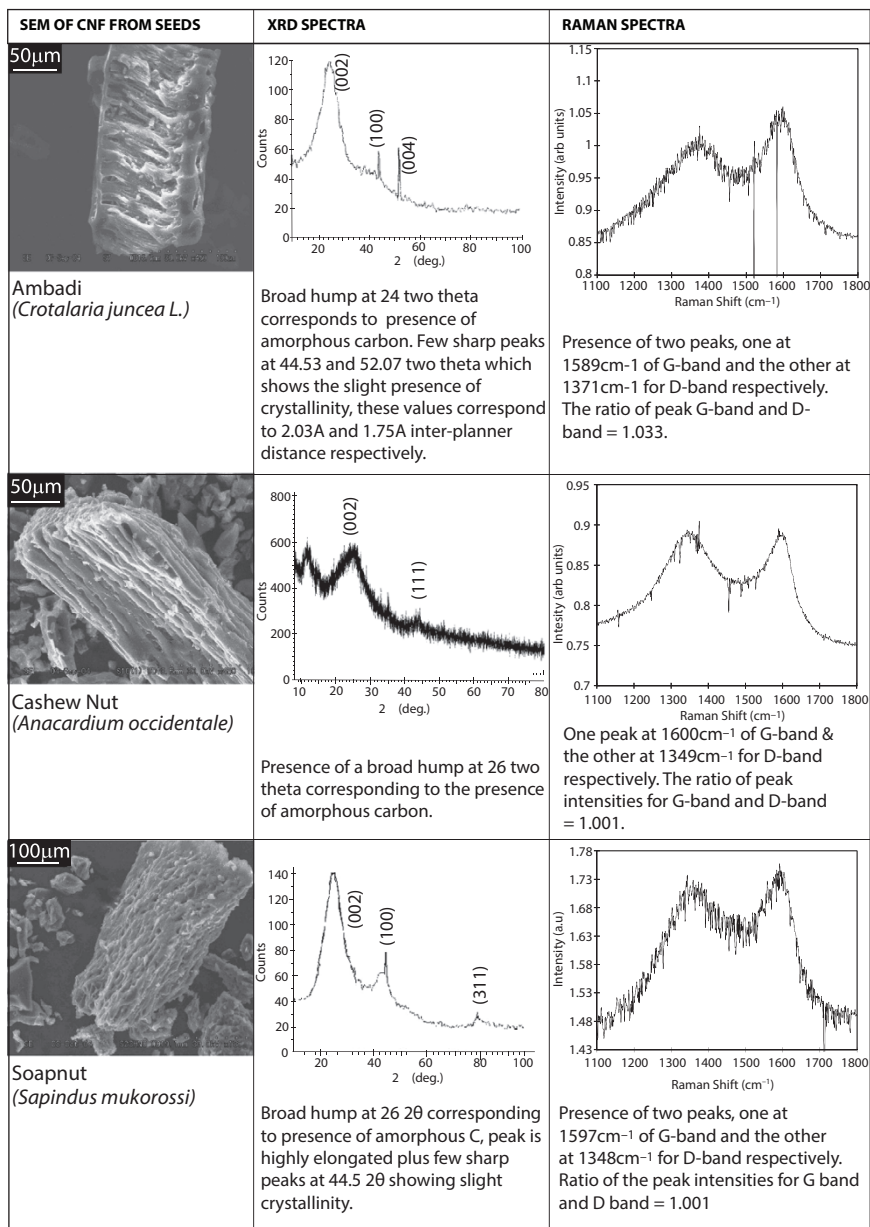
**Figure 2.7** (a) Raman spectra of amorphous carbon film showing an overlapping with a broad G-band and D-band [22, 23]. (b) Diamond showing a sharp D-band [24] and (c) showing intense G-band and small hump of D-band obtained for CNT and intense peak of G-band for HOPG [25].

of G- and D-bands of almost equal intensities, suggesting the presence of graphitic carbon as well as a disordered graphitic structure.

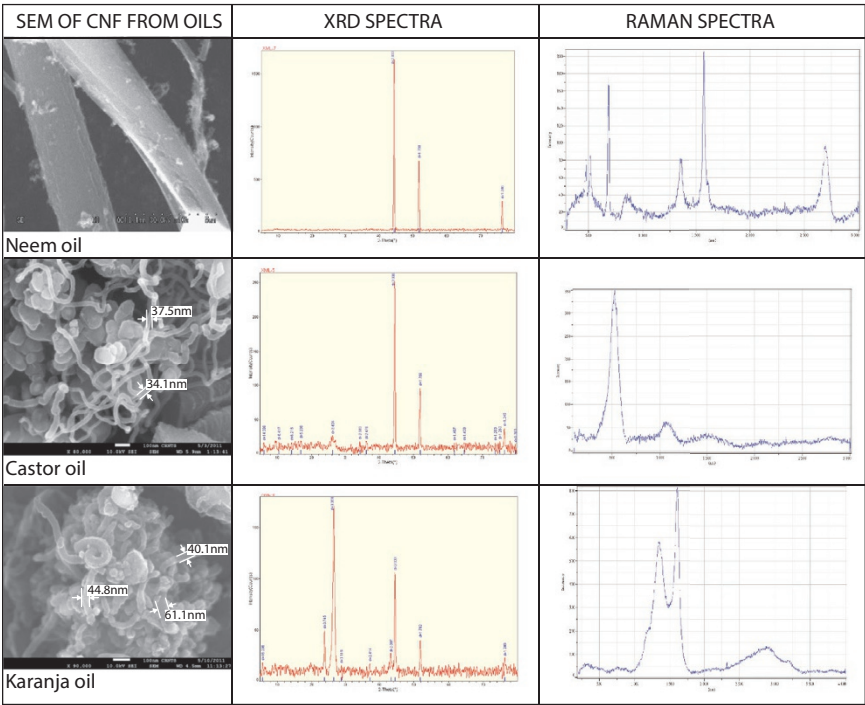
When seeds were pyrolyzed to get CNF, the fibrous tissues present in various seeds yield channel-like fibrous structures which show graphitic nature (Figure 2.8).

### 2.2.2 Plant Metabolites

It has been observed that oils from seeds of plants which are high in concentration of fatty acids (hydrocarbon) serve as excellent precursors for the synthesis of CNMs. Sharon's group has worked with many plant metabolites such as oil, camphor, latex of *Calotropis* and cellulose [6]. There are several other studies about the plant-based oils used as precursors [26–29].



**Figure 2.8** Characterization of CNF obtained by pyrolysis of plants seeds (Courtesy of Sunil Bhardwaj).



**Figure 2.9** Characterization of CNF obtained by pyrolysis of plant oils (Courtesy of Suman Tripathu).

These hydrocarbon metabolites mostly yield CNTs (both SWCNT and MWCNT) and CNB. However, CNF has also been successfully synthesized from plant metabolites. Results of the pyrolysis of some of the oils are presented in Figure 2.9.

2.2.2.1 Characterization of CNF Obtained by Pyrolysis of Plant Metabolites

Plants [30] are a major source of CNM, which can catalytically decompose to liberate carbon atoms and constitute carbon materials of different sizes and shapes.

**XRD analysis** of all the three oils shows a diffraction peak at 26° {002}, which according to [31] is designated to graphitic carbon. Moreover, peak at 44° is also seen in all three graphs that are known to be associated with carbon {111}. A small peak present at 78° of XRD of castor oil depicts the presence of the Silica, which could be due to the boat in which the catalyst was placed.

**Raman Spectroscopic analysis** of all the three oils shows D-band as well as G-band, thus confirming its graphitic nature (Figure 2.9).

Plant parts like straw, stem, etc., are not only composed of pure hydrocarbons but also other chemicals; therefore, they produced plant anatomy-based CNF. Whereas plant-derived oils that are pure hydrocarbon produced defined CNF.

Cellulose is another plant metabolite which is also secreted by many bacteria and extracted from various marine filamentous algae. Cellulose nanofibers are considered as efficient replacements for conventional polymers due to their nano size, ease of preparation, low cost, tunable surface properties and enhanced mechanical properties. CNF obtained from algal sources is less compared to plants and bacterial sources. CNF finds a wide variety of applications such as drug carriers, tissue regenerating scaffolds, water purification, etc. Mulyadi *et al.* (2017) [32] have used doped carbon electrocatalyst from cellulose nanofibrils for metal-free oxygen reduction and hydrogen evolution.

## 2.3 CNF Derived from Parts of Different Plants and Their Applications

The CNF synthesized from different plant-based precursors has been used for various applications. Moreover, CNF has been doped or decorated with metals and conjugated with polymers to enhance its applicability for different purposes.

### 2.3.1 Hydrogen Storage in CNF

Sharon and Sharon (2012) [5] have noted that plant fibers, being rich sources of carbon and having different inherent plant structures, have yielded carbons with different morphologies, pore sizes, surface areas and densities. Depending on these properties, they have shown differences in their capacity to adsorb hydrogen gas. These findings on hydrogen adsorption capacity, and an analysis of the morphology of the carbon material synthesized from different plant fibers, open a new possibility of correlating the finer structure of the synthesized carbon and its various applications. Variation in structures will help in the future in synthesizing desired types of carbon material from waste plant material for different applications. Carbon materials possessing lesser density, larger surface area, and are more graphitic with less sp<sup>3</sup> carbon contribution along with having pore sizes around 10 μm favor hydrogen adsorption. Carbon materials

synthesized from bagasse meet these requirements most effectively, followed by cotton fiber, which was more effective than the carbon synthesized from the other plant fibers.

Hollow CNF synthesized by pyrolysis of cotton at 750 °C in argon atmosphere for 3 h, then treated with  $\text{Ni}(\text{NO}_3)_2$  and thermally treated in argon for 3 h at 850 °C has exhibited a maximum of 8.75 wt.% hydrogen adsorption [6].

### 2.3.2 Removal of Heavy Metals by CNF

Arsenic is a naturally occurring dissolved element in ground and surface waters throughout the world [33]. It exists in a different oxidation state in organic and inorganic forms in many environmental matrices such as natural water and soil. The predominant oxidation states of arsenic are As(III), i.e., arsenite, and As(V), i.e., arsenate ions [34], which can bind to give organic materials commonly present in the environment. Arsenic is a ubiquitous trace element, classified as semi-metal or metalloid. The toxicity, availability and environmental mobility of arsenic are very much dependent on the chemical forms in which it exists [35, 36]. The problem with arsenic is that it is frequently found at higher than acceptable concentration due to anthropogenic contributions, including pesticides, herbicides, industrial waste and the burning of fossil fuels [37]. The health concerns associated with arsenic are well known and generally the word “*arsenic*” is readily associated with “*poison*.” Among its various forms, inorganic arsenic species are known to be more toxic than the organic ones and As(III) is more toxic than As(V). Some of the technologies used for removing this notoriously poisonous material are oxidation, sedimentation, coagulation/co-precipitation, filtration, ion exchange, membrane/reverse osmosis, biological and adsorption modification. Use of nanoforms of carbon is based on the adsorption principle.

For absorbing arsenic, our group has used CNF synthesized from calyx, hair and maize stem by spectrophotometric method using Safranin-O. The method is based on the reaction of As(III) with Potassium Iodate in acidic medium to liberate iodine. The liberated iodine bleaches the pinkish-red color of Safranin-O. The decrease in absorbance at 532 nm is directly proportional to the As(III) concentration and obeys Beer’s Law [38]. As can be seen from Table 2.1, the surface area of CNF is one of the important parameters in adsorbing arsenic from the water.

Sharon’s group [39] have also analyzed the adsorption of arsenic over CNMs prepared from *different oils* using Toluidine blue dye. They have shown that surface area is one of the important concerns in adsorbing

**Table 2.1** Surface area of CNF synthesized from different parts of maize plant and their arsenic adsorbing capacity.

| Plant part of maize | Surface area of synthesized CNF | mg arsenic adsorbed |
|---------------------|---------------------------------|---------------------|
| Cob hair            | 95.018                          | 31                  |
| Corn calyx          | 188.850                         | 53                  |
| Maize straw         | 197.164                         | 61                  |

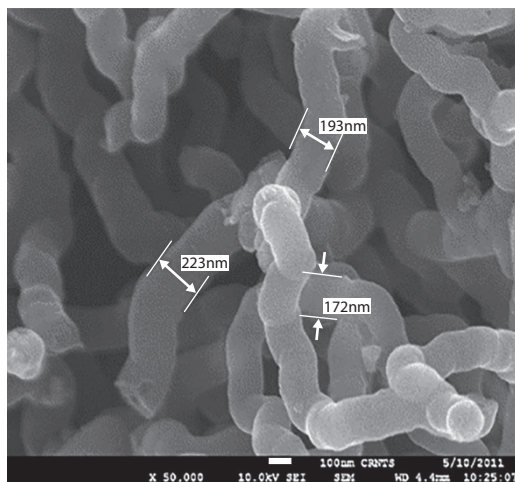
arsenic from the water and have proposed arsenic removal as another application of CNFs. The adsorption was attributed to the presence of dangling bonds on the surface of CNFs. It was felt that CNFs having more dangling bonds on the surface and more surface area can uptake more arsenic

One of the major problems with arsenic removal is that once it has been removed in the form of some materials like ion exchange, etc., is what to do with these materials which contain concentrated solution of arsenic. The advantage with CNF is that it is possible to re-extract absorbed arsenic from CNF into some useful chemical form and use that as a by-product. This facility is not available with any other techniques used for removal of arsenic.

### 2.3.3 Microwave Absorption Capacity of CNF

Multiple uses for morphologically unique plant-derived CNF are being envisaged [40–44]. Sharon's group [28, 45] has shown that these carbon structures have great impact as a radiation absorber. In the present-day scenario of the advancement of wireless communications and microwave communication technology in telecommunication there is a demand to allow the coexistence of various systems and instruments without harmful electromagnetic interferences. Studies have shown that the materials with specific morphology of the plant-derived CNFs will act as microwave absorbing and shielding materials in GHz frequency range, due to their many unique properties. Oil of *Linum usitatissimum* synthesized by CVD method has yielded CNF (Figure 2.10), which has shown an absorption efficiency in the range of ~85–93% and absorption bandwidth of 2.8 GHz in the frequency range of 8–10.8 GHz. This suggests that CNF from *L. usitatissimum* seed oil would be very promising for applications as thinner and lighter absorber as well as SE material in X-band of microwave [46].





**Figure 2.10** CNF synthesized from oil of *Linum usitatissimum* by CVD method.

### 2.3.4 CNF as Electrocatalysts for Microbial Energy Harvesting

CNFs synthesized from biogenic material is being considered as an alternative catalyst for the oxygen reduction reaction. Zhou *et al.* (2016) [47] have fabricated heteroatom-doped (N and S) porous CNFs via pyrolysis of natural spider silk as a precursor. The CNFs have exhibited very good oxygen reduction activity (half-wave potential of 0.85 V and on-set potential of 0.98 V vs. RHE), superior to that of the Pt/C and many metal-free carbon catalysts under alkaline conditions. The catalytic proficiency of the SS-derived CNFs is attributed to the highly positive charges on the carbon atoms due to the presence of the electronegative nitrogen and sulfur atoms within the carbon lattice; and their high surface area and large number of active sites due to their nano-fibrillar structure and abundant pores. They suggested that since these CNFs exhibited excellent oxygen reduction activity in neutral solution (pH 7.0), they used it as cathode catalysts in microbial fuel cells (MFCs), which gave a maximum power density of 1800 mW/m<sup>2</sup> that is 1.56 times more than with a Pt/C cathode.

### 2.3.5 CNF as Regenerative Medicine

Studies are being conducted on CNF for its use in bone regeneration, neural regeneration, scaffolds; the role of adhesive protein adsorption in drug and gene delivery, etc. For such applications CNFs have to be specifically functionalized to improve their biocompatibility. In the field of regenerative

medicine, these nanofibers are becoming increasingly attractive as they can be modified to be integrated into human bodies for promoting tissue regeneration and treatment of various diseases. Despite their tremendous potential, toxicity remains a big concern.

### **2.3.6 CNF as Deodorizer**

The patented work of Sharon and Sharon (2018) has shown the potential of CNF synthesized from agro-waste precursors. Unpleasant odors, mal-odor, stench or stink is caused by food being left out for too long, excreta, urine or any rotting material. Presently, ozone and activated carbon is used for removing bad odor. However, CNF synthesized from agro-waste via pyrolysis is more efficient nanomaterial that can deodorize, as it has higher surface area. It has very high deodorizing property and can remove 99% of odor from a room if temperature, humidity and air circulation (fan speed) is met and can absorb CO, paint odors, noxious vapors, toilet smells, etc.

### **2.3.7 CNF Composites for Strong and Lightweight Material**

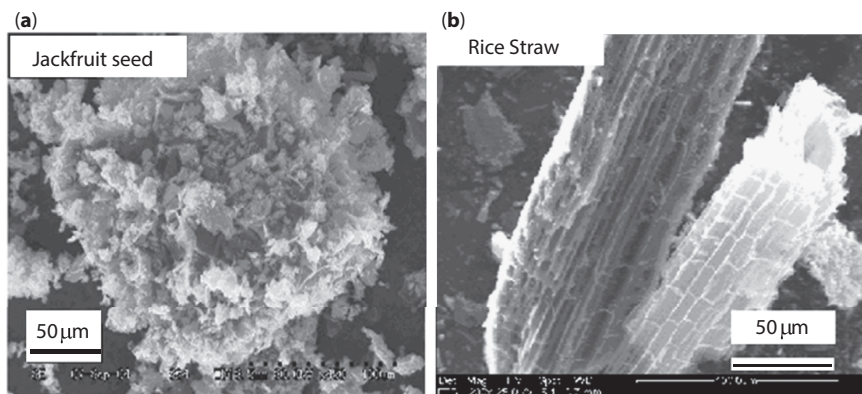
Composites of CNF have been investigated in both fundamental scientific research and practical applications. The need for strong and lightweight materials is being met by promising materials created by reinforcing CNF in polymers for applications that include electrical devices, electrode materials for batteries and supercapacitors, and as sensors. In these applications, the electrical conductivity is a priority need, which depends on the dispersion and percolation status of CNFs in matrix materials. Other important considerations are the effects of the aspect ratio, percolation backbone structure and fractal characteristics of CNFs and the non-universality of the percolation critical exponents on the electrical properties. Apart from the electrical property, the thermal conductivity and mechanical properties of CNF composites also add to the utility of CNF composites, including the melt mixing and solution process, especially for their applications as sensors and electrode materials. Significant application of composite materials has contributed a lot in the defense, aeronautical and automobile industries because of their specific modulus and high strength characteristics. In composite material, CNF-reinforced mat with polymer epoxy resin composites and CNF/polyvinyl alcohol (PVA) mat have been found to improve the flexural strength of the epoxy resin, with 0.015% CNF in PVA giving a better mechanical strength. Cellulose is another plant metabolite which is also secreted by many bacteria and extracted from various marine filamentous algae. Cellulose nanofibers are considered as efficient replacements

for conventional polymers due to their nano size, ease of preparation, low cost, tunable surface and enhanced mechanical properties. CNF obtained from algal sources is less compared to plants and bacterial sources. CNF finds a wide variety of applications such as drug carriers, tissue regenerating scaffolds, water purification, etc.

### 2.3.8 Biogenic CNF as Supercapacitor

Another important application of CNMs is in the development of supercapacitor. Among the CNF obtained from seeds of various plants, it was found by Khairnar *et al.* (2008) that jackfruit seeds gave the highest capacitance of 92F/g [45]. It has been observed that though the CNM from rice straw has a higher surface area ( $140.15 \text{ m}^2/\text{g}$ ) than that obtained from jackfruit seeds ( $114.02 \text{ m}^2/\text{g}$ ), the capacitance obtained from the CNM of rice straw was lower (83F/g) than that of CNM from jackfruit seed. This apparent anomaly has been resolved by analyzing the SEM micrographs of both the CNMs, which show that CNMs from rice straw show channel-type structure while that from jackfruit seeds show porous but block-type structure (Figure 2.11). The cotton fiber-like structure of the CNM from jackfruit helps in forming the electrical double layer which is not so facile in the CNMs from rice straw.

This study established that for getting higher capacitance, in addition to large surface area CNF should also have a large number of pores in a plane parallel to the plane of the electrode for which the surface of CNM should be fluffy like a cotton ball.



**Figure 2.11** CNF synthesized from seeds of Jackfruit and Rice straw by CVD method (Courtesy of Vilas Khairnar).

### 2.3.9 Plant-Derived CNM for Use in Coatings

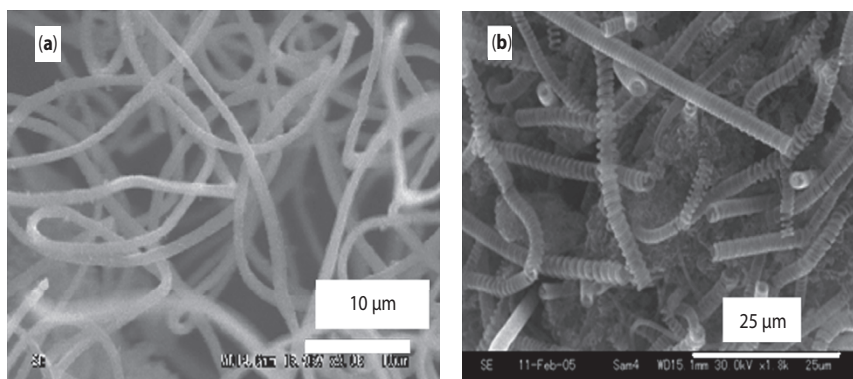
A platform for the development of new environmentally friendly coatings is provided by CNM from burnt grass (*Desmostachya bipinnata*). It is found that a miniscule incorporation of the ash improves the overall property [48] of the composite in manifold ways. Studies of the properties and applications of various CNFs synthesized from plant precursor is still in progress. Hence, it may be concluded that CNF synthesized from plant precursors has potential for significant applications in various fields.

## 2.4 Comparative Structure of Chemically and Biogenically Synthesized CNF

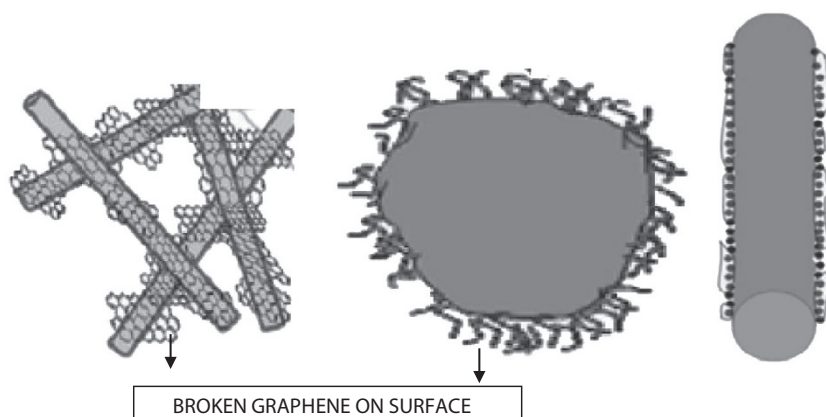
### 2.4.1 CNF Synthesized from Chemical Precursors

Two methods are mainly used to prepare CNF from chemical precursors. One is catalytic thermal chemical vapor deposition (CVD) growth, and the other is electrospinning followed by heat treatment; whereas CNF is usually prepared mostly by CVD from biological precursors, it could be either with or without catalyst. To fabricate CNFs using the catalytic CVD growth method, some metals and alloys (Fe, Co, Ni, Cr, Mo and V) are chosen as the catalysts. Catalyst plays a very important role in deciding the morphology of CNF. Shapes of catalytic nano-sized metal particles decide the structures of the CNF. In the electrospinning process, the polymer types and the carbonization process play the most important roles in the type and quality of the CNFs. Vapor-grown carbon fibers (VGCs) or vapor-grown carbon nanofibers (VGCNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates. Whereas carbon with graphene layers wrapped into perfect cylinders are called carbon nanotubes.

Chemical precursors that have been used for the synthesis of CNF are methane, carbon monoxide, synthesis gas ( $H_2/CO$ ), and liquid organic waste from petrochemical industries, which include acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ) (Figure 2.12), and pyrene ( $C_{16}H_{10}$ ); and various carbon-containing gases, such as carbon monoxide (CO), methane ( $CH_4$ ), etc., are also used as the carbon source. Che *et al.* (1998) have shown that solid carbon nanofibers are formed by increasing the deposition time at 900 °C in a CVD unit when ethylene and pyrene were used as precursor [53]. The morphologies of the CNF synthesized from chemical precursors could be coiled or straight CNFs.



**Figure 2.12** CNF synthesized from chemical precursors: (a) Ethanol and (b) Acetylene using CVD method in our lab.



**Figure 2.13** Schematic illustration of CNF and CNT.

#### 2.4.2 CNF Synthesized from Plant Parts or Plant Metabolites as Precursors

The CVD method is mostly used for the synthesis of CNF from plant parts (stem, leaf, seeds) or plant metabolites that are rich in carbon or hydrocarbons (oil, resins, latex). CNF synthesized from plant parts usually show unique structures that are similar to the carbon-based anatomy of that particular plant part (Figures 2.5, 2.8 and 2.9), whereas plant metabolites produce CNF having similarities with the structure of CNF produced when chemical precursors are used.

## 2.5 Concluding Remarks

In this chapter, carbon nanofibers (CNF) synthesized from plant parts and plant metabolites were investigated both scientifically and for practical applications. Apart from petroleum hydrocarbon-based precursors, natural precursors are accepted as an alternative to the synthesis of CNFs. In this chapter, factors for biogenic synthesis using the CVD system and the factors affecting it were touched upon. Yield of different unique morphologies of CNF that varied with precursors were presented. The impact of a wide range of temperatures on the quality and quantity of yield and effect of temperature on the performance of metal catalysts, such as deciding solubility of carbon, is believed to increase at higher temperatures, and the catalyst and catalyst support systems enhance the rate of growth of CNFs. The effect of carrier gas is not yet very conclusive. Hydrogen seems to have a marked influence on superior CNF synthesis. Despite numerous studies on CNFs being synthesized from natural precursors, there is still room for further understanding of the mechanism of CNF growth by CVD method. CNF composites are able to be applied as promising materials in many fields, such as electrical devices, electrode materials for batteries and supercapacitors, etc.

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# Role of Nanocatalysts in Synthesis of Carbon Nanofiber

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*A positive attitude causes a chain reaction of positive thoughts, events and outcomes. It is a catalyst and it sparks extraordinary results.*

Wade Boggs

## 3.1 Introduction

Catalysis plays a central role in chemical transformations and lies at the heart of countless chemical protocols, from academic research at laboratory level to the chemical industry level. By using catalytic reagents, one can reduce the temperature of a transformation, reduce reagent-based waste and enhance the selectivity of a reaction that potentially avoids the unwanted side reactions. Drivers for development of advanced catalysts include (i) production of high value products with inexpensive raw materials, (ii) energy efficient and environmentally benign chemical conversion processes, (iii) increasingly stringent environmental regulations, and (iv) low-cost catalysts such as with reduction or replacement of precious metals [1].

Catalysis occupies an important place in chemistry, where it develops in three directions, i.e., heterogeneous, homogeneous and enzymatic. Both the homogeneous and heterogeneous catalysis has its own merits and demerits due to which there is urgent need of a new catalytic system, which should be active like homogeneous catalysis, and should also be easily recoverable like heterogeneous catalyst. Considering the advantages of

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these two catalytic approaches, on the one hand heterogeneous catalysts are easy to recover but present some drawbacks, such as the drastic conditions they require to be efficient and mass transport problems; on the other hand, homogeneous catalysts are known for their higher activity and selectivity, but the separation of expensive transition metal catalysts from substrates and products remains a key issue for industrial applications.

Introducing a catalyst increases the speed of a reaction in one of three ways;

- It can lower the activation energy for the reaction,
- Act as a facilitator and bring the reactive species together more effectively, or
- Create a higher yield of one species when two or more products are formed.

## 3.2 Nanocatalysts

Nanomaterials are more effective than conventional catalysts for two reasons. First, their extremely small size (typically 10–80 nm) yields a tremendous surface area-to-volume ratio. Also, when materials are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons account for the versatility and effectiveness of nanocatalyst.

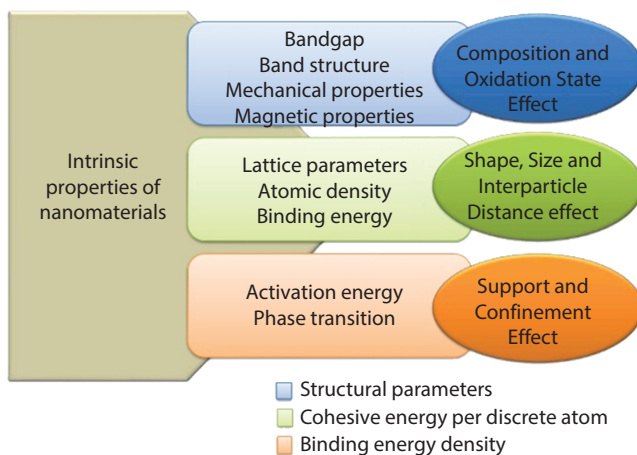
Since the end of the 1990s, with the development of Nanoscience, nanocatalysis has emerged as a domain at the interface between homogeneous and heterogeneous catalysis, which offers unique solutions to answer the demanding conditions for catalyst improvement [2, 3]. The main focus is to develop well-defined catalysts, which may include both metal nanoparticles and a nanomaterial as support. These nanocatalysts should be able to display the ensuing benefits of both homogeneous and heterogeneous catalysts, namely high efficiency and selectivity, stability and easy recovery or recycling. Specific reactivity can be anticipated due to the nano dimension that can afford specific properties which cannot be achieved with regular, non-nano materials. Nano-catalytic system allows rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. Because of its nano size (high surface area) the contact between reactants and catalyst increases dramatically. Insolubility in the reaction solvent makes the catalyst heterogeneous and hence can be separated out easily from the reaction mixture.

Nanoparticles are recognized as the most important industrial catalyst and have wider application ranging from chemical manufacturing to energy conversion and storage. Its variable and particle-specific catalytic activity is due to their heterogeneity and their individual differences in size and shape. The fine tuning of nanocatalyst, in terms of composition (bimetallic, core-shell type or use of supports), shape and size has accomplished greater selectivity. Thus, the question here is how the physical properties of nanoparticles affect their catalytic properties, and how fabrication parameters can in turn affect those physical properties. By a better understanding of these, a scientist can design nanocatalysts, which are highly active, highly selective, and highly resilient. All these advantages will enable industrial chemical reactions to become more resource efficient, consume less energy, and produce less waste, which also helps to counter the environmental impact caused by our reliance on chemical processes.

### 3.2.1 Concept of Nanocatalysis

The concept behind nanocatalysis may be understood by considering the impact of the intrinsic properties of nanomaterials (Figure 3.1) that have a vital impact on their catalytic activity and may be categorized as:

- (i) Quantities that are directly related to bond length, such as the mean lattice constant, atomic density, and binding energy. Lattice contraction in a nano-solid induces densification and surface relaxation.
- (ii) Quantities that depend on the cohesive energy per discrete atom, such as self-organization growth; thermal stability; coulomb blockade; critical temperature for phase transitions, evaporation in a nano-solid; and the activation energy for atomic dislocation, diffusion, and chemical reactions.
- (iii) Properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determine the entire band structure and related properties such as band gap, core level energy, photo-absorption, and photoemission.
- (iv) Properties from the joint effect of the binding energy density and atomic cohesive energy such as the mechanical strength Young's modulus, surface energy, surface stress, extensibility and compressibility of a nano-solid, as well as the magnetic performance of a ferromagnetic nano-solid.



**Figure 3.1** Diagram of effect of intrinsic property on nanocatalyst. (Source: <https://www.slideshare.net/foolishcrack/nanocatalyst-108342252>) [55].

By precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nano components, they can be widely used in catalysis with newer properties and activity.

### 3.2.2 Metallic Nanoparticles (NP) as Catalyst

About two-thirds of chemical elements are metals. Using the molecular orbital description, the generation of a metallic material can simply be understood as the formation of an infinitely extended molecular orbital, leading to energy bands. The development of a metallic band structure requires a minimum number of electronic levels, which have to be very similar in energy so that electrons can move by only thermal activation. The most important properties of a metal are:

- **Its ability to transport electrons**, i.e., the property of conductivity: The conductivity is based on the relation between occupied and unoccupied electronic bands, as electrons can become mobile only if the energy band of which they are part is not fully occupied. Most of the d-type transition metals are characterized by only partially filled d-orbitals so that incompletely filled bands result in any case.  $d^{10}$  elements, such as palladium, platinum or gold, have nearby s-bands that can be used for electron transport.

- **Magnetism:** The existence of unpaired electrons is a condition for magnetism; however, only the uniform orientation of free spins over a large area results in ferromagnetism (for example, the well-known ferromagnetism of iron, cobalt and nickel); while non-oriented free spins produce paramagnetic materials (for example, copper and gold).

Metallic NPs, also called nanoclusters, are pieces of metal at the nanometer scale. They can be nanocrystalline, aggregates of crystallites or single crystallites (nanocrystals). Due to the number of bound metal atoms they contain, metallic nanoparticles display intermediate electronic energy levels in comparison with molecules and metal bulks. (As a result, particular physical and chemical properties are expected for metallic nanoparticles that can lead to applications in various areas such as in catalysis [4]. Metallic nanoparticles are generally considered as intermediate species between metal complexes and metal surfaces, and the term “*nanocatalyst*” is now commonly used to describe them.

For synthesizing carbon nanomaterials (CNMs), typically nanometer-sized metal particles are required to enable hydrocarbon decomposition at a lower temperature than the spontaneous decomposition temperature of the hydrocarbon [4, 5]. The most commonly used metals are iron, cobalt and nickel for two main reasons: i) the high solubility of carbon in these metals at high temperatures, and ii) the high carbon diffusion rate in these metals. Besides that, the high melting point and low equilibrium-vapor pressure of these metals offer a wide temperature window of CVD for a wide range of carbon precursors [6].

Nanoparticles consisting of small metal or metal oxide crystallites in the range of a few nanometers (1–100 nm) are important for catalysis and adsorption. Nanoparticles have higher effective surface area and improved physicochemical properties giving better performance. The uniform shape and size of catalysts are particularly important for structure-sensitive reactions where different types of surface metal atoms, such as corners, edges or terrace atoms, possess quite different properties. Menezes *et al.* (2013) have studied the effect of particle size on catalytic activity of titania-supported Au-Ag (1:1) nanoparticles for CO oxidation. They observed that reactivity of the catalysts increased as size of the nanometals decreased [7].

### 3.2.3 Types of Nanometals as Catalyst

The types of nanometals as catalyst discussed here are based on their physical characteristics.

### 3.2.3.1 *Nanometal Colloids as Catalysts*

In the precursor concept, the nanometal colloids can be tailored for support by modifying them with lipophilic or hydrophilic protective coatings. Adsorption onto the support is achieved by dipping the material into a solution of the particles. Surfactant-stabilized nanometal colloid catalysts have been found to surpass conventional catalysts for hydrogenation and oxidation reactions. The first intramolecular Pauson-Khand reaction in water was successfully carried out by using aqueous colloidal cobalt nanoparticles as the catalyst.

### 3.2.3.2 *Nanoclusters as Catalysts*

Metal nanoclusters have also been found to be good catalysts. Metal clusters retain their activity for extended periods of time and over a range of substrates. Gold nanoclusters have also exhibited catalytic activity for the low temperature oxidation of carbon monoxide, even though bulk gold is inactive. Nanoparticles supported on polymers have been found to catalyze hydrogenations and carbon-carbon coupling reactions. Colloids of bi- and tri-metallic nanoclusters have been shown to be active and selective catalysts in the Suzuki cross-coupling, Pauson-Khand, and hydrogenation reactions.

### 3.2.3.3 *Nanoparticles as Catalysts*

Metal nanoparticles on a variety of supports have also been investigated as catalysts. Zinc and platinum nanoparticles supported on a zeolite matrix exhibited high aromatizing activity in the conversion of lower alkanes. Nanoscale cobalt particles dispersed in charcoal were used as catalyst for the Pauson-Khand, reductive Pauson-Khand, and hydrogenation reactions.

### 3.2.3.4 *Nanopowder as Catalysts*

Usually powder of silica and platinum nanoparticles are used as nanocatalyst. It has exhibited very strong catalytic activity for hydrolyzation reactions. Intradendrimer hydrogenation and carbon-carbon coupling reactions took place in a variety of solvents (water, organics, biphasics, supercritical CO<sub>2</sub>) using dendrimer-encapsulated metal nanoparticles.

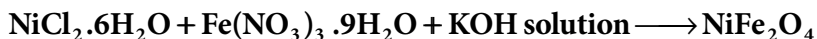
## 3.3 **Methods for the Preparation of Nanoparticles**

It is a challenge to prepare nanoparticles of uniform shape and size by conventional methods. Various new preparation methods are reported that give nanoparticles with narrow size distribution. Some of the reported methods are:

- Hydrothermal method of metal nanoparticles
- Microwave-irradiated method of metal nanoparticles
- Dendrimer-assisted method of metal nanoparticles
- Reverse micelle method of metal nanoparticles
- Co-precipitation method of metal nanoparticles
- Biogenic synthesis of metal nanoparticles

### 3.3.1 Hydrothermal Method of Metal Nanoparticles

In a hydrothermal process, precursor solution in the presence of an alkali is autoclaved at a certain temperature for a specific time. In a typical process, aqueous solution of precursor and KOH is mixed and placed in a Teflon-lined stainless-steel autoclave. The autoclave is maintained at 70–200 °C for 10–24 h depending on the process and then air-cooled to room temperature. Resulting precipitate is collected by filtration, washed and finally dried. For example, nickel ferrite particles prepared by hydrothermal process resulted in particles of size distribution from 40–90 nm [8].



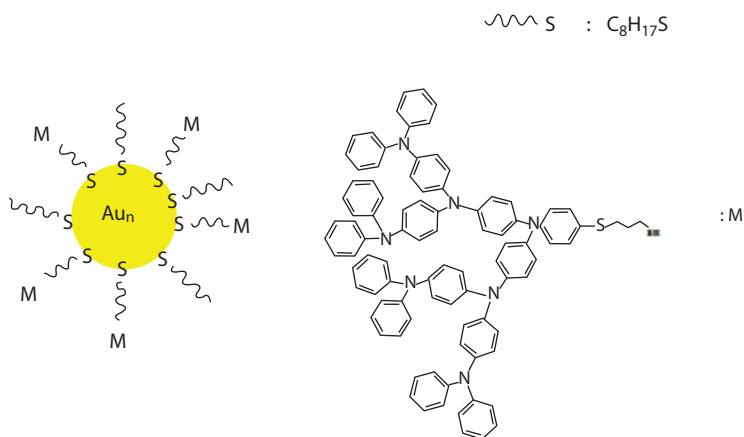
### 3.3.2 Microwave-Irradiated Synthesis of Metal Nanoparticles

Microwave-irradiated synthesis is a new promising technique for the preparation of size-controlled metallic nanostructures. Xu *et al.* (2010) reported the preparation of Pt nanoparticles supported on CNTs [9]. In this method, solutions of Pt precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol and KOH are mixed in a vial and CNTs are uniformly dispersed in mixed solution. The closed vial is then placed in a microwave oven (2450 MHz, 800 W) and heated for the required time. The resulting suspension was filtered and dried at 120 °C. This preparation method resulted in Pt nanoparticles on the surface of CNTs having uniform spherical shape with diameter of  $15 \pm 3$  nm.

### 3.3.3 Dendrimer-Assisted Synthesis of Metal Nanoparticles

Dendrimer is highly ordered branched poly-amidoamine macromolecule with tree-like topology and is used in the preparation of nanomaterial. Dendrimers have multiple coordination sites that are utilized to coordinate metal ions and synthesize metal clusters. In this method, metal ions in solution are complexed to dendrimer, mostly with amine groups in the outer shell of OH-terminated poly-amidoamine. Complexed metal ions are subsequently reduced to metal





**Figure 3.2** Gold clusters with DPA dendron.

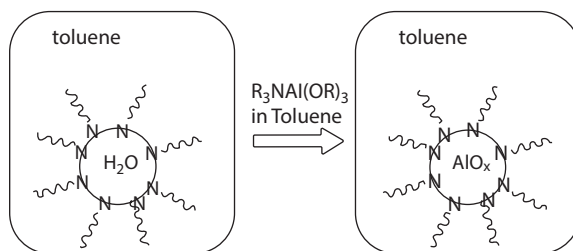
atoms which agglomerate into metal particle. Men *et al.* (2006) [10] reported the synthesis of dendritic polyphenylazomethines (DPA) dendron-encapsulated gold clusters having average cluster diameter of 2.2 nm (Figure 3.2).

### 3.3.4 Reverse Micelle Method of Metal Nanoparticles

Reverse micelles are formed when surfactant molecules possessing polar head group and hydrophobic tail are placed in nonpolar solvent. In reverse micelle structure, surfactant molecules aggregate into nano-sized spherical structures having core of polar head groups and shell of hydrophobic tails. If a small amount of polar solvent is present in the mixture, it would be enclosed in a core of reverse micelles. If this polar solvent contains an oxide precursor, then controlled hydrolysis of precursor will be achieved by mixing a small amount of water and small particles of metal oxide will form at core. For example, nano  $\text{Al}_2\text{O}_3$  is prepared by this method.

A solution of inverse micelles is first formed by adding a long-chain alkyl-amine to a toluene solution. A small amount of water is trapped in the reverse micelle core. Mixing the reverse micelle solution with an aluminum alkoxo amine adducts results in hydrolysis of the aluminum alkoxide adduct and formation of nano-sized particles of aluminum hydroxide after drying (Figure 3.3).

Reverse micelle synthesis method is also reported for preparation of supported metal catalysts. Cheney *et al.* (2011) reported synthesis of alumina-supported Pt/Ni bimetallic catalysts by reverse micelle synthesis method [11]. In this method, two microemulsions were created by mixing 15% water, 10% surfactant and 75% hydrocarbon (cyclohexane and propanol). Ni and Pt precursors were added to microemulsion-1 and hydrazine to the microemulsion-2.



**Figure 3.3** Schematics showing formation of nano-sized particles of aluminum hydroxide by reverse micelle method. (Source [https://edurev.in/studytube/Nano-metal-or-metal-oxide-catalysts--Catalyst-Scie/9b6f7900-95f8-4c67-a444-ef2f86a4b1fd\\_t#](https://edurev.in/studytube/Nano-metal-or-metal-oxide-catalysts--Catalyst-Scie/9b6f7900-95f8-4c67-a444-ef2f86a4b1fd_t#)) [56].

Each mixture was stirred separately for 1 h to allow micelles to equilibrate. In microemulsion-1, reverse micelles were formed having aqueous core and the Pt and Ni precursors were dissolved in aqueous polar core of the reverse micelles. Thereafter, the microemulsion-2 containing the reducing agent was added to the microemulsion-1 for *in-situ* chemical reduction of the metals at reverse micelle core. The alumina support was added to the solution and titrated with acetone to disrupt the micelles and precipitate the nanoparticles onto the support. The supernatant was decanted and the catalyst powder was rinsed with acetone. Residual surfactant was removed by giving heat treatment in oxygen environment.

### 3.3.5 Co-Precipitation Method of Metal Nanoparticles

In the co-precipitation method, the metal catalysts with different compositions are prepared according to the ratio of the metal content required. Solution A was composed of aluminum nitrate, which helps to generate alumina (Al<sub>2</sub>O<sub>3</sub>) to serve as a supporter for the transition metal catalysts in the transition metal nitrate, dissolved in distilled water. The coagulation phenomenon occurs when the temperature is increased. To control the interparticle coagulation of transition metals, such as Fe, Co, and Ni, which all have catalytic activity against the reaction gas during high-temperature reaction, another Solution B, composed of ammonium molybdate and distilled water was added with Solution C made of ammonium carbonate, which serve as a precipitator to precipitate the transition metals and the aluminum included in Solution A. Precipitation was induced by gradual blending of the mixture composed of Solutions A and B and the mixture of Solution C. This step was followed by agitation for stability of the precipitation. These solutions were sufficiently stirred to stabilize the precipitates; moisture was removed by filtering; and they were dried for more than 12 h in a 110 °C oven. Fully dried precipitates were made into powder, and this powder of a metal catalyst was used as the catalyst in the synthesis of carbon nanofibers.

### 3.3.6 Biogenic Synthesis (Green Synthesis) Method of Metal Nanoparticles

Green or Biogenic synthesis is an eco-friendly protocol for synthesis of a wide range of nanomaterials, including metal and metal oxides such as gold (Au), silver (Ag), copper oxide (CuO), and zinc oxide (ZnO), using various biological materials such as bacteria, fungi, algae, and plant extracts. Biogenic synthesis is also called Green synthesis because it prevents or minimizes waste; there is reduction of derivatives and pollution, and the use of safer (or nontoxic) solvent and auxiliaries as well as renewable feedstock. The reaction parameters for biogenic synthesis involve solvent, temperature, pressure, and pH conditions (acidic, basic, or neutral). Availability of effective phytochemicals in various biological materials that act as reducing agents that convert metal salts into metal nanoparticles are ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, reductase, and ascorbic acids. Green synthesis of metallic nanoparticles is a one-pot or single-step eco-friendly bio-reduction method that requires relatively low energy to initiate the reaction.

- **Bacteria** can synthesize metal NP both internally (intra-cellular) and externally (extra-cellular). Some examples of bacterial strains that have been extensively exploited for the synthesis of bio-reduced silver nanoparticles with distinct size and shape morphologies include: *Aeromonas* sp. SH10, *Arthrobacter gangotriensis*, *Bacillus amyloliquefaciens*, *Bacillus cecembensis*, *Bacillus cereus*, *Bacillus indicus*, *Bacillus subtilis*, *Corynebacterium* sp. SH09, *Enterobacter cloacae*, *Escherichia coli*, *Geobacter* spp., *Lactobacillus casei*, *Phaeocystis antarctica*, *Plectonema boryanum* UTEX 485, *Pseudomonas proteolytica*, *Rhodopseudomonas capsulata*, *Shewanella algae*, and *Shewanella oneidensis* [12, 13]. To synthesize metal NPs, microbes, fungi or algae first capture the metallic ions on the surface via electrostatic interactions between ions and negatively charged cell wall enzymes or inside the microbial cells, and then the metal ions are reduced into metal nuclei, which subsequently grow into nanoparticles by the action of enzymes or reducing agents. The two identified reducing agents in the biosynthesis of nanoparticles are NADH (nicotinamide adenine dinucleotide) and NADH-dependent nitrate reductase [14].
- **Fungi**: Fungi-mediated biosynthesis of metal and metal oxide nanoparticles is also a very efficient process for the generation of monodispersed nanoparticles of metal/metal oxide of silver,

gold, titanium dioxide and zinc oxide, with well-defined morphologies. They act as better biological agents for the preparation of metal and metal oxide nanoparticles, due to the presence of a variety of intracellular enzyme [15] as well as enzymes/proteins/reducing components present on the cell surfaces [16].

- **Plants:** Plants have biomolecules like carbohydrates, proteins, and coenzyme with exemplary potential to reduce metal salt into nanoparticles. Various plants, such as *Aloe barbadensis*, *Avena sativa*, *Medicago sativa*, *Ocimum sanctum*, *Citrus limonia*, *Azadirachta indica*, *Hibiscus rosa-sinensis*, *Coriandrum sativum*, *Camellia sinensis*, *Brassica juncea*, *Cymbopogon flexuosus*, *Helianthus annuus*, *Acalypha indica*, and *Calotropis gigantea*, have been utilized to synthesize silver, gold and ZnO nanoparticles [17–19]. Various nano-metal catalyst synthesis approaches are presented in Figure 3.4.

Plant leaf extracts play a dual role by acting as both reducing and stabilizing agents in nanoparticles synthesis [20]. The phytochemicals present in them

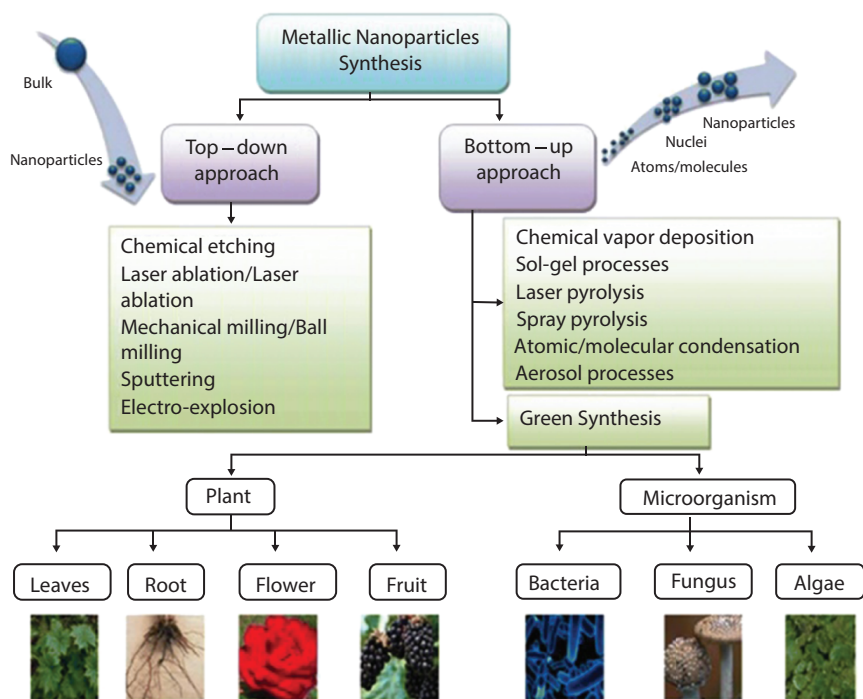
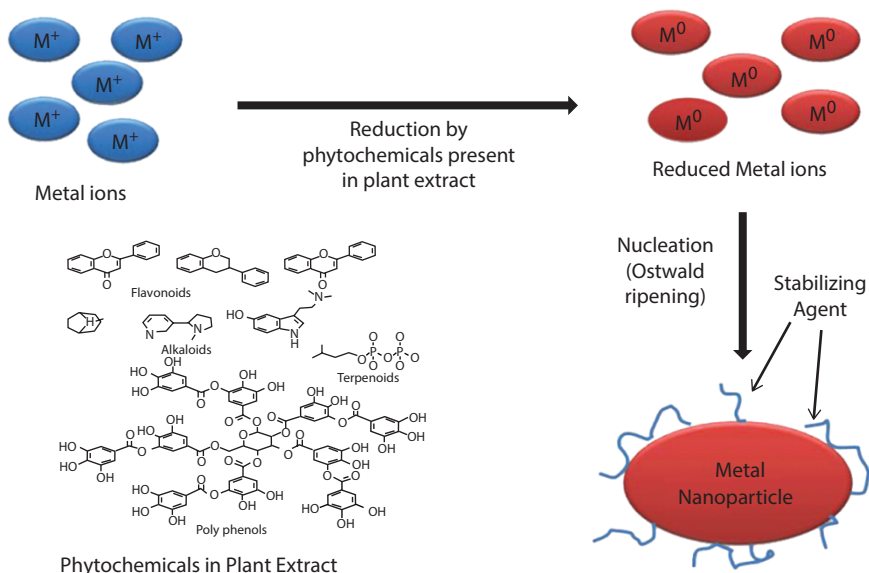


Figure 3.4 Different synthesis approaches available for the preparation of metal catalysts.



**Figure 3.5** The process of nanoparticle formation by plant extract. (Source: Dizai *et al.* 2014) [24].

that support the synthesis of nano-metals by bio-reduction are flavones, terpenoids, sugars, ketones, aldehydes, carboxylic acids, and amides. *Flavonoids* contain various functional groups, which have an enhanced ability to reduce metal ions (Figure 3.5). The reactive hydrogen atom is released due to tautomeric transformations in flavonoids by which the enol form is converted into the keto form. This process is realized by the reduction of metal ions into metal nanoparticles. In sweet basil (*Ocimum basilicum*) extracts, enol to keto transformation is the key factor in the synthesis of biogenic silver nanoparticles [21]. Monosaccharide glucose present in plant is capable of participating in the formation of metallic nanoparticles with different sizes and shapes, whereas fructose-mediated gold and silver nanoparticles are monodispersed in nature [22]. Proteins with functionalized amino groups ( $-NH_2$ ) and amino acids (viz, cysteine, arginine, lysine, and methionine) also have different ways of reducing the metal ions. Moreover, the functional groups (such as  $-C-O-C-$ ,  $-C-O-$ ,  $-C=C-$ , and  $-C=O-$ ) present in phytochemicals, such as flavones, alkaloids, phenols, and anthracenes, are the capping ligands of the nanoparticles and can help to generate metallic nanoparticles [23].

### 3.4 Role of Nanocatalyst in the Production of CNF

It is well known that the mechanical, physical, and chemical properties of nanoparticles may differ considerably from those of bulk substances. The

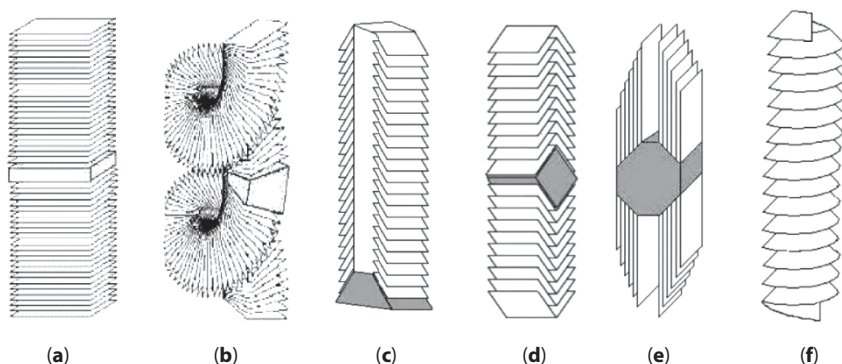
deposition over support often endows particles with novel or improved properties. These changes are provided by the change of electronic and structural properties, strong interaction with the support, and increase of the particle/support interface length taking place with metal dispersion. These factors are closely interrelated and determine, for example, the number of catalytically active sites and adsorption energies during catalytic reactions. Thus, the dispersion of a supported metal can be extremely high, making almost every metal atom accessible to reactants. Advantages of metal dispersing over support widely used for catalytic applications are also applicable for different fields of nanotechnology.

Because of their novel properties, which can be realized in a variety of ways in numerous applications, CNFs have received a great deal of attention from both the research and industrial communities. Several academic and industrial research groups have directed their efforts toward synthesizing and optimizing the growth of these CNFs. In its simplest form, the catalytic synthesis of CNFs consists of formation of these fibers on metallic catalysts in the form of powders, foils, gauzes, or supported particles. The process consists of reducing the catalyst sample in a hydrogen-inert gas stream at a somewhat lower temperature, followed by heating the catalyst up to the reaction temperature, subsequent to which the reaction mixture, consisting of hydrocarbon, hydrogen, and inert gas, is introduced into the system [25–30]. The reaction proceeds for periods ranging from a few minutes to several hours. Several different metallic and bimetallic catalysts can be used. The most commonly used catalysts for CNF synthesis are iron, cobalt, nickel, and copper, both in bulk and in supported form. Lower hydrocarbons, such as methane, ethylene, acetylene, or benzene, and carbon monoxide are the common sources of carbon material. The most common mechanism proposed in the literature for the synthesis of CNFs consists of decomposition of the hydrocarbons on the metal surface, releasing carbon atoms. These carbon atoms then form metal carbides that dissolve and diffuse through the bulk of the metal, resulting in the deposition of CNFs at the other end of the metal particles [31–33]. Despite great advances in synthesis methods and efforts to understand the mechanism of nucleation and growth of CNFs, continuous production of these fibers has proven to be challenging.

### 3.5 Different Types of CNF

Carbon nanofibers of various morphologies have been synthesized (Figure 3.6). Some of them are mentioned below:

- **Platelet-like CNF** is composed of small graphene layers perpendicular to the fiber axis and the fiber must contain a non-negligible



**Figure 3.6** CNF of different morphologies: (a) Platelets, (b) Spiral platelets, (c) Fishbone hollow core, (d) Fishbone solid, (e) Ribbon, (f) Stacked cup.

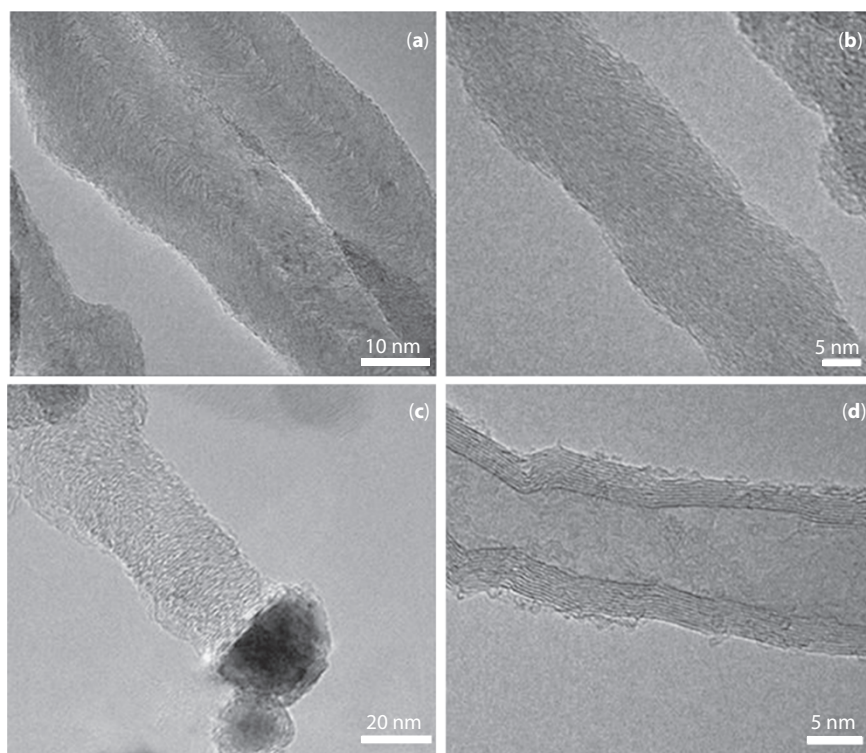
amount of hydrogen or other heteroatoms for the stabilization of the plates. The fibrils can also be coiled, as shown in Figure 3.4a,b [34]. For the growth of platelet, CNFs from propane Ni/Al<sub>2</sub>O<sub>3</sub> catalyst have been found to be good catalyst.

- **Fishbone-like CNF or Herringbone CNF** is where the graphene layers are inclined with respect to the fibril axis. Consequently, hydrogen is also required to stabilize the edges. Fishbone CNFs can have either a hollow core (Figure 3.4c) or a solid core (Figure 3.4d). The herringbone CNFs are synthesized over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst using methane and propane as carbon sources.
- **CBF Ribbons** are comprised of straight, unrolled graphene layers that are parallel to the fibril axis with noncylindrical cross sections (Figure 3.4e). Transition metal Co, originated from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O doped in spinning solution, serves as both template of mesopores and catalyst for graphitic structure [35].
- **Stacked-Cup CNF** This form of CNF is a continuous layer of rolled (spiral) graphene along the fiber axis. The spiral orientation of these nanofibers yields a truncated cone arrangement along the axis with a wide internal hollow space, as shown in Figure 3.4f. SiO<sub>2</sub> particles are used as catalysts for stacked-cup carbon nanotube formation in a spray pyrolysis chemical deposition method from ethanol where SiO<sub>2</sub> particles are reduced to SiC following a carbon dissolution mechanism [36].
- **Thickened Tubular CNFs** are comprised of a base structure of one of the previously mentioned catalytic nano filaments (CNF or CNT) with a variable coating of amorphous carbon produced by CVD method using Fe/Al<sub>2</sub>O<sub>3</sub> catalyst with ethylene as a carbon precursor by CCVD.



Figure 3.7 shows CNF grown using catalytic chemical vapor deposition (CCVD) with methane as carbon source and a hydroxyapatite-supported nickel (Ni/HAp) as catalyst. The catalyst, which contained approximately 14 wt% Ni, was prepared using the incipient wetness method with an aqueous nickel nitrate solution. Three variables were evaluated to optimize the CNF growth process, including the temperature and the time of catalyst reduction as well as the reaction time, at 650 °C. Herringbone bamboo-like CNFs were grown during methane decomposition over Ni/HAp, which was confirmed using transmission electron microscopy [37].

The diameters of the grown CNFs were determined by TEM. As shown in Figure 3.7 the CNF diameters increase as the reduction temperature increases. At 550 °C, CNFs with a diameter of 25–45 nm were grown with a predominant contribution of narrower nanofibers. At 600 °C, a wide distribution of CNF diameters in the range of 25–55 nm was observed. CNFs with a diameter of



**Figure 3.7** TEM images of CNFs with (a & b) herringbone structure without hollow core, synthesized over nickel catalyst using both methane and propane as carbon precursors respectively; (c) The platelet structure in which the graphene layers are aligned perpendicularly to the fiber axis, and (d) the thinnest among the synthesized nanocarbons, with diameters of 10–20 nm [38].



36–55 nm were obtained when the Ni/HAp catalyst was reduced at 650 °C. The shift in the CNF diameter to larger values as the reduction temperature increases was due to an increase in the Ni crystallite size. CNFs with larger diameters were also grown by increasing the reaction temperature [38].

### 3.6 Synthesis of Carbon Nanofiber (CNF) Using Nanocatalysts

Different methods, such as incipient-wetness impregnation, ion exchange, organometallic grafting, electron beam evaporation, and deposition/precipitation followed by reduction, are used to prepare noble metal nanoparticles supported on carbon fibrous materials. In all cases, a delicate optimization of carbon surface chemistry is needed to achieve optimal interaction between the support and metal precursor.

Due to their unique nature, carbon nanofibers are considered as exciting supports for noble metal nanoparticles. Indeed, hollow nanotube cavities can be used to control a particle size and shape. High metal dispersion was obtained on CNTs even if the specific surface area of the support was only 25 m<sup>2</sup>/g. Nanotubes can be filled by metals during the arc-discharge synthesis in the presence of metals or through opening and filling the tubes by a metal precursor followed by reduction. It is also possible to remove unwanted metal particles from the outside surface of CNTs [39]. The process took place via reduction of [PdCl<sub>4</sub>]<sup>2-</sup> anions and simultaneous encapsulation of Pd nanoparticles in CNTs during rolling of graphene sheets from the anode.

Cu particles supported on different types (fishbone, platelet, ribbon, and tubular) of CNFs were deposited from aqueous salt solutions [40]. If Cu nanoparticles were located on the edge sites of nanofibers, they adopted a thin faceted morphology, indicating a strong metal-support interaction. The particles formed in such a way were very stable with respect to sintering. However, the particles tended to acquire a globular geometry if the copper was supported on AC or the basal planes of graphite, showing a very weak interaction with the support. Thus, the fishbone and platelet CNFs were the best supports to provide small particles with a narrow size distribution. A precursor salt and carbon surface functionality also affect the particle size distribution and stability.

Supported Cu nanoparticles (<10 nm) were prepared using CNFs with a diameter ranging from 100 nm. Carbon nanofibers were impregnated with a copper salt solution, dried and treated by H<sub>2</sub> (773 K). The electronic properties of the nanoparticles differed considerably from those of bulk copper. It was noticed that the size of Cu particles was dependent on the

size of CNFs: the smaller the fiber diameter, the smaller the Cu nanoparticle size obtained. However, the nanoparticles were not strongly attached to the support and could be detached by ultrasonic treatment.

The Pd nanoparticles supported on CNFs exhibited a comparable activity in hydrogenation of nitrobenzene to aniline and increased activity in hydrogenation of C=C bond of cinnamaldehyde with respect to the commercial Pd catalyst based on AC. An important advantage of the CNF support is that surface area, size of fibrils, as well as mechanical strength can be controlled and mass transfer limitation can be decreased, because of the absence of micropores. A change of electronic properties of Pd particles provided by interaction with CNFs resulted in a change of their catalytic properties in 1,3-butadiene hydrogenation to butanes. An increase of the Pd<sup>2+</sup> fraction in the catalysts decreases the activity and selectivity.

Pd supported on the fishbone-type CNFs was studied in hydrogen storage. The hydrogen loading of 1.5 wt% was reached at 10 MPa of H<sub>2</sub> pressure for nanofibers with specific surface area of 400 m<sup>2</sup>/g and Pd:C mole ratio close to 1. Hydrogen of 3.1 wt% stored was reported for the 4.1 wt% Pd/MWNT material. However, all these values are well below the 6.5 wt% benchmark set by the U.S. Department of Energy for such kinds of materials.

Carbon nanofibers (CNFs) are hydrophobic, generally without significant functional groups. The diameter of a CNF ranges between 50 nm and 200 nm and that of the carbon nanotubes is usually less than 100 nm. Several methods have been used in the synthesis of CNF.

### 3.6.1 Laser Ablation Method

In laser ablation, a graphite target source with a small amount of catalysts (usually a transition metal) is exposed to a laser beam which vaporizes the graphite and initiates the growth of CNF just in front of the target [41].

### 3.6.2 Chemical Vapor Deposition (CVD)

The CVD method is the most common method for bulk production of carbon nanomaterials. Different hydrocarbons are used as precursor for CNM. At high temperature (between 500 and 1200 °C) under pyrolytic condition, carbon is deposited on various metal catalysts (Fe, Co, and Ni). This method is described in detail in Chapter 1 of this book. The process parameters that are important for the synthesis of CNF are the ratio of hydrogen to carbon source flow, reaction time, and temperature [42].

In the CVD process, CNFs are usually produced by catalytic pyrolysis of hydrocarbons in the presence of a transition metal catalyst and a trace amount

of sulfur to promote the formation of CNF. Precursors that have been successfully used to synthesize CNF by CVD method are methane, carbon monoxide, synthesis gas ( $\text{H}_2/\text{CO}$ ), ethyne or ethane, acetylene, etc. The hydrocarbon or the precursor, along with the catalyst, hydrogen gas, and a sulfur source, are introduced into the reactor. Ferrocene ( $\text{C}_{10}\text{H}_{10}\text{Fe}$ ), dissolved in a suitable solvent, and iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) are commonly used catalyst sources. The organometallic catalyst decomposes, forming clusters of iron (Fe) particles that act as nuclei for the formation and further growth of CNFs. The fibers grow as they move along the reactor, and the diameter of fibers increases by the classic chemical vapor deposition (CVD) mechanism. Both horizontal and vertical reactor configurations have been employed. The fibers coming out of the reactor, along with the off-gases, are trapped and separated via a series of cyclone separators or trap mechanisms located downstream of the reactor. The entire reactor assembly is enclosed within an electric furnace to supply sufficient heat to maintain the pyrolysis temperature of 500 to 1,200 °C. The characteristics of the fibers, such as their thickness and length, are controlled through careful manipulation of the parameters, such as the catalyst concentration, reaction time, and size of the catalyst particles produced. The CNFs prepared by catalytic thermal chemical vapor deposition show different morphologies such as cup-stacked CNF [43] and platelet CNF. For the preparation of CNF by the catalytic vapor deposition growth approach, several types of metal or alloys, which are able to dissolve carbon to form metal carbide, have been used as the catalyst, including iron, cobalt and nickel; chromium, vanadium and molybdenum. Generally, the structures of the CNF are governed by the shapes of the catalytic nano-sized metal particles. The growth mechanism has been proven as the deposition of the hydrocarbons dissolved in the metal particle and precipitated on the metal surface as graphitic carbon.

- **Hydrogen:** The role of hydrogen is to accelerate or suppress the formation of carbon by either decomposing the inactive metal carbides to form active metal [44], or by removing the surface carbon and precursors of carbon which leads to active site blocking.
- **Temperature:** The diffusion and precipitation rates of carbon atoms and availability of carbon atoms are affected by temperature [45]. The precipitation of carbon on the metal catalysts can be either on the surface of CNF or internal. At low temperatures, carbon atoms can only precipitate on the surface areas of the catalyst particles, while the diffusing and dissolution rates of carbon atoms increase with the temperature, and carbon atoms then get into the internal areas of the catalysts to

form CNF [46]. The temperature requirement depends on the precursor used; e.g., methane requires higher temperature than propane due to its higher decomposition energy to carbon and hydrogen (37.8 and 26.0 kJ mol<sup>-1</sup> H<sub>2</sub> for methane and propane, respectively) [47]. Increased reaction temperatures favor the migration of catalyst particles on the support surface, which results in their aggregation, leading to the growth of thicker CNFs [38]. The diameter and the structure of grown CNFs are strongly dependent on the temperature of the CCVD process. The synthesis temperature has an indirect influence on the CNF structure through various diffusion rates of carbon into the catalyst particles and different orientations of the graphene layers precipitated on the metal nanoparticle [38].

- **Growth or Reaction Time:** The growth time plays a major role in tailoring the morphology of nanomaterials in terms of diameter and density of growth [48]. In the initial stage of growth, a part of the metal catalyst (nickel) surface is covered by carbon, leading to formation of relatively catalyst-rich carbon area. In the next stage, dissolved carbon is released to form CNF with the lift-off of the former catalyst-rich carbon particles out of the substrate surface. Generally, the reaction duration is 60 min, while a total time of 3 h is needed for the synthesis of CNF in the decomposition of ethylene over an unsupported Ni-Cu alloy [49].
- **Decomposition of Hydrocarbon:** This is the final stage, where decomposition of hydrocarbon on the new catalyst initiates new deposition of carbons from the same particle, covering the host surface completely by a dense layer of CNF.
- **Size of Catalyst:** It is well known that the diameter of nanofibers is controlled by the size of the catalyst particle responsible for their growth [50]. The parallel orientation of the graphene layers and the lower diameter arose from the changes to the catalyst and the carbon precursor. The use of an iron catalyst promotes the growth of CNTs, whereas nickel favors the formation of herringbone CNFs [51].

### 3.6.3 Self-Propagating High-Temperature Synthesis (SHS) or Combustion Synthesis (CS)

This is a well-known reaction used to fabricate new compounds and structures. Once started, the reaction continues with the help of the energy provided by itself rather than from outside the system. CNF is synthesized by

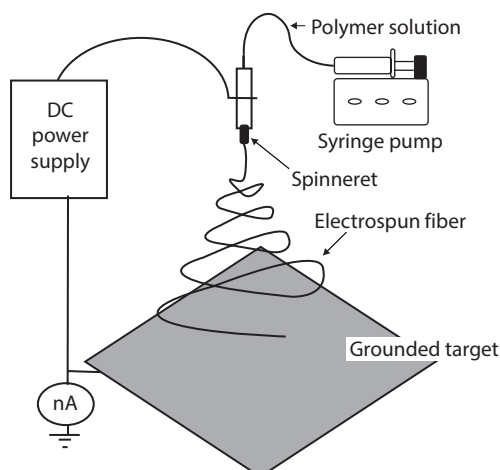
this method, where the exothermic reaction between *aluminum* and *iron oxide* is used for preparing the heat required for SHS. In addition, the iron produced from the reaction can play the role of catalyst for growing the CNFs from activated carbon. Once the process starts, the reaction continues with the help of the energy provided by itself rather than from outside the system. Rapid solidification of products in CS creates nanostructures that would be otherwise difficult to make. Carboniferous materials (soda, limestone, and Teflon) are used along with reducers (magnesium, lithium, and sodium) with the addition of a nickel or iron as a catalyst. The yield of CNTs has shown to be weakly sensitive to the amount of catalyst. They have also found that the carbon source is an important factor: carbonaceous materials which were used required energy to decompose and to take part in the formation of nanostructures, which implies that there are no diluents in the reaction. These conditions cause agglomeration and condensation of the materials, preventing the formation of carbon nanostructures. A simple reaction called a thermite reaction is used to produce CNTs and CNFs in just one step.

#### 3.6.4 Floating Catalyst Method

This is a novel method used to synthesize herringbone-stacked carbon nanofibers in high selectivity using cobaltocene as the catalytic precursor. Thiophene is essential for CNF growth while hydrogen is used as carrier gas at 1100 °C. The conversion rate of the CNFs collected in the cold trap is approximately 1.5 wt% of the initial precursor. The effects of the catalytic precursor temperature, thiophene and acetylene are the parameters that decide the diameter and selectivity of CNF.

#### 3.6.5 Electrospinning Method

Electrospinning is a process that uses an electric potential to overcome the surface tension of a solution to produce an ultrafine jet, which elongates, thins and solidifies as it travels through the electric field to a collector (Figure 3.8). Despite being a relatively simple procedure to undertake in a laboratory, as it requires minimal equipment, the physics behind the process are complex. To gain an understanding of all the variables and interactions involved in electrospinning, consideration must be given to polymer chemistry, electric field interactions, fluid mechanics, environmental conditions and kinetics. CNFs are prepared from acrylonitrile, pitch, polyimide, poly(vinylidene fluoride) and phenol via electrospinning followed by carbonization. The properties of the final CNFs are decided by the types of polymer solution and the processing parameters. Once the polymer



**Figure 3.8** Schematic diagram of the electrospinning setup used for CNF fabrication. (Source: Feng *et al.* 2014) [57].

nanofibers have been successfully prepared, a heat treatment is applied to carbonize the polymer nanofibers to form CNFs. The morphology, purity, crystallinity, diameters and porosity are governed by the parameters of the heat treatment process such as atmosphere and temperature. The carbonization process is followed by heating the polymer nanofiber up to 1000 °C in a specific environment. Generally, volume and weight change occur during the carbonization process, which results in the decrease of the diameter of the CNFs. In most cases, the CNFs prepared by the electrospinning method are prone to form web or mat structures, which are used as electrode materials for batteries, supercapacitors, electrochemical capacitors, anode for lithium-ion rechargeable batteries, catalyst support and composite.

There are two major approaches of CNF production based on the precursor's state of matter: solid-phase synthesis and vapor-phase synthesis. The precursor materials used for CNF production by electrospinning are in their solid state at the initial stage of fabrication. Precursors are aligned in fibers through different spinning techniques, followed by stabilization and carbonization at temperatures up to about 1300 °C. Recently, exploitation of a gaseous state of precursors has also gained in popularity. Vapor-grown carbon fibers (VGCF) are prepared by thermal decomposition or chemical vapor decomposition (CVD) of organic precursors, where stabilization is not necessary. While fibers' solid-phase precursors are obtained as a continuous fiber with different morphologies (monofibers, strands of fibers, woven fabric with diverse woven modes, chopped fibers and also

nonwoven mats), the vapor-grown carbon fibers are relatively short [52]. Some of the common solid phase CNF precursors given below.

#### 3.6.5.1 *Polyacrylonitrile (PAN)*

Carbon fibers derived from PAN have high tensile strength and modulus. The carbon content of acrylonitrile ( $\text{CH}_2=\text{CHCN}$ ) is very high. In order to be suitable as precursor the acrylic fiber should contain at least 85% of acrylonitrile monomer to provide as high a carbon yield and it should preserve the fibrous structure of the polymer precursor throughout the carbonization stage [53].

#### 3.6.5.2 *Pitch*

Pitch-based fibers are produced from low-cost by-products of the destructive distillation of coal, crude oil, or asphalt, and can be separated into two groups: (i) *Isotropic Pitch Fibers*, which have low mechanical properties (Young's modulus of 35–70 GPa) and are relatively cheap, and (ii) *Mesophase Pitch Fibers*, which have very high modulus (above 230 GPa) but are more expensive. The carbon yield for the pitch-based fibers is even higher than for PAN-based ones — it can exceed 60% [52].

#### 3.6.5.3 *Cellulose*

Cellulose-based fibers were developed in the 1960s for aerospace applications and at that time became the first carbon fibers produced commercially. Though they are not as strong as PAN-based fibers they have many advantages, such as abundant resources of the precursor, and are a naturally occurring polysaccharide. But since they consist of D-glucose monomer units joined by 1-4 glucosidic bonds, forming an ether linkage by the elimination of water (one molecule may include up to ten thousand units), these ether linkages together with hydrogen bonds between different units make cellulose relatively stiff and hard to dissolve. They are not soluble in the most common solvents, which leads to extremely difficult processing of cellulose. On the other hand, their derivatives, such as cellulose acetates, are much easier to handle with spinning processes [54]. Cellulose acetates are common esters of cellulose. They are synthesized by reacting cellulose with acetic anhydride or acetic acid in the presence of sulfuric acid. The acetylation makes cellulose more soluble in organic solvents, making it more suitable to produce films from cellulose triacetate. The degree of substitution affects the solubility of cellulose acetate and hence determines the options for further processing for different applications. For example, cellulose acetate with degree of substitution of 2–2.5 is soluble



in acetone, dioxane or methyl acetate, while celluloses with higher degree of acetylation are soluble in dichloromethane.

### 3.7 Summary

Catalysts are known to play an important role in chemical transformations and reactions as they increase the speed of a reaction, lower the activation energy for the reaction, act as a facilitator and bring the reactive species together more effectively, and create a higher yield of one species when two or more products are formed. Recently, nanocatalysts have begun being used because nanomaterials are more effective than conventional catalysts due to their extremely small size and very high surface area-to-volume ratio. Moreover, at the nanoscale, unique properties are found which are not present in their macroscopic counterparts. Hence, for synthesis of CNF, consideration of use of nanocatalyst is very important. In this chapter different types of catalysts and their various preparation methods were presented. Finally, synthesis of carbon nanofiber (CNF) using nanocatalysts were discussed with special emphasis.

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# Carbon Nanofiber and Polymer Conjugate

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*Equipped with his five senses, man explores the universe around him  
and calls the adventure Science.*

Edwin Powell Hubble

## 4.1 Introduction

Nanotechnology is recognized as one of the most progressive and promising fields in recent times. The nano-sized inclusions which range from 1 to 100 nm, including nanoparticles and quantum dots or Q particles, are being widely exploited for different applications and benefits. In material research, the development of polymer nanocomposite is rapidly emerging as a multidisciplinary research activity whose results could broaden its application in various industries ranging from biomedical to aerospace. Polymer nanocomposites are polymers that have been reinforced with small quantities mainly less than 5% weight of nanosized particles having high aspect ratio. Polymer nanocomposites represent a radical alternative to conventional filled polymers or polymer blend. In contrast to conventional polymers where the reinforcement is in the order of microns; polymer nanocomposites are exemplified by discrete constituents with the order of a few nanometers. The development of polymer nanocomposites must simultaneously balance four different areas, i.e., Constituent selection, Cost-effective processing, Fabrication and Performance. A complete understanding of these

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areas and their interdependencies is still in its infancy but with progressive research many prospects will develop for its application in different fields.

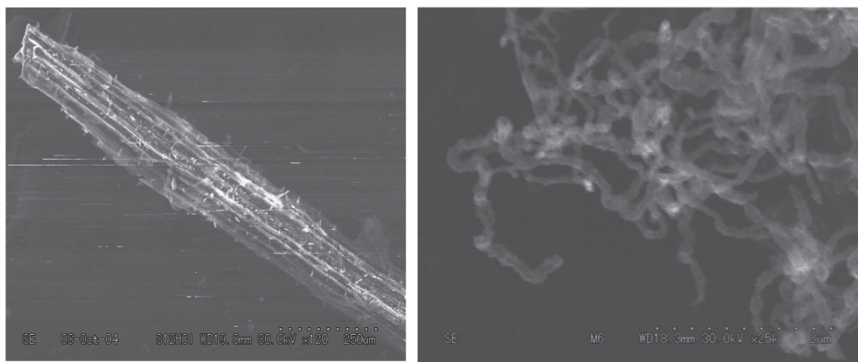
## 4.2 What Is a Composite?

A composite is a material made from two or more components with varied physical and chemical properties, which when combined result in the formation of a new material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure as compared to mixtures and solid solutions. These composites are mainly created with a view to increasing the efficacy of the product, its functionality, durability, sensitivity, longevity, and many other parameters as compared to the traditional materials used for different purposes.

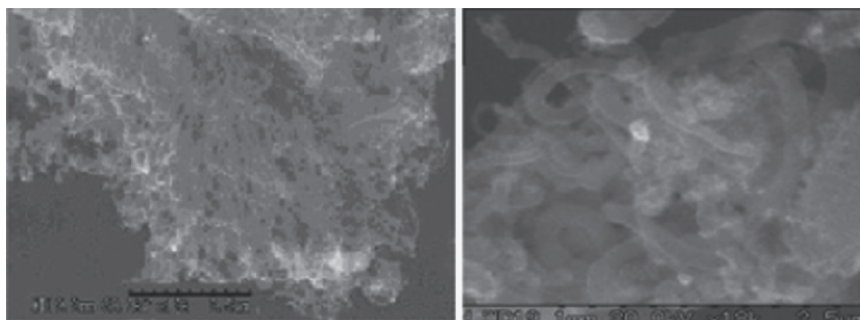
The best examples of composite materials used in our daily life include plywood, which is a composite wood, masonry, fiberglass, ceramic matrix composite, metal matrix composite and many more advanced composites.

Composites may vary in their sizes; depending on their dimensions they may be called microcomposite, measured in micrometers, or nanocomposite, measured in nanometers.

CNF synthesized from both biogenic and chemical precursors are used for fabricating composites (Figures 4.1 and 4.2). This chapter mainly focuses on nanocomposites, especially those nanocomposites of biogenic carbon nanofibers (CNF) (Figure 4.1). Nanocomposite is a multiphase solid material less than 100 nm which is created to design and form new materials with unprecedented flexibility and improved structural, chemical and physical properties. It encompasses large varied systems, such as one-dimensional,



**Figure 4.1** CNF synthesized from biogenic sources: (left) Sugar cane fiber bagasse and (right) Karanja oil.



**Figure 4.2** CNF synthesized from chemical hydrocarbon sources: (left) Plastic and (right) Ethanol.

two-dimensional, three-dimensional and amorphous materials made up of distinctly different components and mixed at nanoscale level. The properties of nanocomposite material not only depend on their individual components but also on their interfacial and morphological characteristics.

In nature, nanocomposites are found in bones, shells, etc., and there are many natural organic and inorganic nanocomposites which exist at different levels depending on their level of complexity.

- **First level** is the simplest level in which the mineral phase is simply deposited into or within the organic structure. For example:
  - Magnetic bacteria that has internal chain of magnetite  $\text{Fe}_3\text{O}_4$  nanocrystals running down their long axis.
  - Many species of grasses that precipitate  $\text{SiO}_2$  within their cellular structures.
- **Second level** is the medium level in which the structure of mineral phase is clearly determined by organic matrix. For example, Bacteria-S layer serves as a protein template for the formation of thin film of meso-structured gypsum.
- **Third level** is the highest level in which the structure of mineral is intimately associated with the organic phase to create a structure with properties superior to those of either the mineral or the organic phase. For example, (i) Sea urchin spine in which a single crystal is composed of calcite containing about 0.02% glycoprotein trapped within the crystal lattice of the spine, (ii) Bone complex structure and function, (iii) Nacreous (mother of pearl) layer of abalone shell consisting of alternating layers of 500-nm-thick aragonite platelets and approximately 30-nm-thick sheets of an organic matrix, etc.

Nanocomposites, depending on their size limit, show different activity as proposed by various researchers: nanocomposites <5 nm for catalytic activity, <20 nm for making hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for superparamagnetism.

Nanocomposites are preferable over conventional composites owing to their following properties:

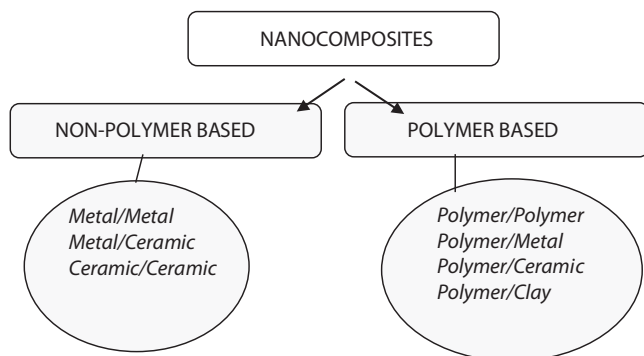
- High surface to volume ratio
- Nanoparticle properties
- Multifunctional capabilities
- Chemical functionalization
- Huge interface zone
- Mechanical properties
- Increased ductility with no decrease in its strength and scratch resistance
- Optical properties (light transmission characteristics depend on particle size)

In Figure 4.3, non-polymer and polymer based different types of nanocomposites are mentioned

The other types of nanocomposites include:

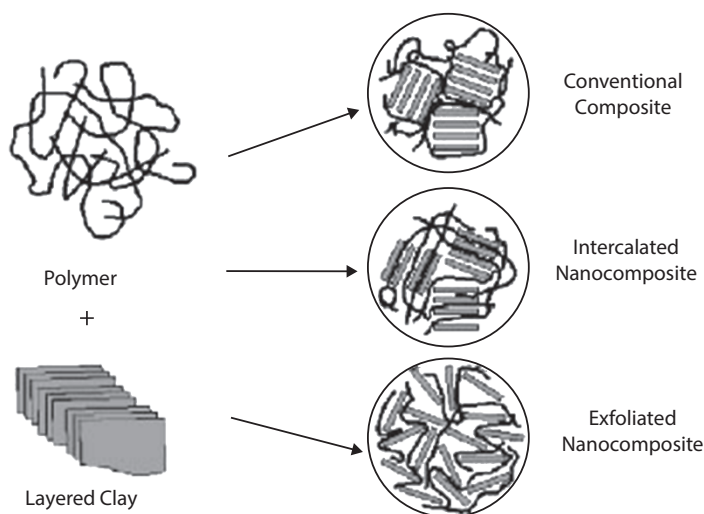
- Intercalated nanocomposites (Figure 4.4)
- Flocculated nanocomposites, and
- Exfoliated nanocomposites (Figure 4.4)

which are categorized based upon the polymer chain ratio. Lamellar nanocomposites can be divided into three distinct classes, intercalated and



**Figure 4.3** Types of nanocomposites based on different polymers used.





**Figure 4.4** Polymer layered nanocomposite. (Source: Denault & Labrecque 2004).

exfoliated. In the first type, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intralamellar space. In the second type, flocculation of intercalated and stacked layers to some extent takes place due to hydroxylated edge-edge interactions of the clay or polymer layer. In exfoliated nanocomposites, the number of polymer chains between the layers is almost continuously variable and the layers stand  $>100 \text{ \AA}$  apart. The intercalated nanocomposites are also more compound-like because of the fixed polymer/layer ratio, and they are interesting for their electronic and charge transport properties. On the other hand, exfoliated nanocomposites are more interesting for their superior mechanical properties [1].

### 4.3 Polymers Used for Conjugating CNF

There are different ranges of polymers available (Table 4.1) which are used in the field of nanotechnology. The wide ranges of natural and synthetic polymers generally used are described below.

#### 4.3.1 Starch

Starch (Figure 4.5) is a complex *polysaccharide*, i.e., many monomeric sugar molecules linked together by glycosidic bond, especially glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ). Starch is found in all plant seeds, tubers and other



Table 4.1 Properties of different nanocomposites.

| Ceramic-based nanocomposite                                                                                                                                                                                                                                                                                                                                                                                                                                    | Metallic-based nanocomposite                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Polymer-based nanocomposite                                                                                                                                                                                                                                                                                                                                                                                     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"><li>Enhances ductility, formability, toughness, super plasticity by nanophase</li><li>Increase in strength, hardness and abrasion by refining particle size</li><li>Change electrical conduction and magnetic properties by increasing the disordered grain boundary interface</li><li>Examples:<br/><math>Al_2O_3/SiO_2</math><br/><math>SiO_2/Ni</math><br/><math>Al_2O_3/TiO_2</math>, <math>Al_2O_3/SiC</math></li></ul> | <ul style="list-style-type: none"><li>Increase hardness, strength and super plasticity</li><li>Lowered melting point</li><li>Increased electrical resistivity</li><li>Increased miscibility of the non-equilibrium components in alloying and solid solution</li><li>Improved magnetic property such as coercivity, superparamagnetism, saturation magnetization and magnetocatalytic properties.</li><li>Examples:<br/><math>Fe-Cr/Al_2O_3</math><br/><math>CoCr</math>,<br/><math>Fe/MgO</math>,<br/><math>Mg/CNT</math></li></ul> | <ul style="list-style-type: none"><li>Electrical, optical, magnetic and catalytic properties arising from the inorganic materials</li><li>Enhanced thermal and mechanical stability originating from the polymeric matrix</li><li>Examples:<br/><math>Polyester/TiO_2</math><br/><math>polymer/CNT</math>, <math>polymer/layered</math> silicates,<br/><math>polymer/layered double hydroxides</math></li></ul> |

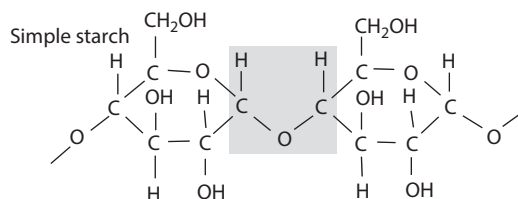


Figure 4.5 Molecular structure of starch.

plant-derived foods such as bread, potatoes, pasta, and rice. Apart from being consumed as food, starch is used for making cotton and linen. This complex polysaccharide is mostly present as amylose and amylopectin, arranged in linear or branched form. Starch is organic, white, tasteless, insoluble in cold water, alcohol, or other solvents. The simplest form of starch is the linear polymer amylose; amylopectin is the branched form. This polysaccharide is produced by most green plants as energy storage.

### 4.3.2 Cellulose

Cellulose is also a *polysaccharide* consisting of a linear chain of several hundred to many thousands of  $\beta$ -linked D-glucose units (Figure 4.6). This organic compound with the formula  $(C_6H_{10}O_5)_n$ , has a molar mass of 162.1406 g/mol and density of 1.5 g/cm<sup>3</sup>. Cellulose is an important structural component of the primary cell wall of all green plants, algae and oomycetes; and also fibers of plants. Some species of bacteria secrete cellulose to form biofilms.

### 4.3.3 Collagen

Collagen is a major structural *protein* which is made up of amino-acids: glycine, proline, hydroxyproline, and arginine (Figure 4.7). It is found in skin, hair, nails, gut and connective tissues. Collagen is the most abundant protein

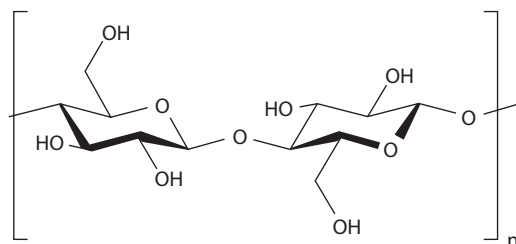
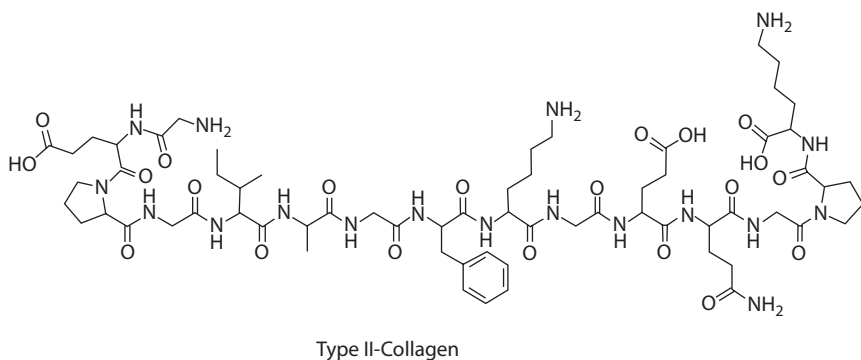
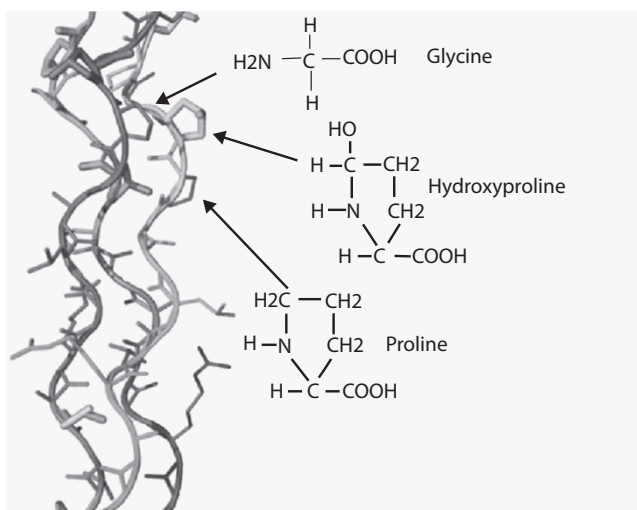


Figure 4.6 Molecular structure of cellulose.



**Figure 4.7** Molecular structure of collagen.



**Figure 4.8** Triple-helical structure of collagen.

present in mammals, making up 25% to 35% of the whole-body protein content. The triple-helical structure of collagen arises from an abundance of three amino acids: glycine, proline, and hydroxyproline. Hydrogen bonds linking the peptide bond NH of a glycine residue with a peptide carbonyl (C=O) group in an adjacent polypeptide help hold the three chains together (Figure 4.8).

#### 4.3.4 Chitosan

Chitosan is a linear *polysaccharide* composed of randomly distributed  $\beta$ -linked D-glucosamine and N-acetyl-D-glucosamine (Figure 4.9). It is

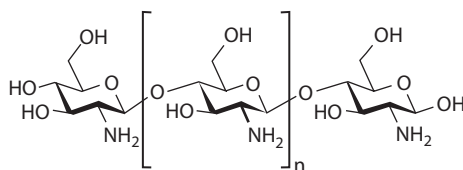


Figure 4.9 Molecular structure of chitosan.

synthesized commercially from deacetylation of chitin shells of shrimp and other crustaceans and also cell walls of some fungi, with sodium hydroxide, for many biomedical uses. Chitosan is water-soluble and acts as a bioadhesive by readily binding to negatively charged surfaces such as mucosal membranes.

### 4.3.5 Gelatin

Gelatin is a heterogeneous mixture of single or multi-stranded *polypeptides* (Figure 4.10), each with extended left-handed proline helix conformations. It contains 50–1000 amino acids. Gelatin (also known as hydrolyzed collagen, collagen hydrolysate, gelatin hydrolysate, hydrolyzed gelatin, and collagen peptides) is a translucent, colorless, brittle, flavorless ingredient derived from collagen obtained from various animal body parts.

### 4.3.6 Fibrin

Fibrin ( $C_5H_{11}N_3O_2$ ), as the name suggests, is a fibrous, non-globular *protein* (Figure 4.11). It is formed by polymerization of fibrinogen (an insoluble protein) by the action of protease thrombin during clotting of blood. It forms a fibrous mesh that stops the flow of blood.

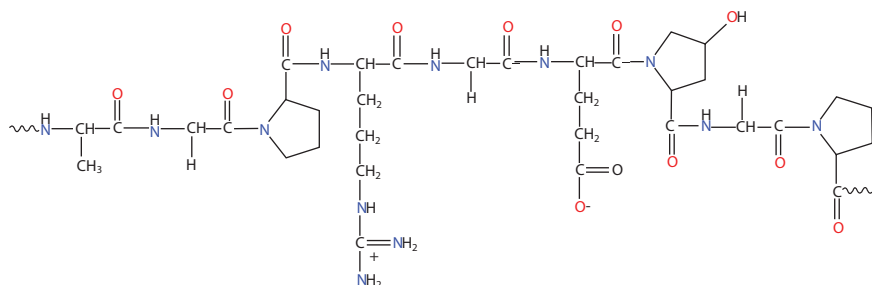
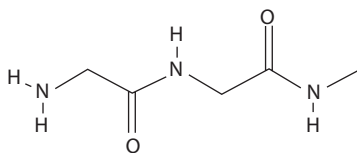


Figure 4.10 Molecular structure of gelatin.



**Figure 4.11** Molecular structure of fibrin.

### 4.3.7 Alginate

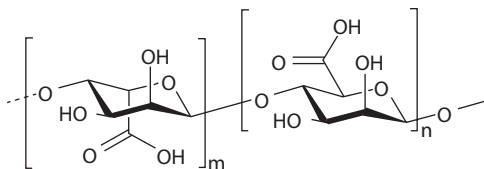
Alginate is a *polysaccharide*. In nature, it occurs in brown algae in the range of 30 to 60% (on a dry weight basis). Alginic acid (Figure 4.12) accumulates in brown seaweeds and forms a structural component of their cell walls.

### 4.3.8 Poly Vinyl Alcohol (PVA)

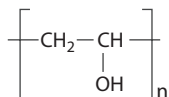
Poly vinyl alcohol (Figure 4.13) is a white, odorless, water-soluble synthetic polymer  $(C_2H_4O)_x$ . Generally other vinyl polymers are prepared by polymerization of their corresponding monomer, but PVA is synthesized by partial or complete hydrolysis of polyvinyl acetate so as to remove acetate groups. It has many applications such as in papermaking, textiles, and a variety of coatings. It is used in smart textiles as it has a melting point of  $200^\circ\text{C}$  and boiling point of  $228^\circ\text{C}$ . The properties are  $1.19\text{ g/cm}^3$ .

### 4.3.9 Poly Ethylene Glycol (PEG)

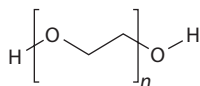
Poly ethylene glycol ( $C_{2n}H_{4n+2n+1}$ ) is a *polyether* compound (Figure 4.14) also known as polyethylene oxide or poly(oxyethylene), depending on its molecular



**Figure 4.12** Molecular structure of alginic acid.



**Figure 4.13** Molecular structure of poly vinyl alcohol (PVA).



**Figure 4.14** Molecular structure of poly ethylene glycol (PEG).

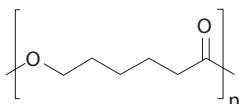
weight. It is water soluble with molar mass of  $18.02 + 44.05n$  g/mol and 1.125 density. It is used in areas from medicine to industrial manufacturing.

#### 4.3.10 Poly Caprolactone (PCL)

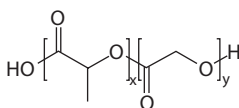
Poly Caprolactone ( $C_6H_{10}O_2$ )<sub>n</sub> is biodegradable *polyester* (Figure 4.15) with a low melting point of around 60 °C and a glass transition temperature of about -60 °C. In the human body, PCL is degraded by hydrolysis of its ester linkages in physiological conditions. PCL is a very suitable material for production of speciality polyurethanes; therefore, it has received a great deal of attention for use as a long-term implantable biomaterial and for controlled drug release.

#### 4.3.11 Poly Lactic-co-Glycolic Acid (PLGA)

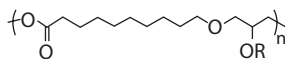
Poly lactic-co-glycolic acid is a copolymer which is synthesized by means of ring-opening co-polymerization of two different monomers, the cyclic dimers of glycolic acid and lactic acid (Figure 4.16). PLGA is naturally amorphous. Though separately both poly(*lactic*) and poly(*glycolic*) acid have poor solubility in most solvents, PLGA dissolves in many solvents, including tetrahydrofuran, acetone, ethyl acetate and chlorinated solvents. Being biocompatible and biodegradable, it has found applications in many drug delivery and food administration applications and is approved for therapeutic devices.



**Figure 4.15** Molecular structure of poly caprolactone (PCL).



**Figure 4.16** Molecular structure of poly lactic-co-glycolic acid (PLGA).



**Figure 4.17** Molecular structure of poly glycerol sebacate (PGS).

#### 4.3.12 Poly Glycerol Sebacate (PGS)

Poly glycerol sebacate (Figure 4.17) is a comparatively newly discovered [2] synthetic, biodegradable, thermosetting and tough polymer that is used in making many composites. According to Wang it is cheap, bioresorbable, biodegradable and has nontoxic degradation products. Due to its many unique desired properties, such as having surface degradation and elastomeric behavior, physicochemical, mechanical, thermal and morphological properties. PGS and its composite forms have been researched for both *in-vitro* and *in-vivo* studies for numerous tissue engineering applications. Especially the combination of PGS with  $\beta$ -tri-calcium phosphate ceramics has been recently proposed by Tevlek *et al.* [3] for guided bone regeneration [3].

### 4.4 Approaches Involved in Synthesizing Polymer/CNF Nanocomposites

Carbon nanofiber is generally fabricated either by catalytic chemical vapor deposition growth or by electrospinning. Fabrication methods are detailed in Chapter 1 of this book. The overall performances of the CNF/Polymer composites are largely governed by the dispersion of the CNF in the polymer matrix. Therefore, the dispersion technique plays a key role in the synthesizing of CNF composites. In the following paragraphs a few of the commonly used fabrication techniques for CNF/Polymer nanocomposites are described.

In the preparation of any composite there are three main material constituents:

- The matrix
- The re-enforcement material (CNF)
- The interfacial region

The dispersion of CNFs in polymer matrix are realized by three approaches:

1. **Melt Mixing Process** which is the most widely used method due to its low cost, simplicity and availability. Processes like

extrusion or roll mill [4, 5]; Haake torque rheometer [6] and mini-max molder [7, 8] all belong to the melt mixing method.

2. **Sonication Process** in low viscosity solutions. In this method, to obtain a good dispersion condition for CNF in polymer matrix, a high shear mixing condition is usually required. Although the high shear mixing leads to a relatively good dispersion of the CNF, the aspect ratio, which is another key parameter governing the overall performances of the CNF/Polymer composites, gets decreased during the mixing process. It was found that the decrease of the aspect ratio results in the degradation of some properties [9, 10]. Therefore, the investigation of the relatively low shear mixing approach without sacrificing the dispersion is still a challenge for the preparation of CNF/polymer composites by the melt mixing approach.
3. **Chemical Surface Treatment of CNFs** method helps dispersion of CNF in the polymer matrix. The compatibility between the grafting functional groups and the polymer matrix is the main factor that decides the CNF dispersion and performances of the composites. In this process, CNF surface is oxidized by soaking it in sulfuric/nitric acid at various temperatures followed by acylation. And then the functional group is grafted onto the surface of the CNF by the reaction between the oxidized CNF and the functional groups. Li *et al.* (2005) have prepared and characterized the surface-treated CNF by using diamines or triamines as linker molecules. The amine group acts as a bridge connecting the CNF and the  $-NH_2$  to form the CNF-C(O)-NH- structure [11].

Using these three approaches and different chemical and biological polymers; CNF/Polymer composites have been prepared by different scientists for various applications. The method of synthesis, CNF content, fabrication temperature and the polymer selected, has helped in producing composites of different properties.

## 4.5 Various CNF Composites

In composite material development, nanofibers reinforcement is one of the most recently developed methods. Electrospun mat of CNF, reinforced with polymer epoxy resin, has been studied by many [12]. Sharma *et al.* (2016)



performed a molecular level analysis of CNF-reinforced polypropylene (PP) composites. Using CNF reinforcement in polypropylene (PP) matrix, molecular dynamics (MD) simulation was studied by them to know the effect of CNF volume fraction ( $V_f$ ) and aspect ratio ( $l/d$ ) on the mechanical properties of CNF/PP composites using Materials Studio 5.5 software as a tool for finding the modulus and damping in composites [13]. They varied CNF composition in PP by volume from 0 to 16% and aspect ratio of CNF from  $l/d=5$  to  $l/d=100$ . Results have also been obtained for longitudinal loss factor ( $\eta_{11}$ ) and, as they have claimed, *to date (2016) there has been no study, either experimental or analytical, which predicts  $\eta_{11}$  for CNF-PP composites at nanoscale*. They have shown that with only 2% addition by volume of CNF in PP,  $E_{11}$  increases by 748%. Thereafter, the increase is at a lower rate. Increase in  $E_{22}$  is much less in comparison to the increase in  $E_{11}$ . With increase in CNF aspect ratio ( $l/d$ ) till  $l/d=60$ , the longitudinal loss factor ( $\eta_{11}$ ) decreases rapidly. Thereafter, the decrease is smaller.

#### 4.5.1 CNF/Epoxy Composites

Using the sonication method, Pervin *et al.* (2005) fabricated nanocomposites composed of SC-15 epoxy and CNF. The mixing process was carried out through a high-intensity ultra-sonication of the CNF and SC-15 epoxy. Once the sonication was completed, the hardener was added to the mixture, followed by high-speed mechanical stirring, and then cured at room temperature [14].

Simultaneously in another attempt, Kellarakis and coworkers [15] prepared CNF/ethylene/propylene (EP) random copolymer composite using a similar process, i.e., oxidizing the CNF surface by  $H_2SO_4$  and then reducing it by sodium borohydride in absolute ethanol to form the CNF-OH structure. After that, the hydroxylated CNF was dispersed in dichlorobenzene and a polypropylene-graft-maleic anhydride polymer to form the CNF-O- structure. Apart from the melt mixing processing for the CNF/thermoplastic polymers, the dispersion of the CNF in thermosetting polymers to prepare the CNF/thermosetting polymers (mostly epoxy resins) composites mainly counts on the solution approach with the help of sonication. In this process, the CNFs were dispersed in the liquid epoxy form by sonication before being mixed with the hardener. Usually, acetone or other solutions are needed to help the effect of sonication. In addition, to avoid increasing temperature during the sonication process, external cooling devices are necessary in most cases.

The preparation of the CNF/epoxy nanocomposite [16] showed that ozone surface treatment of the CNF is helpful for its dispersion in the epoxy matrix. The CNFs were dispersed in acetone by sonication and stirring them at room temperature.

Bal and Saha (2015) studied the influence of amount of CNF (1.5, 2 and 2.5 wt% of CNFs) on the mechanical and viscoelastic behavior of epoxy-based nanocomposites [17]. The composite synthesis was done at room temperature (27 °C) and at low temperature of 4 °C. It was found that flexural modulus was improved to 50% and 25% for composites containing 1.5 wt% CNF, and 83% and 79% for 2 wt% CNF respectively, for all the room temperature cured composites. And low temperature cured composites; maximum improvement in flexural modulus was 83% and 128%. According to the authors, this improved storage modulus and glass transition. The temperature of these specimens show good interfacial adhesion.

No further improvement at higher CNF content of 2.5 wt% was observed, which was due to the appearance of aggregated phases in the composites.

#### **4.5.2 CNF/Phenolic Resin Composites**

Joshi and Bhattacharya (2004) [18] used CNF dispersed into the phenolic resin (prepared by condensing phenol and formaldehyde and then refluxing them at 70 °C) by three different processes: (i) Sonication, (ii) Mechanical stirring with 0.2% nonionic surfactant, and (iii) Mechanical stirring followed by sonication. The surfactant helps in proper dispersion of the CNF into the matrix. Finally, they prepared the composite by dipping the fabric in the resin and then drying overnight. The fiber impregnated composite was taken for compression-molding at curing temperature of 150 °C for 2 h using 3 metric ton-force. Textile structured CNT/CNF composites help in the preparation of carbon-carbon composites [19]. This composite has found application in spacecraft re-entry frames. Incorporation of carbon nanomaterial enhances the mechanical properties of the composites and gives better thermal stability. CNF-reinforced polymeric matrix composites with carbon fiber reinforcement are examples of unique three-phase nanocomposite systems.

#### **4.5.3 CNF/Polyaniline (PANI) Composites**

Polyaniline (PANI) is a conducting polymer. Owing to its high capacitance, good environmental stability, and low cost combined with the ease of preparation, PANI materials have been widely studied as supercapacitors [20]. PANI has also been considered to promote the electrochemical capacitance of flexible CNT and graphene papers. Researchers have used electrospinning to produce flexible carbon nanofiber (CNF) paper. This electrospinning process is simple and fast, and the CNFs are relatively inexpensive compared with CNTs or graphene. More importantly, they

have demonstrated the preparation of a freestanding CNF–PANI composite paper by a simple rapid-mixture polymerization of aniline monomers on the CNF paper. The obtained composite paper maintains the pristine flexibility of the CNF paper and displays improved electrical conductivity and electrochemical performances compared with the CNF paper.

#### 4.5.4 CNF/Poly (Ether Ether Ketone) Nanocomposite

Vapor-grown CNF/Poly(ether ether ketone) nanocomposite is a high-temperature semi-crystalline polymer nanocomposite. CNF was homogeneously dispersed and aligned in a thermoplastic matrix using the standard polymer processing techniques of extrusion and injection molding. They were evaluated for their mechanical properties, which revealed a linear increase in tensile stiffness and strength with nanofibers loading fractions up to 15 wt% while matrix ductility was maintained up to 10 wt%. Differential scanning calorimetry showed that an interaction between matrix and the CNF occurs during processing that changes the polymer morphology due to the presence of nanoscale filler. The addition of low CNF contents resulted in a linear increase in tensile and bending stiffness and tensile yield stress and strength without negatively affecting the matrix ductility at loadings up to 10 wt%. The intrinsic stiffness of vapor-grown CNF was very low [5].

#### 4.5.5 CNF/Biopolymers Nanocomposites

Recently, CNF has been reinforced in polylactic acid (PLA) (as a strategy to control degradation *in vitro* of CNF-reinforced PLA composites, by combining fiber modification and pulsed electromagnetic fields [21]. PLA is biodegradable and bioactive thermoplastic aliphatic polyester. It is derived from corn starch, cassava roots, chips or starch, sugarcane, etc. It is used in food handling and medical implants that slowly biodegrade within the body. Since CNF/PLA composites are a human bone-fixation material, which controls the degradation of materials, Zhang *et al.* 2018 [21] studied CNF/PLA, both in modified and unmodified forms. During subsequent degradation process, they selectively applied pulsed electromagnetic field (PEF) and found that the interfacial ester bonding between modified CNF and PLA matrices significantly affected degradation *in vitro* of C/PLA composite. However, PEF affected the degradation performance of C/PLA composites and, after PEF treatment, the material's water absorption, mass retention, and bending and shearing strengths were changed to varying degrees.

#### 4.5.6 CNT/CNF-Epoxy Nanocomposites

Multi-walled carbon nanotubes (MWCNT) grown on CNF-reinforced epoxy has been used to improve physical and electrical properties. An improvement in sizing-sensitive mechanical and physical properties, such as the interfacial adhesion, shear properties and handling of the fibers, whilst retaining resin-infusion capability has been observed [22]. The CNT-modified carbon fiber composite offers improvements of 146% increase in Young's modulus; 20% increase in ultimate shear stress; 74% increase in shear chord modulus and an 83% improvement in the initial fracture toughness. Moreover, it is found that addition of CNTs imparts electrical functionalization to the composite and 400% enhancements in the surface direction, thus it may be a suitable route for developing sizing-free composites with enhanced mechanical and electrical functionality.

### 4.6 Possible Futuristic Applications of CNF/Polymer Composites

Carbon nanofiber composites have been investigated for both fundamental scientific research and applications in many fields, such as electrical devices, electrode materials for batteries and supercapacitors and as sensors. For these uses the electrical conductivity is an important consideration. The electrical property of CNF composites counts on the dispersion and percolation status of CNFs in the matrix. The thermal conductivity and mechanical properties of CNF composites also decide their applications as sensors and electrode materials.

CNF is used as a reinforcement material in composites, especially reinforced plastic (CFRP) composites, because it offers higher strength-to-weight ratio, stiffness-to-weight ratio, lightweight, high-strength, and high-stiffness composite materials. These are crucial for the development of an energy-efficient transportation industry, enabling vastly improved power generation, new mechanisms for storing and transporting reduced carbon fuels and enhancing renewable power production in wind turbines, aerospace (commercial and military aircraft, space launch vehicles), pressure vessel industries for increased strength to weight and stiffness, in sports and leisure composites (e.g., skis, snowboards, bicycles and hockey sticks), and in aviation and automotive industries.

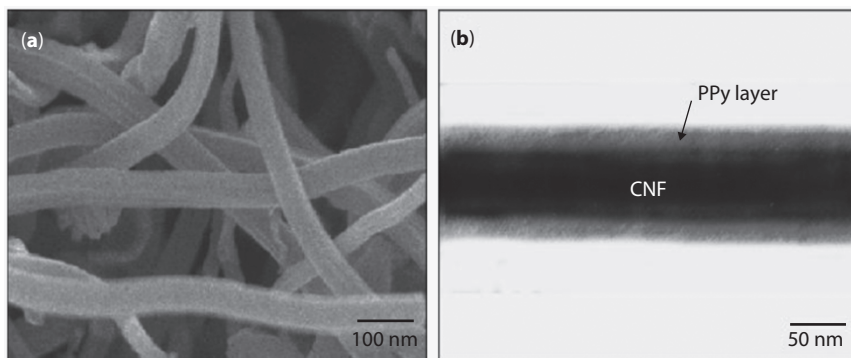
The properties of CNF composites are governed by the dispersion condition of the CNFs in the matrix materials. The electrical property of the CNF composites largely depends on the dispersion and percolation

condition of the CNFs in the matrix; therefore, the method of dispersing CNF plays a very important role. The main electrical transport mechanism is the tunneling effect. Therefore, the surface treatment methods, the dispersion approaches and the polymer types are extremely important for the enhancement of the electrical properties.

It has been found that nanocomposites are more advantageous and offer improvements over conventional composites, especially in their thermal, mechanical, electrical and barrier properties; hence, there is the possibility of a variety of applications in the automotive, construction, aerospace, food packaging, electrical and electronics industries, among others.

#### 4.6.1 Sensors

The suitability of CNF composites for their self-sensing function is due to the variation in their electrical properties caused by the change of the external conditions, such as stress/strain and the gas environment. The electrical conductivity of the CNF composites reversibly changes by several orders of magnitude with the reversible change of the external conditions. Jang and Bae (2007) fabricated CNF/PPY (polypyrrole) coaxial nanocable toxic gas sensor for detecting  $\text{NH}_3$  and  $\text{HCl}$  [23]. This sensor was prepared by one-step vapor deposition polymerization method, and had an ultrathin and uniform PPy layer on the surface of CNF (Figure 4.18). When this sensor is exposed to the  $\text{NH}_3$  or  $\text{HCl}$ , there is a change in oxidation level of PPy layer, resulting in the reaction between the PPy and



**Figure 4.18** SEM and TEM images of the PPy-coated CNF as a toxic gas sensor. (Source: Jang & Bae, Carbon nanofibers/polypyrrole nanocable as toxic gas sensor. *Sens. Actuators B Chem.* 122, 7-13, 2007) [23].

the  $\text{NH}_3$  or  $\text{HCl}$ , and the electrical conductivity due to the decrement in the charge carrier density.

Li *et al.* (2008) prepared graphitic CNF-poly(acrylate) polymer brushes as gas/vapor sensors. It was found that the vapor can be detected via a five orders of magnitude change in the electrical conductivity [24]. Later, Zhu *et al.* (2011) prepared CNF/elastomer (VM2) composites for sensing strain that causes mechanical deformation [25]. This composite has a percolation threshold of 1 wt% as strain sensors for reflecting large mechanical deformation. The electrical conductivity of the composite could reversibly change 102–103 orders of magnitude upon stretching to 120% strain and recovery to 40% strain.

Though CNF composites have been used for sensing strain/stress or gas, there is a need to also investigate the possibility of using CNF composites for sensing temperature, humidity, magnetic field and light.

#### 4.6.2 Batteries

For good performance of supercapacitors and batteries, one of the requirements is highly porous electrode, so as to contain enough electrolytes and satisfy fast and long-term ion transport. For this purpose, CNF composites have been found to be a very suitable material and have been widely studied in batteries and supercapacitors. Ji *et al.* (2009) [26] prepared and used as an anode material for lithium-ion batteries a highly porous CNF with magnified surface areas and defects; prepared by the carbonization of electrospun PAN/ $\text{SiO}_2$  composite nanofibers and then resolving the  $\text{SiO}_2$  nanoparticles with hydrofluoric acid (HF). A unique 3D CNF deposited on graphene sheet composite by CVD was prepared [27] [Fan *et al.* (2011)], which had 1D CNF grown on the 2D graphene nanosheets. This composite has many cavities, open tips and edges of graphene nanosheet, and they used it as high-performance anode materials for lithium-ion batteries.

Hollow carbon nanofiber-encapsulated sulfur cathodes for high specific capacity rechargeable lithium batteries was developed by Zheng *et al.* (2011) [28], which had a reversible capacity of about 730 mAh/g. Another effective CNF composite was fabricated by doping porous CNF webs with nitrogen [29], which guaranteed a reversible capacity of 943 mAh/g with a current density of 2 A/g, even after 600 cycles. Hollow CNF has also been used as freestanding electrodes in a flexible lithium-ion battery; it improved their mechanical properties by repeated electrochemical reactions with lithium ions, because inserted Li ions are envisaged to form irreversible FCC crystals in the hollow CNF cavities and act as the reinforcement second phase of the carbonaceous matrix.

### 4.6.3 Food Packaging

Conventional food packaging systems passively protect the food packed in them and act as a barrier between the food and the surrounding environment. On the other hand, an active food packaging system not only acts as a passive barrier but also interacts with the food in some desirable way, e.g., by releasing desirable compounds (antimicrobial or antioxidant agents), or by removing some detrimental factor (such as oxygen or water vapor). The consequences of such interactions are usually related to improvements in food stability. Antimicrobial food packaging systems have received considerable attention since they help to control the growth of pathogenic and spoilage microorganisms on food surfaces. Antimicrobial nanocomposite systems are particularly interesting, since materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. Nanomaterials are thus more efficient, because they are able to attach more copies of microbial molecules and cells. Nanoscale materials have been investigated for antimicrobial activity as growth inhibitors [30], killing agents [31], or antibiotic carriers.

As far as CNF composites in food packaging system are concerned, it is still at the initial stage of development. Rather than using CNF derived from chemicals or plant metabolites; attention is being focused on the use of cellulose nanofibers [32]. Instead of synthetic plastics, the use of biodegradable polymers appears to be a more lucrative packaging solution as they are decomposable and are also derived from renewable sources [33–35].

Protein-based biopolymers, such as whey protein isolates (WPI), have been successfully used as packaging material, as they have excellent barrier to oxygen, which protects food by avoiding the oxidation process, and act as a barrier to aromas, have high transparency and film-forming ability and can be used as active packaging for transporting food additives, antioxidants, antimicrobial agents, nutrients, etc. However, due to the presence of amino acid chain these biopolymers are hydrophilic, which directly influences the water vapor barrier and solubility properties [36]. To improve biopolymer packaging performance, the addition of nanoscale materials to the biopolymer is being tried, as nanoscale materials have a larger contact surface area per weight of material than macroscale, allowing greater interaction with the polymer matrix of the film and leading to better performance of the material. Cellulose-derived nanofibers (CNF) are one such nanomaterial that have great potential as a reinforcing material in polymeric matrices. Cellulose is a component of plant fiber. It is obtained from cotton, eucalyptus, wood, flax, sugarcane bagasse, sugar beet, etc. [37]. Apart from being economic, it has a



hydrophilic nature, leading to high affinity with protein-based polymer formulations and also with most natural polymers [38]. When added to packaging, CNFs are capable of imparting high rigidity, vapor permeability and water solubility reduction [39, 40]. Carvalho *et al.* (2017) [32] have shown that depending on the quantity of CNF added to WPI films, it caused a reduction in thickness of the films, the composite was more resistant to water, and the mechanical properties of the films were improved, making the films more resistant and elastic. Addition of 4% (w/w) of CNF decreased the permeability by about 30%. Addition of 6% (w/w) CNF did not change the mechanical properties and water vapor permeability, which was related to nanoparticle agglomeration when added to the polymer matrix in excess. When 2 or 4% (w/w) CNF was added in WPI the transmittance of the films decreased.

## 4.7 Summary

Carbon nanofiber (CNF) is accepted as an important nanoform of carbon. It is competing with CNT in many applications in both fundamental scientific research and practical applications. It is a promising material for an additive in polymers for its application in many fields. The electrical property of CNF composites largely depends on the dispersion and percolation status of CNFs in matrix materials. In this chapter, properties and applications of CNF nanocomposites are dealt with. Fabrication methods of CNF composites have also been discussed in brief.

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# Characterization of Carbon Nanofiber

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*A painstaking course in qualitative and quantitative analysis by John Wing gave me an appreciation of the need for, and beauty of, accurate measurement.*

Paul D. Boyer

## 5.1 Introduction

This chapter deals with Nanometrology, i.e., characterization of nanoparticles. Characterization of nanoparticles is done to assess their physical and chemical properties. This is very important because nanoparticles exhibit unique properties that are not found in their bulk counterparts. Moreover, these novel properties of nanomaterials are the base for deciding their various applications. There is a wide range of instruments used to measure the properties of nanoparticles.

## 5.2 Microscopic Characterization Techniques

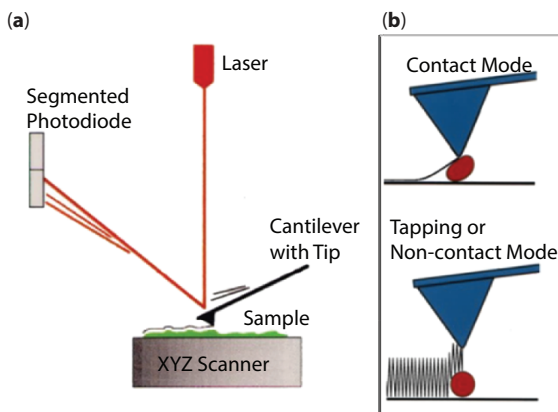
Surface and morphological characterization of CNFs is of paramount importance due to their nano size, complex surface morphology, and deviation in properties between the surface and bulk, due to variations in physical and chemical structure. The chemical structure of CNFs is influenced by a variety of covalent bonding arrangements provided by orbital hybridization, primarily due to the allotrope formation ability of carbon,

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**Figure 5.1** Schematic of AFM: (a) Principle of operation, (b) Modes of operation.

with different kinds of carbon-carbon bonds such as  $sp^2$ -based graphite and  $sp^3$ -based diamond.

Enhancement of the application spectrum of CNFs is highly dependent on the surface properties, since it is the surface that dynamically interacts with the environment. Due to these reasons, it has become increasingly important to characterize the CNF surface with advanced tools and techniques that figure into the nanoscale properties.

We now discuss a few, but important and versatile, surface and morphological characterization techniques that fall within these boundaries. These techniques include atomic force microscopy (AFM), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray analysis.

### 5.2.1 Atomic Force Microscopy (AFM)

Scanning probe microscopy (SPM) techniques, including atomic force microscopy (AFM) and scanning tunneling microscopy (STM), are capable of providing high surface sensitivity with atomic-level resolution. However, the yield of acceptable images is low and image interpretation can be difficult. When performing high-resolution scans, large numbers of images must be taken to ensure the data is representative.

Atomic Force Microscopy (AFM) is a mechanic-optical instrument able to detect forces of the order to piconewtons ( $10^{-12}$  N). AFM works by scanning the sample surface with a tip or probe, either in the contact or non-contact scanning mode [1], to obtain high lateral resolution images

with z-height discrimination from all types of surfaces—even those that are wet or insulating. Figure 5.1, schematically explains the principal of operation and mode of operation of AFM.

A typical AFM scan measures the attractive or repulsive forces between the tip and the sample either in constant height or constant force mode. According to the sample the force can be any of the following: electrostatic, magnetic, mechanical and even van der Waals force.

The interactive force is detected by a series of photodetectors which collect the laser beam scattered at different directions due to the deflection of the probe. This results in formation of a 3D image carrying the information of the topography of the CNF surface. A major advantage of AFM is the non-requirement of conducting surfaces for the analysis, although the method requires a large number of scanned images for ensuring authentic data representation.

Furthermore, the AFM exhibits sensitivity to chemical changes via molecular recognition and friction imaging.

Paredes *et al.* (2002 and 2003) developed an AFM-based approach to resolve hydrophilic oxygen group regions on carbon surfaces [2, 3]. This method is based on the detection of phase changes in the noncontact tapping mode of the AFM to detect and map the oxygen functionalized content of CNF surfaces.

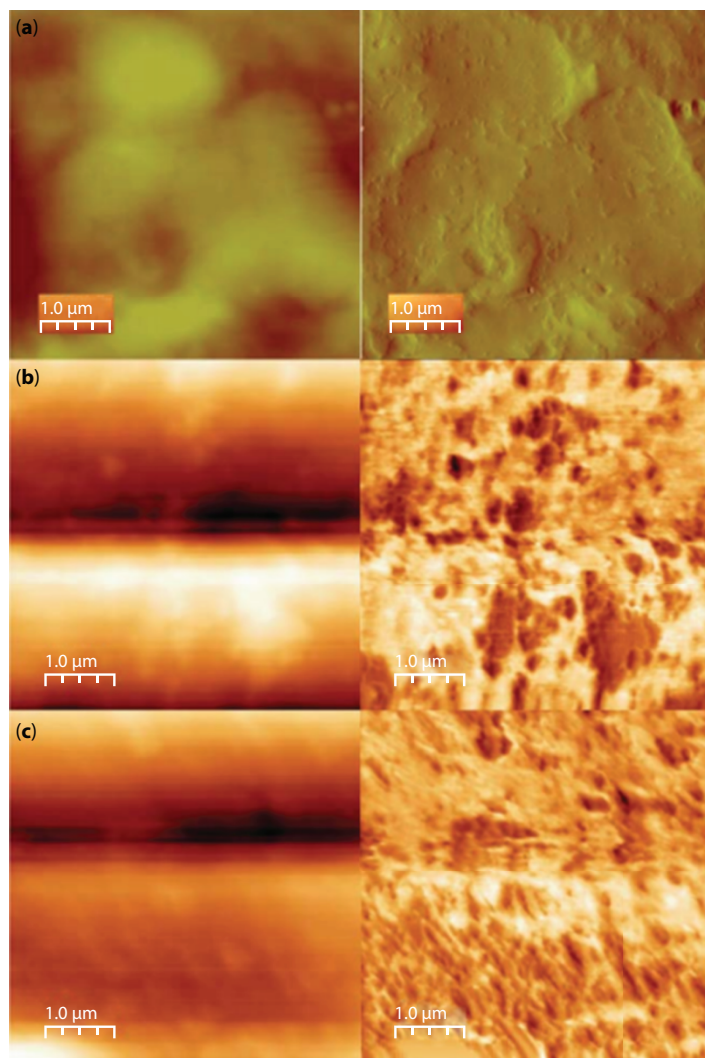
Line profiles from the noncontact tapping mode phase images of a CNF deposited on HOPG (Highly Oriented Pyrolytic Graphite) before and after oxygen plasma treatment show abrupt changes in surface topography and also lead to phase contrast. Typical phase profiles implied that the phase of the untreated CNF was very similar within  $1^\circ$  to that of the HOPG substrate, while the phase of the plasma-treated CNF was consistently  $3^\circ$  higher than the HOPG substrate. This  $3^\circ$  shift had been previously reported for oxygenated planar HOPG surfaces as well [4].

In another application, dispersion of CNTs in rubber matrices by AFM was studied and reported by different authors [5–10].

Effect of application of macroscopic strain, its suppression and second stretching behavior of CNTs/Styrene Butadiene Rubber (SBR) was studied using cost-effective AFM in tapping mode.

When the tip passes through a sample of CNTs/Styrene Butadiene Rubber, the AFM's oscillation phase can change according to the different interaction conditions between the tip and the sample. This results in phase image contrast and it is commonly used to distinguish different domains or different blend components [7].

In another application of AFM, the dispersion of nanometric fillers and morphology in nanocomposites and polymer blends based on elastomers was studied by Fabiula *et al.* (2014) [12]. A novel method was used



**Figure 5.2** AFM images representing height images (left) and phase images (right) of (a) Pure TPU and TPU/CNF nanocomposites with (b) 4 wt% CNF loading and (c) 10 wt% CNF loading. (Source: AK Barick, DK Tripathy, *J. Appl. Polym. Sci.* 124, 765–780, 2012 ©Wiley) [11].

by Barick and Tripathy (2012) [11] to prepare nanocomposites of TPU/CNFs by melt intercalation technique followed by compression molding. AFM was used to analyze the dispersion of CNFs in these nanocomposites. According to the AFM images, CNFs presented a high level of dispersion via either covalent or ionic bonds between CNF and TPU. The nanofibers

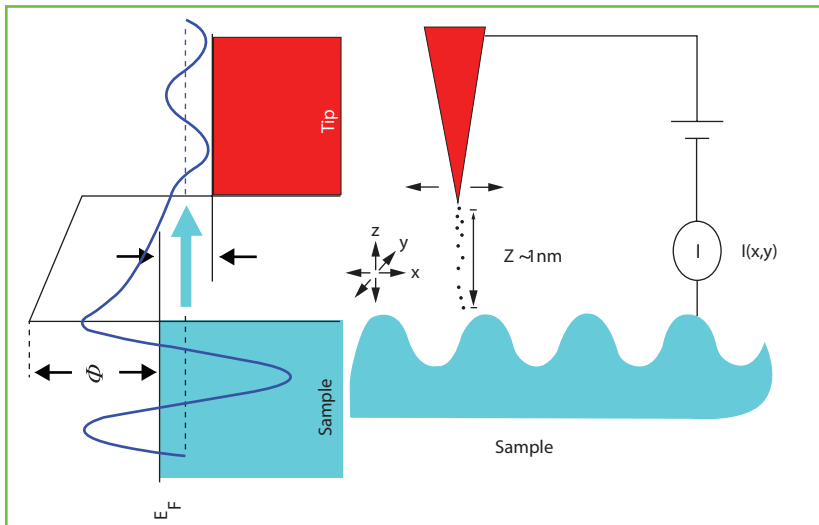
are preferentially associated with the soft segment of the TPU matrix, which developed sufficient wetting and interphase adhesion of the CNF with TPU (Figure 5.2). Due to the CNFs presence, the mechanical reinforcement of the TPU matrix was obtained.

### 5.2.2 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy is a companion to AFM in characterization of CNF's surfaces by STM. STM can map the surfaces of electrically conductive materials with sub-Angstrom vertical resolution. STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them (Figure 5.3). The resulting tunneling current is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample [13].

Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form on a computer screen.

Paredes *et al.* used STM observations to address the atomic-scale reorganization of the CNF surface after oxidation [2, 3]. STM images of nanofiber



**Figure 5.3** Schematic diagram of STM's operation principle of Quantum Mechanical Tunneling.



surface before and after a 5 min oxygen plasma treatment, showed that untreated CNF surfaces displayed basal graphite characteristics at a local scale of several atom lengths, but lacked long-range atomic order. While, oxygen plasma treatment resulted in the annihilation of the short-range basal graphitic order, leading to a significant and uniform increase in the atomic-scale disorder of the CNF surface. Paredes *et al.* (2005) [14] monitored the graphitization process of CNF surfaces at various annealing temperatures by using STM imaging. These images provided clear, atomic-scale evidence for the evolution of the CNF surface consistent with spatially averaged characterization results obtained by X-ray diffraction (XRD) and Raman spectroscopy.

In particular, STM revealed a nanoscale surface transformation from platelet morphology to larger ordered areas and finally to atomically flat terraces on faceted nanofibers at 2800 °C.

This corresponded in the atomic-scale images to a conversion from small, highly defective crystallites coalescing to form larger, defective crystallites and finally to true graphitic domains in many areas. Endo *et al.* also observed similar graphitization results using STM imaging [15].

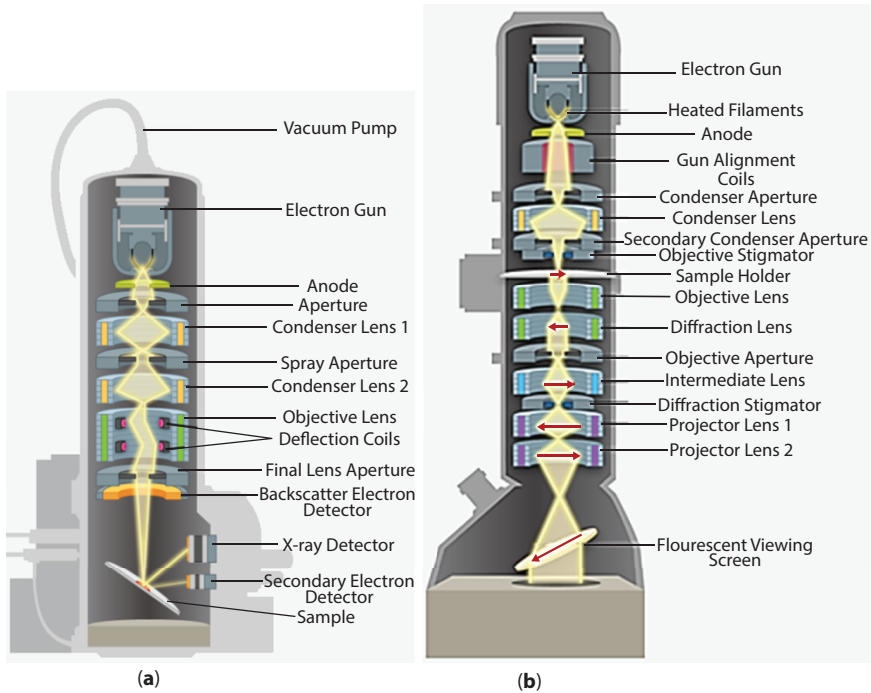
Another STM study by Yoon *et al.* found that graphitized platelet CNFs are actually assembled of carbon nanorod units, where the edges of the graphene layers formed closed caps [16].

### 5.2.3 Electron Microscopy for Morphology and Surface Characterization

#### 5.2.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a widely used technique for characterizing the morphological structure and topography of CNFs. In particular, SEM is useful in the examination of length, diameter and morphology of CNFs. Typical penetration depth of the SEM electron beam is about 5 to 50 nm, while the resolution is around tens of nm. The signals collected by the various detectors are mainly secondary electrons (SE), backscattered electrons (BSE), X-rays, and cathode-luminescence light. These signals are then amplified, analyzed and transferred as images of the topography. Electron Dispersive Energy Analysis (EDAX) gives additional information on the chemical composition by analysis of the emitted characteristic X-rays. An energy dispersive X-ray analysis (EDAX) spectrometer is a common tool available with both SEM and TEM (Figure 5.4).

EDAX gives the elemental composition of the sample spot irradiated due to the incoming electron beam. It mainly consists of a semiconductor



**Figure 5.4** Schematic diagrams of (a) SEM along with the EDAX detector and (b) TEM. (Source: <http://library.open.oregonstate.edu/microbiology/chapter/microscopes/>).

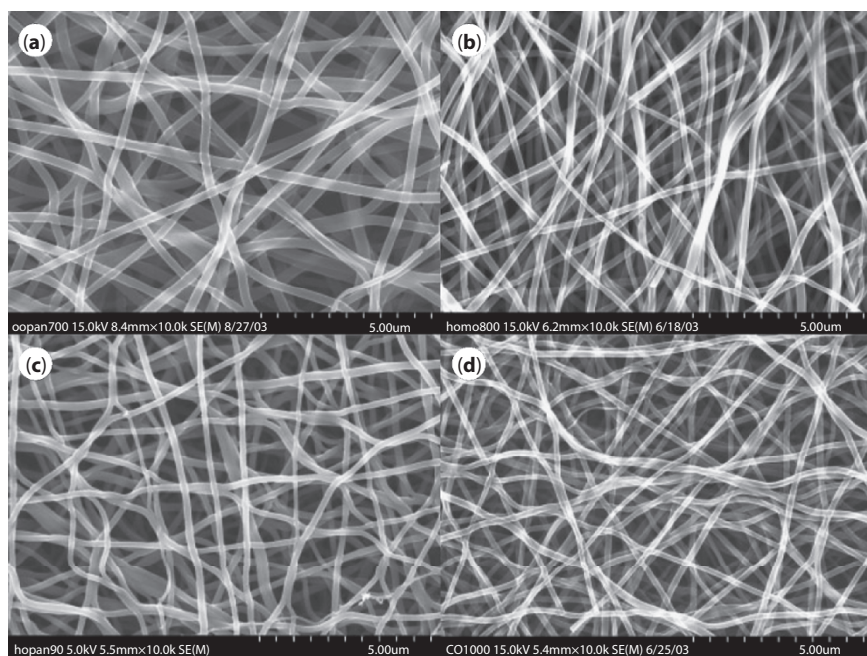
diode that detects each incoming X-ray photon emitted due to the simultaneous ejection of an inner shell electron by the primary electron beam, and consequent replacement of the resulting vacancy with an outer shell electron. The resulting spectrum, which captures the differences in BE of the electron shells involved in the relaxation process, is unique for each element, and helps in identification of the elements present in the CNFs. Data can be analyzed to give the exact chemical composition of the CNFs under study. EDAX information is a function of energy of the electron beam, and the density and chemistry of the CNF specimen. In EDAX, the lateral spatial resolution can range from micrometers to tens of nanometers, while the depth resolution is a fraction of the incident beam range and so is on the scale of hundreds of nm or less.

Xia *et al.* (2005) [17] generated secondary CNFs with diameters in the range from 10 to 20 nm grown from cyclohexane catalyzed by the sintered metallic iron nanoparticles under reducing conditions.

The morphological transition from smooth fibers to those with protrusions from the surface, correlates with the processing steps taken to grow secondary fibers from iron oxide particles deposited on the oxidized CNFs. The resulting increase in the surface area is well captured by the SEM image.

In an important study SEM was used [18] to ascertain the decrease in average diameter of polyacrylonitrile-based (PAN-based) carbon nanofibers from 350 to 250 nm with increase in carbonization temperature (Figure 5.5) in the HTT (Heat Treatment Temperature) range.

In another study, SEM was used [4] to document the change in surface morphology of vertically aligned carbon nanofibers (VACNFs) grown from a  $\text{Fe}_x\text{Co}_{100-x}$  gradient film. The growth conditions, such as temperature, gas flow ratio, pressure, and plasma current, were kept the same for all compositions for the sake of proper comparison of magnetic properties of nanoparticles that underwent the same treatment. SEM images revealed that the nanofiber growth conditions were optimal for the Co-rich alloys, while the Fe-rich alloys catalyze better in a higher energy process. SEM



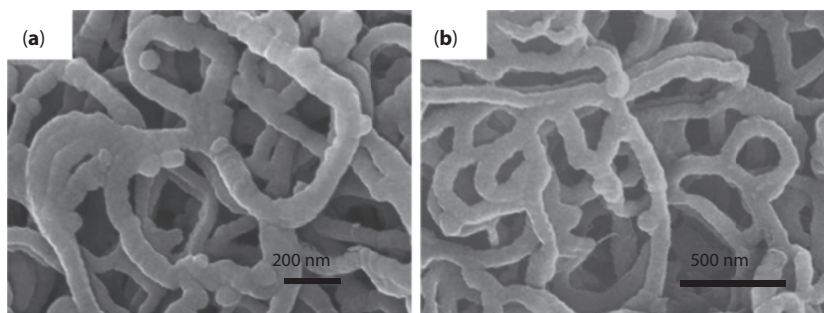
**Figure 5.5** SEM images of PAN-based CNFs as a function of HTT: (a) 700; (b) 800; (c) 900; (d) 1000 °C. (Source: Chan Kim, Sang-Hee Park *et al.* *J. Raman Spectroscopy*, 35, 928–933, 2004 © Wiley) [18].

images of the VACNFs were studied as a function of composition in the 115-nm-thick gradient film. At lower Fe concentrations, the samples have the appearance of a rather uniform “forest” of nanofibers with a narrow diameter distribution (100–200 nm). However, as the Fe concentration is increased to 50%, a bimodal distribution in diameters was observed, where smaller particles that are able to break away from the film grow into tall fibers and the larger particles (300–500 nm) remain behind. Finally, at high Fe concentrations, it appeared that it is difficult to break up the film and large angular particles are formed, which are not highly active catalysts under these conditions.

In another research conducted by Klein *et al.* (2005) [19] SEM was used to document the change in morphology of VACNFs with catalyst composition. Small levels of Cu in Ni-rich alloy catalysts resulted in split particles and branching nanofibers. However, as the composition became Cu-rich the nanofibers became more conical. This suggested that Cu-rich alloys were not highly active catalysts for carbon growth, but rather the Ni portion segregated to catalyze a very thin CNF, which served as a scaffold for the condensation of predominantly silicon species from the plasma.

A facile way to synthesize N-doped porous CNF webs as anode materials for lithium-ion batteries via using polypyrrole as a precursor was reported by Qie *et al.* (2012) [20]. The high-level N-doping and the nanostructure of the CNF webs guaranteed a reversible capacity of 943 mAh/g with a current density of 2 A/g, even after 600 cycles. Figure 5.6a gives the SEM microstructure of the PPy nanofiber webs and Figure 5.6b of CNF webs. Thus SEM proves to be a useful microstructure analysis tool for CNF nanocomposites.

Weng *et al.* (2004) [21] reported significantly enhanced field emission FE properties from VACNFs on a Si substrate treated briefly with an argon plasma.



**Figure 5.6** The SEM microstructure of (a) PPy nanofiber web and (b) CNF webs. (Source: Qie *et al. Adv. Mater.* 24, 2047–2050, 2012. © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim) [20].

Analysis by electron microscopy and EDX, suggests that a structural transformation of the fibers is a result of a co-sputtering/deposition process by energetic plasma ions, revealed by the Si counts increasing with longer Ar plasma treatment. They attributed the field emission enhancement to the combined effect of additional Si/C layer coverage, catalytic nanoparticle removal, and the physical sharpening of the CNFs tips. However, with longer treatment times 5 min, structural damage effects were seen to decrease the effectiveness of the plasma treatment as conveyed by the FE measurements.

Hang *et al.* (2005) [22] found EDX mapping useful in their search for the best nanocarbon material for Fe/C composite air battery anodes. Hollow- and herringbone-type CNFs exhibited favorable results, including improved conductivity and higher redox currents of the Fe/C electrode. EDX revealed that on the Fe/nanofiber surface, iron was more dispersed than on Fe/graphite after cycling. They concluded that such a high dispersion of iron on nanofiber surfaces may improve the electrochemical behavior of the iron redox species.

It is important to state that surface charging is one of the main impediments that may result in spurious secondary electron signals. These losses can be minimized by coating the sample with thin films of conducting substance, i.e., gold, silver, or conducting carbon.

#### 5.2.3.2 *Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM)*

Other useful tools of electron microscopy are transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The signal consists of electrons transmitted through the ultra-thin sample, prepared either by FIB (focused ion beam) for bulk material or dispersion of CNF powder in ethanol, and adding the resulting solution dropwise to a copper grid, followed by desiccation for at least 10 hours. In case of 2D CNFs, a single CNF can be used for analysis. The TEM operates either in image mode or diffraction mode. The latter mode reveals the crystal structure of the CNF under investigation. Both these tools convey information about the nanostructure of CNF as a whole, in addition to revealing the presence of surface layers and atomic structure of the surface interface by high-resolution TEM (HRTEM).

The surface as well as internal structure of CNFs can be analyzed using STEM or TEM. Both real space “image” and reciprocal space “diffraction” data, together with chemical and electronic analytical information derived from EDX or EELS, can be obtained from the same nanoscale area.

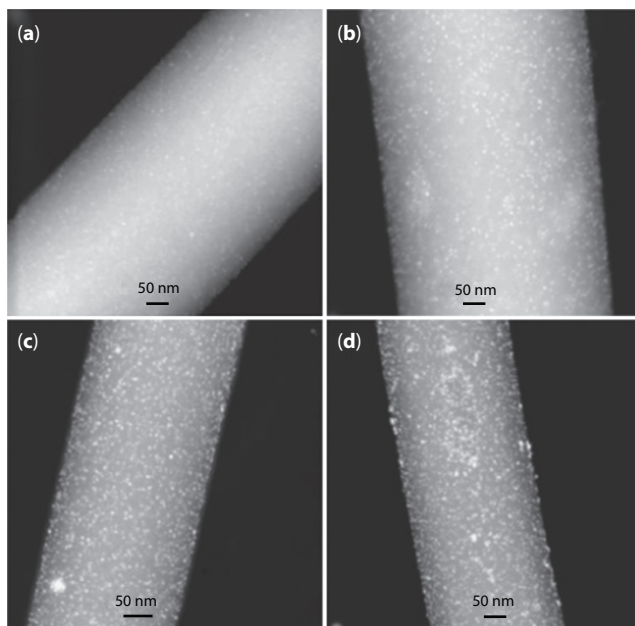
The TEM and STEM therefore provide a wide and deep range of data about the specimen of interest.

For instance, TEM images of the catalyst particles following nanofiber growth were studied for pure Co, for  $\text{Fe}_{41}\text{Co}_{59}$  and for pure Fe initial films [23].

Again, the Co-rich elongated and teardrop-shaped catalyst particles (worked well for VACNF synthesis under the present growth conditions. As the concentration of Fe increases, the catalyst particles become more angular and less active in the production of carbon leading to minimal fiber production at the Fe rich composition.

In an important study involving Atomic Layer Deposition (ALD) of Pd Nanoparticles on N-Doped Electrospun Carbon Nanofibers, Mohammad Aref Khalily *et al.* (2019) [24] used STEM imaging (Figure 5.7) to confirm increase of Pd incorporation with increase in ALD cycles. Later this result was also confirmed by XRD studies.

A study on the nanofiber structural effects of different catalysts (Ni versus Pd) was performed [25]. The STEM images indicated that the Ni-catalyzed fibers have graphitic planes ending on sidewalls of the fiber in a herringbone fashion, whereas the Pd-catalyzed fibers have multi-walled



**Figure 5.7** STEM images of Pd10/nCNF (a), Pd20/nCNF (b), Pd30/nCNF (c), and Pd40/nCNF (d). Pd10/nCNF means nCNF subjected to 10 ALD cycles. (Source: Mohammad Aref Khalily, Bhushan Patil *et al.* *ChemNanoMat*, 05, 1–8, 2019 ©Wiley) [24].



nanotube-like layers on the outer walls of the fiber. Ominami *et al.* (2005) attributed the increased electrical conductivity along the length of the Pd catalyzed CNFs to this improvement in the graphitic structure and lower interface resistance with the substrate.

Similarly, Naguib *et al.* (2005) [26] used HRTEM to analyze the nanofiber wall structure in order to compare processing methods for biological applications. They reported that heat treatment of CNFs at 3000 °C formed graphitic loops on their surface, eliminating chemically active dangling bonds and leading to hydrophobic behavior. However, CNFs that were pyrolytically stripped in carbon dioxide to remove hydrocarbon layers from their outer surface had significantly more disordered surfaces and exhibited hydrophilic behavior. As a result of improved wetting and increased protein binding capacity of the nanofiber surface, Naguib *et al.* concluded that antibody coatings were more successful on the pyrolytically stripped CNFs.

The work by Hang *et al.* (2005) [22] is also a good example of the utility of TEM for surface characterization. TEM imaging, can give an idea of the degree of functional sites available by the dispersion of gold nanoparticles on the surface of the fibers. Additionally, the HRTEM image gives useful insight on how the graphitic planes are terminated by a gold nanoparticle.

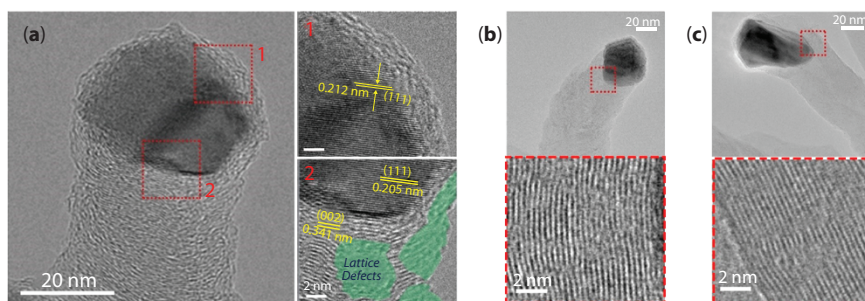
Similarly, the work by A. Asokan *et al.* (2020) [27] on Carbon Nanofibers Encapsulated Nickel-Molybdenum Nanoparticles, uses TEM images of the catalysts synthesized at 400–600°C. The images confirm the increase in particle size of NiMo@Ni with respect to CVD temperature, resulting in different fiber thickness and length. In addition TEM images clearly show the direction of carbon growth which is perpendicular to NiMo@Ni metal head in case of the catalysts synthesized at 400 and 500°C (Figure 5.8 a, b), and parallel growth of carbon for the catalyst at 600°C (Figure 5.8 c). Furthermore, the interlayer d-spacing values of NiMo and carbon were calculated to be 0.205 and 0.341 nm, respectively, which are consistent with the calculated d-spacing values of Ni (1 1 1) plane and graphite (0 0 2) plane obtained from XRD.

Tongfei Li *et al.* (2018) [28] compared the SEM, TEM and HRTEM images to study the morphology of Encapsulated Ni<sub>3</sub>Fe Nanoparticles in N-Doped Carbon Nanotubes.

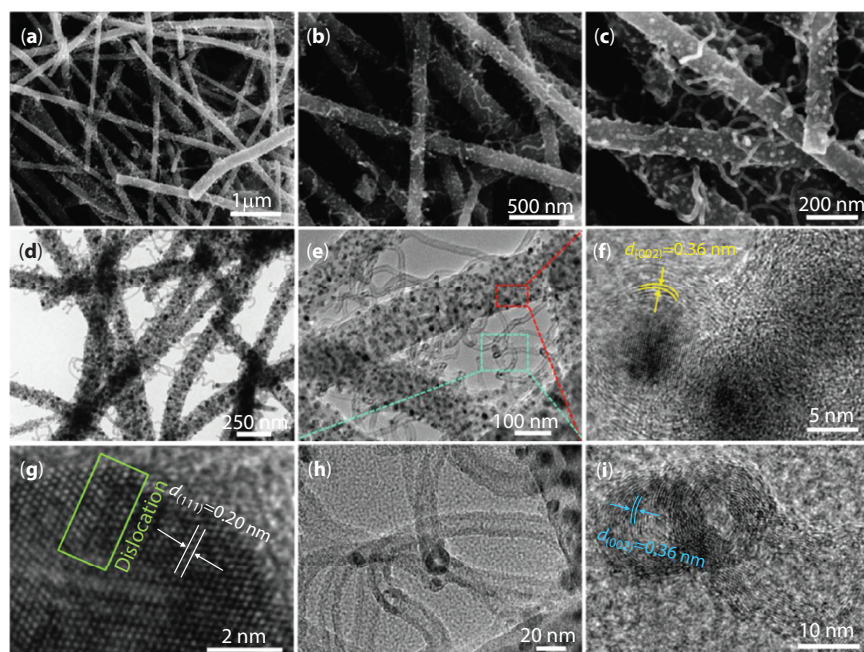
SEM images revealed nanofibers with lengths of tens of micrometers possess a very smooth surface and uniform diameter of ≈300 nm. The shrinking in the size to ≈100 nm due to the carbonization of PVP and the decomposition of metal nitrates is shown in Figure 5.9 b, and c.

Typical transmission electron microscopy (TEM) images (Figure 5.9 c, d, e) further confirm the fibrous skeleton of the fabricated Ni<sub>3</sub>Fe@N-C NT/

NFs, while High-resolution TEM (HRTEM) image in Figure 5.9 f-i, indicates that the  $\text{Ni}_3\text{Fe}$  nanoparticles are coated with several graphitic carbon layers, with the observed interplanar spacing in the onion-like carbon layers to be 0.36 nm, corresponding to the C (002) plane. Figure 5.9 g shows the

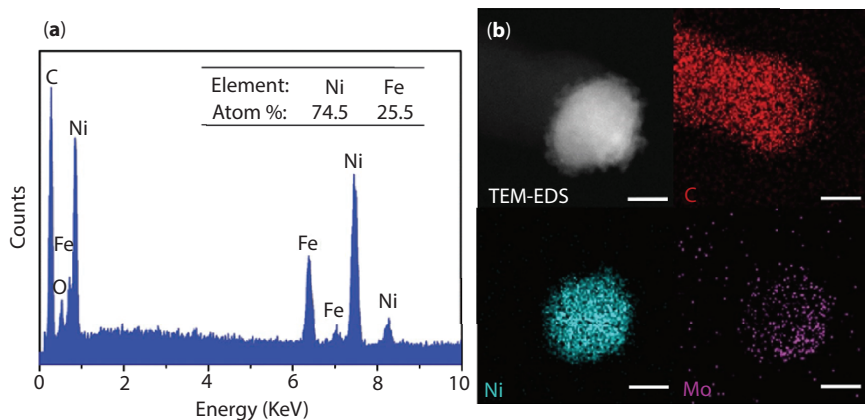


**Figure 5.8** TEM images of NiMo/CNF synthesized at (a) 400°C, (b) 500°C, and (c) 600°C (red square: high-magnification images). (Source: Arunchander Asokan, Chaehyun Lim *et al. ChemNanoMat*, 06, 937-946, 2020 ©Wiley) [27].



**Figure 5.9** Morphological examinations of the as-synthesized  $\text{Ni}_3\text{Fe}@\text{N-C}$  NT/NFs. (a-c) SEM images. (d-e) TEM images. (f-i) HRTEM images. (Source: Tongfei Li, Gan Luo, *et al. Adv. Funct. Mater.* 28, 1805828, 2018©Wiley) [28].





**Figure 5.10** (a) EDX spectrum of s Compositional analyses of the as-prepared Ni<sub>3</sub>Fe@N-CNT/NF spectra of as-prepared Ni<sub>3</sub>Fe@N-CNFs. (Source: Tongfei Li, Gan Luo, *et al. Adv. Funct. Mater.* 28, 1805828, 2018©Wiley). (b) EDS mapping of NiMo/CNF-400 for C, Ni, and Mo. (Source: Asokan, Chaehyun Lim *et al. ChemNanoMat*, 06, 937–946, 2020©Wiley) [27].

HRTEM image of an individual Ni<sub>3</sub>Fe nanoparticle with some dislocations. The measured lattice spacings of 0.20 nm correspond to the (111) facets of Ni<sub>3</sub>Fe. A closer observation (Figure 5.9 i) reveals the highly graphitic and multiwalled features of the rooted carbon nanotubes.

Energy Dispersive X-ray Spectroscopy (EDX) is an extension of SEM, and is used for determination of elemental composition of materials. In their studies on encapsulation of Ni<sub>3</sub>Fe Nanoparticles in N-Doped Carbon Nanotube.

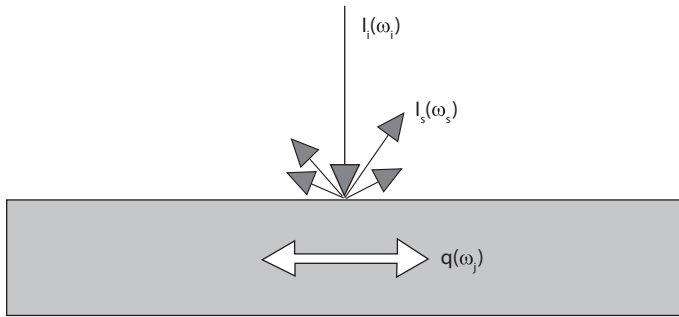
Tongfei Li *et al.* (2018) [28] used the SEM-EDX or the energy-dispersive X-ray (EDX) spectrum (Figure 5.10 a) to verify the Ni/Fe atomic ratio of 74.5:25.5, which is in consistence with the stoichiometric value of 3:1.

Similarly TEM too is associated with a tool for elemental compositional mapping known as EDS (Energy Dispersive X-ray Spectroscopy and is same as EDX). Asokan *et al.* (2020) [27] used STEM image and the corresponding EDS mapping of NiMo/CNF-400 to determine the dispersion of Ni and Mo in a CNF synthesized at 400°C (Figure 5.10 b).

### 5.3 Spectroscopic Characterization

#### Spectroscopic Analysis of CNF by Raman Spectroscopy

The Raman signal originates from interaction of light (photons) with vibrations (phonons in a crystal). When light from a laser source, with



**Figure 5.11** Photon-Phonon reaction.

frequency  $\omega_j$ , interacts with phonons in the sample (frequency  $\omega_j$ ), as shown in Figure 5.11, there can be an exchange of energy between light and phonons. This may result in an energy gain or loss of the phonons. Therefore, the frequency of the scattered light ( $\omega_s$ ) can change:  $\omega_s = \omega_i \pm \omega_j$ .

The spectrum of the scattered light will show frequency components at a frequency  $\omega_j$  higher or lower than the frequency of the incident laser light. So, from the spectrum, one is able to know the characteristic frequency of the material vibrations  $\omega_j$ .

### 5.3.1 Raman Spectroscopic Studies of Carbon Nanofibers

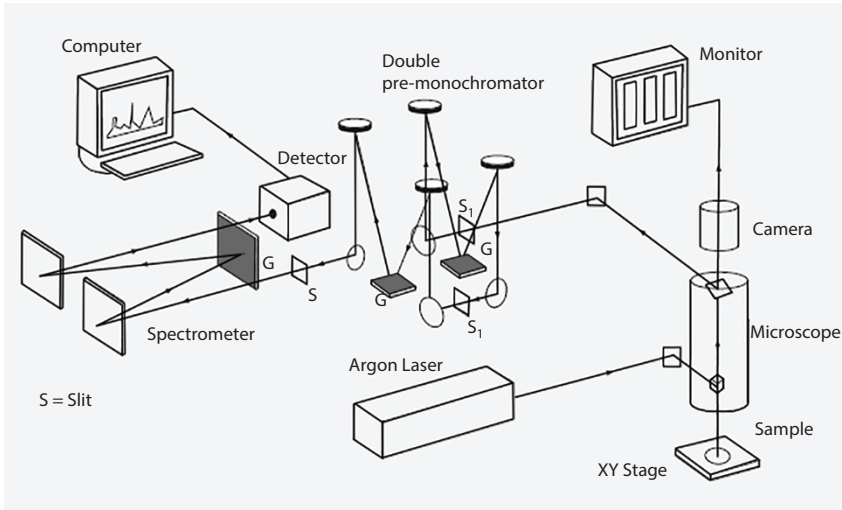
Raman spectroscopy is the most important tool for studying the structural properties of carbonaceous materials like CNFs. Raman spectra provide useful insights on the crystalline perfection of graphite-based materials.

Figure 5.12 shows a typical Raman spectroscopy instrument. Laser light is focused on the sample through a microscope. The scattered light is collected and its spectrum is analyzed (pre-monochromator, spectrometer). This spectrum contains information on the Raman signal of the CNF sample.

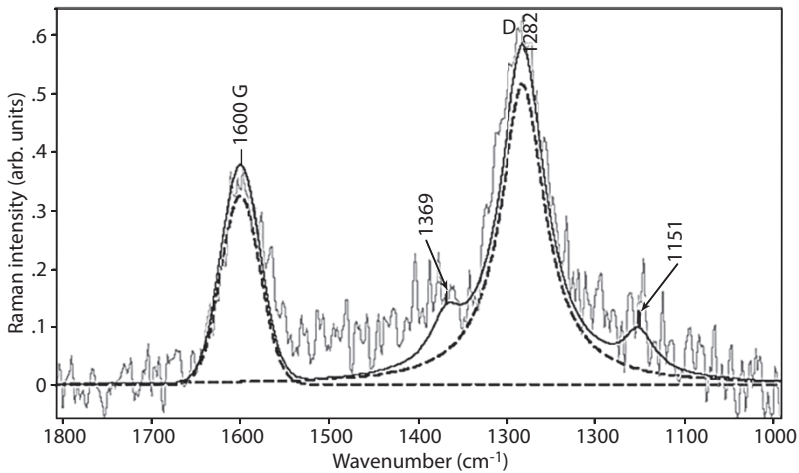
A typical Raman plot of CNFs (Figure 5.13) shows G-band at  $1600\text{ cm}^{-1}$  is usually related to graphite layer and the D-band at  $1282\text{ cm}^{-1}$  related to disordered structures in carbon materials.

The additional two weak noisy bands observed at around  $1150$  and  $1370\text{ cm}^{-1}$  can be assigned to the mixed bonds between  $\text{sp}^2$  and  $\text{sp}^3$  carbon for amorphous carbon structures.

The ratio of intensities of D-band to G-band ( $I_D/I_G$ ) is found to have a value of 1.69.



**Figure 5.12** A typical Raman spectroscopy setup. (Source: Recreated from Jian Chen, M. Chan and I. De Wolf, “Local stress measurements in packaging by Raman spectroscopy,” Proceedings of 3rd Electronics Packaging Technology Conference (EPTC 2000) (Cat. No.00EX456), Singapore, 2000, pp. 159–162) [29].



**Figure 5.13** Typical Raman plot of CNFs.

An increase in relative intensity of the D-band near infrared excitation (1064 nm) is related to a larger electron-phonon interaction for D-band with respect to G-band.

In one such study Endo *et al.* 1999 [30], studied the variations of the properties of submicron vapor-grown carbon fibers (VGCFs) and nanofibers,

with diameters around 0.1–0.2 microns and 80–100 nm respectively, are observed by Raman spectroscopy as a function of heat treatment temperature. The micro-structural evolution strongly depends on the original properties of the material, such that the main transition temperatures associated with the onset for establishing 2D graphene ordering are defined below 1500 °C for the nanofibers and 2000 °C for the submicron VGCFs. Ratio of intensities of D-band to G-band ( $I_D/I_G$ ) is found to have a value for carbon-based VGCFs and nanofibers as 3.44 and 1.35, while those for the corresponding graphitized samples are 0.393 and 0.497 respectively [31] (Wang *et al.* 2003). Ultrafine fibers were spun from polyacrylamide (PAN)/N,N-dimethyl formamide (DMF) precursor solution using a homemade electrospinning setup, and then pyrolyzed in vacuum at 873, 1073, 1273 and 1473 K respectively. The pyrolyzed fibers, with diameter of the order of 100 nm, were characterized using Raman microspectrometry. Their Raman scattering spectra manifested D and G peaks, characteristic of disordered carbon and graphite respectively. The D and G peak parameters were fitted using a Gaussian-Lorentzian mixed shape and graphitic crystallite size and mole fraction in the nanofibers were estimated from the ratio of the integrated intensity of D and G peaks.

In another study [32], nanostructure in the PAN-based carbon fibers was investigated by means of Raman spectroscopy, which was performed using a series of different excitation wavelengths. UV-Raman measurements showed the predominance of  $sp^2$  carbon for the carbon fibers. The excitation wavelength dependence of the spectral line shape implied the presence of the graphitic ( $sp^2$  carbon layers) as well as the amorphous carbon-like component ( $sp^2$  carbon clusters) in these fibers. These studies served as valuable inputs for developing an analytic model, providing essential keys towards development of new generation carbon nanofibers.

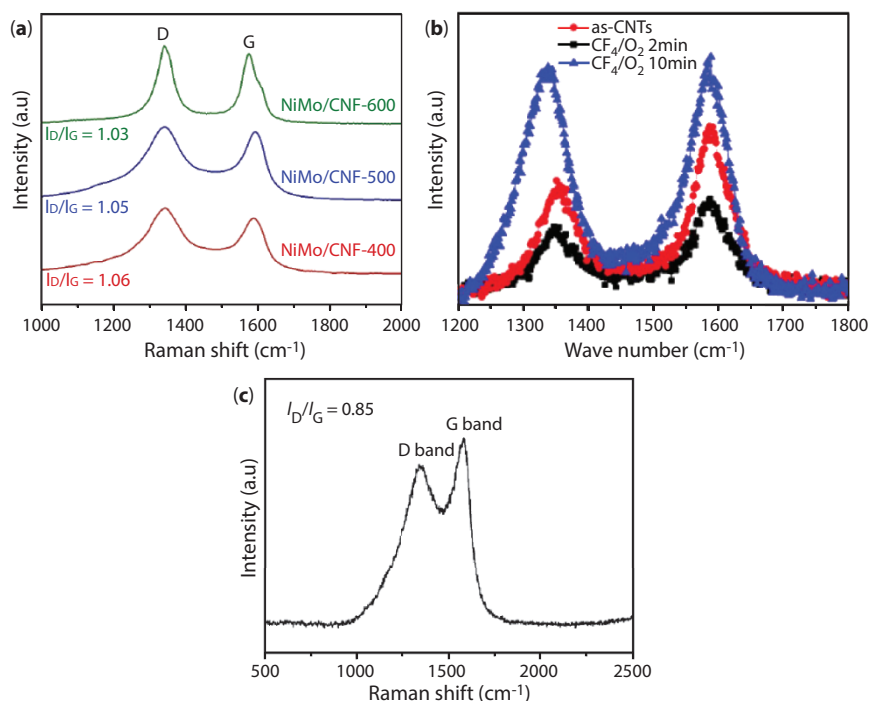
For example, from visual inspection of the excitation wavelength dependence of the Raman spectra, it was found that the PAN-based carbon fibers could be regarded as nanocomposites that are made up of the  $sp^2$  carbon layers and the  $sp^2$  carbon clusters. Raman studies also led to the development of an analytical model based upon the Tuinstra-Koenig relation that could reproduce the experimental behavior of the peak intensity ratio  $I_D/I_G$  reasonably well.

In their research work on encapsulation of CNFs by NiMo, Asokan *et al.* (2020) [27] used Raman spectroscopy to quantify the lattice defects on the catalysts. The characteristic D and G bands are observed at  $\sim 1340$  and  $1590\text{ cm}^{-1}$  for synthesis temperatures of 400 and 500 °C. A red shift is observed for the samples synthesized at 600°C and was attributed to oxidized carbon

structures. The intensity ratios  $I_D/I_G$  were also studied to estimate the quantitative degree of the disorder (Figure 5.14a).

Chien-Huang Tsai (2012) [33] reported similar bands for CNFs synthesized using microwave plasma-enhanced chemical vapor deposition (Figure 5.14b). The ratio of intensities of Raman peaks  $I_D/I_G$ , increased with the slightly appearance of noncrystalline subpeaks implying that the degree of disorder in CNF increased at 10 min  $CF_4/O_2$  plasma treatment. The plot also indicated that from the relative intensity of the as-grown CNFs, the overall crystalline quality is lower than that of  $CF_4/O_2$  plasma post-treatment time of 2 min on CNF. Thus Raman studies can be successfully used to study crystalline disorders.

In another Raman study of encapsulated  $Ni_3Fe$  Nanoparticles in N-Doped CNF by Tongfei Li *et al.* (2018) [28], the Raman spectrum



**Figure 5.14** (a) Raman spectra of NiMo/CNF with various synthetic temperature. Source: Asokan, Chaehyun Lim *et al. ChemNanoMat*, 06, 937–946, 2020 [27]. (b) Raman spectra of (a) as-grown CNF with the various fluorocarbon and oxygen  $CF_4/O_2$  plasma treatment times of (b) 2 min and (c) 10 min. Source: Chien-Huang Tsai, *Surf. Interface Anal.* 44, 573–577, 2012©Wiley [33]. (c) Raman spectrum of as prepared as-prepared  $Ni_3Fe@N-C$  NT/NFs. Source: Tongfei Li, Gan Luo, *et al. Adv. Funct. Mater.* 28, 1805828, 2018©Wiley [28].

(Figure 5.14c) exhibits disordered carbon-induced D band and graphitic carbon-induced G band, respectively. The intensity ratio between the D and G bands ( $I_D/I_G$ ) is calculated to be 0.85, further confirming a highly graphitic carbon. Thus the ratio of the intensities plays a major role in identification of disordered carbon or graphitic carbon.

The last example we take in this section is the studies [18] of Chan Kim, *et.al* (2004) performed on PAN based CNFs prepared by electro spinning at various HTT (Heat Treatment Temperature). Viz. 700°C, 800°C, 900°C and 1000°C (Figure 5.15).

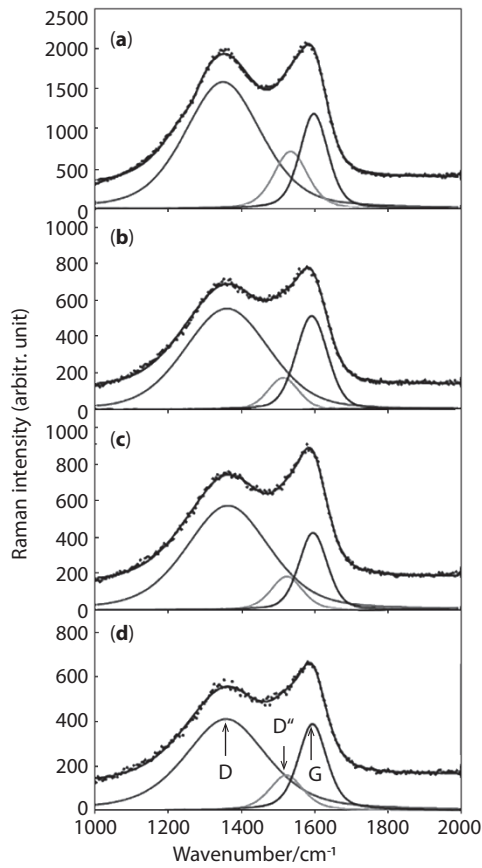
As discussed in the previous examples of Raman studies on CNFs, the ratio of the relative intensities of the D-band to the G-band, known as the R-value, depends on both the degree of graphitization and the alignment of the graphitic planes. In the example under discussion, the 'R' value of the PNA-based novel CNFs are greater than unity and decreases with increasing HTT. This suggest the increased transformation of disordered carbon into graphitic carbon, during the carbonization process. Chan Kim *et al.*, went a step further and calculated the crystallite domain size of graphite as  $L_a = 44/R$ .

Thus,  $L_a$  increased from 1.6 to 3.2 nm with increase in HTT (Table 5.1).

## 5.4 Spectroscopic Analysis of CNF by XRD

The techniques of XRD and Raman spectroscopy are used to complement the local information obtained by STM on CNFs. In one such study, CNFs have been chosen mainly for two reasons: (i) they are of particular interest in their graphitized state for some applications, for example, as a filler to improve the performance of Li-ion batteries [16, 34] and (ii) from a fundamental carbon-science perspective, they offer the opportunity to study in detail potentially new aspects in the graphitization of carbon materials confined to the nanometer scale.

Typical X-ray diffractograms for the as-grown and heat-treated CNF samples are presented in Figure. As expected, the most visible feature is the graphite (002) diffraction line, located at  $\sim 26^\circ$ . Also discernible are the (100) and (101) reflections, which appear in the region between 42 and 45° forming a broad band, and the (004) line near 55°. We note that the (002) peak narrows and increases in intensity with increasing heat-treatment temperature, and a similar trend is observed for the other lines, which indicates a general development of both intra- and inter-plane graphitic order. Likewise, it is apparent that the (002) peak of the



**Figure 5.15** Raman spectra of PAN-based carbon nanofibers as a function of HTT: (a) 700; (b) 800; (c) 900; (d) 1000 °C. (Source: Chan Kim, Sang-Hee Park *et al. J. Raman Spectroscopy*, 35 928–933 2004) [18].

**Table 5.1** XRD results for PAN-based carbon nanofibers.

| HTT/°C | 2 $\theta$ /° | $d_{(002)}$ /nm | $L_{c(002)}$ /nm | $L_{a(10)}$ /nm | $L_{c(002)}/d_{002}^a$ |
|--------|---------------|-----------------|------------------|-----------------|------------------------|
| 700    | 24.51         | 0.363           | 1.85             | 2.23            | 5.1                    |
| 800    | 24.59         | 0.363           | 1.94             | 3.18            | 5.3                    |
| 900    | 24.63         | 0.361           | 2.11             | 3.33            | 5.8                    |
| 1000   | 24.65         | 0.360           | 2.15             | 3.36            | 6.0                    |

<sup>a</sup>Number of graphite layer planes.

as-grown sample has a broad shoulder on its low-angle side. Indeed, the peak can be deconvoluted [35] to yield a sharp line centered at about  $26.3^\circ$ , characteristic of an ordered graphitic phase, and a broad band at  $24.7^\circ$ , indicative of only partially ordered carbon. Considering the known duplex structure of this CNF, the ordered phase can be ascribed to the graphitic inner filament and the less ordered phase to the relatively amorphous carbon outer layer. Table lists some crystallographic parameters deduced for the two phases: the interlayer spacing ( $d_{(002)}$ ) and the apparent crystallite size along the c axis ( $L_c$ ).  $L_c$  was calculated using Scherrer's formula as given below:

$$d_{(002)} = \frac{\lambda}{2 \sin \theta} \quad (5.1)$$

$$L_c = \frac{0.9\lambda}{\beta \cos \theta} \quad (5.2)$$

$$L_a = \frac{1.84\lambda}{\beta \cos \theta} \quad (5.2a)$$

where " $\theta$ " was the scattering angle, " $\lambda$ " was the wavelength of X-ray, " $\beta$ " was the width of the diffraction peak measured at half its height in radian, and the coefficient (pre-factor) of "0.9" was included in "Scherrer's Equation" because the Gaussian distribution was adopted.  $L_a$  is the apparent crystallite size along the 'a' direction.

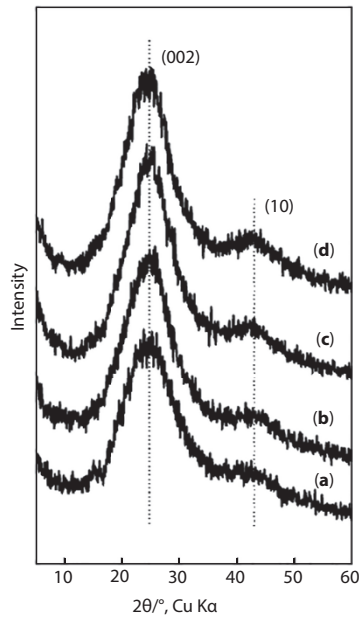
Chan Kim *et al.* (2004) [18] studied the XRD patterns of the PAN-based carbon nanofiber webs (Figure 5.16). The two XRD peaks near  $2\theta = 24$  and  $44^\circ$  correspond to the (002) and (10) layers of the graphite structure.

The values of  $L_a$  and  $L_c$  are tabulated in Table 5.2. The table shows that the values of  $L_a$  and  $L_c$  increase with increase in HTT. This fact has been earlier confirmed from Raman studies performed on the same samples.

Nguyen *et al.* (2014) [36] conducted another study on CNF, where XRD is used as an important analysis tool for crystallographic characterization of modified iron encapsulated CNF.

The research utilized calcination of CNF, in nitrogen gas flow to detach acidic and basic groups from the surface of as-synthesized CNF and remove the amorphous carbon phase. This is because functional oxygen





**Figure 5.16** XRD patterns of PAN-based carbon nanofibers as a function of HTT: (a) 700; (b) 800; (c) 900; (d) 1000 °C. Source: Chan Kim, Sang-Hee Park *et al.* *J. Raman Spectroscopy*, 35, 928–933, 2004 © Wiley [18].

**Table 5.2** XRD results for PAN-based carbon nanofibers.

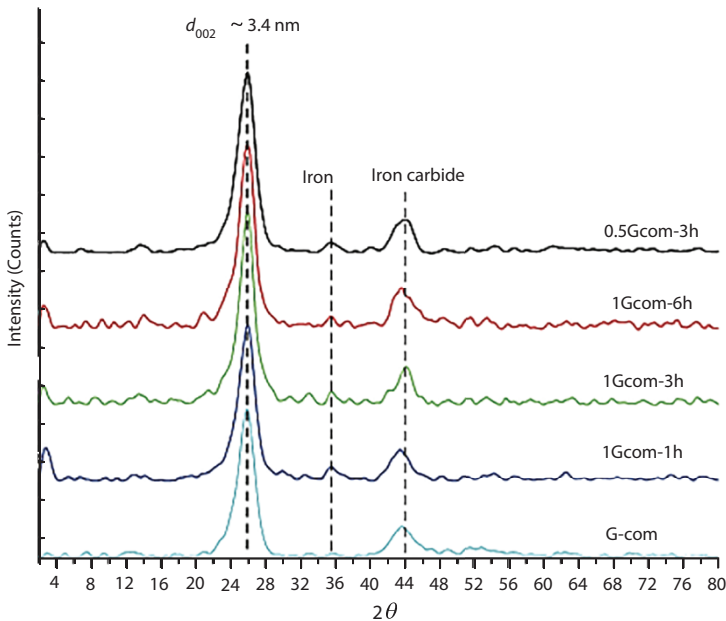
| HTT/°C | 2θ/°  | $d_{(002)}/\text{nm}$ | $L_{c(002)}/\text{nm}$ | $L_{a(10)}/\text{nm}$ | $L_{c(002)}/d_{002}^a$ |
|--------|-------|-----------------------|------------------------|-----------------------|------------------------|
| 700    | 24.51 | 0.363                 | 1.85                   | 2.23                  | 5.1                    |
| 800    | 24.59 | 0.363                 | 1.94                   | 3.18                  | 5.3                    |
| 900    | 24.63 | 0.361                 | 2.11                   | 3.33                  | 5.8                    |
| 1000   | 24.65 | 0.360                 | 2.15                   | 3.36                  | 6.0                    |

<sup>a</sup>Number of graphite layer planes.

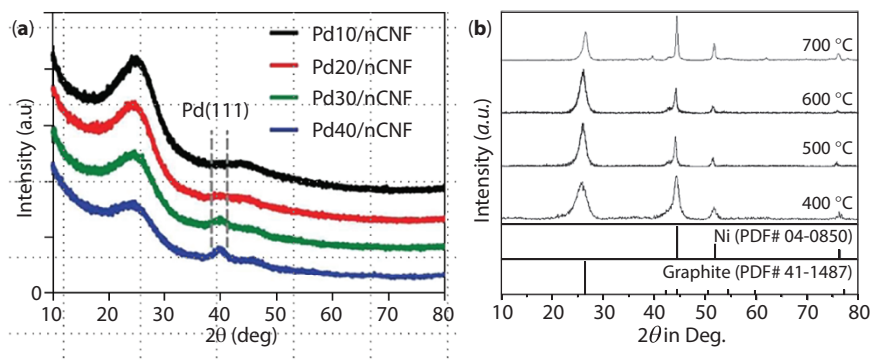
groups and the amorphous carbon phase inhibit the supported catalyst during nitrogen hydrogenation [37, 38] (Li *et al.* 2004; Bartholomew 2001). The degree of graphitization of samples and their relative amorphous values were assessed by the Bruker AXS D8 Advance XRD system using copper Kα radiation (wavelength,  $\lambda = 0.154 \text{ nm}$ ) and 2 theta from 2–80°. The CNF XRD pattern shows more information of d-spacing interlayer

of graphite and existing elements in samples. The data of iron, iron carbide, and CNF were matched with reference data of 13-0534, 35-0772, and 75-2078 based on JCPDS, respectively. Figure 5.17 shows that no change occurred in the d-spacing interlayer of crystalline graphite in  $2\theta = 20\text{--}30^\circ$ . The iron carbide changes did occur in  $2\theta = 40\text{--}48^\circ$  [39]. The modified samples (1Gcom-1h, 1Gcom-3h, 1Gcom-6h, and 0.5Gcom3h) each displayed iron peaks between  $30$  and  $40^\circ$  that were not present in the G-com sample [40] (Wu *et al.* 2010). This indicated that the treatment abolished amorphous carbon layers and revealed encapsulated iron.

Mohammad Aref Khalily *et al.* (2019) [24] used XRD analysis to determine the effect of number of ALD cycles on the loading of Pd into nCNF (Figure 5.18a). Asokan *et al.* [27] studied the XRD pattern of NiMo/CNF catalyst synthesized at different temperatures ( $400$ ,  $500$ ,  $600$  and  $700^\circ\text{C}$ ), to confirm the presence of Ni and graphite peaks at lower temperatures and the inclusion of carbide in the catalyst at higher temperatures of  $700^\circ\text{C}$  (Figure 5.18b).



**Figure 5.17** X-ray diffraction results for CNF and modified CNFs. (Source: Nguyen *et al.*, *J. Nanomater.* vol. 2014, Article ID 631069, 2014 Copyright © 2014 Thien Duc Nguyen Van *et al.*) [36].



**Figure 5.18** (a) XRD of Pd/nCNF samples with variation in ALD cycles. Source: Mohammad Aref Khalily, Bhushan Patil *et al. ChemNanoMat*, 05, 1–8, 2019, ©Wiley [24]. (b) XRD patterns of NiMo/CNF synthesized at 400 °C, 500 °C, 600 °C, and 700 °C. Source: Arunchander Asokan Chaehyun Lim *et al. ChemNanoMat*, 06, 937–946, 2020 ©Wiley [27].

## 5.5 Measurement of Mechanical Properties of CNF

CNFs are known to possess high mechanical strengths and moduli, superior stiffness, excellent electrical and thermal conductivities, as well as strong fatigue and corrosion resistance. Various applications of CNF depend on these properties, particularly for the development of large load-bearing composites. These properties depend on the method of synthesis, precursor, and various synthesis parameters used such as catalyst, temperature, duration of reaction, etc.

### 5.5.1 Tensile Strength Testing/Tension Testing

Endo *et al.* (1999) [30] reported the mechanical tensile properties of sub-micron vapor-grown carbon fiber (s-VGCF), where the tensile strength of graphitized s-VGCF increases with decreasing the fiber diameter. For example, tensile strength of s-VGCF having a diameter of 100 and 300 nm were 2.2 GPa and 1.77 GPa, respectively.

It is apparent that the tensile strength and tensile modulus of s-VGCF is higher than that of general grade CF. On average, the tensile strength and tensile modulus of the s-VGCF are 2 and 200 GPa, respectively. Tibbetts and Beetz (1987) [41] grew large diameter VGCFs and directly measured their tensile properties. The effect of the fiber's diameter on tensile properties was studied for the diameter range of 6.5–31.5  $\mu\text{m}$ . The tensile properties decrease with increasing VGCF diameter. For a 7.5  $\mu\text{m}$  diameter

VGCF, the tensile strength and tensile modulus were 2.92 GPa and 237 GPa, respectively.

So far, the mechanical properties of CNF have been discussed. However, to enhance properties of CNF for various applications CNF composites or polymer-reinforced CNF is used. The mechanical properties of the polymer reinforced by adding carbon nanomaterials have been investigated for decades [42]. Generally, the mechanical properties of the polymer will increase with increasing CNF content. Bortz *et al.* (2011) [43] reported that the resistance to fracture increased by 66% and 78%, with a 0.5 wt% and 1.0 wt% addition of CNFs in CNF/epoxy composites. The CNF-reinforced thermal-plastic polyurethane (TPU) composites were prepared by the melt mixing method [11]. In this composite, the tensile strength of the nanocomposites increased 49% with the CNF filling content of 4 wt% compared with the neat TPU. However, the tensile strength of the CNF-reinforced nanocomposites reduced dramatically with a higher CNF dosage, because of the increase in voids or other defect densities resulting from the CNF bundles, which will lead to stress concentration under dynamic loading and finally results in a premature failure at low strain values.

Moreover, as per findings of Okuda *et al.* (2018) [32], UV-Raman measurements showed the predominance of sp<sup>2</sup> carbon for the carbon fibers with Young's moduli ranging from 55 to 440 GPa.

### 5.5.2 Young's Modulus

Apart from the strength, the microhardness of the CNF composites was also found to increase with increasing CNF content [44]. The microhardness of the epoxy matrix improved by 53% with 0.5 wt%, 62% with the addition of 0.75 wt% and 100% with 1.0 wt% CNF. The high aspect ratio and high modulus strength of CNFs contributed to the reinforcement, thus improving the hardness value. The reinforcement mechanisms have been systematically studied, as well, and many successful results have been extensively reported to demonstrate the relationship between the mechanical properties of the composites and the reinforcement fillers. The most widely accepted model is the mixture model expressed as:

$$\rho_{mix} = \rho_r f_r + \rho_m f_m \quad (5.3)$$

where  $P_{mix}$  is the mechanical properties of a composite, such as strength, Young's modulus or fracture toughness,  $f_r$  and  $f_m$ , and  $p_r$  and  $p_m$  are the filling contents and the mechanical properties of the reinforcement phase

and the matrix, respectively. Especially if the reinforcement materials are fibrous materials, such as CNTs or CNFs, this model should be modified as (Esawi *et al.* 2011):

$$\rho_{mix(p)} = \mu_1 \mu_2 \rho_r f_r + \rho_m f_m \quad (5.4)$$

where  $\mu_1$  represents the length efficiency factor and  $\mu_2$  represents the orientation efficiency factor. The Cox model is a typical model to predict the Young's modulus of CNF-reinforced polymer based on the rule of mixtures (Cox 1952). It is written as:

$$E_c = (1 - V_f)E_m + nV_f(\rho_f E_f) \quad (5.5)$$

$$\rho_f = 1 - \frac{\tan h \beta}{\beta} \quad (5.6)$$

$$\beta = \frac{l}{d} \sqrt{\frac{E_m}{(1 + \nu)E_f \ln \sqrt{\frac{\pi}{4V_f}}}} \quad (5.7)$$

where  $E_c$  is the modulus of the composite;  $V_f$  is the filling content of the filler;  $E_m$  is the Young's modulus of the polymer matrix;  $\rho_f$  is the efficiency factor of the filler;  $E_f$  is the Young's modulus of the filler;  $n$  is an orientation constant ( $n = 1/6$  for random orientated fibers in 3D,  $n = 1/2$  for random orientated fibers in 2D and  $n = 1$  for aligned fibers);  $l$  is the average fiber length;  $d$  is the diameter; and  $\nu$  is Poisson's ratio. Other models based on the rule of mixtures were further developed in fibrous, reinforced composites. The elastic modulus of the composites can be expressed as (Omidi *et al.* 2010):

$$E_{c/m} = (E_{r/m} - 1)V_r \text{ (lower bound)} \quad (5.8)$$

$$E_{c/m} = \frac{(E_{r/m} - 1)V_r}{E_{r/m} + (E_{r/m} - 1)V_r} \text{ (upper bound)} \quad (5.9)$$

where  $V_r$  is the filling content of the reinforcement;  $E_{c/m} = (E_c - E_m)/E_m$ ;  $E_{r/m} = E_r/E_m$ ; and  $E_c$ ;  $E_r$ ; and  $E_m$  are the longitudinal elastic moduli of the composites, reinforcement phase and the matrix, respectively. However,

some experimental results claimed that the mechanical property of composites as a function of reinforcement filling content is not linear, especially when the filling content takes large values. Consequently, a revised form of the rule of mixtures was developed with an exponential form [45]:

$$E_{c/m} = (\varepsilon_l \varepsilon_0 \varepsilon_w E_{r/m} - 1) V_r \exp \alpha V_r \quad (5.10)$$

$$\text{Where, } \alpha = \frac{\ln \beta}{\widehat{V}_r}, \beta = \frac{\widehat{E}_{c/m}}{(\widehat{\varepsilon}_l \varepsilon_0 \varepsilon_w E_{r/m} - 1) \widehat{V}_r}, \quad \widehat{E}_{c/m} = (\widehat{E}_c - E_m)/E_m \quad (5.11)$$

The hat sign means that the values need to be determined by experimental results, and  $\varepsilon_l$ ,  $\varepsilon_0$  and  $\varepsilon_w$  are constants. Another well-accepted model is the Halpin-Tsai equation [46–48], which gives the prediction of the tensile modulus of nanocomposites, expressed as:

$$E_c = \left[ \frac{3}{8} \times \frac{1 + 2 \left( \frac{l}{d} \right) \rho_L V_r}{1 - \rho_L V_r} + \frac{5}{8} \times \frac{1 + 2 \rho_D V_r}{1 - \rho_D V_r} \right] \quad (5.12)$$

$$\rho_L = \frac{\left( \frac{E_r}{E_m} \right) - \left( \frac{d_m}{4t} \right)}{\left( \frac{E_r}{E_m} \right) + \left( \frac{l_m}{2t} \right)}, \quad \rho_D = \frac{\left( \frac{E_r}{E_m} \right) - \left( \frac{d_m}{4t} \right)}{\left( \frac{E_r}{E_m} \right) + \left( \frac{d_m}{4t} \right)} \quad (5.13)$$

where  $E_c$  and  $E_m$  represent the Young's moduli of the composite and the matrix;  $l/d$  and  $V_m$  are the aspect ratio and the filling content of the nanofibers or nanotubes; and  $t$  is the thickness of the graphite layer. Apart from the models mentioned above, the composite sphere method (CSM) was also developed to predict the modulus of composites, which can be written as [49]:

$$K_{com} = K_r + \frac{V_m}{\frac{1}{K_m - K_r} + \frac{3V_r}{(3K_r + 4G_r)}} \quad (5.14)$$

$$G_{com} = G_r + \frac{V_m}{\frac{1}{K_m - K_r} + \frac{6V_r}{(3K_r + 2G_r)/(5G_m(3K_r + 4G_r))}} \quad (5.15)$$

where  $K_{com}$  and  $G_{com}$  are the bulk and shear moduli of composites;  $V_m$  and  $V_r$  are the filling content of the matrix and the reinforcement phase;  $K_m$ ,  $G_m$  and  $K_r$ ,  $G_r$  are the bulk moduli and shear moduli of the matrix and the reinforcement phase, respectively.

Although the mechanical properties of CNF-reinforced composites have been extensively studied, and numerous methods have been applied to characterize the relationship between the fillers and the final properties, the disagreement between some experimental results and theoretical models, which resulted from the complexity of the reinforcement phase, is always a problem that needs to be solved, especially that of how to quantitatively predict the mechanical properties of the composites with different geometrical structures of reinforcements, which is still one of the most challenging topics in composite science and technology. Further studies need to be focused on the influence of the geometrical structure of the CNF on the mechanical properties of the composites. One thing to be noted here is that the overall properties of CNF-modified composites are largely decided by the CNFs-matrix interfaces. Cu/CNF composites with high thermal conductivity were prepared via three different powder metallurgy approaches [50]. It was found that the interfaces are very clear and strong, and a high density of dislocations of the Cu matrix can be observed at the interface area, which is an important factor that decides the thermal properties of the composites. Lu *et al.* (2010) [51] prepared CNF/epoxy-based shape memory polymer composites, and the electrical and thermal properties of the composites were tested. It was also claimed that the CNF/polymer interfaces play a key role in the final properties of the composites. Sandler (2002) [52] studied the mechanical properties of vapor-grown CNF-reinforced poly-ether-ether-ketone (PEEK) composites. The interfaces between the CNFs and the PEEK were observed by SEM and TEM. It was found that the interface remained intact during the preparation process, which guarantees the strengthening effect of the CNFs. In spite of many experimental studies having demonstrated that the interface between the CNFs and the matrix is considerably important to the overall performances, limited theoretical models have been developed to quantitatively explain the effect of the interfaces on the properties, such as the bonding types, bonding strengths and dislocation densities. The bonding between the CNF and the matrix is different from the CCF and CNT due

to the different external surface structures of CNFs, CCFs and CNTs. This should be considered as an important factor before developing a theoretical model to explain the relationship between the performances and the CNF/matrix interfaces.

Both tensile strength and Young's modulus became substantially higher with increase of the final carbonization temperature. The 1000 °C carbonized nanofiber bundle had the tensile strength and Young's modulus (mean standard deviation) of (32515) MPa and (404) GPa, respectively. For the 2200 °C carbonized nanofiber bundle, the tensile strength and Young's modulus were increased to (54245) MPa and (586) GPa, respectively. Thus, the tensile strength was improved by w67%, while Young's modulus was improved by w45%. Similar to electrical conductivity, mechanical properties of the bundles cannot be directly interpreted as those of individual carbon nanofibers in the bundles. The tensile strengths and Young's moduli of commercially available PAN-based carbon fibers (such as the T-series carbon fibers produced by Toray Industries, Inc.) are 3–7 GPa and 200–400 GPa [53, 54], respectively; both are approximately an order of magnitude higher than the acquired results for bundles. Generally speaking, the mechanical properties of the prepared electrospun carbon nanofiber bundles are attributed to two factors, including (i) the mechanical properties of individual carbon nanofibers in the bundles, and (ii) the alignment of carbon nanofibers in the bundles. In order to measure the mechanical properties of individual carbon nanofibers, the testing methods for measuring mechanical properties of CNTs may be appropriate, and such study is in progress. It is well-known that the moduli of carbon fibers can be improved by increasing the carbonization temperature; however, the increase of tensile strength with higher carbonization temperature is abnormal since the strongest PAN-based carbon fibers usually possess turbostratic microstructures instead of highly graphitic microstructures [53, 54]. This is probably because the acquired moduli were measured from the bundles instead of the individual nanofibers; as described before, higher carbonization temperature may result in stronger binding and/or improved contacting at the locations among the entangled nanofibers, thus can prevent the nanofibers from separating and/or slipping from each other.

## 5.6 Optical Property Analysis of CNF

Carbon nanofibers play a major role in enhancing the absorption edge and photoelectric activities and in extending the absorption edge. These unique nanostructures hold great promise for applications in solar cells because of



their excellent optical and electronic transport properties [55]. The analysis of optical properties of CNF has been tried using different methods.

### 5.6.1 Ellipsometric Method for CNF and MCNF

Ellipsometry is a nondestructive, well-established technique for characterizing thin films. It is possible to use ellipsometry to characterize two-dimensional (2D) photonic crystal (PC) slabs and determine their band structure [56], as well as symmetry directions and lattice parameters. It was done by using CNF as components of planar photonic crystals. Square and rectangular lattices and random patterns of vertically aligned CNFs were fabricated and their properties studied using ellipsometry. Two-dimensional PC slabs are materials with a periodic modulation of the refractive index in a 2D plane and a finite extension in the perpendicular direction. These systems have generated much interest in recent years as a means to control light at length scales on the order of a wavelength. In their study, Rehammar *et al.* (2010) reported on the properties of 2D PC slabs consisting of free-standing CNFs grown on a metallic substrate. The optical properties have been investigated using the technique of variable-angle spectroscopic ellipsometry [56].

An ellipsometer is a dual-rotating compensator which provides all 16 elements of the reflection Mueller matrix, from which the generalized ellipsometry parameters can be derived. The full Mueller matrix is measured at different angles of incidence,  $\theta$ , and different rotations of the sample  $\psi$  the symmetry directions and the band structure of these novel materials are extracted from considerations of the polarization state in the specular beam. An interesting find was value of the refractive index of the individual CNF, that was found to be  $n_{\text{CNF}} = 4.1$ .

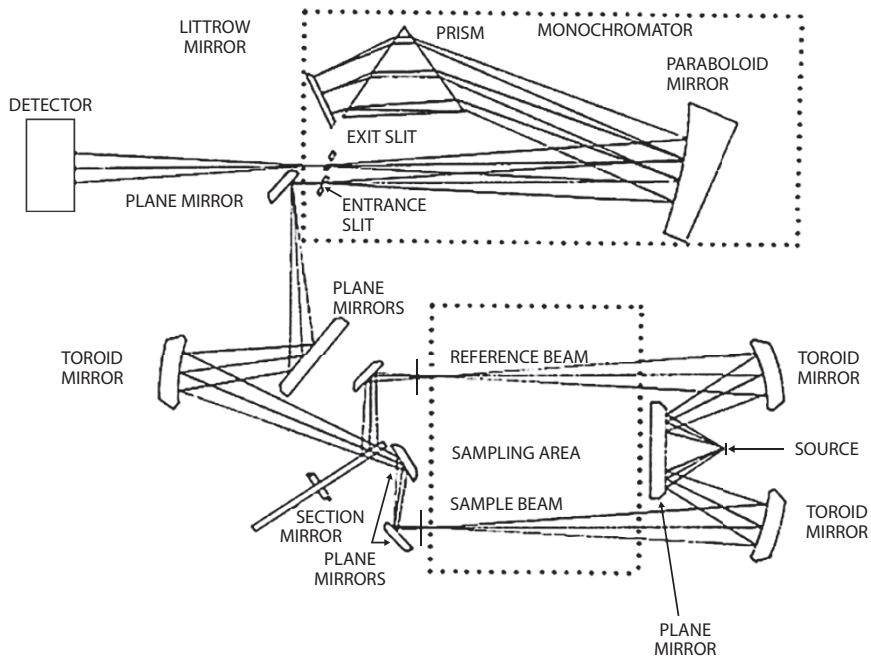
Photonic crystals (PCs) have emerged as exciting optical systems with promising properties such as the ability to have ultra-slow light propagation [57], negative refraction [58] and extreme light confinement [59]. Recently, there has been an increasing interest in developing antennas operating in the optical regime [60–63], which requires the fabrication of structures with controlled dimensions on the order of the wavelength of visible light. In another study, Rehammar *et al.* (2010) [56] explored the diffraction properties of a square planar photonic crystal composed of carbon nanofibers, fabricated using e-beam lithography and chemical vapor deposition. In this study, the 2D PC slabs operating in the optical range, were achieved through growth of arrays of nanowires or carbon nanofibers (CNF) using plasma-enhanced chemical vapor deposition (PECVD). The pattern of the structures was controlled by lithographic deposition of nanoscale metal particles that seed the PECVD growth [64]. An additional

advantage of using conducting CNFs is that they can potentially be electrically actuated, providing a convenient and practical means of tuning the optical properties of the PCs. In order to achieve this, the CNFs were grown on conducting substrates to understand the optical properties of the static arrays. The diffraction properties of the system were characterized experimentally and compared with theory and numerical simulations.

The intensities of the  $(-1; 0)$  and  $(-1; -1)$  diffraction beams were measured as functions of the angles of incidence for both  $s$  and  $p$ -polarization. The obtained radiation patterns are explained using a simple ray interference model, in terms of the aspect ratio of the nanofibers and the excitation of surface plasmon polaritons at the substrate interface.

### 5.6.2 UV-Vis-NIR Spectrophotometric Method for ACNF Analysis

Currently attention is being paid to developing activated carbon nanofiber (ACNF) by electrospinning method [65]. The optical properties of ACNF layer are investigated using a UV-Vis-NIR spectrophotometer. Schematic details of a standard monochromatic spectrophotometer is presented in a block diagram in Figure 5.19. The optical constants, such as refractive



**Figure 5.19** Block diagram of a spectrophotometer. Model: Jasco V670.

index, extinction coefficient and dielectric constants, are evaluated using reflectance and transmittance spectra for ACNF layer. The optical energy gap of ACNF layer is determined as 1.07 eV. The optical constants are obtained by using the transmission spectrum.

The ACNF layer is assumed to be homogeneous with a uniform thickness. The reflectance (R) and transmittance (T) characteristics of the ACNF layer were obtained for the normal incidence of light between 200 and 2000 nm at room temperature.

The optical constants, such as refractive index, extinction coefficient and dielectric constants, are evaluated using reflectance and transmittance spectra for ACNF layer. The optical energy gap of ACNF layer is determined as 1.07 eV. The optical constants are obtained by using the transmission spectrum.

The present study aims to prepare high-quality thin films of ACNFs by a low-cost technique, i.e., electrospinning. The ACNF layer is assumed to be homogeneous with a uniform thickness. The reflectance (R) and transmittance (T) characteristics of the ACNF layer were obtained for the normal incidence of light between 200 and 2000 nm at room temperature.

R and T can be expressed by the following relations [66, 67]:

$$R = \left( \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \right) \quad (5.16)$$

$$T = \left( \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \right) \quad (5.17)$$

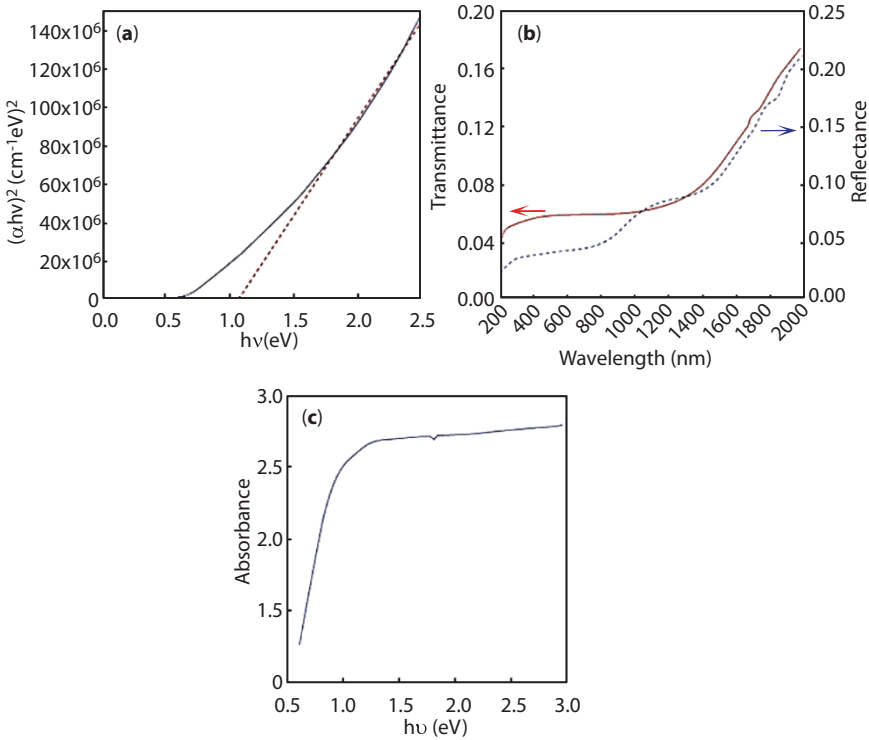
where  $\alpha$  is the absorption coefficient,  $k$  is the extinction coefficient,  $n$  is the refractive index and  $d$  is the thickness. Figure 5.20b shows the transmittance and reflectance spectra against wavelength of ACNF layer.

From these spectra, the average values of the optical transmittance and reflectance in the visible range (400–700 nm) were measured ranging from 5.577 to 5.992% and from 3.883 to 4.657%, respectively.

The absorption coefficient ( $\alpha$ ) of ACNF layer was calculated from the reflectance and the transmittance measurements, using the following equations [66–68]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (5.18)$$

where  $d$  is the thickness. The thickness of ACNF layer is calculated as 5.65  $\mu\text{m}$  by means of a profilometer. Figure 5.20 c shows the absorption coefficient ( $\alpha$ ) of ACNF layer in the wavelength range 200–2000 nm.



**Figure 5.20** Typical plots of (a) photon energy dependence of  $(\alpha h\nu)$  of ACNF layer (b) Optical transmittance and reflectance spectra of ACNF layer as a function of wavelength (c) absorption coefficient ( $\alpha$ ) variation of ACNF layer with photon energy.

According to Figure 5.20c, we can evaluate that absorption coefficient is not a constant. While the wavelength increases, the absorption coefficient value of ACNF layer shows slowly decreasing behavior up to 1200 nm and then sharply decreasing behavior up to 2000 nm.

### 5.6.3 Measuring Optical Band Gap

Energy gap determination of ACNF layer: The optical band gap ( $E_g$ ) of ACNF layer can be found from the calculated values of the absorption coefficient ( $\alpha$ ). Not only does it give the basic absorption limit of the layer, but it also reflects the optical band structure of the layer. To determine the band gap of ACNF layer, the relationship between the optical band gap and the absorption coefficient can be expressed by the following relationship [69–71]:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (5.19)$$

where  $h\nu$  is photon energy,  $\alpha$  is absorption coefficient and  $B$  is energy independent constant. Figure 5.20a shows the curve of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ) of the electrospun ACNF layer at room temperature. The optical band gap ( $E_g$ ) value of ACNF layer was taken as the intercept of  $(\alpha h\nu)^2$  versus ( $h\nu$ ) at  $(\alpha h\nu)^2 = 0$  according to Tauc's relation for the allowed direct transition. According to Figure, the ACNF layer has an energy gap value.

The calculated band gap energy ( $E_g$ ) of the electrospun ACNF layer is about 1.07 eV.

Liao *et al.* (2009) [72] synthesized the mesoporous carbon nanofibers (MCNFs) within the pores of AAO through an easy one-step template method. Based on transmission loss vs. wavelength, they have estimated that the value of band gap energy of the MCNFs is 1.07 eV.

## 5.7 Thermal Properties and Thermal Effect Analysis

### 5.7.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a method of thermal property. TGA measures the mass of a sample over time as the temperature changes, i.e., the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time.

The measurement is done in an atmosphere of nitrogen, helium, air, or in vacuum. Or one can describe it as a technique in which, upon heating a material, its weight increases or decreases. Hence, the concept of TGA is that it measures a sample's weight as it is heated or cooled in a furnace. A plot of wt% vs. temperature is known as a *thermogravimetric curve*.

Thermogravimetric analysis is a simple technique. The method of operation is selected from pre-loaded operating software of TGA. The setup of TGA consists of a sample pan that is supported by a precision balance. A platinum pan containing weighed (5 to 15 mg) sample is placed in a furnace and TGA analysis is performed by gradually increasing the temperature of a sample and simultaneously its weight is measured on an analytical balance that remains outside of the furnace. The loss in mass during TGA is due to the loss of volatile component or thermal decomposition.

The residual ash content is investigated by TGA. A typical instrument used for this is Q5000IR TGA (TA Instruments Inc., New Castle, Delaware, USA). Birch *et al.* (2013) [73] utilized two methods to determine residual ash content. The results for the two methods were averaged, with standard

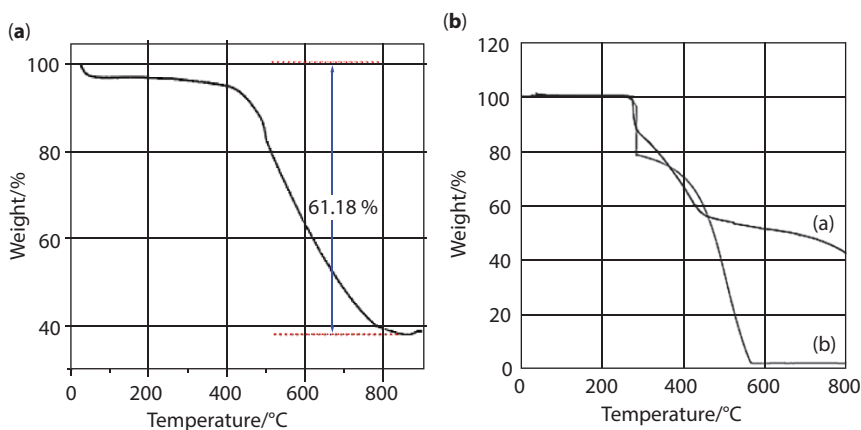
deviations reported. It was observed that complete oxidation occurred with both methods; results were equivalent and thus averaged.

- **The first method** was started at room temperature then increased by 50 °C per minute to 850 °C in nitrogen. The sample in the oven was held at 850 °C for 2 min and then cooled to 500 °C. The gas was switched to air, and the temperature was then increased at 50 °C per minute to 920 °C and held at 920 °C for 2 min.
- **The second method** was performed in air, ramping from room temperature to 920 °C at 5 °C per minute. For all samples, mass loss rates near the end of the analysis were near zero.

The TGA results for the residual ash contents of three samples were  $0.59 \pm 0.44\%$ ,  $1.2 \pm 0.31\%$  and  $1.48 \pm 0.60\%$ , respectively.

Thermogravimetric analysis of the purified CNM carried out under nitrogen flow gives an idea about the presence of defective carbon structure, which thermally disintegrates at lower range of temperatures (350–400 °C). CNM under the flow of nitrogen does not thermally disintegrate, but under the flow of air it does [74].

Tongfei Li *et al.* (2018) [28] used TGA under an air atmosphere to quantify the  $\text{Ni}_3\text{Fe}$  content in the  $\text{Ni}_3\text{Fe@N-CNFs}$  (Figure 5.21a). As shown in Figure, the final residue (38.8 wt%) is composed of  $\text{NiO}$  and  $\text{Fe}_3\text{O}_4$ .



**Figure 5.21** (a) TGA curves of as-prepared  $\text{Ni}_3\text{Fe@N-CNFs}$ . Source: Tongfei Li, Gan Luo, *et al. Adv. Funct. Mater.* 28, 1805828, 2018©Wiley [28]. (b) Thermal analysis of electrospun PAN CNFs: (a)  $\text{N}_2$  and (b) air atmosphere. Source: Chan Kim, Sang-Hee Park *et al. J. Raman Spectroscopy*, 35, 928–933, 2004©Wiley [18].

TGA is a useful tool to determine the starting temperature of oxidative stabilization and carbonization of PAN. This was demonstrated by Chan Kim *et al.* (2004) [18], wherein TGA analysis was performed for electrospun PAN-CNFs in an inert atmosphere of N<sub>2</sub> and in atmospheric air (Figure 5.21b). In the inert atmosphere the weight was found to decrease sharply in the temperature range 250–400 °C while in air atmosphere, the weight loss occurred in two steps which was interpreted as reactivity of PAN-CNFs with oxygen at 200 °C, loss of volatiles at 300 °C and inception of combustion at 400 °C.

### 5.7.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of sample and reference are measured as a function of temperature. The difference between TGA and DSC is the method of measuring the changes in samples that are caused by heat. The technique and equipment were developed by E. S. Watson and M. J. O'Neill in 1962 [75]. The term DSC was coined to describe this instrument, which measures energy directly and allows precise measurements of heat capacity.

DSC of weighed CNF sample is measured by keeping it in the thermal analyses chamber in the temperature range at 30–200 °C with heating ramp rate of 10 °C/min. Nitrogen flow rate is usually maintained at 30 ml/min. Noise level of the instrument needs to be set on 1 μW. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. There are two types of DSC:

- **Power-compensated DSC** keeps power supply constant.
- **Heat-flux DSC** keeps heat flux constant.

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. Results are expressed as a graph of Temperature (°C) vs. Heat flow (mW). There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition.

The following example gives valuable guidelines for interpretation of DSC plots for CNF. The DSC study of well-staged brominated P-120 CNF samples shows a phase transition at 100 °C, due to in-plane melting of the bromine superlattice [76]. This transition was not observed in the poorly graphitized pitch-based fibers [77], but a small endothermic peak was found by Chung at −2 °C for P-100 and E-130 fibers during heating, while no corresponding peak appeared during the subsequent cooling. This suggests that there is no phase transition between 25 and 250°C. However, an endothermic peak was observed around −10 °C. DSC scans were carried between −50 and +25 °C at a heating rate of 5 °C/min.

This peak was assigned to an order-disorder transition. No exothermic peak was detected during the cooling of the sample, but a second run with the same sample shows the presence of the endothermic peak at the same temperature. This suggests a reversible transition.

### 5.7.3 Differential Thermal Analysis (DTA)

Differential thermal analysis is very similar to DSC. Both DSC and DTA provide similar information. DSC measures the energy required to keep both the reference and the sample at the same temperature whereas DTA measures the difference in temperature between the sample and the reference when the same amount of energy has been introduced into both. But in this technique, it is the *heat flow* to the sample and reference that remains the same rather than the temperature. Hence, both the sample and reference are heated identically; phase changes and other thermal processes cause a difference in temperature between the sample and reference.

### 5.7.4 Thermal Conductivity

More continuous crystalline planes and a reduction in residual catalyst particles are expected to increase phonon mean free path (MFP) and thus increase the lattice (phonon) thermal conductivity in MWCNTs [78]. The most simplistic steady-state thermal conductivity measurement method is the “self-heating” technique. In general, the self-heating method requires samples to be electrically conductive, transport heat diffusively, and the temperature coefficient of resistance of the sample to be known. The self-heating method was first applied to a bundle of CNTs [79] and subsequently to individual MWCNTs [80].

Many studies have explored thermal properties of test specimens by measuring the third harmonic voltage in a  $3\omega$  experimental setup, as the sample is Joule heated with an alternating current. The “T-type probe” is



one method that can employ third harmonic voltage detection to make thermal conductivity measurements. For the T-type probe method, a suspended wire of known electrical resistivity and temperature coefficient of resistance is Joule heated by a current source until it reaches a steady state. A sample is attached, and the reduction in the spatially averaged temperature of the probe wire is measured via the change in voltage. The sample thermal conductivity is determined from the average temperature drop and the sample geometry. The method has been used to great effect in studying thermal transport in individual nanostructures, including CFs and multi-walled carbon nanotubes. A widely used method for thermal conductivity of both heat-treated and non-heat-treated CNF specimens is the  $3\omega$ , Wollaston wire, T-type probe method.

Use of commercially available Wollaston wire has the advantage of being extremely cost-effective when compared to conventional micro-fabrication methods and allows for a large volume of samples to be characterized in a short span of time (Bifano *et al.* 2013). In the present investigation, all thermal property characterization studies are conducted inside a high-resolution scanning electron microscope equipped with nano-manipulators and a gas injection system. Moreover, the choice of materials and package design allows for multiple Wollaston T-type probes to be prepared with varying thermal resistances and, thus, measurement sensitivities. The configuration, technique, and analysis used in this study for making the thermal conductivity measurements of CNFs are described in detail by Bifano *et al.* (2010) [78].

The platinum probe wire is heated by an alternating current

$$I(t) = I_{1\omega} \sin(\omega t) = I_{1\omega, RMS} \sqrt{2} \sin(\omega t) \quad (5.20)$$

where  $I_{1\omega}$  is the current amplitude and  $I_{1\omega, RMS}$  is the RMS current.

The Joule heating in the wire is given by the equation:

$$Q(t) = I^2(t)R_{e0} = I_{1\omega, RMS}^2 R_{e0} (1 - \cos 2\omega t) \quad (5.21)$$

where  $R_{e0}$  is the electrical resistance of the probe wire at zero current. The spatially averaged temperature of the wire above the ambient temperature,  $\bar{\theta}(t)$ , is directly proportional to the Joule heating by the thermal transfer function  $Z_0$  such that

$$\bar{\theta}(t) = Z_0 Q(t) \quad (5.22)$$

The electrical resistance of the probe wire changes according to

$$R_e(t) = R_{e0}[1 + \alpha \bar{\theta}(t)] \quad (5.23)$$

where  $\alpha$  is the temperature coefficient of resistance of the wire. The RMS Joule heating is defined to be:

$$Q_{RMS} = I_{1\omega, RMS}^2 R_{e0} \quad (5.24)$$

When the wire is Joule heated, the third harmonic voltage across the wire is given by,

$$V_{3\omega, RMS} = \frac{1}{2} \alpha Z_0 I_{1\omega, RMS} Q_{RMS} R_{e0} \quad (5.25)$$

Defining the third harmonic RMS electrical resistance as:

$$R_{e3\omega, RMS} = \frac{V_{3\omega, RMS}}{I_{1\omega, RMS}} \quad (5.26)$$

The third harmonic resistance is found to be directly proportional to the RMS Joule heating by:

$$R_{e3\omega, RMS} = \frac{1}{2} \alpha Z_0 Q_{RMS} R_{e0} \quad (5.27)$$

The thermal transfer function is determined experimentally by measuring the slope of

$$R_{e3\omega, RMS} \text{ versus } Q_{RMS} \quad (5.28)$$

The steady-state response of the probe wire is modelled in one dimension by:

$$k_p \frac{d^2 \theta}{dx^2} = -\frac{Q_{RMS}}{A_p L_p} \quad (5.29)$$

Here,  $x$  is the position marked from the midpoint of the wire,  $k_p$  is the thermal conductivity of the wire,  $A_p$  is the cross-sectional area of the wire, and  $L_p$  is the length of the wire.

Heat loss due to convection and radiation are neglected, as the experiments are conducted in vacuum involving small temperature rises.

Using constant ambient temperature boundary conditions at the wire ends, and a heat flux out of the wire at the point of attachment of the sample, the solution of the differential equation leads to the spatially averaged temperature as:

$$\bar{\theta} = \frac{1}{12} Q_{RMS} R_{th,P} \left[ 1 - \frac{3}{4} (1 + \eta^{-1})^{-1} \right] = Q_{RMS} Z_0 \quad (5.30)$$

The thermal resistance of the probe and sample are given respectively by:

$$R_{th,P} = \frac{L_p}{k_p A_p} \text{ and } R_{th,s} = \frac{L_s}{k_s A_s}$$

$\eta$  is the ratio of the thermal resistances, defined as:

$$\eta = \frac{R_{th,P}}{4R_{th,S}} \quad (5.31)$$

**Experimental Procedure:** When no sample is attached, i.e.,  $\eta = 0$ , the thermal resistance of the probe is deduced using Equations (5.30) and (5.31) as:

$$R_{th,P} = \frac{24}{\alpha R_{e0}} \left( \frac{R_{e3\omega,RMS}}{Q_{RMS}} \right) \quad (5.32)$$

The ratio of the slopes is then defined as:

$$\emptyset = \frac{\left( \frac{R_{e3\omega,RMS}}{Q_{RMS}} \right)_{with\ sample}}{\left( \frac{R_{e3\omega,RMS}}{Q_{RMS}} \right)_{No\ Sample}} \quad (5.33)$$

The sample thermal resistance can be found from Equations

$$R_{th,s} = \frac{1}{4} R_{th,p} \left( \frac{3}{4(1-\phi)} - 1 \right) \quad (5.34)$$

The thermal conductivity of the CNF is determined from

$$k_s = \frac{L_s}{R_{th,s} A_s}, \quad (5.35)$$

Where, the cross-sectional area is  $A_s = \pi(r_0^2 - r_i^2)$ .

In the study the inner radius  $r_i$  is much smaller than the outer radius  $r_0$ , such that  $\frac{r_i^2}{r_0^2} \ll 1$ .

Hence, the effective cross-sectional area of the CNF sample is approximated to  $A_s = \pi r_0^2$ .

The heat-treated batch produced a mean thermal conductivity of  $160 \pm 139$  versus  $4.5 \pm 3.1$  W/m-K for the non-heat-treated samples. The results of the study indicate that significant improvements in thermal conductivity are obtained by heat treatment of CNFs to 2800 °C for 20 h. The average measured thermal conductivity of the heat-treated batch is 160 W/m-K when compared to the much lower average of 4.5 W/m-K for the as-grown non-heat-treated samples. The highest measured thermal conductivity when adjusted for TCR is  $449 \pm 39$  W/m-K. Raman spectroscopy also indicated an improvement in the degree of crystallinity for the heat-treated samples. The results suggest that the quality and heat treatment of CNFs are important considerations for potential use in thermal management applications.

In another study [78], the average thermal conductivity of the heat-treated MWCNT specimens is 228 W/m-K, with the highest measured thermal conductivity being  $765 \pm 150$  W/m-K.

## 5.8 Specific Surface Area (SSA) Determination of CNF

Knowledge of SSA of CNF is a preliminary requirement for determining their applications. Moreover, SSA also provides valuable insight into the properties of carbon nanomaterials, which can differ vastly depending on synthesis parameters and post-production treatments. Specific surface area is defined as “*The accessible area of solid surface per unit mass of material.*”

Because the surrounding phase can modify the surface area, each method that was studied for measuring surface area had shortcomings.

Usually, to enhance the surface area of CNFs they are given further treatments like adding to polymers or decorating with nano-metals, etc. SSA is also correlated and confirmed by other characterization tools such as SEM, TEM, XRD, Raman, etc.

Two common SSA measurement tests are described below.

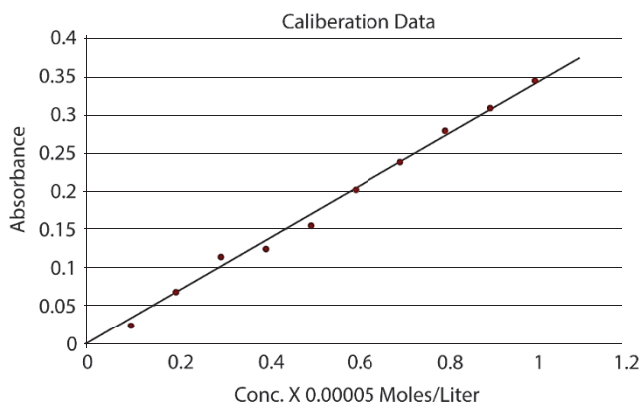
### 5.8.1 Methylene Blue (MB) Test

The method of adsorption of MB in liquid phase for specific surface area determination has been widely adopted for various natural solids [81], activated carbon [82], charcoal [83] and clay [84]. Methylene blue is known for strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material.

Methylene blue solution is prepared with distilled water and the concentration of Methylene blue solutions is analyzed by measuring their absorbance (OD) at 670 nm on a double beam spectrophotometer. This wavelength corresponds to the maximum absorption peak of the Methylene blue ( $\lambda_{\max}$ ). A calibration curve of OD of Methylene blue against its standard concentration (ranging from  $0.1 \times 10^{-5}\text{M}$  to  $1 \times 10^{-5}\text{M}$ ) has to be plotted first (Figure 5.22).

The molar extinction coefficient value obtained from the slope is  $3.9 \times 10^4$ ; this value lies in the broad range  $3.9 \times 10^4$  to  $9.5 \times 10^4$  reported [85, 86].

For analyzing surface area by MB test, known amount of CNF is taken in methylene blue solution of known concentration ( $5 \times 10^{-5}\text{M}$ ). The mixture



**Figure 5.22** A typical calibration curve of absorbance of Methylene blue vs. concentration of MB.

is stirred until the CNF is submerged in the dye solution. This mixture is kept at room temperature for 24 hours and periodically shaken, considering that the complete equilibrium for the adsorption of Methylene blue is attained in 24 hours. After 24 hours, the Methylene blue uptake onto CNF is calculated from the difference between the Methylene blue concentration before and after adsorption onto the carbon and the difference corresponds directly to active surface area of CNF.

Let the concentration difference be  $C$  moles/dm<sup>3</sup> which was adsorbed by  $W$  grams of CNF in  $V$  ml of solution.

Therefore, the amount adsorbed by the CNF in grams is given by:

$$\text{Wt of Methylene blue adsorbed} = \left( \frac{M \times C \times V}{1000} \right) \text{grams} \quad (5.36)$$

where  $M$  is the molecular wt of Methylene blue.

Therefore, number of molecules adsorbed is:

$$n = \frac{6.023 \times 10^{-23}}{M} \times \left( \frac{M \times C \times V}{1000} \right) \text{grams}$$

$$\therefore n = \frac{6.023 \times 10^{-23}}{1000} \times (C \times V) \text{grams}$$

If the surface area of a single molecule of Methylene blue is  $a$ , then the total surface area of the adsorbed molecules will be

$$\text{SurfaceArea} = n \times a = 6.023 \times 10^{-26} CVa \quad (5.37)$$

This is the surface area of  $W$  grams of carbon, so the surface area is

$$\text{SurfaceArea} = \frac{6.023 \times 10^{-26} CVa}{W} \text{A}^{\circ 2}/\text{gm} \quad (5.38)$$

To convert it into square meters the equation must be divided by  $10^{-20}$ .

$$\text{SurfaceArea} = \frac{6.023 \times 10^{-26} CVa}{W} \text{m}^2/\text{gm} \quad (5.39)$$

If average surface area is determined for carbon materials as classified in three groups is calculated as suggested earlier it appears that those carbon materials which are either channel type or whose crystals are not well developed (i.e., whose XRD signals are weak), have more surface area ( $\sim 73 \text{ m}^2/\text{g}$ ) as compared to carbon materials ( $\sim 60 \text{ m}^2/\text{g}$ ) which are crystalline (i.e., whose XRD signals are strong).

### 5.8.2 Brunauer–Emmett–Teller (BET) Specific Surface Areas

The BET method is widely employed for determining the BET area,  $a(\text{BET})$ , of many kinds of porous and non-porous materials. For this purpose, nitrogen at 77 K is the most popular adsorptive, although argon at 87 K is beginning to be favored by some investigators. Two stages are involved in the evaluation of  $a(\text{BET})$  from a physisorption isotherm. The BET monolayer capacity,  $n_m$ , must first be derived from the linear part of the BET plot.

The BET equation is conveniently expressed in the linear form as:

$$\frac{p/p^0}{n \left( 1 - \frac{p}{p^0} \right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \left( \frac{p}{p^0} \right) \quad (5.40)$$

Here,  $n = n^a/m^s$  is the amount adsorbed at relative pressure  $\frac{p}{p^0}$  and  $n_m = n_m^a/m^s$  is the monolayer capacity.

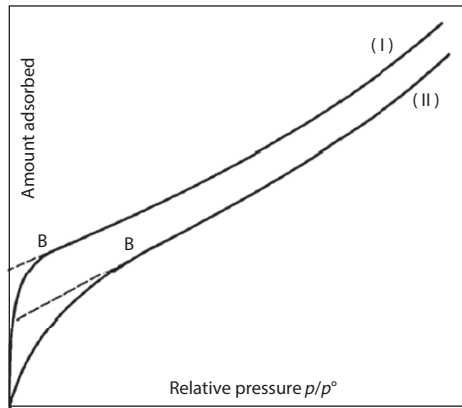
According to the BET equation, the BET plot of  $\frac{p/p^0}{n \left( 1 - \frac{p}{p^0} \right)}$  vs.  $\frac{p}{p^0}$  is a straight line with slope

$$s = \frac{C-1}{n_m C} \text{ and intercept } i = \frac{1}{n_m C}$$

$$\text{Hence, } n_m = \frac{1}{s+i} \text{ and } C = (s+i)+1.$$

If possible, this should straddle the knee of a Type II or Type IV isotherm (i.e., be located around Point B as in Figure 5.23).

The application of a few criteria is recommended to ensure that the BET range is selected objectively. If the BET C value lies outside the range of  $\sim 50$ – $150$ , the validity of  $n_m$  is questionable: thus, if  $C < 50$ , there is an appreciable overlap of monolayer and multilayer adsorption; if  $C > 150$ , there is either strong localized adsorption or a micropore filling contribution.



**Figure 5.23** Typical Type II isotherms: (i) with sharp “knee,” (ii) with rounded knee.

Micropore filling is clearly evident in the case of a Type I isotherm, so the physical validity of  $n_m$  is doubtful and should not be regarded as a true monolayer capacity.

The BET method is strictly not applicable to Type III or Type V isotherms. In the second stage of the BET method, the calculation of  $\alpha(\text{BET})$  from  $n_m$  requires the effective molecular area,  $s$ , to be known or assumed.

$$\text{The specific area, } a(\text{BET}) = n_m \cdot L \cdot \sigma \quad (5.41)$$

Here,  $L$  is the Avogadro number and  $\sigma$  is the average area occupied by each molecule in the completed monolayer.

In applying the “standard” BET method, the completed nitrogen monolayer is assumed to be close-packed at 77 K so that  $\sigma(\text{N}_2) = 0.162 \text{ nm}^2$ . Provided that certain conditions are fulfilled, the BET area derived from a nitrogen isotherm of Type II or Type IV can be regarded as an effective surface area available for nitrogen adsorption at 77 K.

Although the BET area derived from a Type I isotherm should not be treated as a “real” surface area, it is useful as an indication of adsorbent “activity.”

Possible relationships between the Brunauer–Emmett–Teller specific surface areas (SSAs) and their physical and chemical properties have been established by Birch *et al.* (2013). SSA is influenced by the number of walls/diameters, impurities, and surface functionalization with hydroxyl and carboxyl groups.

The most widely used method for determining the SSA of CNM is the BET gas adsorption method.



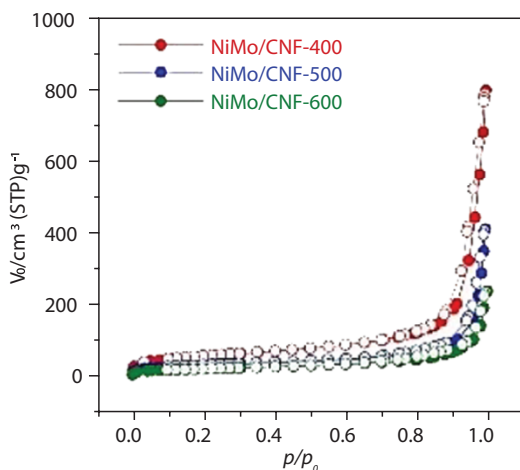
For the BET surface area analysis, either a Micromeritics Gemini 2375 instrument or a Micromeritics TriStar II 3020 instrument is used. For analysis, typically 200 mg or more of CNF sample is taken and degassed in ultra-high purity (UHP) nitrogen for 30 min at 90 °C and then for 90 min at 200 °C. The free space is measured using UHP helium gas. The SSAs is determined by a 5-point BET measurement with UHP nitrogen as the adsorbate and liquid nitrogen as the cryogen. The following relative pressures ( $P/P_0$ ) are used: 0.05, 0.10, 0.15, 0.2, and 0.25. A 50-point nitrogen isotherm analysis is also performed to determine BET surface area. Surface area is calculated from the BET adsorption isotherm.

In one such study [73], samples of CNFs (labeled as 19-21) from a major manufacturer also were analyzed for the BET SSA study. Three samples were examined: two raw materials from two different reactors (Samples 19 and 20) and a final, processed product (Sample 21). The CNFs analyzed have an OD in the range of ~50–200 nm. The two raw products (Samples 19 and 20) have SSAs of 2 and 19  $\text{m}^2\text{g}^{-1}$ , respectively, while the SSA of the final processed product (Sample 21) is 35  $\text{m}^2\text{g}^{-1}$ . From TEM analysis, the diameters of the nanofibers from reactor 1 (Sample 19) ranged mainly from 50–70 nm, similar to those from reactor 2 (Sample 20), which were mainly 50–80 nm. The final product (Sample 21) consisted of fibers mainly in the diameter range 50–80 nm. In conclusion, the relationship between the diameter of the CNFs discussed here and SSA is not straightforward. It seems that multiple parameters (e.g., impurities, morphology, and structure) play a role for these particular products.

In another study [87], the BET adsorption studies for a pristine three-dimensional carbon nanosheet modified carbon nanofiber (3DCNF)—as a multifunctional host for high performance LIS batteries—provided a surface area as low as 30  $\text{m}^2\text{g}^{-1}$ .

In contrast, after being modified with carbon nanosheets, the surface area, again determined by BET analysis, was dramatically increased to 500  $\text{m}^2\text{g}^{-1}$ , i.e., 16 times higher than that of the pristine carbon nanosheets. Among the four samples, the pore volume of 3DCNF12 showed the highest pore volume value of 0.65  $\text{cm}^3\text{g}^{-1}$ . In contrast, the pristine CNF, 3DCNF11 and 3DCNF21 only had a pore volume of 0.036, 0.29 and 0.29  $\text{cm}^3\text{g}^{-1}$ , respectively.

Ashokan *et al.* [27] used the Brunauer- Emmett-Teller (BET) technique from  $\text{N}_2$  adsorption and desorption results (Figure 5.24) to obtain the SSA, Pore size, and Pore volume depicted in Table 5.3. From the values listed, he concluded that SSA decreases with increasing synthesis temperature of NiMo encapsulated CNFs.



**Figure 5.24** BET plots of  $N_2$  adsorption and desorption for NiMo encapsulated CNFs synthesized at different temperatures. Source: Ashokan *et al. ChemNanoMat*, 6, 937–946, 2020 © Wiley [27].

**Table 5.3** The specific surface area of NiMo/CNF with various synthesis temperature.

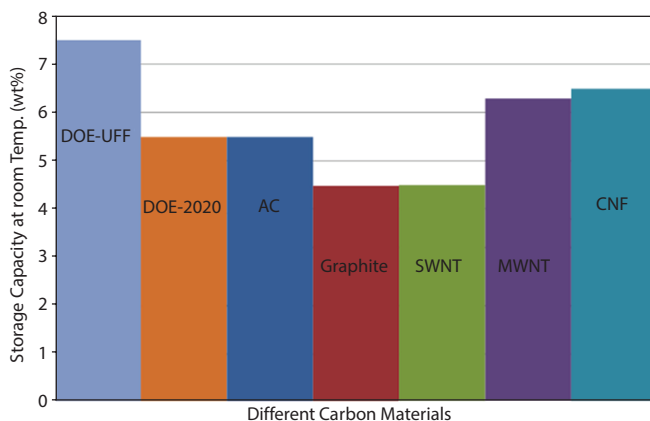
| Synthesis temperature [°C] | Specific surface area [m <sup>2</sup> g <sup>-1</sup> ] | Pore size [nm] | Pore volume [cm <sup>3</sup> g <sup>-1</sup> ] |
|----------------------------|---------------------------------------------------------|----------------|------------------------------------------------|
| 400                        | 204.46                                                  | 22.5           | 1.15                                           |
| 500                        | 113.52                                                  | 21.2           | 0.60                                           |
| 600                        | 78.10                                                   | 16.0           | 0.31                                           |

Source: Ashokan *et al. ChemNanoMat*, 6, 937–946, 2020 © Wiley [27].

The hydrogen storage capacity can be determined by using  $H_2$  adsorption and desorption isotherms. As shown in the bar chart below (Figure 5.25 [103]) CNF has a remarkable hydrogen storage capacity in comparison with other forms of carbon material. These studies are spinoffs of BET plots to determine SSA of different carbon materials.

## 5.9 Characterization of Electrical Properties

The electrical properties are measured under both DC and AC voltage. Before measuring the electrical properties, the disks of samples are pre-treated at 90 °C for 24 h to remove any trace of moisture, solvents or



**Figure 5.25** Hydrogen storage capacity of different carbon material. Source: Manmohan *et al.* 2019, *Energy Storage*, 1:e35. 2019 © Wiley.

impurities. Then, both sides of the samples are metalized with silver paint (Alpha Silver Coated Copper Compound Screening, with a resistivity of  $0.7 \Omega\text{-square}$ ) so as to reduce the effects of surface roughness and to ensure Ohmic contacts. The measurement system is composed by a Keithley 6517A multimeter with function of voltage generator (max  $\pm 1000 \text{ V}$ ) and voltmeter (max  $\pm 200 \text{ V}$ ) and a HP34401A ammeter (having resolution of  $10 \text{ nA}$ ). The AC properties are evaluated in the frequency range  $100 \text{ Hz}$ – $1\text{MHz}$  by using a Quadtec7600 dielectric analyzer and by applying a sinusoidal stimulus of amplitude  $0.1\text{V}$  or  $1\text{V}$  for specimens above or below the electrical percolation threshold (EPT), respectively. This is done in order to avoid measurements around the current saturation limit ( $100 \text{ mA}$ ) of the instrument for samples with low resistivity.

The first carbon fiber (CF), which was prepared by carbonizing cotton and bamboo, was used as the filament of a light bulb in 1879 by Thomas Edison and since then this property of carbon fiber has developed tremendously in both fundamental scientific research and practical applications.

Endo *et al.* (1976) [88] were the first to report the intrinsic conductivity of highly graphitic vapor-grown carbon fiber, which was  $5 \times 10^{-5} \Omega \text{ cm}$  at room temperature, which is near the resistivity of graphite. Due to their high electrical conductivity and high aspect ratio, CNFs can impart equivalent electrical conductivity to a composite at lower loadings than conventional conductive fillers. By controlling the loading, one can produce composites with different electrical resistivity values so that it can be used for applications that require a resistivity in different ranges such as electrostatic dissipation (ESD)  $\{10^6\text{--}10^8 \Omega\text{-cm}\}$ , electrostatic painting

$\{10^4 - 10^6 \Omega \cdot \text{cm}\}$ , EMI shielding  $\{10^3 - 10^1 \Omega \cdot \text{cm}\}$ , and lightning strike protection  $\{<10 \Omega \cdot \text{cm}\}$ .

CNF is the most important member of CF especially due to its size; hence, it is applied as promising materials in many fields such as energy conversion and storage, reinforcement of composites and self-sensing devices. Except for their nano-scale diameter; the structures of the CNFs are evidently different from traditional carbon fibers. The typical CCFs were prepared from high-strength polyacrylonitrile (PAN) or meso-phase pitch (MP), varying the preparing conditions, including the oxidation atmosphere, the raw materials chosen and the heat treatment temperatures. The different preparing conditions will result in different properties of the prepared conventional CF. Whereas CNF is prepared either by catalytical vapor deposition of a hydrocarbon or by electrospinning.

Because of its electrical properties, CNF is being used to provide electrical conductivity to polymers. A uniformly dispersed CNF in the polymer matrix results in a more uniform stress distribution and minimizes the presence of agglomerates that can act as stress concentration centers which decrease the general strength and modulus of the composite.

Leer (2010) [89] determined that the electrical properties of CNF are affected by its aspect ratio, percolation backbone structure and fractal characteristics of CNFs and the non-universality of the percolation critical exponents.

Figure 5.26a represents percolation curves possible with different CNF loading levels and shear conditions. Higher shear levels during composite processing lead to higher percolation thresholds.

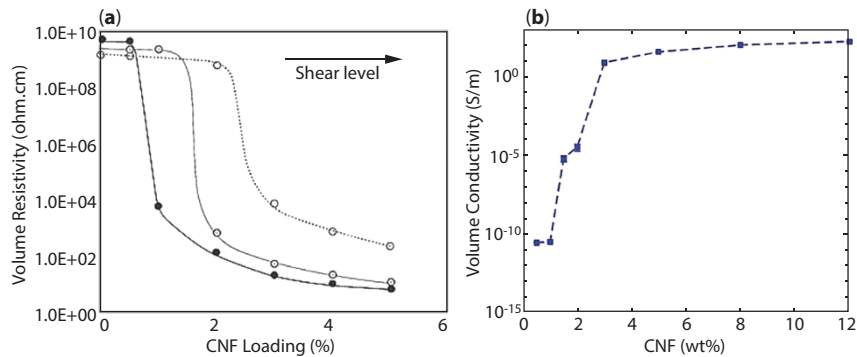
Chowdhury *et al.* (2018) [90] examined the volume electrical conductivity of nanocomposites with different CNF weight concentration.

The application under study was use of these CNF nanocomposites in flexible sensors, where electrical conductivity is a key material property. Electrical conductivity increased in orders of magnitude, with increase in CNF content, due to formation of more conductive networks are created by the dispersed CNFs (Figure 5.26b).

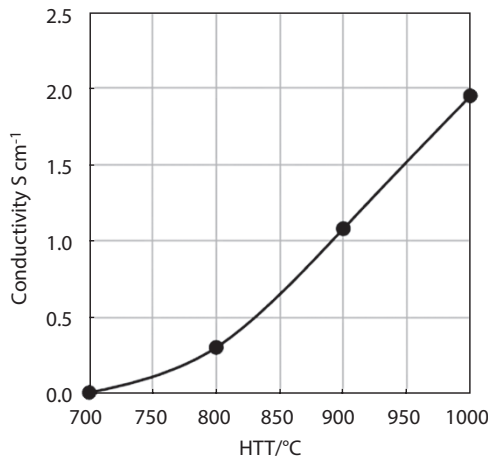
Chan Kim *et al.* (2004) [18] studied the Electrical conductivity of PAN-CNFs function of carbonization temperature (Figure 5.27).

The electrical conductivity increased with increasing carbonization temperature by several orders of magnitude suggesting that carbonization and ordering of crystals proceeded at the elevated temperature.

Two common methods of assessing electrical properties of CNF and CNF composites are the two-probe and four-probe methods. They are now discussed.



**Figure 5.26** (a) Volume electrical resistivity of the composites made with CNF, as a function of fiber weight loading. Source: C. Leer, Carbon nanofibers thermoplastic nanocomposites: Processing – morphology – properties relationships. PhD Thesis, University of Minho, Portugal, 2010 [89]. (b) Volume electrical conductivity of prepared nanocomposites as a function of CNF content. Source: Shoieb A. Chowdhury *et al.*, *Adv. Mater. Technol.*, 1800398(1–10), 2018. © Wiley [90].



**Figure 5.27** Electrical conductivity of PAN-based carbon nanofibers as a function of HTT from 700 to 1000 °C. Source: Chan kim, Sang-Hee Park *et al.* *J. Raman Spectrosc.* 35: 928–933, 2004©Wiley [18].

### 5.9.1 Two-Probe and Four-Probe Methods for Resistivity Measurement

The two-probe method is a standard and commonly used method for the resistivity measurement of very high resistivity samples like sheets/films of polymers. The two-probe setup has two spring load contact probes. These

probes move in a pipe and are insulated by Teflon washers. This probe arrangement is mounted on a suitable stand, which also holds the sample plate and RTD sensor. The stand also serves as the lid of PID temperature-controlled oven. Teflon-coated leads are provided for connecting with High Voltage Power Supply EHT-11 and Digital Picoammeter DPM-111. With the setup assuming maximum voltage = 1500V; current  $100 \times 10^{-12}$  A (max) and thickness of sample 1 mm, the resistivity of the sample could be measured up to 1014 ohm.cm.

In the two-probe method electrical properties of the pure CNF are measured by using a Keithley Electrometer 617 having maximum input resistance  $\sim 10^{17} \Omega$  [44]. The composites are cut into rectangular bars with dimension of 8 mm  $\times$  4 mm  $\times$  5 mm (length, width and thickness) by a diamond saw. The two end surfaces are coated with silver for ohmic contact. Electrical resistivity and the respective conductivity were calculated using the measured resistance and the geometry of the sample.

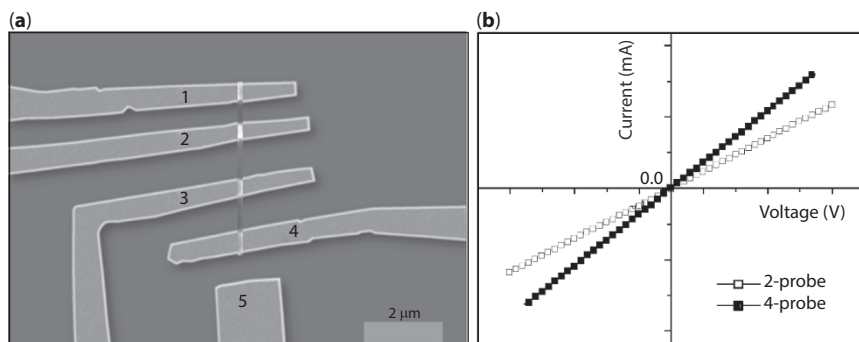
It has been found [91] that two-probe measurements of CNF prepared by CVD (using pyrene as the precursor) and Ni-catalyzed CVD (using ethylene as the precursor) are conducting. The conductivity ranged between 0.1 and 3.0 S/cm. Whereas CNF prepared by Ni-catalyzed CVD using pyrene as the precursor is non-conducting. This result was attributed to the defects in the thin wall or broken tubes (as observed by the SEM). Moreover, if heat treatment is given to the fibers, it causes breaking of fiber and decrease in the conductivity.

### 5.9.2 Four-Probe Methods for Resistivity Measurement

Four-probe measurement of I–V characteristics are essential for measuring inherent charge transport behavior, as the potentially large and nonlinear behavior of contact resistance limits the accuracy of two-probe measurements [92].

A PID controlled oven is a high-quality temperature-controlled oven suitable for a four-probe setup (to be discussed later). The oven is designed for fast heating and cooling rates, which enhances the effectiveness of the controller. While the basic design of the controller is around the PID configuration for its obvious advantages, wastage of power is avoided by using a pulse width modulated (PMW) switch. This combination has the advantages of both on-off controller and linear PID controller. The result is a good stable and accurate temperature control.

Zhang *et al.* (2004) [92] reported four-probe charge transport measurements made on individual VACNFs taken from a VACNF forest, grown on silicon using a DC PECVD process. The height of VACNFs was 10 mm,



**Figure 5.28** (a) A typical four probe nanoscale device with four to five metal electrodes, contacting the nanofiber. (b) Typical I–V curves for the four-probe electrodes 1, 2, 3, and 4 of the device in Figure a and two-probe ~electrodes 2 and 3 measurements.

and the diameter was approximately 150 nm. VACNFs were removed from the substrate by scratching with a needle and dropped onto a Si/SiO<sub>2</sub> chip on which alignment marks had been defined. The position of individual VACNFs was mapped out relative to the alignment marks by scanning electron microscope. Poly(methyl methacrylate) (495 K, A8) was spun at 2300 rpm onto the substrate to achieve a thickness of 800 nm, and was then patterned by electron beam lithography and resist removal. After 12 s of reactive ion etch (RIE) Ti (200 nm thick) and Au (200 nm thick) were deposited on the substrate, and lift-off was performed to leave patterned four or five electrodes on the fibers for successful four-probe measurements at room temperature (similar to Figure 5.28a). The RIE was performed in the presence of optimized flow rate of oxygen for a predefined time interval that leads to formation of ohmic contacts between VACNF and metal electrodes. These measurements demonstrate that VACNFs exhibit linear I–V behavior (similar to Figure 5.28b) at room temperature, with a resistivity of approximately  $4.2 \times 10^{-3} \Omega\text{-cm}$ . These measurements are consistent with a dominant transport mechanism of electrons traveling through intergraphitic planes in the VACNFs as reported earlier by Kelly (1981) in his book entitled *Physics of Graphite* [93].

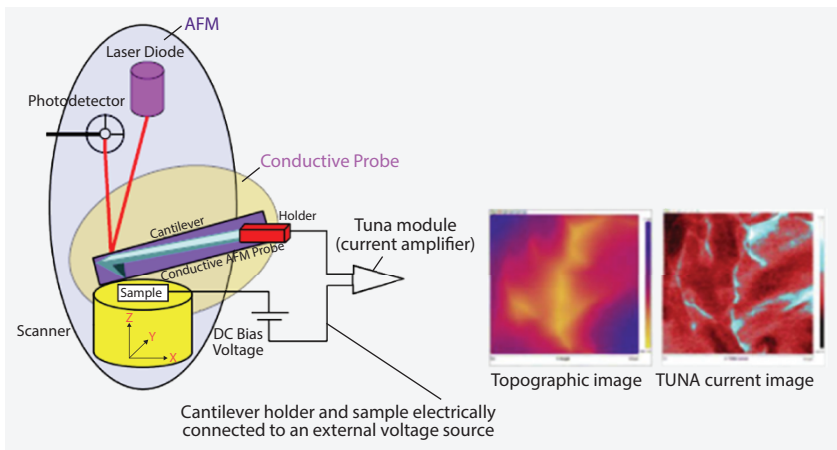
### 5.9.3 Tunneling Atomic Force Microscopy (TUNA) Analysis

Tunneling atomic force microscopy is officially abbreviated as “TUNA” by its manufacturer, Bruker. It is a very sensitive technique that can measure ultra-low currents (<1 pA) ranging from 80 fA to 120 pA [94]. Using TUNA, tunneling current can be obtained from a nano sharp tip attached

to a cantilever which moves the tip across the surface of the sample and simultaneously measures the topographical data. Unlike standard STM that requires smooth sample surfaces (on the nanometer scale), TUNA can investigate surfaces with an RMS roughness of several microns. The advantages of TUNA is that (i) the surface can be studied over scan areas up to hundreds of square microns, thus giving a wider picture of the morphology, (ii) unlike the constant-current mode of STM, the physical tracking of TUNA means that the height data collected from the deflection of the cantilever avoids possible artefacts due to variations in the conductivity of the sample surface and (iii) TUNA has very high current sensitivity with a noise level of 50 fA [95].

**The TUNA Setup** has a conductive AFM probe, an external voltage source (to apply a potential difference between the tip and the sample holder) and a current amplifier (to convert the analogical current signal into digital voltages) that can be read by the computer [96, 97].

TUNA operated with a cantilever holder and an epoxy nano filled sample (containing conductive CNF is electrically connected to an external voltage source (see Figure 5.29). In TUNA the sample is fixed on the sample holder using a conductive tape or silver paste. The principle of the TUNA mode is illustrated in Figure 5.29. The ohmic contact formed between the conductive AFM tip and the sample surface is the same as C-AFM, by which simultaneous topographic imaging and current imaging are obtained.



**Figure 5.29** Illustration of tunneling AFM (TUNA) setup. Source: Raimondo *et al.*, *Compos. B Eng.* 140, 44–56, 2018. Copyright © 2018 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license. [97] <http://creativecommons.org/licenses/by/4.0/>.



The TUNA-AFM technique has proven to be a really powerful tool for measuring electric transport through the CNF-based epoxy network.

**Electrical measurements** of the samples have the same contact mode as AFM, the z-feedback loop uses the DC cantilever deflection as a feedback signal to maintain a constant force between the tip and the sample to generate the topography image [98]. During scanning, a constant DC bias voltage is applied between the tip and the sample. The resulting current through the sample is measured with a current amplifier to get the desired electrical information.

### 5.9.4 Hall Effect Measurement

The application of carbon nanofibers in electronic and photonics [99] requires micro-electronic property investigation. Carrier concentration and mobility are two such parameters that are measured using Hall coefficient measurement.

Gupta *et al.* (1995) [100] measured the transport properties (electrical conductivity, Hall coefficient, transverse magnetoresistance) of the pristine and intercalated fibers (pitch-based highly graphitic P-120 CNF as procured from Amco) at room temperature and at 77 K with a magnetic field strength of 0.75 T. In such a low field,  $\mu_H \ll 1$  and the Hall coefficient is field independent. However, for increased accuracy, alternative current was used instead of direct current, and detection was performed with a lock-in amplifier. The experimental values for carrier mobility and carrier concentrations are obtained from measurements of the Hall coefficient  $\mu_H$ , conductivity  $G$ , and magnetoresistance  $\Delta R/R$  are presented for Pristine P-120 sample.

The sign of the Hall coefficient is observed to be negative for pristine fibers. This value changes to positive for intercalated fibers, due to the creation of a large number of holes in the valence band, as a result of the charge transfer from bromine to carbon.

These results can be interpreted with a two-carrier model: electrons of concentration  $n_e$ , and charge  $-e$ , and holes of concentration  $n_h$  and charge  $+e$ . In the low magnetic induction approximation (we never used more than 0.75 T), the conductivity ( $\sigma$ ), Hall coefficient ( $R_H$ ), and positive magnetoresistance ( $\Delta R/R$ ) of the fibers can be expressed as:

$$\sigma = e(n_e \mu_e + n_h \mu_h) \quad (5.42)$$

$$R_H = e(n_h \mu_h^2 - n_e \mu_e^2) / \sigma^2 \quad (5.43)$$

$$\Delta R/R = e^2 B^2 n_e \mu_e n_h \mu_h (\mu_h + \mu_e)^2 / 2\sigma^2 \quad (5.44)$$

Typical values for bromine intercalated carbon fibers were found to be  $0.147 \text{ m}^2/\text{V.s}$  and the concentration was of the order of  $10^{24} \text{ m}^{-3}$  for both electrons and holes [100].

Difficulties arising in measurements of transport properties due to the nano size of the CNFs can be circumvented by measuring the Hall mobility alternatively through the magnetic field dependence of negative magneto-conductance, i.e., positive magnetoresistance.

In one such study [101] Santiago-Aviles *et al.* (2003), two-probe conductance measurement ( $G$ ) was made at 300 K, on PAN fibres with a transverse  $B$ , varying between  $-9$  and  $+9$  T using a Model 6000 Quantum unit in conjunction with a Keithley 237 high-voltage source-measure unit.

For measuring the length  $l$  and cross-section area  $S$  using a scanning probe microscope in tapping mode, the conductivity was determined using:

$$\sigma = \frac{Gl}{S} \quad (5.45)$$

Magnetoresistance is defined as:

$$\frac{\sigma}{\sigma} = \frac{\sigma(B)}{\sigma(0)} - 1 \quad (5.46)$$

where  $\sigma(0)$  and  $\sigma(B)$  are conductance measured at transverse magnetic field zero and  $B$ .

The magnetoconductance shows a definite negative sign, and the  $B$  dependence of  $\frac{\sigma}{\sigma}$  resulted in a **parabolic** equation [102]:

$$\frac{\sigma}{\sigma} = (\mu_H B)^2 \quad (5.47)$$

This resulted in a value of  $\mu_H$  as  $(4.25 \pm 0.01) \times 10^{-3} \text{ m}^2/\text{V} \cdot \text{s}$ .

Furthermore, the conductivity of the PAN CNFs was determined as  $27535 \pm 527 \text{ S/m}$ . Assuming contribution due to holes and electrons to the conductivity, and equal values of mobilities, for an intrinsic CNF, we can approximate conductivity as:

$$\sigma = 2n\mu e \quad (5.48)$$

Another approximation that is applicable for CNF is the equality of Hall mobility  $\mu_H$  and the conductivity mobility  $\mu$ .

The resulting carrier concentration was,  $n = (2.02 \pm 0.04) \times 10^{25} \text{ m}^{-3}$ . The order of magnitude was found to be in agreement with the as-received P-120 fiber.

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# Carbon Nanofiber – A Potential Superconductor

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*Superconductivity helped broaden my professional phase space. When I started my work, it was already known that magnetic fields could quench superconductivity. I found that the transition was not continuous, that superconductivity was initially enhanced in the presence of magnetic fields, and then it would suddenly fall off.*

Mildred Dresselhaus

## 6.1 Introduction

Broadly speaking, there are four states of matter, viz. solid, liquid, gas and plasma. Many other states such as glass or liquid crystal, Bose-Einstein condensates, neutron-degenerate matter, and quark-gluon plasma are also known to exist. Most of the useful materials are found to exist in solid state with unique physical, chemical and electrical properties. Solids are further classified as metals/conductors, insulators or semiconductors based on their electrical properties like conductivity or resistivity and energy bands. Conductors are those materials whose electrical conductivity is very high. They conduct charges very easily. Copper, silver, aluminum and tungsten are some of the well-known conductors. Insulators are the materials whose electrical conductivity is either very small or zero. Therefore, they do not conduct charges. For example, glass, rubber and wood are the most commonly used insulators. The third kind of materials, popularly

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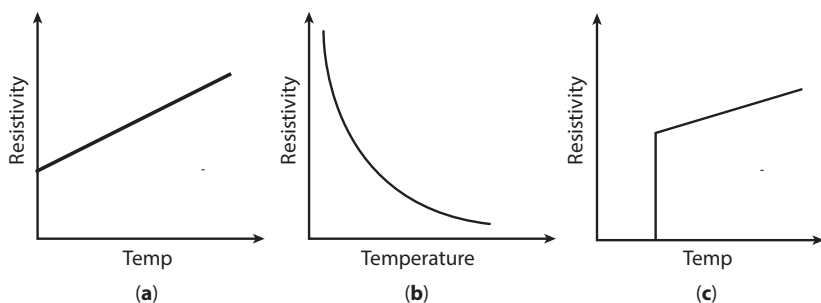


known as semiconductors, are the backbone of the electronic industries. These are the materials whose electrical conductivity lies in between insulators and conductors. They can conduct charges but not as easily as in the case of conductors. Germanium and silicon are the most commonly used semiconductors.

As mentioned above, conductors have high electrical conductivity. What does that mean? It means that these materials allow the current to flow through them. But each material has a tendency to oppose the flow of current passing through them. And this tendency to oppose the flow of current is called electrical resistivity. In other words, electrical resistivity is a fundamental property of a material that quantifies how strongly that material opposes the flow of electric current. A low resistivity indicates a material that readily allows the flow of electric current. Resistivity is commonly represented by the Greek letter  $\rho$ . Each conductor has a unique resistivity value in the range of  $10^{-8}$  Ohm-meter. The value of resistivity is temperature dependent. Normally the resistivity of the metals increases with increase in temperature, as represented in Figure 6.1.

But there is some unique behavior shown by some of the solid materials at low temperature. One of the most interesting properties of the solids at low temperature is that, in many metals and alloys, electrical resistivity decreases drastically and becomes zero below certain temperature depending upon the material. This phenomenon of showing zero resistivity by certain material below certain temperature is called *superconductivity* and the materials exhibiting this property are called *superconductors*.

Since this book is devoted to carbon nanofibers (CNF) and their applications, it is only natural to examine whether CNF by introducing some suitable properties can show superconductivity and, if so, can such material show  $T_c$  (temperature at which its conductivity goes down to 0.0000 °C)



**Figure 6.1** Resistivity vs. Temperature curve of (a) metal, (b) semiconductor, and (c) superconductor.

as low as room temperature or nearby. Hence, efforts are being made to explain certain salient features which a material should possess for superconductivity so that it would be possible to introduce superconductivity in CNFs. This chapter, therefore, discusses the theory of superconductors, the techniques of superconductivity; and studies the different aspects of the reported superconducting metal and alloys including mixed oxides and chalcogenides. Superconductivity identified in some organic compounds like fullerene is also a point of discussion in this chapter. The chapter closes by establishing evidence on how the existing properties of CNF/CNFs exhibit the possibility of CNFs being a superconductor too.

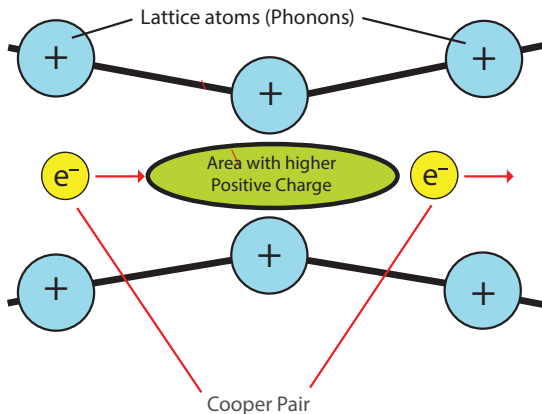
## 6.2 Superconductors

To understand the importance of superconductors, let us consider an example of power station situated at place A. If there are three different places—B, C, D—situated at a distance of 10 Km and are delivered a current of 50 amperes from the power station through the wires made of different conductors, it can be observed that place B gets a current of 40 amperes and place C gets a current of 45 amperes, whereas place D gets a current of 50 amperes. Now, what is the factor which leads to the decrease in the current reaching point B and C? It is nothing but the resistance of materials of the wire used to carry the current. And if place D gets 100% of the delivered current, the material used to carry the current is not an ordinary conductor but is a special material which must have zero resistance. Such materials with zero resistance are called superconductors. The evidence of existence of superconductivity in any material is the property of diamagnetism shown by the material. It is found that superconductors repel a magnetic field if exposed to magnetic lines of force below a certain critical temperature. This effect of diamagnetism is popularly known as the Meissner effect [1]. This effect is discussed in detail in Subsection 6.2.2.

### 6.2.1 Theory of Superconductors

Superconductivity was discovered by Dutch physicist Heike Kamerlingh Onnes on April 8, 1911 in Leiden when experimenting on conductivity of metals at low temperature [2]. Onnes found that Mercury, when cooled to temperature as low as 4.2 °K, was found to show a sudden decrease in the resistivity essentially equal to zero. He noticed that above 4.2 °K, mercury had a small but finite resistance. But below that temperature the resistivity became zero. It means that at that temperature, the transition takes place

from some finite value of resistance to zero resistance. The temperature at which the transition takes place is called the *critical temperature* ( $T_c$ ) or *transition temperature*. The state of matter below the critical temperature is called the *superconducting state*. Onnes also noticed that the superconducting transition is reversible. That is, the normal state of the materials is obtained when heated above  $T_c$ . Although the credit for the discovery of superconductivity goes to Onnes [3], the first theory on superconductors was published by Bardeen, Cooper and Schrieffer (BCS) in 1957 [4], which is commonly known as the BCS theory. They showed that superconductivity occurs when a special state of affairs exists between the conduction electrons. According to the BCS theory, a Coulomb attraction exists between the electron and the crystal lattice. An electron in the lattice will cause a slight increase in positive charges around it. This increase in positive charge will, in turn, attract another electron. These two electrons are known as a *Cooper pair*. The energy required to bind these electrons together always has to be higher than the energy from the thermal vibrations of the lattice. Therefore, to obtain superconductivity, low temperatures are required so that the thermal vibration of the lattice is small enough to allow the forming of Cooper pairs. In superconductor, the flow of current is due to the motion of these Cooper pairs, rather than individual electrons. So, Cooper pairs are formed by Coulomb interactions with the crystal lattice. This is also what overcomes resistance. Remember, an electron inside the lattice causes a slight increase of positive charge due to Coulomb attraction. As the Cooper pair flows, the leading electron causes this increase of charge, and the trailing electron is attracted by it. This is illustrated in Figure 6.2.



**Figure 6.2** Orientation of Cooper pair and lattice atoms in BCS theory.

According to this theory, an electron attracts lattice ions towards itself, so that it is surrounded by a region of positive charges. Another gets attracted to this region at high positive ion concentration. Thus, an electron-lattice-electron interaction results in an electron pair formation called *Cooper pairs*. They can be scattered only if the energy involved is sufficient to break them up into two single electrons. Copper pair electrons are of opposite momenta and spin ( $K$  and  $-K$ ). In addition, a Cooper pair does not obey Pauli's exclusion principle and hence any number of Cooper pairs can be accommodated into a single quantum state. Since an electron pair has a lower energy than the two normal electrons, there is an energy gap between the paired and the two single electrons. As long as Cooper pair electrons remain in Cooper pair states, they do not suffer scattering and hence resistivity will be zero. When the temperature is raised, to overcome the energy gap, Cooper pair electrons get separated into normal single electrons, which may undergo scattering due to the presence of imperfections in the crystal or lattice vibrations, which leads to a finite resistivity.

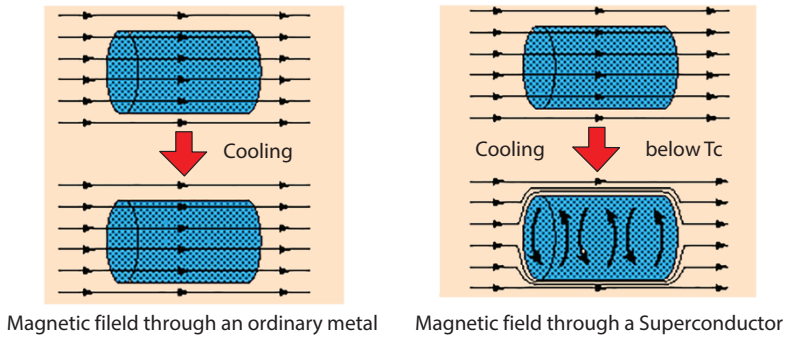
### 6.2.2 Measurement Technique of Superconductivity

One of the most popularly known tools to identify the existence of superconductivity in any material or to confirm superconductivity in a material is the *Meissner effect*. According to this effect, in addition to zero resistance value, if superconductors are cooled below their critical temperature and exposed to magnetic field, it is observed that the magnetic lines of force do not pass through the superconductor metal or, in other words, the magnetic flux density inside the superconductor metal is zero ( $B=0$ ).

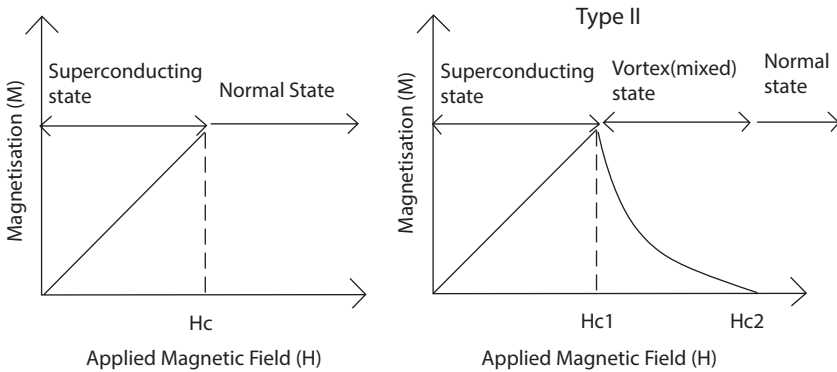
It is also noticed that if the same Meissner effect is studied with an ordinary metal, the lines of Magnetic lines of force pass even after cooling to the lowest temperature. The schematic illustration in Figure 6.3 explains the Meissner effect.

### 6.2.3 Types of Superconductors

Superconductors are classified as soft (Type I) and hard (Type II) superconductors. A superconductor which exhibits complete Meissner effect is called Type I and the other which does not obey complete Meissner effect is called Type II superconductor. Figure 6.4 distinguishes Type I and Type II superconductors based on magnetization ( $M$ ) as a function of applied magnetic field ( $H$ ) curve.



**Figure 6.3** Meissner effect applied to an ordinary metal and a superconductor.



**Figure 6.4** Magnetization ( $M$ ) as a function of applied magnetic field ( $H$ ).

As seen in Figure 6.4, Type I superconductor keeps out the whole magnetic field until a critical applied field,  $H_c$ , is reached. Above that field, Type I superconductor is no longer in its superconducting state. A Type II superconductor will only keep the whole magnetic field out until a first critical field  $H_{c1}$  is reached. Then vortices start to appear. A vortex is a magnetic flux quantum that penetrates the superconductor. Where the vortex appears the superconducting order parameter drops to zero. In this region the metal is no longer a superconductor. Around the vortex a current starts to circulate. Even though the vortices have formed, the rest of the metal remains superconducting. If the field is increased to the second critical field,  $H_{c2}$ , the metal stops to be superconducting.  $H_{c2}$  is usually a lot bigger than  $H_c$ , which is why Type II superconductors are typically used for superconducting magnets.

### 6.3 History of Existing Superconductors

After German researchers Walther Meissner and Robert Ochsenfeld discovered in 1933 that superconducting materials repel a magnetic field [1], in subsequent decades, in addition to the superconducting elements (mentioned in Table 6.1), other superconducting metals, alloys and compounds have also been discovered.

**Table 6.1** Critical temperature ( $T_c$ ) of some known superconductor element [5].

| Element    | Symbol | $T_c$ (°K) | Elements   | Symbol | $T_c$ (°K) |
|------------|--------|------------|------------|--------|------------|
| Aluminium  | Al     | 1.75       | Lead       | Pb     | 7.2        |
| Beryllium  | Be     | 0.03       | Rhenium    | Re     | 1.7        |
| Cadmium    | Cd     | 0.52       | Ruthenium  | Ru     | 0.49       |
| Gallium    | Ga     | 1.08       | Tin        | Sn     | 3.72       |
| Hafnium    | Hf     | 0.13       | Tantalum   | Ta     | 4.47       |
| Mercury    | Hg     | 4.15       | Technetium | Tc     | 7.8        |
| Indium     | In     | 3.41       | Thorium    | Th     | 1.38       |
| Iridium    | Ir     | 0.11       | Titanium   | Ti     | 0.4        |
| Lanthanum  | La     | 4.88       | Tellurium  | Tl     | 2.38       |
| Molybdenum | Mo     | 0.92       | Vanadium   | V      | 5.4        |
| Niobium    | Nb     | 9.25       | Tungsten   | W      | 0.02       |
| Osmium     | Os     | 0.66       | Zinc       | Zn     | 0.85       |
| Lead       | Pb     | 7.2        | Zirconium  | Zr     | 0.61       |
| Rhenium    | Re     | 1.7        | Tin        | Sn     | 3.72       |
| Ruthenium  | Ru     | 0.49       | Tantalum   | Ta     | 4.47       |
| Technetium | Tc     | 7.8        | Vanadium   | V      | 5.4        |
| Thorium    | Th     | 1.38       | Tungsten   | W      | 0.02       |
| Titanium   | Ti     | 0.4        | Zinc       | Zn     | 0.85       |
| Tellurium  | Tl     | 2.38       | Zirconium  | Zr     | 0.61       |

To name a few, in 1941 niobium-nitride was found to be superconducting at 16 K. In 1953, vanadium-silicon displayed superconductive properties at 17.5 K. In 1962, scientists at Westinghouse developed the first commercial superconducting wire with an alloy of niobium and titanium (NbTi). Then, in 1986, a truly breakthrough discovery was made in the field of superconductivity. K. Alex Müller and J. Georg Bednorz [6], researchers at the IBM Research Laboratory in Rüschlikon, Switzerland, created a brittle ceramic compound that super conducted at 30 K, the highest temperature known at that time. The following year, they were awarded the Nobel Prize in Physics for their discovery of the first superconducting copper-oxides. It was later found that tiny amounts of this material were actually superconducting at 58 K, due to a small amount of lead having been added. In 1986, J. Georg Bednorz and K. Alex Müller discovered superconductivity in a lanthanum-based cuprate perovskite material, which had a transition temperature of 35 K (Nobel Prize in Physics, 1987), which was the first of the high-temperature superconductors [6]. It was shortly found by Ching-Wu Chu that replacing the lanthanum with yttrium, i.e., making YBCO, raised the critical temperature to 92 K, which was important because liquid nitrogen could then be used as a refrigerant (at atmospheric pressure, the boiling point of nitrogen is 77 K). In 2001, superconductivity of magnesium diboride ( $\text{MgB}_2$ ) was found with  $T_c = 39$  K. In 2008, the oxypnictide or iron-based superconductors were discovered, which led to a flurry of work in the hope that studying them would provide a theory of the cuprate superconductors. In 2013, room-temperature superconductivity was attained in YBCO for picoseconds, using short pulses of infrared laser light to deform the material's crystal structure. In 2015, hydrogen sulfide ( $\text{H}_2\text{S}$ ) under extremely high pressure (around 150 gigapascals) was found to undergo superconducting transition near 203 K ( $-70^\circ\text{C}$ ), due to the formation of  $\text{H}_3\text{S}$ , a new record high temperature superconductor. In 2017 it was suggested that undiscovered superhard materials (e.g., critically doped beta-titanium Au) might be a candidate for a new superconductor with  $T_c$  substantially higher than  $\text{HgBaCuO}$  (138 K), possibly up to 233 K, which would be higher even than  $\text{H}_2\text{S}$ . A lot of research suggests that, additionally, nickel could replace copper in some perovskites, offering another route to room temperature.  $\text{Li}^+$ -doped materials can also be used, i.e., the spinel battery material  $\text{LiTi}_2\text{O}_x$  and the lattice pressure can increase  $T_c$  to over 13.8 K. Also,  $\text{LiHx}$  has been theorized to metallize at a substantially lower pressure than H and could be a candidate for a Type 1 superconductor. Table 6.2 enlists some of the other known superconducting alloys reported so far with their critical temperatures.

**Table 6.2.** Some known superconducting compounds with critical temperatures. (Source: [https://en.wikipedia.org/wiki/List\\_of\\_superconductors](https://en.wikipedia.org/wiki/List_of_superconductors)).

| Compound                                       | T <sub>c</sub> (°K) | Compounds          |  | T <sub>c</sub> (°K) | Compound                           |  | T <sub>c</sub> (°K) |
|------------------------------------------------|---------------------|--------------------|--|---------------------|------------------------------------|--|---------------------|
| Ba <sub>8</sub> Si <sub>46</sub>               | 8.07                | Nb <sub>3</sub> Al |  | 18                  | C <sub>3</sub> Na                  |  | 2.3–3.8             |
| C <sub>6</sub> Ca                              | 11.5                | Nb <sub>3</sub> Ge |  | 23.2                | C <sub>2</sub> Na                  |  | 5.0                 |
| C <sub>6</sub> Li <sub>3</sub> Ca <sub>2</sub> | 11.15               | NbO                |  | 1.38                | C <sub>8</sub> Rb                  |  | 0.025               |
| C <sub>8</sub> K                               | 0.14                | NbN                |  | 16                  | C <sub>6</sub> Sr                  |  | 1.65                |
| C <sub>8</sub> KHg                             | 1.4                 | Nb <sub>3</sub> Sn |  | 18.3                | C <sub>6</sub> Yb                  |  | 6.5                 |
| C <sub>6</sub> K                               | 1.5                 | NbTi               |  | 10                  | C <sub>60</sub> Cs <sub>2</sub> Rb |  | 33                  |
| C <sub>3</sub> K                               | 3.0                 | SiC:B              |  | 1.4                 | C <sub>60</sub> K <sub>3</sub>     |  | 19.8                |
| C <sub>3</sub> Li                              | 0.35                | SiC:Al             |  | 1.5                 | C <sub>60</sub> Rb <sub>x</sub>    |  | 28                  |
| C <sub>2</sub> Li                              | 1.9                 | TiN                |  | 5.6                 | FeB <sub>4</sub>                   |  | 2.9                 |
|                                                |                     |                    |  |                     | YB <sub>6</sub>                    |  | 8.4                 |
|                                                |                     |                    |  |                     | ZrN                                |  | 10                  |
|                                                |                     |                    |  |                     | ZrB <sub>12</sub>                  |  | 6.0                 |
|                                                |                     |                    |  |                     | LaFePO                             |  | 4                   |
|                                                |                     |                    |  |                     | FeSe                               |  | 65                  |
|                                                |                     |                    |  |                     | InN                                |  | 3                   |
|                                                |                     |                    |  |                     | In <sub>2</sub> O <sub>3</sub>     |  | 3.3                 |
|                                                |                     |                    |  |                     | LaB <sub>6</sub>                   |  | 0.45                |
|                                                |                     |                    |  |                     | MgB <sub>2</sub>                   |  | 39                  |



## 6.4 Superconductivity in Organic Materials

Superconductivity in organic compounds built of carbon and hydrogen (Table 6.3), which are among the most common elements on earth compared to copper or osmium, have been of great interest not only for scientists who are looking for room-temperature superconductivity but also for daily life issues as organic compounds. The recent studies indicate that some organic substances might be able to display metallic characteristics. It was realized that conduction and valence bands in organic molecules can be made partially filled if planar organic molecules are combined with anions that are nonorganic elements to make the compounds superconducting at reasonably high temperature above absolute zero. As of 2007 the highest achieved critical temperature for an organic superconductor at standard pressure is 33 Kelvin, observed in the alkali-doped fullerene  $\text{RbCs}_2\text{C}_{60}$ . The 1980s were a decade of significant discovery in the field of superconductivity. The first organic superconductor,  $(\text{TMTSF})_2\text{PF}_6$ , was synthesized by Klaus Bechgaard in 1980 [7]. But before that, in 1964 Bill Little of Stanford University had suggested the possibility of organic (carbon-based) superconductors.

**Table 6.3** Organic superconductors with their critical temperatures. (Source: [https://en.wikipedia.org/wiki/Organic\\_superconductor](https://en.wikipedia.org/wiki/Organic_superconductor)).

| Compounds                   | T <sub>c</sub> (°K) |
|-----------------------------|---------------------|
| $\text{K}_3\text{C}_{60}$   | 18                  |
| $\text{Rb}_3\text{C}_{60}$  | 30.7                |
| $\text{K}_2\text{CsC}_{60}$ | 24                  |
| $\text{K}_2\text{RbC}_{60}$ | 21.5                |
| $\text{K}_5\text{C}_{60}$   | 8.4                 |
| $\text{Sr}_6\text{C}_{60}$  | 6.8                 |
| $\text{C}_3\text{Na}$       | 2.3–3.8             |
| $\text{C}_2\text{Na}$       | 5.0                 |
| $\text{C}_8\text{Rb}$       | 0.025               |
| $\text{C}_6\text{Sr}$       | 1.65                |

The first of these theoretical superconductors were successfully synthesized in 1980 by Danish researcher Klaus Bechgaard of the University of Copenhagen and three French team members.  $(\text{TMTSF})_2\text{PF}_6$  had to be cooled to an incredibly cold 1.2 K transition temperature and subjected to high pressure to superconduct. Also, from Tables 6.1 and 6.2 it is evident that although carbon does not fall into the category of superconductors, many superconductors, viz.  $\text{C}_6\text{Ca}$ ,  $\text{C}_6\text{Li}_3\text{Ca}_2$ ,  $\text{C}_8\text{K}$ ,  $\text{C}_3\text{K}$ ,  $\text{C}_3\text{Li}$ ,  $\text{C}_2\text{Li}$ ,  $\text{C}_6\text{Sr}$ ,  $\text{C}_6\text{Yb}$ ,  $\text{C}_{60}\text{Cs}_2\text{Rb}$ ,  $\text{C}_{60}\text{K}_3$ , etc., have been reported with the various forms of carbons when mixed with other elements.

Guo-meng Zhao and Yong Sheng Wang of the University of Houston in Texas found suitable signs of superconductivity in carbon nanotubes [8]. Although it was not zero resistance, it was the closest anyone reported so far. Zhao thought that all the experimental results were consistent with superconductivity but could not rule out other explanations. The researchers did not see zero resistance in their bundles. They thought that it was because the connections between the tiny tubes never become superconducting. But they did see more subtle signs of superconductivity within the tubes themselves. For example, when they put a magnetic field across a bundle at temperatures up to 400 Kelvin (127 °C), the bundle generated its own weak, opposing magnetic field. Such a reaction can be a sign of superconductivity. They also observed that when the bundles were cooled they turned the external field off. A current running around within the tubes could generate this lingering field if there isn't any resistance to make it fade away. While each effect could have a more prosaic explanation, they varied in similar ways as the temperature of the bundles changed. The correlation suggests superconductivity was responsible. Although their paper was argued on many fronts, the idea revealed possibilities of CNTs as potential superconductors. Another group from Ural Federal University together with their colleagues from Lomonosov Moscow State University have discovered a mathematical method to calculate the temperature at which SWCNTs can become superconductors and developed a way to increase it, thus opening new prospects for superconductive materials application [9].

## 6.5 Can Carbon Nanofiber Also Be a Possible Superconductor?

In this chapter, no mention is made of the theory of superconductivity, mainly because to date there has been no standard theory developed which can explain the superconductivity for all materials. Theories have only

been developed to explain the superconductivity observed for a particular material, which cannot be taken as universal theory. There is thus a need to develop a theory which can be universally accepted for any materials.

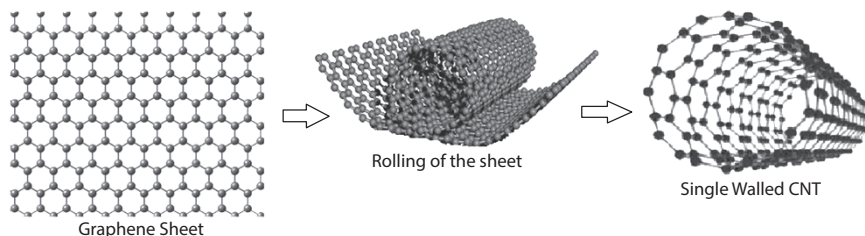
However, examining the structures of materials which had shown superconductivity, suggest that material should possess structure such that electrons can migrate along a particular direction without being disturbed by other sets of electron's migrations. This means there seems to be horizontally parallel axis (C-axis) separated from each other such that wavelength of electrons while migrating along the c-axis does not interact with waves of electrons of other parallel c-axis.

If this hypothesis is assumed to be correct, then in CNF the arrangement of electrons in the structure should meet these requirements. CNF contains both  $sp^3$  and  $sp^2$  carbons and their alignments should be such that electrons migrations should not be affected by the presence of either of these configured carbons. Though it is known that conductivity of electron in CNFs is favored along the length rather than in ab-axis; hence, one needs to develop or improve the structure of carbon such that migration of electrons along the c-axis is not affected by other electrons. Thus, there is a need to synthesize CNF or dope it suitably such that these requirements can be met.

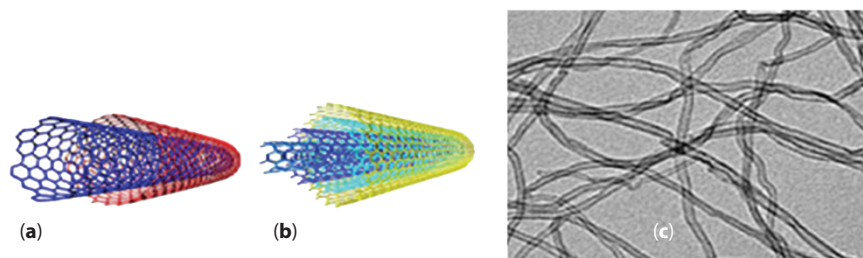
CNTs are basically tubular form of carbon with diameter varying from 1 nm to a few micrometers. Configurationally they are equivalent to a 2D graphene sheet rolled into a tube, as shown in Figure 6.5.

On the other hand, if two or more graphene sheets separated by a distance on the order of nanometers are rolled into a cylindrical shape, it takes the shape of double-walled carbon nanotubes (DWCNT) or multi-walled carbon nanotubes (MWCNT). Normally it is not possible to distinguish the SWCNT and DWCNT from their physical appearance, but from the TEM images of the cross sections of the tubes structure of SWCNT and MWCNT can be visualized (Figure 6.6).

However, when broken sheets of multiple graphene sheets are rolled into a cylinder, it takes the shape of carbon nanofiber. CNFs appear as



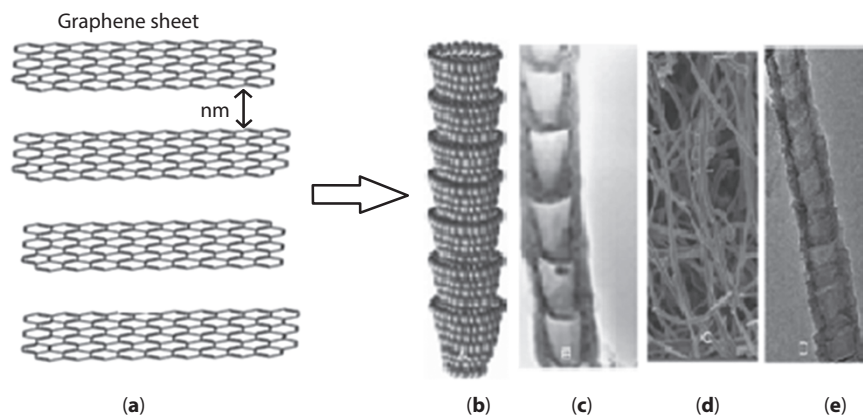
**Figure 6.5** Graphene sheet converted into carbon nanotubes.



**Figure 6.6** Structures of various forms of carbon nanotubes: (a) Single-walled CNT, (b) Double-walled CNT, (c) TEM image of MWCNT.

cylindrical nanostructures with graphene layers organized as packed cones, cups or plates (Figure 6.7). Surface area of carbon nanofiber is much larger compared to MWCNT of the same dimension.

The ability of carbon to form flat, one-atom-thick graphene sheets has attracted the attention of scientists. Rolling such a sheet to make a tube produces another interesting structure, SWCNT. These structures are highly tensile, refract light in an unusual manner, and may be used in many areas from electronics to biomedicine. Atoms inserted in the walls of such tubes may change their properties, including conductivity. It may depend on the orientation of hexagons that form the carbon layer, on the filling of the tube, or on additionally inserted or attached atoms of other elements.



**Figure 6.7** Various images of CNF. (a) Broken sheet of graphene, (b) Schematics of stacked CuO CNF, (c) TEM of packed cones/cups, (d) SEM image of CNF, (e) TEM image of MWCNT showing stacked cup-like structure. (Source: Figures A, C, & D are taken from Chapter 1 of this book; and B is reinforced carbon polymer composite, pp. 11-26, Part of Springer Briefs in Materials Book series).

SWCNTs are actively studied as prospective superconductors. However, their diameter equals only 0.4 nanometers. Therefore, they are close to 1D materials. At temperatures close to absolute zero, so-called Cooper pairs of electrons form within them. In the absence of curvature, Cooper pairs do not form, and no superconductivity is observed. However, the 1D structure may be modified in order to increase the temperature of superconductive transition. It is said that when SWCNTs are piled together, Cooper pairs may stabilize and a superconductor may be formed. However, such piles will require quite low temperatures to exhibit superconductive properties above absolute zero. CNFs have similar structure and properties as that of CNTs. They possess excellent mechanical properties, high electrical conductivity, electromagnetic shielding and high thermal conductivity. The CNFs have average diameters ranging from 125 to 150 nm depending upon the precursors and technique used to manufacture them and have lengths ranging from 50 to 100  $\mu\text{m}$ . Electrical conductivity in CNFs depends upon the nature of the network and their alignment in the matrix. Therefore, for good electrical conductivity, good fiber dispersion and the continuation of the network is necessary. Also, by controlling the loading amount of CNF in the composite, different electrical resistivity values can be achieved.

Endo *et al.* (1995) [10] first reported the intrinsic conductivity of highly graphitic vapor-grown carbon fiber at room temperature to be  $5 \times 10^{-5} \Omega\text{-cm}$ , which is near the resistivity of graphite. Since virtually all of the electrical conductivity is through the network of carbon nanofibers, it is clear that good fiber dispersion and maintenance of fiber length will aid in achieving high composite electrical conductivity at even a low fiber loading. Due to their high electrical conductivity and high aspect ratio, CNF can impart equivalent electrical conductivity to a composite at lower loadings than conventional conductive fillers. Also, by controlling the loading, one can produce composites with different electrical resistivity values. This is of particular importance for applications that require a resistivity in different ranges such as electrostatic dissipation (ESD)  $\{10^6 - 10^8 \Omega\text{-cm}\}$ , electrostatic painting  $\{10^4 - 10^6 \Omega\text{-cm}\}$ , EMI shielding  $\{10^3 - 10^1 \Omega\text{-cm}\}$ , and lightning strike protection  $\{< 10 \Omega\text{-cm}\}$ . Research in the field of nanowires and nanofibers indicates that depending on their composition and dimensions, they can become superconducting too. Several interesting effects appearing at nanoscale are discussed by Buzea *et al.* (2018) [11] regarding superconductivity in wires made of non-superconducting materials due to superconducting electrodes, a switch in electrical behavior from metallic to semiconducting with chirality of CNTs, and metallicity of one-dimensional materials confined inside nanotubes that are semiconducting in bulk. They said that due to their small dimensions, nanowires and nanofibers show

interesting electrical properties. Some materials fabricated as nanowires, while non-superconducting in bulk form, show superconductivity only on the nanowire surface.

Therefore, it is evident that CNFs are the potential superconductor; if not in pure form then at least after due doping with some inorganic elements and optimized synthesis techniques.

## 6.6 Summary

An effort was made in this chapter to discuss the various features of superconductors, viz. theory, types, measurement techniques, etc. A chronological history of development in the fields of superconductivity with the mixed oxides and chalcogenides to the organic superconductors are also discussed. Efforts were also made to explain the basic differences and similarities between CNF and CNT; and to prove that if CNTs can be superconducting, there is a possibility that CNF can also be a potential superconductor.

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# Carbon Nanofiber for Hydrogen Storage

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*Energy and persistence conquer all things.*

**Benjamin Franklin**

## 7.1 Introduction

Due to population growth along with an ever-increasing list of luxuries becoming necessities across all strata of society, the present day level of generation of energy is unable to cope with the galloping increase in demand. Moreover, fossil fuel stock is dwindling faster than ever before and hydro-energy and nuclear energy have inherent drawbacks. Hence, it has become a requirement to explore various new renewable sources of energy.

It is believed that most of the future energy requirements can be satisfied by the use of hydrogen as a source of energy. Although the technology of hydrogen fuel cells has been developed, what remains to be developed for its use commercially is the facility to store enough hydrogen in a small package to be carried easily.

In this chapter, carbon nanofiber (CNF) for hydrogen storage, the pros and cons of use of hydrogen as a source of energy, and various methods of storing hydrogen are presented.

The search for a clean and sustainable fuel that can be transported easily, ends with HYDROGEN. One may differ and advocate for nuclear energy, wind energy and the like, not to mention solar energy. Though these are

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formidable competitors, all these forms have their inherent drawbacks particularly when the question of transportation arises. It is also necessary to discuss the different methods of storing hydrogen, as many such methods have drawbacks to be considered like dead weight, technology, refueling ability, economy, etc. It is desirable to find a material or method that can be used to store enough hydrogen as envisaged by the U.S. Department of Energy (DOE) and at the same time free of most of the drawbacks mentioned earlier.

## **7.2 Hydrogen – Its Advantages and Disadvantages as Source of Energy**

Henry Cavendish discovered the element hydrogen in 1766. It is the smallest element with atomic number 1. There are three isotopes of hydrogen with mass numbers 1, 2 and 3 named hydrogen, deuterium and tritium respectively. A hydrogen molecule consists of two atoms of hydrogen joined by a single covalent bond. As such, a hydrogen atom consists of one proton and one electron. Each proton has an associated magnetic moment; hence, molecular hydrogen occurs in two isomeric forms. The molecule with protons spin aligned parallel forms a triplet state, which is known as ortho-hydrogen; the other with protons spin aligned anti-parallel is a singlet state and is known as para-hydrogen. At room temperature and thermal equilibrium, hydrogen consists of 25% para-hydrogen and 75% ortho-hydrogen. These two allotropes are chemically and physically identical, except that they slightly differ in spectra and specific heats.

Hydrogen gas is regarded as the fuel of the future. Its energy can be transformed into electrical energy without the emission of carbon dioxide or other pollutants. In 1959, Francis Bacon produced a 5-kW fuel cell system to prove that hydrogen and air can be used as a source of energy [1]. In addition, the source of hydrogen, i.e., water, does not face the danger of becoming depleted like fossil fuel. The impending energy crisis scenario has made it a necessity to explore alternative sources of energy which do not depend on fossil fuel and are non-polluting or carbon neutral. Due to increasing global energy demands and environmental concerns, hydrogen has become a good candidate for alternative fuel. The main challenge for commercialization of hydrogen fuel cells is storage of an adequate quantity of hydrogen on board to match the current requirements. Thus, hydrogen is the probable solution towards feasible safe reliable and completely sustainable energy source.

### 7.2.1 Advantages

- **Abundance:** Hydrogen is available in plenty as future fuel, as it can be easily generated from renewable energy sources as well as from water [2].
- **Energy:** 1 Kg of hydrogen contains the same amount of energy as 2.1 Kg of natural gas or 2.8 Kg of gasoline. Thus, it is much more efficient than any other fuel available. Hydrogen energy can be transformed into electrical energy with high efficiencies (up to 50–60%). It can be used in a fuel cell [3, 4]. If used in an internal combustion engine, it behaves like any other known fuels; hence, hydrogen can be accepted as a perfect and sustainable fuel.
- **Green fuel:** Gasoline and other petroleum-based fuels are highly toxic and hazardous to humans and flora and fauna alike when released into the environment. Hydrogen has very high diffusibility in air. If hydrogen spillage occurs accidentally, it will evaporate easily and unlike petrol, hydrogen being the lightest element escapes to upper atmosphere quickly before it has any chance to spread horizontally. Petroleum-based fuels on the other hand, require immense cleanup efforts with the result that most of the spilled toxic hydrocarbons seep into the surrounding ecosystem wrecking irreparable damage. Hydrogen is non-polluting and forms water as a harmless by-product.
- **Safety:** Though hydrogen is highly inflammable, its ability to disperse rapidly into the atmosphere makes hydrogen safer in case of leakage. Propane, gasoline or similar hydrocarbons, due to their higher densities and slow dispersal, allow the fuels to concentrate near the ground, increasing the risk of explosion. Gasoline's concentration has to reach only 1% before the danger of explosion arises, while hydrogen has to reach a concentration of 4% in the surrounding atmosphere of air before it poses a danger [5].

### 7.2.2 Disadvantages

The flame of hydrogen runs back to the cylinder in which it is stored, causing an explosion; hence, storing in a cylinder needs some facility to prevent backflash of hydrogen flame.

Hydrogen gas is about fourteen times lighter than air, with a very low flash point [6]. The kinetic molecular diameter of hydrogen is 0.289 nm. It is smaller than the interlayer spacing in graphitic materials (0.335–0.350 nm).

The above discussion emphasizes the need to explore and find a suitable method to store large quantities of hydrogen in a small lightweight container.

## 7.3 Methods of Hydrogen Storage

Methods of hydrogen storage depend on the state in which it is stored, viz. storage of liquid or gaseous hydrogen.

### 7.3.1 Storage of Liquid Hydrogen

Melting point of hydrogen is  $-259.20^{\circ}\text{C}$ ; hence, cryogenic conditions are necessary for storing liquid hydrogen [7, 8]. To achieve liquid state and to compress the hydrogen gas, energy equivalent to about 30% of the stored energy of hydrogen is lost. The storage tanks require effective insulation and sustained energy to maintain the hydrogen in a liquid state [9]. Thus, use of liquid hydrogen as fuel is not economical.

### 7.3.2 Storage of Gaseous Hydrogen

There are various methods to store gaseous hydrogen. These are discussed below.

#### 7.3.2.1 *In Metal Hydride Storage Tanks*

Metal hydrides are specific combinations of metallic alloys that possess a unique ability to absorb hydrogen and release it later, either at room temperature or at higher temperature or by decreasing the external pressure. Magnesium-based hydrides have hydrogen storage with reversible hydrogen capacity up to 7.6 wt.% for on-board applications. The percentage of gas absorbed to volume of the metal is still relatively low. Metal hydrides offer the advantage of safely delivering hydrogen at a constant pressure. The life of a metal hydride storage tank and ability to store hydrogen gradually reduces as the impurities keep on getting adsorbed by metal hydride and which are not desorbed during the heating process. Important limitations in the application of metal hydrides for hydrogen storage are slow

kinetics and poor reversibility. Hydrogen storage by  $\text{NaAlH}_4$  showed that the nano-range particle size of hydrides not only reduces desorption temperature but also decreases the activation energy. Moreover, decreasing the particle size lowers the reloading pressure [10]. Sodium borohydride ( $\text{NaBH}_4$ ) was presented as a promising hydrogen storage material but based on their findings the U.S. DOE recommended a no go for  $\text{NaBH}_4$  for on-board automotive hydrogen storage [11]. Through direct hydrogenation of  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$ , it is possible to reversibly store >11 wt.% hydrogen [12]. One may synthesize Mg-B-H compounds directly and use them as hydrogen storage system [13]. Various metal hydrides, including lanthanides, have been used as hydrogen storage material but with different degrees of success.

### 7.3.2.2 *Storage of Compressed Hydrogen in High-Pressure Tank*

Hydrogen can be compressed into a high-pressure storage tank. The process requires a large quantity of energy to accomplish and the space that the compressed gas occupies is usually quite large, resulting in a lower energy density. Hence, compressing or liquefying the gas is expensive. Hydrogen can be compressed into high-pressure tanks where each additional cubic foot compressed into the same space requires another atmospheric pressure of 14.7 bar. High-pressure tanks can sustain a hydrogen pressure of 6,000 bars but since hydrogen molecule is smaller in size it gets easily diffused into the matrix of the metal of the container at 200 bars, making the container brittle. Moreover, the total weight of the container becomes larger than the amount of hydrogen stored in the cylinder. Thus, the vehicle has to carry the additional weight of the cylinder, which makes the system uneconomical.

### 7.3.2.3 *Hydrogen Storage in Glass Microspheres*

Glass spheres are small hollow glass micro-balloons whose diameter ranges between 25–500  $\mu\text{m}$  and wall thickness about 1  $\mu\text{m}$ . These spheres are filled with hydrogen at high pressure and temperature and cooled to ambient temperature; the hydrogen is trapped inside the spheres [14]. Hydrogen gas is released by heating or crushing the spheres. The crushing prevents the reuse of spheres and is not a very favorable option being that it is uneconomical. The glass spheres can also cause accidents when breaking down if not handled properly. The storage capacity of spheres is about 5–6 wt.% at 200–490 bar [15].

#### 7.3.2.4 *Storage in Array of Glass Micro Tubules/Capillaries*

A multinational team of researchers from Israel, Russia and Germany developed a lightweight hydrogen storage technology. They discovered a way to pack hydrogen into glass filaments/capillaries that, once completed, becomes slightly thicker than a human hair. The glass hairs, or “capillaries,” are then bundled into a glass tube, 370 at a time, forming a “capillary array” about the width of a drinking straw. It was predicted that 11,000 of such arrays would fuel a car for 240 miles, will occupy less than half the space and weight of a conventional hydrogen cylinder [16].

#### 7.3.2.5 *Storage of Hydrogen in Chemicals*

Chemical compounds like methanol ( $\text{CH}_3\text{OH}$ ) and methyl cyclohexane ( $\text{CH}_3\text{C}_6\text{H}_{11}$ ) containing hydrogen can also be considered for hydrogen storage [17, 18]. At NTP conditions, all of these compounds are in liquid form and thus the infrastructure for gasoline could be used for transportation and storage of the compounds. This system is advantageous as compared to compressed hydrogen gas cylinder, which requires leak-proof piping and vessels. These chemical compounds have fairly good hydrogen storage capacity, i.e., 8.9 wt.% for  $\text{CH}_3\text{OH}$  and 13.2 wt.% for  $\text{CH}_3\text{C}_6\text{H}_{11}$ . The containers for these chemicals can be made of lightweight composites or even plastic in some cases.

Chemical storage of hydrogen also has some disadvantages as this storage method is nonreversible. The compounds have to be produced in a centralized plant and the reaction products have to be recycled. Besides which, it also produces carbon monoxide, which is also unfavorable [18]. However, methanol has been used as a reformer in alkaline fuel cell to provide hydrogen. Ammonia, another candidate for chemical storage of hydrogen, has about 15.1 wt.% hydrogen storage capacity but produces environmentally toxic nitrogen oxides.

Lithium and sodium borohydride, ammonia borane, hydrazine, formic acid, etc., are promising candidates of the same class having relatively high hydrogen content.

#### 7.3.2.6 *Storage of Hydrogen in Metal Amidoboranes*

Alkali- and alkaline-earth metal amidoboranes contain  $[\text{NH}_2\text{BH}_3]^-$  units.  $\text{LiNH}_2\text{BH}_3$  and  $\text{Ca}(\text{NH}_2\text{BH}_3)_2$  in tetrahydrofuran have been reported to improve the dehydrogenation properties of ammonia borane. Therefore, metal amidoboranes, with accelerated desorption kinetics and suppressed

toxic borazine, are of great interest for their potential applications for hydrogen storage [19].

### 7.3.2.7 *Storage of Hydrogen in Metal Organic Framework System*

Metal-organic frameworks (MOFs) provide unique systems with large overall pore volumes and surface areas, adjustable pore sizes, and tunable framework-adsorbate interaction by ligand functionalization and metal choice. These remarkable materials can potentially fill the niche between other physisorbents, such as activated carbon, which have similar uptake at low temperatures but low affinity for hydrogen at ambient temperature, and chemical sorbents such as hydrides, which have high hydrogen uptakes but undesirable release kinetics and thermodynamics [20].

The large void space generated by cages in MOFs is not completely utilized for hydrogen storage application owing to weak interactions between the walls of MOFs and hydrogen molecules. The unutilized volumes in MOFs can be effectively utilized by incorporation of other microporous materials, such as single-walled carbon nanotubes, into the pores of MOFs, which could effectively tune the pore size and pore volume of the material towards hydrogen sorption [21].

The hydrogen adsorption capacity of the materials increases not only at cryogenic temperatures but also at ambient temperatures. Thus, metal-organic framework seems to be a very promising and effective candidate for hydrogen storage, though a lot of work needs to be done before the entire potential can be realized.

Zr-based metal-organic framework (Zr-MOF) and reduced graphene oxide (rGO) composite was synthesized to study the possibility of transfer of some of the graphene's attractive properties to the MOF materials. There was an increase in SSA of the rGO/Zr-MOF composite when compared to that of Zr-MOF with enhanced hydrogen storage capacity. The synergistic effect of interactions of rGO sheets with hydrogen and the possible expansion of the pore volume in the Zr-MOF induced by the presence of the graphene-like material are the reasons for the enhancement [22, 23].

## 7.4 **Different Forms of Carbon and Nanocarbon for Storage of Hydrogen**

Carbon and carbon-based materials have received considerable attention in the context of physisorption. Sorption processes require porous materials with a large number of sorption sites per unit mass or volume of an

adsorbent; in other words, materials with high specific surface area (SSA) (either gravimetric or volumetric) accessible to the sorbate. Carbon structures, known to have high SSA, are activated carbon, exfoliated graphite, fullerenes, carbon nanotubes (CNT), carbon nanofibers (CNF), to name a few. Investigations of hydrogen storage in carbons as a function of SSA have been reported over the last three decades, and activated carbons with SSA up to  $\sim 3000 \text{ m}^2/\text{g}$  have been produced [24]. The interest is also due to the following factors, viz. adsorption capacities from 0 to 67 wt.% have been claimed [25] along with the possibility of using these materials for hydrogen storage for subsequently use in fuel cells and automobiles [26].

Reports of very high and reversible adsorption in carbon nanomaterials have stimulated many experimental works and theoretical calculations worldwide. However, owing to the low apparent density of CNTs and CNFs, doubts have been raised as to whether their volumetric hydrogen storage capacity could meet the volumetric target value set by the U.S. DOE hydrogen plan! Numerous claims have been put forward regarding different potential methods for storing hydrogen in carbon systems at ambient temperature for use in transportation systems. Some of the results of hydrogen storage by different types of CNMs are discussed below.

#### 7.4.1 Activated Carbon

Activated carbons are highly porous structures providing large surface area, some in excess of  $3000 \text{ m}^2/\text{g}$ . The importance of micropore volume relative to the hydrogen capacity of a carbon material was elucidated and hydrogen adsorption of 2 wt.% at  $-196^\circ\text{C}$  was detected [24]. Different scientist reported 1.3 wt.% gravimetric capacity of hydrogen adsorption on microporous carbon materials or hydrogen adsorption capacity of up to 1.5 wt.% by isothermal gravimetric analysis, using a microbalance at hydrogen pressures up to 125 bars at  $238^\circ\text{C}$  [27, 28]. One has to understand that hydrogen adsorption capacity depends on both the micropore volume as well as the micropore size distribution [29]. An astonishing amount of adsorption of hydrogen on activated carbon was observed, to the extent of 23.76 wt.%. It was observed that when the adsorption pressure reached about 80 MPa, the adsorption potential was 0 kJ/mol and no more adsorptive molecules could enter into the adsorbent micropores [30]. If the adsorption pressure was above 80 MPa, the structure of the adsorbent would be destroyed and some micropores would be enlarged into mesopores or macropores; thus, some supercritical hydrogen that has been adsorbed on the super-activated carbon would be desorbed.



Doping of activated carbon by alkali metals, etc., resulted in an increase in hydrogen adsorption. The mechanism of hydrogen adsorption by activated carbon, prepared mechanically by ball milling, is due to hydrogen adsorption into the pores in the carbon in the form of hydrogen molecules, and a combination of dangling bonds created by ball milling [31]. Chemisorption of hydrogen gas was found to increase when microporous activated carbons were doped with Li and K, but the isotherm profiles of doped activated carbon at 77 K show no clear enhancement of the sorption ratio compared to the raw activated carbon [32]. The enhanced release of hydrogen from such systems like the K-doped super-activated carbon at high temperatures (440–1370 K) is mainly due to chemisorptions [33]. Reversible hydrogen uptake on these carbons was reported to be almost proportional to surface area and to micropore volume. Modification of activated carbon fiber (ACF) by decorating with different metals alters the adsorption of hydrogen and is more than as-obtained carbon fibers due to chemisorptions [34]. The hydrogen adsorption properties of ACF oxidized with ammonium dithionate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  or reduced in a hydrogen flow at 1073 K were evaluated at 77 and 303 K over the hydrogen pressure range of 0–3.5 MPa. The amount of adsorbed hydrogen was decreased by oxidation and increased by reduction. Activated carbon prepared from coconut shell was doped with potassium, the maximum hydrogen adsorption capacity of 0.85 wt.% at 100 bars, 298 K was obtained in these materials [35]. To obtain a gravimetric density of 6 wt.%, it was calculated that a specific surface greater than  $4000 \text{ m}^2 \text{ g}^{-1}$  would be required. Accordingly, carbon sample was prepared by chemical activation of anthracite with KOH, which had a surface area of  $3183 \text{ m}^2/\text{g}$  but showed a hydrogen uptake of only 3.2 wt.% at ambient temperature and 200 bars [36, 37]. This suggested that surface area alone is not responsible for giving higher hydrogen adsorption; other parameters like pore size and pore volume may also be responsible for giving higher storage capacity.

The hydrogen adsorption capacity as calculated by Zhang (2003) to be 23 wt.% has not been achieved so far by anyone [38]; only Strobel *et al.* (2006) [36] reached up to 6 wt.% with activated carbon with very high surface area ( $4000 \text{ m}^2/\text{g}$ ). Nickel was impregnated in commercial activated carbon to study the extent of hydrogen adsorption in those particles. Various factors influencing the level of hydrogen uptake (metal precursor, metal content and method of preparation) were investigated. It was concluded that the hydrogen stored is loosely chemisorbed on the carbonaceous material surface as spill-over species through hydrogen dissociation on the metal phase then migration onto the support [39]. Many researchers used the method



of doping to increase the hydrogen adsorption but they could only succeed in getting desorption up to 2 wt.%. Potassium hydroxide activation of the activated carbon created remarkable microporosity in the frameworks. One of the resultant porous carbons exhibited a high surface area of up to  $3190 \text{ m}^2 \text{ g}^{-1}$  and large gravimetric hydrogen uptake capacity of 7.08 wt.% at 77 K and 20 bar, which is one of the largest data reported for the porous carbon materials [40].

These results suggest that the porous carbon with large amounts of active sites, high surface area and high micropore volume related to optimum pore size could achieve high gravimetric hydrogen storage. The theoretical analysis suggests that surface is an important parameter for getting very high hydrogen adsorption capacity. Reversible hydrogen uptake by these carbons was reported to be almost proportional to surface area and to micropore volume [41].

#### 7.4.2 Single-Walled Carbon Nanotubes (SWCNTs)

Single-walled carbon nanotubes were prepared by co-evaporation of cobalt and graphite using an electric arc. The hydrogen storage capacity of this material and activated carbon through temperature-programmed desorption (TPD) measurements were investigated [42]. It was observed that the hydrogen desorbed from both the nanotubes and the activated carbon samples at the same temperature  $\sim 133 \text{ K}$ . However, when the nanotubes sample was heated in a vacuum, a second peak appeared at a higher temperature  $\sim 290 \text{ K}$ . This indicates that a second type of hydrogen adsorption must have taken place, probably inside the SWCNTs. This high-temperature desorption was not observed in either activated carbon or in arc generated soot produced without a catalyst. This phenomenon was described as cutting method to produce samples with a high concentration of short SWCNTs having open ends that ensure the entry of hydrogen molecules [43]. Using such structures, it was possible to achieve hydrogen adsorption, estimated to be at  $\sim 3.5\text{--}4.5 \text{ wt.}\%$  at room temperature and 0.65 bars of hydrogen pressure, while crystalline ropes of SWCNTs can adsorb hydrogen up to 8 wt.% at pressures higher than about 40 bars at 80 K [44]. Furthermore, when these tightly packed rope structures of highly crystalline pure SWCNTs were ruptured by sonicating them in dimethyl formamide (DMF), the diameter distribution of the SWCNT ropes were broadened and the number of SWCNT terminations were increased within the ropes. The solvent, DMF, was extracted by vacuum filtration. The highest gravimetric hydrogen storage capacity achieved in SWCNT material treated in this manner was 8.25 wt.% at a temperature of 80 K and a pressure of  $\sim 7 \text{ MPa}$  [45].

In the case of CNTs, hydrogen molecule can exist in the empty space inside nanotubes and the storage capacity of hydrogen in an empty space increases linearly with tube diameter. The maximum storage capacity is restricted by the repulsive energies between hydrogen molecules inside nanotubes and those between hydrogen molecules and the tube wall [46]. It was predicted that hydrogen storage capacity in (10,10) nanotube can exceed 14 wt.% (160 kg H<sub>2</sub>/m<sup>3</sup>). When the ropes of SWCNT were split into individual tubes, the surface area available for physisorption also increased [47]. The removal of catalyst tip by thermal treatment added to the possibility of increased hydrogen adsorption. An interesting observation was that the CNT films obtained from chemical vapor deposition (CVD) have a hydrogen storage capacity of 8.0% and the CNT films produced by catalytic decomposition have even higher hydrogen storage capacity than that of the former [48].

The adsorption of hydrogen is favored by certain specific sites in the SWCNTs. Arrays of SWCNTs with open ends accommodate hydrogen in at least two sites: inside the nanotubes (endohedral adsorption) and in the interstitial pores formed between nanotubes (exohedral adsorption). Aligned CNTs of 50–100 nm in diameter were synthesized which were capable of hydrogen adsorption up to 5–7 wt.%. The hydrogen adsorption capacity was further improvised to 13 wt.% with the help of pretreatments and heating the samples to 300 °C [49]. Hydrogen atoms can be stored on the tube wall by breaking the C-C mid bond, while preserving the wall stability of CNTs after complete hydrogen insertion [50]. Chemisorption of hydrogen reduces the gas storage capabilities of carbon nanotubes, while the opening of cavities by oxidation tends to increase the mass of stored hydrogen gas in terms of both gravimetric and volumetric capacity [51]. The gravimetric storage capacity, including endohedral and exohedral adsorptions, of hydrogen on open nanotube arrays of 2.719 nm is 7.1 wt.% at 77 K and 40 bars, while the total excess adsorption of hydrogen on open isolated nanotubes of 2.719 nm reaches 9.5 wt.% at the same temperature and pressure [38]. It can be concluded here that the extent of hydrogen adsorption depends on the exposed specific surface area of the carbon material.

Surprisingly, macroscopic ropes of well-aligned SWCNTs having 1.72 nm diameter, synthesized by semicontinuous hydrogen arc discharge (with discharge capacity of 503 mAh/g), could adsorb 1.84 wt.% hydrogen [52]. Whereas purified SWCNT bundles at room temperature only had an adsorption capacity of 0.9 wt.% [53]. These results indicate that the results may not be reproducible. A number of researchers subsequently synthesized SWCNTs by various methods and studied their hydrogen adsorption

capacity at different temperatures and pressures, but none were able to get a hydrogen adsorption of more than 3 wt.% [54–58]. Nitric acid treatment enhanced the amount of hydrogen adsorbed on SWCNT due to opening up the nanotubes and changing the bundle structure. The heat treatment further increased the hydrogen adsorption capacity of acid-treated SWCNT sample owing to the removal of the functional groups introduced by the nitric acid treatment [59, 60].

A new direction was chartered to the saga of hydrogen adsorption by SWCNTs when it was found that nickel-dispersed single-walled CNTs are capable of releasing ~10 wt.% H<sub>2</sub> at around room temperature [61]. SWCNTs synthesized from methane and their hydrogen adsorption on as-obtained as well as nanocrystalline platinum-dispersed SWCNTs were studied using high pressure Sievert's apparatus with expected results [62]. SWCNTs encapsulated by thin palladium layers can achieve a net capacity of 8–12 wt.% hydrogen [63]. SWCNTs were prepared from natural gas by decomposition at 900 °C, over cobalt-molybdenum nanoparticles supported by nanoporous magnesium oxide during CVD process. Unfortunately, the maximum adsorption capacity found was 0.8 wt.% in the case of CNTs with 95% purity and was raised up to 1 wt.% after some purification. It was concluded that there was no considerable hydrogen storage in CNT and activated carbons at room temperature due to insufficient binding between hydrogen molecules and carbon nanostructures. In addition, hydrogen must be adsorbed via interaction of atomic hydrogen with the storage environment in order to achieve the U.S. DOE target, because the hydrogen atoms have a very stronger interaction with carbon nanostructures [64].

A calculation on extent of adsorption of hydrogen on coiled carbon nanotube concluded that when the nanotube surface is fully covered with one molecule per graphitic hexagon, pentagon and heptagon, a 6.8 wt.% storage capacity is obtained [65]. Density functional calculations to investigate the interaction of hydrogen molecules with Li-doped charged SWCNTs was carried out. It was found that binding of hydrogen on positively charged Li-doped SWCNTs is enhanced compared with that on uncharged systems. Also, as the charge of the Li-doped SWCNTs increases, the binding energy of hydrogen increases. The study of the chemisorption process pathway of hydrogen atoms onto the exterior wall of (5,5) CNTs revealed that the adsorptions of hydrogen atoms onto the sidewall of CNTs are energetically favorable and the most stable state is to form two H–C  $\sigma$ -bonds while the original  $\sigma$ -bond between the carbon atoms is totally severed. Further study of the molecular thermodynamics properties for the reaction at a range of temperatures from 77 K to 1000 K was conducted,

and the results suggest that the reaction is possible at ambient temperature, but is less favorable than that at lower temperature [66]. Similar observations were made while studying hydrogen adsorption on platinum-decorated CNTs [67].

### 7.4.3 Multi-Walled Carbon Nanotubes (MWCNTs)

It was expected that MWCNTs might exhibit higher hydrogen storage capacities than SWCNTs. The experimental results show that the purified MWCNTs have opened tips, simpler chemical state, larger micropore volume, hence, much higher hydrogen storage capacity. Gravimetric hydrogen storage capacities of the purified MWCNTs obtained was 6.3 wt.% [68]. Accordingly, when the ends of MWCNTs were opened by ball milling with magnesium oxide for one hour, a hydrogen adsorption capacity of 0.69 wt.% was obtained at room temperature under a pressure of 80–90 bars [69]. The hydrogen adsorption and desorption of 3.7 wt.% and 3.6 wt.% respectively were observed on MWCNT/NiMgO system at 69 bars. Hydrogen storage in MWCNTs was enhanced via the catalytic activity of NiMgO [70]. The hydrogen storage capacity of the purified and pretreated MWCNTs was proportional to their diameter and hydrogen in all types of MWCNTs measured was not completely desorbed at room temperature and ambient pressure. Furthermore, the microstructural and surface characterizations reveal that the pore structure and surface modification are important for enhancing the hydrogen uptake capacity of MWCNTs [68]. MWCNTs synthesized by pyrolysis of acetylene over mischmetal-based hydride catalyst had over 90% purity. A maximum hydrogen storage capacity of 3.2 wt.% at 60 bars was obtained at 125 K for purified CNTs [58].

An independent study found that single-walled, double-walled, and multi-walled nanotubes, as well as CNF show hydrogen adsorption capacity to be below 1 wt.% over a range of conditions [71]. Potassium hydroxide treated MWCNTs were annealed at high temperatures; structure of CNTs got damaged after being activated by potassium hydroxide at 550 °C in hydrogen atmosphere. The hydrogen storage capacity on the untreated and KOH treated CNTs was 0.71 and 4.47 wt.%, respectively, under ambient pressure and at moderately high temperature [72]. Interestingly, in MWCNT synthesized from acetylene but over Dy-Ni alloy hydride catalyst, the maximum hydrogen storage capacity was found to be 3.5 wt.% at 143 K and 75 bars [73]. Microwave treatment of MWCNT makes the surface microporous, thereby increases the hydrogen adsorption capacity [74]. Platinum particles homogeneously distributed on MWCNT were a better candidate for hydrogen adsorption than as obtained ones [75].

A similar work carried out shows hydrogen storage capacity can be improved in the decorated MWCNT by Co, Fe, Ni, and Ca metals in two approaches: (i) hydrogen adsorption via Kubas interaction and (ii) dissociation of  $H_2$  molecules on the metal particles. Palladium seems to be a better option than Co, Fe, Ni and Ca. It was also found that dissociation of hydrogen occurs on the palladium particle, and hydrogen atoms enter into the spaces between adjacent carbon layers. This creates loose bonds of  $CH_x$  species and  $Pd-C-H_x$  complex, which can be decomposed easily at lower temperatures as compared to C-H chemical bonds. It can be concluded that hydrogen adsorption capacity by MWCNTs would be higher than SWCNTs due to the storage of hydrogen between the layers of carbon. The adsorption capacity of 6.3 wt.% was modified to 20 wt.% by doping and other treatments. The presence of metal can improve the adsorption capacity in a very similar manner to SWCNT.

#### 7.4.4 Metal-Doped Carbon Nanotubes

In an attempt to enhance the hydrogen adsorption capacity of CNTs, many efforts have been made to dope the CNTs with metals. The metal-doped CNTs show greater hydrogen adsorption capacity than pristine CNTs.

Significantly high hydrogen adsorption property in alkali-metal-doped carbon nanotubes (AMDNTs) from methane was observed at ambient pressure and slightly elevated temperatures. Doping of the carbon nanotubes was done by reactions with Li- or K-containing compounds such as carbonates and nitrates. The best result found in the case of Li-doped CNTs was 20 wt.% gravimetric storage compared to virtually negligible (0.4 wt.%) storage in undoped CNTs [76]. Similar observations that A-MDNTs exhibit higher hydrogen uptake than conventional SWCNTs were made by other researchers [77]. This phenomenon is due to the charge transfer from the alkali metal to the tube which polarizes the hydrogen molecule, and this charge-induced dipole interaction is responsible for the higher hydrogen uptake of the A-MDNTs. Adsorption of hydrogen gas was also studied in microporous doped carbons; activated carbon having SSA 1600  $m^2/g$  with satisfactory results [32]. Potassium-doped super-activated carbon adsorbs hydrogen at room temperature greater than that of potassium-doped graphite. The mechanism is likely due to high surface area [33].

Aluminum- and nickel-doped CNTs were also found to adsorb more hydrogen than those without doping. The mechanism of adsorption of hydrogen in such CNTs was due to the stabilization of hydrogen atoms on the inner and outer walls of the doped CNTs [78, 79]. In these findings,

the surface area of CNMs plays an important role in addition to the doped metal.

#### 7.4.5 Graphene and the Like

Graphene, the base structure of nanoforms of carbon, has also been tried as a hydrogen storing material. Nanosheets of graphene having surface area  $640 \text{ m}^2/\text{g}$  were prepared by the reduction of a colloidal suspension of exfoliated graphite oxide. These sheets do not show any enhanced hydrogen adsorption at cryogenic temperature [80]. Ca-decorated zigzag graphene nanoribbon (ZGNR) could reach the gravimetric capacity of 5 wt.% hydrogen [81]. Li-decorated porous graphene is much stronger than that of regular Li-doped graphene due to the natural separation of Li cations, leading to a potential hydrogen storage gravimetric capacity of 12 wt.% [82]. Whereas, graphene sheet with Al adsorbed on both sides can store up to 13.79 wt.% hydrogen [83]. The process of hydrogen chemisorption was simulated on corrugated graphene and released under the application of time-dependent mechanical deformations. The results show that the corrugated graphene multilayer system can potentially reach gravimetric capacities up to 8 wt.% and reversibly store and release hydrogen by external control of the local curvature at room conditions and with fast kinetics [84]. Though very high hydrogen adsorption capacity is expected with graphitic carbon fibers, a large amount of variation is observed in the reported data as it is highly influenced by the methods used for synthesizing them. Very thin amorphous carbon film (10–30 nm), when bombarded with sputtered Cr nanoparticles, causes atom displacement and rearrangement into graphene layers. The process was carried out at ambient temperature. The synthesis of graphitic microporous carbon terminated with few-to-multilayer graphene walls has been confirmed by Raman spectroscopy and SEM. Such graphene layers have been used to study hydrogen storage [85].

One of the major questions raised by various scientists is why it has been almost impossible to reproduce results on hydrogen adsorption reported by scientists in different laboratories. In addition, it has also not been possible to establish whether any particular type of activation, doping, surface area, pore volume, pore size among others are really the unique parameters to give the highest storage capacity of carbon material be it activated carbon, CNT, MWCNT, SWCNT. These are the burning questions concerning this universal problem in hydrogen adsorption research work that need to be answered.



The above discussion also indicates that different methods of synthesis and treatments of synthesized carbon, weight of carbon used for measurement, method of density calculation to get hydrogen adsorption values, etc., maybe also be responsible in controlling the hydrogen adsorption. Therefore, to get reproducible results it is important to standardize the synthesis of SWCNTs and different treatment procedures.

To study the effect of particle size of the dispersed/decorated particles on adsorption of hydrogen, palladium nanoparticles of different sizes (2, 6 and 18 nm) dispersed on high surface area graphite powder were used. Using cyclic voltammetry, the influence of the particle size can be studied directly from electrochemical signals and pressure-composition isotherms under ambient conditions. The study confirms that as the Pd particle size is reduced, the hydrogen content increases [86]. Li-decorated 6,6,12-graphyne is a new candidate for hydrogen storage. Due to the unique sp hybridization in graphyne, Li atoms bind strongly to carbon atoms and avoid the formation of Li clusters on the surface of graphyne. This material has hydrogen storage capacity up to 19.3 wt.% with an average adsorption energy of -0.230 eV, which is in the ideal adsorption energy range for practical application of hydrogen economy [87]. Hydrogen storage property of light alkali metal, viz. Li and Na, functionalized fluorographene monolayer (FG) were the subject of a study. The metal adatoms bind to the FG with higher binding energy than their cohesive energies. The metal adatoms get uniformly distributed on the FG monolayer and consequently ensure reversibility. The difference of electronegativities ensures that each metal adatom transfers a substantial amount of its charge to the FG monolayer and attains a partial positive state. This enhances the adsorption of hydrogen molecules around the adatoms by electrostatic as well as van der Waals interactions [88]. Exfoliated graphite oxide with SSA of  $2300 \text{ m}^2\text{gm}^{-1}$  shows hydrogen adsorption not more than 1 wt.% at 120 bars of hydrogen and at ambient temperature [89]. This possibly can be attributed to the absence of nanometal-propelled hydrogen adsorption. This theory was further exemplified when a study of the kinetics of de/hydrogenation of nano-confined  $\text{MgH}_2$  by using functionalized mesoporous carbon scaffolds (N doped or Ni decorated) was carried out. In the case of reduced graphene oxide (rGO) doped with palladium and nickel, it was observed that nickel-doped rGO had reduced hydrogen adsorption. In addition, the extent of oxidation of graphene was inversely responsible for adsorption of hydrogen [90]. Interestingly, the thermal analysis and hydrogen sorption isotherms reveal that Ni-decorated or N-doped structures can significantly promote both the hydrogen storage capacity and kinetics [91]. In a recent study on the effect of temperature on hydrogen adsorption/desorption by Mg-Al,

it was found that the presence of graphene-titanium (III) fluoride significantly reduced both the temperatures, thus enhancing hydrogen storage [92]. This phenomenon is attributed to the synergistic effect of graphene- $\text{TiF}_3$  on Mg-Al. An identical effect was observed with Mg-Li alloy due to graphene.

Functionalized nanostructures, especially two-dimensional materials like graphdiyne (GDY) nanosheets doped with light metals Li, Na, K, Ca, Sc and Ti, have a uniform distribution over GDY due to their strong binding and charge transfer mechanism. It was found that at 11% of metal functionalization, GDY changes into a metallic state from being a small band-gap semiconductor. This turns the dopants into a partial positive state favoring adsorption of  $\text{H}_2$  molecules [93].

## 7.5 Carbon Fibers for Storage of Hydrogen

In CNF, graphitic planes are aligned randomly in any orientation relative to the axis of the filament, other than parallel alignment. CNF can also be described in different words, viz. nanofilaments, nanowires and nanofibers. Graphenated CNTs are a relatively new hybrid that combines graphitic foliates grown along the sidewalls of MWCNT or bamboo-like CNTs. “Chemically bonded graphene leaves” were grown along the sidewalls of CNTs [94].

The graphitic nanofibers are capable of adsorbing and retaining in excess of 20 L (STP) of hydrogen per gram of carbon when the nanofibers are exposed to the gas at pressures of 120 atm at 298 K, a value that is over an order of magnitude higher than that found with conventional hydrogen storage systems [93, 95, 121]. Vapor-grown CNFs (VGCNFs) are able to adsorb in excess of 10 wt.% of hydrogen. Unlike the metal-alloy hydrogen storage materials that begin to adsorb hydrogen gas after a short period of incubation, the VGCNFs start to adsorb hydrogen as soon as they interact with hydrogen gas [96]. Graphitic carbon fibers were prepared by decomposition of ethylene over a series of Fe-Ni-Cu alloys and used as possible hydrogen sorbets. The storage levels of adsorption in excess of 6.5 wt.% have been observed by such fibers [97].

Many experimentations yielded disappointing findings, contrary to expectations. The presence of different nickel-copper ratios in the catalyst particles leads to a change in crystalline structure and specific surface area of the CNF synthesized. At room temperature such CNFs adsorb hydrogen up to 0.7 wt.% at 105 bars [98]. Similarly, CNF synthesized by catalytic decomposition of methane using Ni-MgO catalyst after heat treatment at



1473 K in nitrogen atmosphere exhibited hydrogen adsorption capacity of 1.4 wt.% at 120 bars and 298 K [99]. Ball milling of graphite to obtain graphitic carbon for the purpose also did not help positively [100], while hydrogen uptake of the CNFs increased to 5.1 wt.% at the moderate temperatures of 303–873 K by a thermogravimetric system on CNF-doped using  $\text{KNO}_3$  [101].

It has to be remembered that activation under severe conditions destroys the fiber structure of CNF [102]. Activation of CNF by KOH is a better option than by carbon dioxide. The former yields higher surface area carbons (up to  $1000 \text{ m}^2 \text{ g}^{-1}$ ). The increased surface area, however, did not result in a proportionate increase in hydrogen adsorption capacity though high surface areas are important for hydrogen storage on solid surfaces [103]. Activated carbon fibers (ACFs) with high surface area and pore volume were further modified by nickel doping and fluorination. After fluorination treatment, although the micropore volume of ACF was decreased, amounts of hydrogen storage were found to increase. Additionally, micropore volume on ACFs was found to be unchanged with nickel doping, and hydrogen storage capacities were considerably increased due to the effect of catalytic activation of nickel [104]. The use of aqueous precursors for palladium impregnation rather than organic and functionalized CNFs leads to increases in the adsorption capacity close to 100% compared to the parent CNF at ambient pressure [105]. It has been further concluded that the defects on the surface and expandable graphitic structure are important keys to increasing the hydrogen uptake in CNFs [106]. These results on CNF suggest that this material should be explored for the storage of hydrogen. The storage capacity can be improved by suitably synthesizing CNF and suitably doping as well as activating with suitable chemicals.

## 7.6 Pyrolyzed Natural Fibers from Plant/Animals to Store Hydrogen

Natural fibers from plants and animals have been converted to graphitic carbon having well-preserved inherent pores by standard carbonization/pyrolytic method, with or without using any catalyst. These carbonaceous structures have been tried for storage of hydrogen.

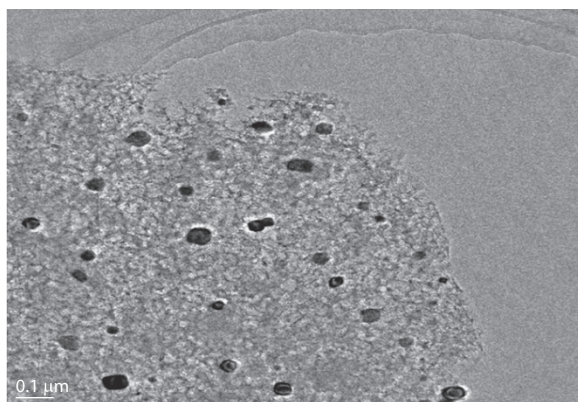
### 7.6.1 Carbonization/Pyrolysis

In this method, carbon-containing plant material or animal fiber material (precursor) is heated to desired temperature (500–1000 °C), usually in an

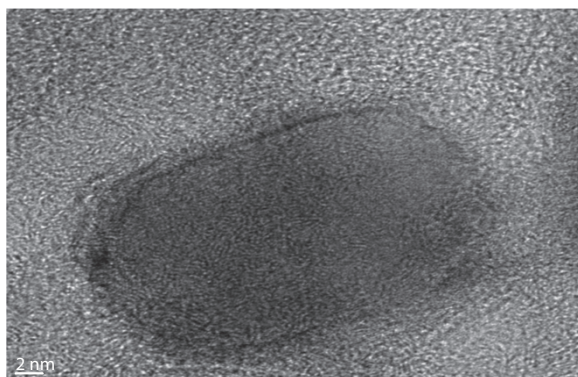
inert atmosphere like argon or nitrogen. In some cases hydrogen gas or carbon dioxide has also been used. The main advantage of this method is that the carbon structures obtained are very unique compared to the ones synthesized by the methods stated earlier. Hard plant tissue is structurally transformed into a rather well-defined carbon replica. It has been confirmed by analytical techniques like SEM and HRTEM that the original carbon structure of the precursor is retained even after carbonization. The remaining elements, except traces of metals, present in the precursor are removed as gaseous products. The microstructure of the carbon materials obtained from plant materials to some extent depend on the temperature of pyrolysis, carrier gas used and duration of carbonization [107–111].

The SEM image of the biogenic CNF prepared using nickel shows fairly evenly distributed nickel nanoparticle (Figure 7.1). The HRTEM image of the same sample shows that the nickel nanoparticles are embedded in the carbon and have a size of about 50 nm (Figure 7.2) and they are graphitic in nature (Figure 7.3).

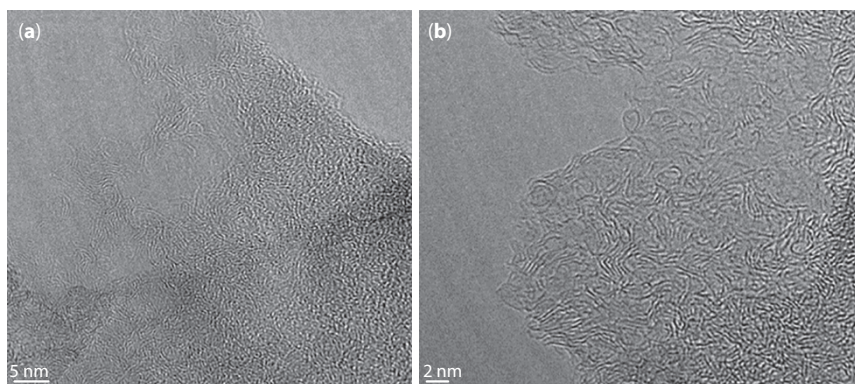
Though activated carbons from coconut shell impregnated with phosphoric acid, and also activated by potassium, were synthesized much earlier [112, 113], it was only in 2007 that researchers lead by Sharon and his research group took the lead in studying hydrogen adsorption by such carbon materials. Carbon materials synthesized employing different conditions of temperature, atmosphere, activation, etc., from oil seeds and fibrous plant materials of thirty different plant-based precursors were used to study hydrogen adsorption. The extent of hydrogen adsorption obtained was substantially below 6.4 wt.%. Efforts were made to correlate the hydrogen adsorption capacity with Raman spectra's intensities and peak



**Figure 7.1** SEM image of CNF showing evenly distributed nickel nanoparticles.



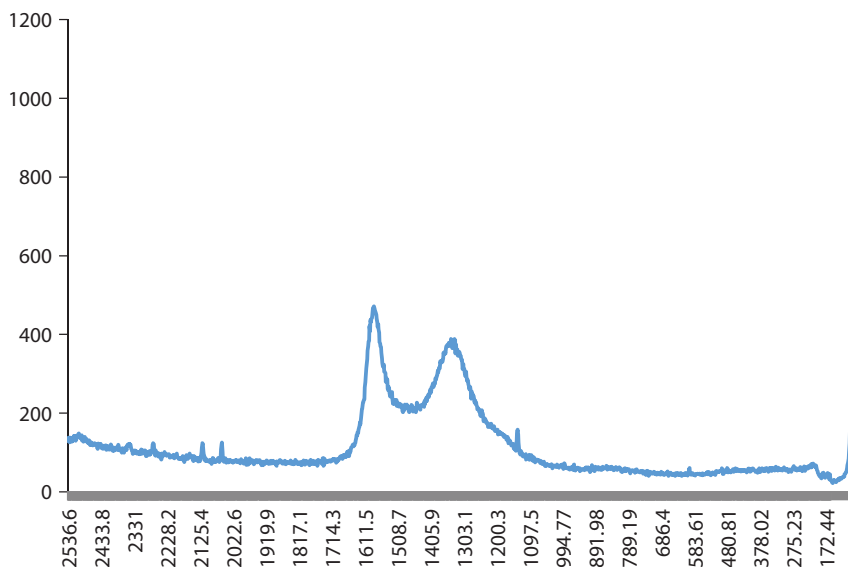
**Figure 7.2** HRTEM image showing nickel particle embedded in the carbon nanofiber.



**Figure 7.3** (a) and (b) are graphitic layers obtained by pyrolysis of cotton filaments (HRTEM).

positions of G- and D-band obtained with carbon materials synthesized from plant-based precursors. Carbon materials' G-band is around  $1575\text{ cm}^{-1}$  and the intensity of D-band is less compared to G-band (Figure 7.4), which are more useful material for studying hydrogen adsorption [108].

Activated mesoporous carbon was prepared from rice bran having SSA of  $652\text{ m}^2\text{ g}^{-1}$  and a pore volume of  $0.137\text{ cm}^3\text{ g}^{-1}$  [114]. KOH activated carbon was synthesized from waste coffee beans with huge specific surface area of  $2070\text{ m}^2/\text{g}$ . The pore size was in the range of approximately 0.6 to 1.1 nm. Unfortunately, the hydrogen storage obtained was only 0.6 wt.% [115]. The hydrogen adsorption capacity of the highly porous novel corn grain-based carbon monoliths (CG-CMs) at 77 K (up to 1 bar) and 298 K (50 up to bar) were studied. The observations suggested that the hydrogen



**Figure 7.4** Raman spectrographs of carbon nanofiber obtained from cotton filaments shows G-band is around  $1575\text{ cm}^{-1}$  and the intensity of D-band is less compared to G-band.

adsorption abilities of the prepared CG-CMs were similar or higher than the other super-activated carbons or carbon monoliths [116]. In an identical study on activated carbon from waste coffee beans, the hydrogen storage ability was found to be dependent on the pore structure of porous carbon materials. Also, the hydrogen storage ability at 298 K increased linearly with an increase of specific surface area [115]. Pyrolyzed chicken feather fiber (PCFF) with an estimated adsorption energy of 5–6 kJ/mol was found to be in the range of physisorption materials, indicating the easy recovery of hydrogen. However, PCFF showed very poor hydrogen adsorption capacity [117]. In spite of some of these having very high surface area, the extent of hydrogen adsorption observed so far is very poor.

Nanoporous carbon materials were obtained using a nanocasting method with agglomerated porous silica nanoparticles from rice husk having SSA  $749\text{ m}^2/\text{g}$  and a pore volume of  $1.44\text{ cm}^3/\text{g}$ . The hydrogen adsorption was found to be 2.41 wt.% achieved at 77 K and 7.3 MPa [118]. Nickel nanoparticles-decorated CNFs were synthesized from cotton filaments. The SSA of these fibers was in the range of  $640\text{ m}^2/\text{g}^{-1}$  to  $1018\text{ m}^2/\text{g}$ . The hydrogen adsorption was found to be up to 8.75 wt.% at 60 bars and ambient temperature [108, 110, 111].

The author synthesized CNF using various methods employing different parameters of pretreatment of cotton filament, activation of carbon

material, temperature of pyrolysis, duration of heating during annealing, etc., and decorated the CNF with different metals, and as control CNF without metal decoration. The variation in adsorption of hydrogen by these CNFs was as expected due to the variations in methods of synthesis. But the analysis revealed a startling observation, that is, an apparent relation was found between tap density of the carbon materials and hydrogen adsorption (Table 7.1).

This relation is independent of the SSA of the carbon nanofiber and is not proportional to the skeleton density. The extrapolation of the graph tap density against wt.% of adsorption of hydrogen, rekindles the possibilities of reaching 15 wt.%, as was predicted by Lee *et al.* (2000) [46]. Figure 7.5 shows a graph exhibiting an apparent relation between tap density of synthesized CNF and adsorption of hydrogen.

Few of the experiments were scaled-up in terms of mass of carbon material used for adsorption of hydrogen from about one gram to ten grams synthesized using identical methods and the findings were repeated. CNF synthesized from petroleum products yields some specific structure while CNF synthesized from plant-based materials contains its inherent structure (which nature has produced). These structures are very difficult to synthesize otherwise. In addition, CNF from petroleum products is expensive while CNF from plant-based precursors is extremely economical and, if suitable, CNF obtained from some specific plants would make a product commercially viable. Hence, there is a need to explore various plant-based precursors to find suitable CNF.

Various scientists [120–124] have used Sievert's apparatus to study hydrogen adsorption on carbon nanomaterials at low pressure as well as at high pressure. The calculation of the adsorption capacity is based on *ideal gas law*

$$PV = nRT \quad (7.1)$$

The symbols having their accepted significance.

As the hydrogen gas molecules do not behave like an ideal gas at high pressure, van der Waals correction factors for the intermolecular force 'a' and molecular size correction 'b' have been applied to the ideal gas equation to improve the accuracy of the result. Accordingly, the equation is modified as

$$\left[ P_r + a \left( \frac{n}{V_r} \right)^2 \right] (V_r - nb) = nRT \quad (7.2)$$

**Table 7.1** Tap density of CNF (synthesized from cotton using different metals for decoration) and their impact on wt.% hydrogen storage capacity.

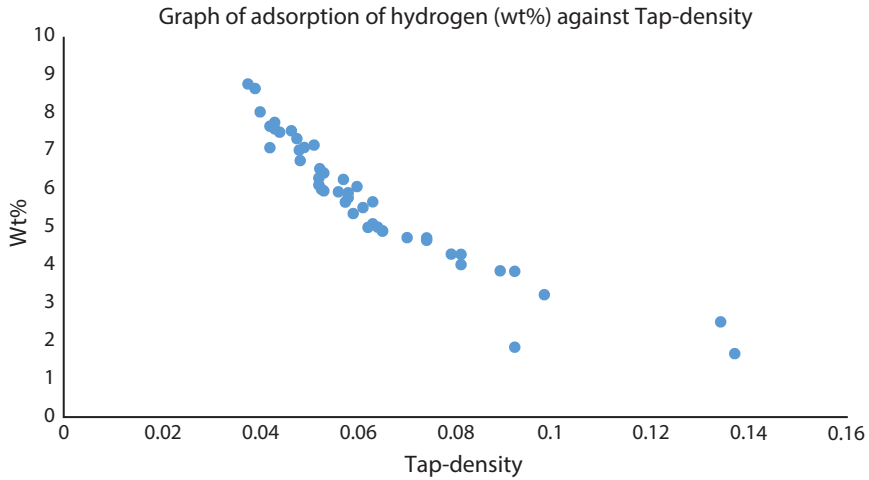
| Sr. No | Metal used to decorate CNF synthesized from cotton | Tap density (g/cm <sup>3</sup> ) | Wt.% hydrogen storage |
|--------|----------------------------------------------------|----------------------------------|-----------------------|
| 1      | Fe                                                 | 0.063                            | 5.65                  |
| 2      | Fe                                                 | 0.058                            | 5.89                  |
| 3      | Fe                                                 | 0.079                            | 4.27                  |
| 4      | Fe                                                 | 0.081                            | 4.01                  |
| 5      | Fe                                                 | 0.049                            | 7.08                  |
| 6      | Fe                                                 | 0.134                            | 2.50                  |
| 7      | Fe                                                 | 0.092                            | 3.83                  |
| 8      | Fe                                                 | 0.098                            | 3.21                  |
| 9      | Ni                                                 | 0.064                            | 4.99                  |
| 10     | Ni                                                 | 0.081                            | 4.27                  |
| 11     | Ni                                                 | 0.058                            | 5.76                  |
| 12     | Ni                                                 | 0.070                            | 4.71                  |
| 13     | Ni                                                 | 0.056                            | 5.92                  |
| 14     | Ni                                                 | 0.037                            | 8.75                  |
| 15     | Ni                                                 | 0.053                            | 5.94                  |
| 16     | Ni                                                 | 0.042                            | 7.64                  |
| 17     | Ni                                                 | 0.074                            | 4.64                  |
| 18     | Ni                                                 | 0.062                            | 4.98                  |
| 19     | Ni                                                 | 0.042                            | 7.08                  |
| 20     | Ni                                                 | 0.039                            | 8.64                  |
| 21     | Ni                                                 | 0.063                            | 5.07                  |
| 22     | Ni                                                 | 0.089                            | 3.84                  |
| 23     | Co                                                 | 0.137                            | 1.66                  |

(Continued)

**Table 7.1** Tap density of CNF (synthesized from cotton using different metals for decoration) and their impact on wt.% hydrogen storage capacity. (*Continued*)

| Sr. No | Metal used to decorate CNF synthesized from cotton | Tap density (g/cm <sup>3</sup> ) | Wt.% hydrogen storage |
|--------|----------------------------------------------------|----------------------------------|-----------------------|
| 24     | Co                                                 | 0.092                            | 1.83                  |
| 25     | Co                                                 | 0.065                            | 4.89                  |
| 26     | None                                               | 0.043                            | 7.57                  |
| 27     | None                                               | 0.061                            | 5.50                  |
| 28     | None                                               | 0.052                            | 6.28                  |
| 29     | None                                               | 0.051                            | 7.14                  |
| 30     | None                                               | 0.048                            | 6.73                  |
| 31     | None                                               | 0.059                            | 5.35                  |
| 32     | None                                               | 0.047                            | 7.32                  |
| 33     | None                                               | 0.053                            | 6.41                  |
| 34     | None                                               | 0.057                            | 5.64                  |
| 35     | None                                               | 0.046                            | 7.52                  |
| 36     | None                                               | 0.052                            | 6.09                  |
| 37     | None                                               | 0.044                            | 7.49                  |
| 38     | None                                               | 0.043                            | 7.74                  |
| 39     | None                                               | 0.060                            | 6.05                  |
| 40     | None                                               | 0.074                            | 4.70                  |
| 41     | None                                               | 0.048                            | 7.01                  |
| 42     | None                                               | 0.052                            | 6.52                  |
| 43     | None                                               | 0.057                            | 6.24                  |
| 44     | None                                               | 0.065                            | 4.89                  |
| 45     | None                                               | 0.053                            | 5.99                  |
| 46     | None                                               | 0.040                            | 8.02                  |





**Figure 7.5** A graph of tap density against adsorption of hydrogen (wt.%).

On solving the Equation (7.2)

$$abn^3 - aV_r n^2 + (RT + P_r b)V_r^2 n - P_r V_r^3 = 0 \quad (7.3)$$

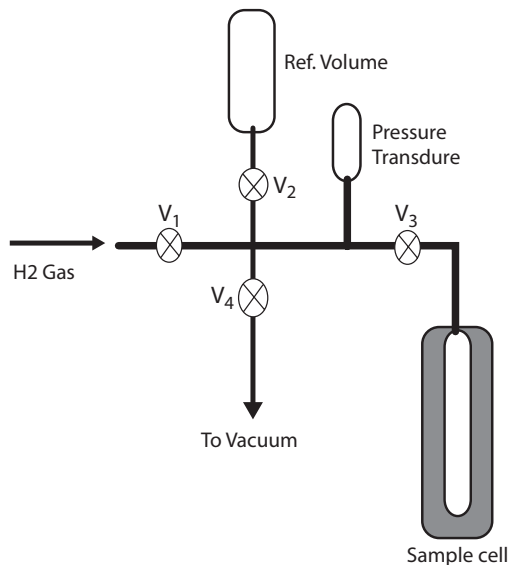
$$\text{i.e.,} \quad P_r V_r^3 + aV_r n^2 - (RT + P_r b)V_r^2 n - abn^3 = 0 \quad (7.4)$$

The constants 'a' and 'b' have positive values and are characteristic of the individual gas. For hydrogen gas 'a' is  $2.45 \times 10^{-2} \text{ Pa.m}^3$  and 'b' is  $26.61 \times 10^{-6} \text{ m}^3/\text{mol}$  [125].

Sievert's apparatus (Figure 7.6) is made up of stainless-steel tubes, needle valves, and T and elbow joints which can withstand up to a maximum pressure of 100 bars. Strain gauge-based pressure transducer is used to measure hydrogen gas pressure in the system, which works in the pressure range of 0 to 100 bars with least count of 0.01 bar. In the diagram, needle valves are represented as V with suffixes (1 to 4) to designate the various valves. The reference volume (Ref Volume), which is a container for storing the hydrogen gas, is attached to the valve  $V_2$ . Valve  $V_1$  allows hydrogen gas into the system. A specially designed "Sample cell," which can withstand high pressure and high temperature, is housed inside a resistance furnace.

The temperature of the furnace is controlled using a temperature controller with an accuracy of  $\pm 1^\circ \text{C}$ . Valve  $V_3$  isolates the sample section from the measuring section. A high vacuum diffusion pump is connected to the unit through the valve  $V_4$ .





**Figure 7.6** Schematic diagram of a Sievert's apparatus modified to function at 100 bars and to use up to 40 grams of CNF.

The sample is introduced in the sample holder and a leak test is performed on the system to rule out any leakage, as even a negligible loss of pressure will be detrimental to the final outcome. The surface of the sample is cleaned by heat and vacuum.

The reference volume of the Sievert's apparatus is then filled with hydrogen gas to the predefined pressure and allowed to attain equilibrium. When the equilibrium is reached the valve  $V_3$  is opened to allow the hydrogen gas enter the sample holder containing carbon sample and once again allowed to attain equilibrium. The hydrogen gas should be filled very slowly as temperature of the gas as well as that of the steel container increases due to friction.

The initial pressure ( $P_r$ ), i.e., the pressure of hydrogen gas filled in the volume  $V_r$  gives the number of moles of hydrogen ( $n_1$ ). The equation is:

$$Pr V_r^3 + aV_r n_1^2 - (RT + P_r b)V_r^2 n_1 - abn_1^3 = 0 \quad (7.5)$$

The final pressure ( $P_f$ ) and the total volume ( $V$ ) when substituted in the Equation (7.4) gives the number of moles of hydrogen unadsorbed ( $n_2$ ). The equation is presented as:

$$P_f V^3 + aV n_2^2 - (RT + P_f b)V^2 n_2 - abn_2^3 = 0 \quad (7.6)$$

Thus, the number of moles of hydrogen adsorbed ( $n$ ) will be the difference of  $n_1$  and  $n_2$ .

Avogadro's law states that one mole of a substance contains  $6.023 \times 10^{23}$  particles. Thus, the number of molecules of hydrogen is calculated. The product of number of moles ( $n$ ) and molecular weight give the weight of hydrogen. This weight, say, 'X' gm of hydrogen is adsorbed in 'Y' gm of carbon, then,  $100 X/Y$  gives the weight percentage of adsorbed hydrogen.

## 7.7 Summary

In this chapter, a review of the advantages and disadvantages of storage of hydrogen under different physical conditions as well as in different types of materials, viz. carbon and other materials, were presented. It was observed that an effective hydrogen-storage material should have specific properties like high hydrogen storage capacity per unit mass and unit volume as it determines the amount of available energy, low dissociation temperature, moderate dissociation pressure, fast kinetics, long cycle life, low cost of recycling and charging infrastructures and high safety.

Different carbon materials, like activated carbon, nanofibers, SWCNTs, MWCNTs, graphene sheets, metal-doped and metal-decorated carbon nanomaterials, have shown hydrogen adsorption capacity. These CNMs have been prepared from petroleum products. Since petroleum deposits are on the verge of being depleted, these studies will ultimately be confined to academic purposes only.

So far, the best possible option for hydrogen storage material has not yet been achieved, although CNF obtained from plant fibers promises to be a strong contender at ambient temperature. Some of the researchers have explained this on the basis of the diameter of the tube, some on the surface area, some on the pore size and some on the basis of doping, while others have attributed it to the activation by nanometals. The hydrogen storage capacity recorded has varied in the range of 0.1 w% to 68 wt.%. Hence, the adsorption of hydrogen by CNM is still an open topic and a thorough investigation is needed to understand the factors which control the hydrogen adsorption to give the required and reproducible results.

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# Carbon Nanofiber for Microwave Absorption

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*When grand plans for scientific and defense technologies are made, do the people in power think about the sacrifices the people in the laboratories and fields have to make?*

A. P. J. Abdul Kalam

## 8.1 The Need to Develop a Microwave Absorber

Microwave absorbers are used in both civil and military applications on account of their ability to eliminate electromagnetic wave pollution and to reduce radar signatures. The first electromagnetic wave absorber came to light in the mid-1930s to improve front-to-back ratio of a 4 GHz antenna [1, 2]. With the development of radar, there has been a growing and widespread interest in radar-absorbing material technology. As the name implies, radar-absorbing materials or RAM are coated on the target whose electrical and magnetic properties have to be altered to give absorption of microwave energy at broadband or discrete frequency [3]. The use of radar-absorbing materials to coat the metallic surface of ships is one method of reducing the radar signatures of targets by the reduction of radar cross section, i.e., the actual area “seen” by a radar system when its transmitted wave is reflected from a given object [4]. Recently, a lot of development has taken place in the telecommunication market due to the fast advancement of wireless and microwave communication technology.

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The demand for various kinds of microwave absorbers has increased in the frequency range of 1–20 GHz because of their two-fold use such as electromagnetic wave interference (EMI) shielding and countermeasure to radar detection (countermeasure involves the radiation of noise power in the operating band of the radar to confuse or deceive the radar as communication system). Out of these two-fold uses, the suppression of EMI and meeting the electromagnetic compatibility (EMC) have become an essential requirement in industries dealing with high-speed wireless data communication systems operating at 1.9 GHz for personal handy-phone system (PHS) and 2.4 GHz wireless for local area networks (LANs). This kind of system is also employed in mobile communication fields, such as the electric toll collection (ETC) system at 5.8 GHz, where it prevents incorrect operation [5]. In addition to mobile communication systems, the satellite communication systems and automatic teller machines (ATM) also operate in the GHz range [6–8]. Therefore, in order to allow the coexistence of all those various system and instruments without harmful electromagnetic interferences, there is a need to develop new shielding and absorbing materials, which especially require anti-electromagnetic interference coatings, self-concealing technology and microwave darkrooms [9–12] with high performance and a large operating frequency band [13]. The application of the appropriate microwave-absorbing material in electronic equipment helps to control the excessive self-emission of electromagnetic waves and ensures undisturbed functioning of the equipment in the presence of external electromagnetic interference.

## 8.2 Types of Microwave Absorbers

The microwave absorbers are categorized into various forms such as resonant absorber, broadband absorber, magnetic absorber, dielectric absorber and metal absorber.

It is seen that all these absorber materials should have dielectric, magnetic and conductive losses because of the manner by which the properties change with frequency that reflects the performance of the absorber [14, 15]. In general, absorbers work by allowing the wave to penetrate into a region where the electric and/or magnetic fields experience loss. All lossy materials are frequency dependent. The frequency dependence constrains the values of real and imaginary parts of the relative permittivity ( $\epsilon_r$ ) and relative permeability ( $\mu_r$ ) of the material. Conductivity is another loss mechanism; however, it also affects the material's impedance, since  $\epsilon = \sigma/\omega\epsilon_0$ .

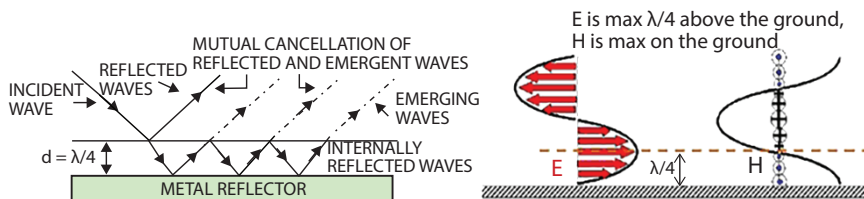
Thus, a metal ( $\sigma = 10^7$  mhos/m) is both highly lossy if it is used as conductive filler and highly reflective if its thickness is greater than the skin depth.

Therefore, based on the principle of absorption, the microwave absorbers are categorized as resonant absorber, broadband absorber, magnetic absorber and dielectric absorber. These four types of absorbers are discussed below.

### 8.2.1 Resonant Absorber

The resonant absorbers are much thinner than the other types; they are preferred for most applications where wide operational bandwidth is not a requirement. They are customarily chosen to improve antenna patterns by covering parts of antennas and to improve radar performance by covering nearby reflecting surfaces. Their physical flexibility is often useful in coating surfaces of complex shape. Usually, these absorbers are directly mounted on the metal, causing the reflection. Even the surface is sharply curved or small in terms of wavelengths. Some reduction in performance is to be expected with the application of this absorber. For cases where the material cannot be mounted directly on metal, it is necessary to provide a conducting rear surface, such as foil or silver paint, to achieve low reflection at the resonant frequency. Loss mechanism in these absorbers is discussed here.

**Loss mechanism of resonant absorber:** In resonant absorber a wave incident upon the surface of the layer of dielectric material is partially reflected and partially transmitted (Figure 8.1). The transmitted portion undergoes multiple internal reflections to give rise to a series of emergent waves. At the designed frequency, the sum of the emergent waves is equal to amplitude of incident wave, which is  $180^\circ$  out of phase with the initial reflected portion (Figure 8.1). This causes the absorption by destructive



**Figure 8.1** Resonant absorber showing out-of-phase condition existing between reflected and emergent waves.

interference at the material's front surface. A dielectric layer with phase thickness equal to a quarter wavelength ( $\lambda/4$ ) of incident wave (frequency of  $\lambda=1/f$ ) is required to cause such destructive interference at the material's front surface for absorption of the incident microwave energy.

The basic principle of open-end microwave resonator is normally used to design such resonant absorber. Any field excited in the resonator is reflected from the ends. The waves add in phase or the resonator resonates when at every point of the line (transmission line) waves add in phase, i.e., the total phase shift in the propagating waves must be  $2\pi$  or its multiple. If  $\phi_1$  and  $\phi_2$  are the phases introduced by the reflections at the two ends and 'l' is the length of the resonator, then the condition for the resonance will be,

$$\phi_1 + \phi_2 + 2 \beta d = 2n\pi \quad (8.1)$$

where,  $\beta$  is phase constant, the imaginary part of propagation constant, measured in radians per meter; 'd' is the thickness of absorber layer and

$$n = 1, 2, 3 \dots \text{are integers.}$$

For open-end resonator,  $\phi_1 = 0$ ,  $\phi_2 = \pi$ , so

$$2 \beta d = (2n-1) \pi \quad (8.2)$$

or

$$\lambda_r = 4d/(2n-1) \quad (8.3)$$

Where,  $\lambda_r$  is resonant wave length,

$$n = 1, 2, 3 \dots \dots \dots$$

As  $\lambda_r = 2 \pi / \beta$  or  $\beta \lambda_r = 2 \pi$ .

Here,  $\lambda_r$  is defined as the distance over which the sinusoidal waveform passes over a full cycle of  $\pi$  radians.

For a resonator of definite length  $l$ , various resonant modes are possible having resonant wavelengths  $\lambda_r = 4d, 4d/3, 4d/5, \dots$  and so on. The lowest mode corresponds to a resonator length  $= \lambda/4$  and hence this type of resonator is also designated as the quarter-wave co-axial resonator or open-end resonator. However, the transverse component of the electric and magnetic fields in the resonator are displaced through a phase corresponding

to a quarter guide wavelength. This phase shift arises from pure standing waves. There is no energy transfer in any direction, i.e., the Poynting vector  $E \times H$  is zero.

As the resonant absorber is like open-end resonator, the quarter wavelength mechanism is also applicable to the resonant absorber.

In the case of a metal-backed single-layered absorber (resonant absorber), the normalized input impedance ( $Z_{in}$ ) with respect to the impedance in free space and reflection loss (RL) with respect to the normal incident plane wave in hyperbolic form are given by,

$$Z_{in} = (\mu_r / \epsilon_r)^{1/2} \tan h[j2\pi/c(\mu_r \epsilon_r)^{1/2}fd] \quad (8.4)$$

where  $\mu_r$  and  $\epsilon_r$  are the relative complex permeability and permittivity of the absorber medium; 'f' and 'c' are, respectively, the frequency of microwave in free space and the velocity of light; and 'd' is the thickness of an absorber. The impedance matching condition representing the perfectly absorbing properties is given by  $Z = 1$ .

Since the reflection loss is a function of  $Z_{in}$ , which is expressed as,

$$\text{Reflection loss [dB]} = 20 \log ( | Z_{in} - 1 | ) / ( | Z_{in} + 1 | ) \quad (8.5)$$

the attenuation of the Microwave can be calculated at a given  $f$  and  $d$ .

Equations (8.4) and (8.5) are used to determine the reflectance (reflection loss) of an absorber. It is determined at the surface by six parameters; namely, frequency ( $f$ ), thickness of layer ( $d$ ), and real and imaginary components of permeability ( $\mu' - j\mu''$ ) and permittivity ( $\epsilon' - j\epsilon''$ ). The relation given by Equation (8.4), with these parameters for zero reflection condition, can be evaluated numerically. In these absorbers, theoretically zero reflection takes place at the given frequency; but in practice, absorption of greater than 30dB (99.9%) may be achieved (less reflection and transmission lead to high absorption). These absorbers generally operate over a relatively narrow frequency range.

The limited reflectivity characteristics of resonant absorbers lead to the use of the thicker broadband types in many applications.

### 8.2.2 Broadband Absorbers

In contrast to resonant absorbers, which use the back-face reflection to good advantage, broadband-type absorbers must have sufficient attenuation so that any energy reflected from the back face should be able to leave the material with a very low-level reflection. To get this degree of



attenuation in practice, the absorber should have appreciable thickness in terms of wave length. Hence, it might be expected that a material of higher loss tangent and higher dielectric constant would provide adequate loss at reduced thickness. It is important to note that a medium with such properties would also have impedance quite different from that of free space and, therefore, will show a higher value in front-face reflection. Such front-face reflections can be significant in a lossy medium and would strongly deteriorate the performance of the absorber.

**Loss mechanism of broadband absorber:** To understand the broadband absorber principle, one must understand the concept of tapered impedance. These absorbers are designed by varying the impedance from that of free space at its incident surface to lower impedance, where there is more lossy material at its rear (back) surface. When microwave incident energy is absorbed on such absorbers, incident energy “sees” free space as it enters the material and is attenuated as it propagates through a medium which becomes lossier. Instead of having a medium of uniform properties, the dielectric constant can be adjusted to be very low at the front surface and increase it to a relatively high number at the rear. Consequently, the front-face reflection and the overall thickness, which are required to make the back-face reflection negligible, are greatly reduced, since very high impedance can be tolerated in the lossy material at the rear. Extremely low reflection levels can be achieved in this manner, resulting in performance more than 60 dB below the incident energy levels under best conditions.

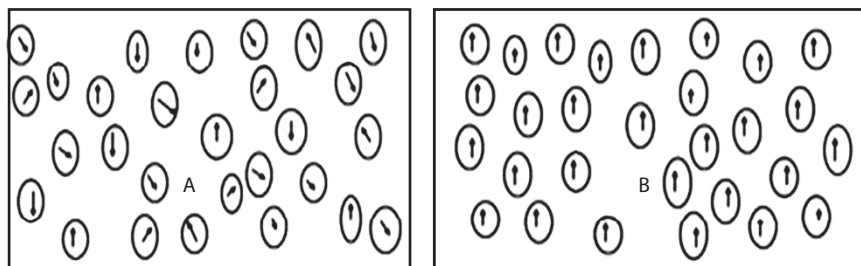
An example of broadband absorber is a graded dielectric absorber. It consists of different layers of conductive carbon which is pyramidal in shape in polyurethane foam. The principle of operation of such absorber is quite different from that of the resonant type. Absorption is achieved by a gradual tapering of impedance from that of free space to a highly absorbing state (lossy state). If the transition from free space to a highly absorbing state is done smoothly, little reflection from the front face will result, making it a good absorber. Absorption levels of greater than 50 dB can be obtained with pyramids of many materials with different thicknesses (thickness in terms of wave length) with the graded dielectric absorber. Good levels of reflectivity reduction (greater than 20 dB) can be achieved in the materials of thickness less than  $1/3$  wavelength. In this case, very open-celled (10 pores per inch) foam is used. In this type of absorber gradual transition, i.e., free space to a highly absorbing state, is achieved via a conductive carbon coating. These types of absorbing materials are used for “broadband” absorption characterized by a gradual tapering from the

impedance of free space to that of the medium over/above appreciable thickness.

### 8.2.3 Magnetic Absorbers

Magnetic absorbers, such as ferrites, iron and cobalt-nickel alloys, alter the permeability for the absorption of microwave and alter the dipole orientation (Figure 8.2). For the purposes of analysis of microwave absorption, the magnetic properties such as permeability (which has complex numbers with real and imaginary parts) are used. The strong magnetism properties of magnetic absorbers make them a good microwave absorber [16]. Magnetic absorbers, particularly ferrites, are special kinds of absorbing materials due to their dielectric and magnetic losses in microwave frequency band [17]. Ferrites are complex solids, represented by  $M^{+2}OFe_2O_3$ . Whereas  $M^+$  is the ion of a divalent metal [cobalt (Co), nickel (Ni), zinc (Zn), cadmium (Cd), iron (Fe), manganese (Mn), chromium (Cr), copper (Cu), etc., or a mixture of these]. The specific resistance of ferrites is very high (of the order of  $10^7$ – $10^8$  ohm-m), which is  $10^{14}$  times as high as those of metals.

The relative permittivity for ferrites is of the order of 10–15 and loss tangent  $\tan \delta = 10^{-4}$  (low loss at microwave frequencies). The relative permeability of ferrites is several thousand. As the ferrites are transparent to the electromagnetic waves, an electromagnetic ray propagating through the ferrites encounters strong interaction with spinning electrons and gives rise to desirable magnetic properties in ferrites. Spherical ferrite and carbonyl iron powders are among the most popular conventional magnetic fillers. Usually, the microwave-absorbing properties of the ferrites are dominated by the magnetic and dielectric losses [11]. The material that exhibits both



**Figure 8.2** A schematic representation of the effect of microwave absorption by magnetic materials (A) before and (B) after absorbing the microwave.

dielectric and magnetic parameter is known as four-parameter material, which plays an important role as an absorber [3].

**Loss mechanism of magnetic absorbers:** As the resistivity of the ferrites is very high, the magnetic loss of these materials results from their ferromagnetism. The dielectric loss (low loss) for ferrites originates from the electron transferring between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and the magnetic loss comes from the moments and spin relaxation of magnetic domains [18]. Therefore, it can be concluded that in ferrites absorber, the microwave loss is closely related to the ferromagnetism of the samples. Loss occurring via other mechanisms, such as molecular polarization phenomena, is insignificant. As mentioned earlier, usually the microwave-absorbing properties of the ferrites are dominated by the magnetic and dielectric losses [3]. In order to know the parameter that dominates the absorption, one should examine the complex dielectric permittivity ( $\epsilon' - j\epsilon''$ ) and magnetic permeability ( $\mu' - j\mu''$ ); with the help of these parameter the frequency dependence of the dielectric and magnetic absorption losses are given by,

$$\tan \delta_e = \epsilon''/\epsilon' \quad (8.6)$$

and

$$\tan \delta_m = \mu''/\mu' \quad (8.7)$$

Here, the materials with  $\tan \delta > 1$  are considered “lossy” materials. Loss tangents ( $\tan \delta$ ) of the order of 10 are considered to indicate strong absorption at a given frequency [19].

#### 8.2.4 Dielectric Absorber

Dielectric absorber is material in which the electrical and magnetic properties have been altered to allow absorption of microwave energy at discrete or broadband frequencies. The common dielectric materials used as absorbers are foams, plastics and elastomers. These materials do not have magnetic properties, giving them permeability of ‘1’. High dielectric materials, such as carbon, graphite and metal flakes, are used to modify the dielectric properties of such materials so that they are able to absorb better. For dielectric absorbers, loss is primarily generated via the finite conductivity of the material. Incident EM waves impinging upon a conductive surface induce current as the electric field of electromagnetic wave interacts with mobile electrons within the material. Additional loss can also

occur via molecular polarization phenomena such as dipole rotation. Loss mechanism in these materials is discussed below.

**Loss mechanism of dielectric absorber:** In order to study propagation of EM waves in such (dielectrics) medium, Maxwell introduced dielectric constant in his famous equation as,

$$\nabla \times \mathbf{H} = \mathbf{J} + \partial \mathbf{D} / \partial t \quad (8.8)$$

Here,  $\mathbf{D} = \epsilon \mathbf{E}$

where  $\epsilon$  is a constant of the medium that measures efficiency of transfer of electric charge, which is known as dielectric constant of the medium.

This equation shows that the magneto motive force ( $\nabla \times \mathbf{H}$ ) around a closed path is equal to the sum of conduction current ( $\mathbf{J} = \sigma \mathbf{E}$ ) and the displacement current  $\partial \mathbf{D} / \partial t$ . Here,  $\mathbf{D}$  being an electric displacement in the medium, is a function of dielectric properties through any surface bounded by the path. Furthermore, Maxwell showed that the velocity 'c' of an electromagnetic wave (EM) in a given medium is a function of medium parameters such as  $c = 1/\sqrt{\mu\epsilon}$ ; where,  $\mu$  is the permeability and  $\epsilon$  is the electric permittivity (dielectric constant) of the medium.

In microwave electronics we generally come across sinusoidally time-varying fields of the form  $e^{j\omega t}$ . Consequently, using the phasor representation (vector representing the phase of the wave), the time derivative  $\partial/\partial t$  may be the factor  $(j\omega)$ .

Since  $\partial/\partial t (e^{j\omega t}) = j\omega \cdot e^{j\omega t}$ , Maxwell's equations with steady-state sinusoidal time dependence becomes,

$$\nabla \times \mathbf{H} = \sigma \mathbf{E} + j\omega \epsilon \mathbf{E} \quad (8.9)$$

or

$$\nabla \times \mathbf{H} = j\omega (\epsilon - j\sigma/\omega) \mathbf{E} = j\omega \epsilon^* \mathbf{E} \quad (8.10)$$

$$\text{where,} \quad \epsilon^* = (\epsilon - j\sigma/\omega) \quad (8.11)$$

$\epsilon^*$  is known as complex dielectric constant. Let  $\epsilon_0$  be the dielectric constant of vacuum (free space) which has a value  $(36\pi \times 10^9)^{-1}$  farad/meter. Dividing Equation (8.11) by  $\epsilon_0$ , we have,

$$\epsilon^*/\epsilon_0 = \epsilon_r = (\epsilon/\epsilon_0 - j\sigma/\omega\epsilon_0) = \epsilon' - j\epsilon'' \quad (8.12)$$

where  $\epsilon_r$  is the ratio of the complex dielectric constant to the dielectric constant of vacuum and is known as relative or normalized complex dielectric constant. Furthermore, separating Equation (8.12) into real and imaginary parts we find that the real part  $\epsilon' = R_e(\epsilon^*/\epsilon_0)$  is associated with the ability of the dielectric material to store electrical energy, while the imaginary part  $\epsilon'' = -\text{Im}(\epsilon^*/\epsilon_0)$  is associated with the losses occurring in the dielectric.

Also, rewriting Equation (8.12) as,

$$\epsilon_r = \epsilon'(1 + \epsilon''/\epsilon') = \epsilon'(1 + \tan\delta) \quad (8.13)$$

where  $\tan\delta$  represents the ratio of power lost in the dielectric ( $\epsilon''$ ) to the energy stored per cycle ( $\epsilon'$ ) in the dielectric is known as *loss tangent*. In dielectrics the variation of  $\tan\delta$  with frequency is more commonly used than that of  $\epsilon'$ . In addition, dielectric constant ( $\epsilon'$ ) depends upon frequency but its variation is quite gradual and is constant over a narrow band of frequencies. Thus, a low loss medium is characterized by a complex permittivity  $\epsilon^*$ , whose real part is the permittivity of the lossless medium and imaginary part represents the losses.

The complex permittivity is sometimes written as,

$$\epsilon^* = \epsilon(1 - j \tan\delta) \quad (8.14)$$

Here, the loss tangent  $\tan\delta = \epsilon''/\epsilon'$  is a good measure of microwave absorption. Materials with  $\tan\delta > 1$  are considered as “lossy” materials. Loss tangents ( $\tan\delta$ ) of the order of 10 are considered to indicate strong absorption at a given frequency [19].

### 8.2.5 Metal Absorber

In most of the absorbers, the metal particles or the conducting material's particles are used as filler. These particles alter the electrical properties such as permittivity and conductivity, etc., of the material. Hence, it is essential to discuss EM wave propagation in pure conductor material. Since in practice no conductor is perfect, i.e., it has a finite conductivity  $\sigma$ , this imperfection of the conductor results in a very small portion of energy entering the conductor from free space (air), i.e., the second medium. However, due to the high value of  $\sigma$ , the waves are highly attenuated in the conductor.

If propagation constant for a conductor is,

$$k = \eta \sigma_m. \quad (8.15)$$

Where,  $\eta$  is the intrinsic impedance and  $\sigma_m$  is conductivity of medium,

as, 
$$\eta = (\mu/\epsilon)^{1/2}$$

we have, 
$$\alpha = \sigma_m / 2(\mu/\epsilon)^{1/2} = \sigma_m / 2. H \quad (8.16)$$

Since  $\alpha$  is a function of  $\sigma$ , the attenuation depends upon the nature of the metal.

The property of the metal to attenuate the fields is expressed in terms of a quantity defined as the depth of the penetration or skin depth. It is defined as the distance within the metal in which the amplitude of the traveling wave is attenuated to  $1/e$  or 36.8 percent of its value just above the metal surface. Then, by definition if  $d$  is the skin depth,

$$\alpha d = 1 \text{ or } d = 1/\alpha \quad (8.17)$$

For copper and silver,  $d$  values are 0.00667 mm and 0.00637 mm respectively at 100 MHz frequency. Thus, in good conductors such as copper, silver, etc., the wave is attenuated to a negligibly small value within a few thousands of a centimeter.

In addition to the above-discussed absorbers, the composite materials also play an important role as an absorber. These materials allow the convenient use on surfaces and good control over mechanical properties. These properties along with the variation of microwave properties, depend on the proper selection of matrix material and different inclusions, which are either dielectric, conductive, or ferromagnetic [19–22]. These magnetic absorption materials made by dispersing magnetic fillers in an insulating matrix continue to play a leading role in the investigation and application of microwave absorption [23, 24]. Although many kinds of ferrites with particle sizes from micron to millimeter magnitude have been utilized for this purpose, the coatings of these absorbers are still too thick and heavy to meet the practical demands [25].

### 8.3 Considerations for Nano Absorbers

The technical requirements for an absorber, such as wide frequency range, zero external magnetic field and thin absorption layer, limit the number of

ferromagnetic materials applicable in the microwave frequency range to the range of a few gigahertz [26–28]. Compared with conventional materials, it is observed that nanocrystalline materials possess a tremendous surface area. Also, when the particle size is in nanoscale, the structure of crystalline may form the multiple magnetic domains to the single, and the coercive force of the material increases greatly. This may lead to large hysteresis attenuation and the absorbing properties can be improved greatly [11].

Therefore, nanostructured materials have an attraction for microwave radiation-absorbing materials in the GHz frequency range due to their unique chemical and physical properties. In addition, the volume-to-weight ratio of absorber material is very important in microwave-absorbing materials for lightweight and strong absorption properties [11] that can be achieved using nano absorber.

### **8.3.1 Nanoferrite Absorber**

Nano-size ferromagnetic particles have properties that are different from those of the bulk materials or large particles. They can also somewhat vary with size selection and method of preparation [29, 30]. This could extend the applicability of ferrites already in use and allow further fine-tuning of the absorber characteristics [11]. Since the evaluation of absorber characteristics depends on desired properties, the emphasis can be given to various parameters such as thickness, weight [20], wide band absorption in some frequency ranges, etc.

#### *8.3.1.1 Limitations of Ferrites*

It has been a challenge to develop an electromagnetic wave absorber for the desired matching frequency because the ferrite materials used are manufactured by a complex process involving conditions like controlled sintered temperature, pressure, and a specific ratio of composite materials [31], which makes it difficult to develop a material which can absorb the microwave in a wide range of the frequency band. Also, since these magnetic absorbers tend to be heavy, their virtue lies in the ability to provide extended frequency performance with reasonable material thickness of few mm (in some case from 1–5 mm thickness) [14]. Unfortunately, these materials need a thick coating to meet practical demands. Therefore, there is a need to develop materials so that even thin coating should be sufficient to absorb microwaves [32].

## 8.4 The Radars

### 8.4.1 Detection and Ranging

Radar is a detection system that uses radio waves to determine the range, angle, or velocity of objects. It can be used to detect aircraft, ships, spacecraft, guided missiles, motor vehicles, weather formations, and terrain. A radar system consists of a transmitter producing electromagnetic waves in the radio or microwaves domain, a transmitting antenna, a receiving antenna (often the same antenna is used for transmitting and receiving) and a receiver and processor to determine properties of the object(s). Radio waves (pulsed or continuous) from the transmitter reflect off the object and return to the receiver, giving information about the object's location and speed. Radar was developed secretly for military use by several nations in the period before and during World War II. A key development was the cavity magnetron in the UK, which allowed the creation of relatively small systems with submeter resolution. The term *RADAR* was coined in 1940 by the United States Navy as an acronym for **R**Adio **D**etection **A**nd **R**anging. The term *radar* has since entered English and other languages as a common noun, losing all capitalization. The modern uses of radar are highly diverse, including air and terrestrial traffic control, radar astronomy, air-defense systems, antimissile systems, marine radars to locate landmarks and other ships, aircraft anti-collision systems, ocean surveillance systems, outer space surveillance and rendezvous systems, meteorological precipitation monitoring, altimetry and flight control systems, guided missile target locating systems, ground-penetrating radar for geological observations, and range-controlled radar for public health surveillance. High tech radar systems are associated with digital signal processing, machine learning and are capable of extracting useful information from very high noise levels. Radar is a key technology that the self-driving systems are mainly designed to use, along with sonar and other sensors. Other systems similar to radar make use of other parts of the electromagnetic spectrum. One example is "lidar," which uses predominantly infrared light from lasers rather than radio waves. With the emergence of driverless vehicles, radar is expected to assist the automated platform to monitor its environment, thus preventing unwanted incidents.

### 8.4.2 Multi-Band 3D Radar

Imaging radar is a kind of radar equipment which can be used for imaging. A typical radar technology includes emitting radio waves, receiving their



reflection, and using this information to generate data. For imaging radar, the returning waves are used to create an image. When the radio waves reflect off objects, some changes will be made in them that can provide data about the objects, including how far the waves travelled and what kind of objects they encountered. Using the acquired data, a computer can create a 3D or 2D image of the target. Imaging radar has several advantages. It can operate in the presence of obstacles that obscure the target, and can penetrate ground (sand), water, or walls. It has various applications which include surface topography and crustal change; land-use monitoring, agricultural monitoring, ice patrol, environmental monitoring; weather radar-storm monitoring, wind shear warning; medical microwave tomography through wall radar imaging; 3D measurements, etc.

The capacity to measure the range to the first scatter within every pixel requires 3D imaging. Hence, an array of range counters is needed. A monolithic approach to an array of range counters is being developed. This technology must be coupled with highly sensitive detectors of eye-safe wavelengths.

### 8.4.3 Quantum Radar

Quantum radar is an emerging remote-sensing technology based on input quantum correlations (in particular, quantum entanglement) and output quantum detections. If it is successfully developed, it will allow the radar system to pick out its own signal even when swamped by background noise. This allows it to detect stealth aircraft, filter out deliberate jamming attempts, and operate in areas of high background noise, e.g., due to ground clutter. The first feasible design of a quantum radar was proposed in 2015 by an international team and is based on the protocol of Gaussian quantum illumination.

The basic concept is to create a stream of entangled visible-frequency photons and split it in half. One half, the “signal beam,” goes through a conversion to microwave frequencies in a way that preserves the original quantum state. The microwave signal is then sent and received as in a normal radar system. When the reflected signal is received it is converted back into photons and compared with the other half of the original entangled beam, the “idler beam.”

Although most of the original entanglement will be lost due to quantum decoherence as the microwaves travel to the target objects and back, enough quantum correlations will still remain between the reflected-signal and the idler beams. Using a suitable quantum detection scheme, the system can pick out just those photons that were originally sent by the radar,

completely filtering out any other sources. If the system can be made to work in the field, it represents an enormous advance in detection capability.

One way to defeat conventional radar systems is to broadcast signals on the same frequencies used by the radar, making it impossible for the receiver to distinguish between their own broadcasts and the spoofing signal (or “jamming”). However, such systems cannot know, even in theory, what the original quantum state of the radar’s internal signal was. Lacking such information, their broadcasts will not match the original signal and will be filtered out in the correlator. Environmental sources, like ground clutter and aurora, will similarly be filtered out.

There is considerable discussion of the use of quantum radar as an anti-stealth technology. Stealth aircraft are designed to reflect signals away from the radar, typically by using rounded surfaces and avoiding anything that might form a partial corner reflector. This so reduces the amount of signal returned to the radar’s receiver that the target is (ideally) lost in the thermal background noise. Although stealth technologies will still be just as effective at reflecting the original signal away from the receiver of a quantum radar, it is the system’s ability to separate out the remaining tiny signal, even when swamped by other sources, that allows it to pick out the return even from highly stealthy designs.

#### 8.4.4 LIDAR (Light Imaging Detection & Ranging)

Lidar is a surveying method that measures distance to a target by illuminating the target with pulsed laser light and measuring the reflected pulses with a sensor. Differences in laser return times and wavelengths can then be used to make digital 3D representations of the target. The term *lidar*, now used as an acronym of *light imaging, detection, and ranging*, was originally a portmanteau of *light* and *radar*.

Lidar is sometimes called *3D laser scanning*, a special combination of a 3D scanning and laser scanning. It has terrestrial, airborne, and mobile applications. Lidar originated in the early 1960s, shortly after the invention of the laser, and combined laser-focused imaging with the ability to calculate distances by measuring the time for a signal to return using appropriate sensors and data acquisition electronics. Its first applications came in meteorology, where the National Center for Atmospheric Research used it to measure clouds. The general public became aware of the accuracy and usefulness of lidar systems in 1971 during the Apollo 15 mission, when astronauts used a laser altimeter to map the surface of the moon. Laser radar is used for multidimensional imaging and information gathering. In all information gathering modes, lasers that transmit in the eye-safe region

are required as well as sensitive receivers at these wavelengths. A lidar instrument principally consists of a laser, a scanner, and a specialized GPS receiver. Airplanes and helicopters are the most commonly used platforms for acquiring lidar data over broad areas. Two types of lidar are topographic and bathymetric. Topographic lidar typically uses a near-infrared laser to map the land, while bathymetric lidar uses water-penetrating green light to also measure seafloor and riverbed elevations. Lidar systems allow scientists and mapping professionals to examine both natural and manmade environments with accuracy, precision, and flexibility. NOAA scientists use lidar to produce more accurate shoreline maps, make digital elevation models for use in geographic information systems, to assist in emergency response operations, and in many other applications.

Lidar is commonly used to make high-resolution maps, with applications in geodesy, geomatics, archaeology, geography, geology, geomorphology, seismology, forestry, atmospheric physics, laser guidance, airborne laser swath mapping (ALSM), and laser altimetry. The technology is also used in control and navigation for some autonomous cars.

## 8.5 Role of CNF in Microwave Absorption

Fortunately, we have an abundance of cheap low-conducting carbon materials. It is possible to construct synthetic materials from carbon that can have tailored conductivity, from very poor (insulated grains of carbon black) to very high (connected chains of graphite). Therefore, the carbon-based absorbers essentially follow the electric field loss mechanism. In these materials, the induced currents caused by the electric field from electromagnetic wave dissipate the electromagnetic energy into heat. Therefore, the conductivity mechanism can be a broadband loss mechanism for such conducting materials.

Among the various types of carbon nanomaterials CNF has some peculiar properties like lightweight, corrosion resistance, good conductivity, low electrical resistance, large surface area because of longer length, good mechanical strength and are easy to fabricate as compare to other nanomaterials. Microwave absorption is caused in CNF due to loss during its transmission through material; at that time the electromagnetic waves interact with free charge carriers present inside the material. Here, the electric field of electromagnetic waves interacts with more mobile electrons within the material as compared to other materials, which results in the induced current. Moreover, the CNFs are oriented in different directions and thus could effectively attenuate electromagnetic waves by internal reflection even if

the waves are incident from any direction. The rough surface of CNF also helps to enhance the internal reflection to cause more loss of microwave energy. These processes dissipate the microwave energy, resulting in a low reflection of microwave in CNF films. So, the CNFs are more advantageous as a microwave absorber compared to other materials.

As an example, dense population of randomly grown CNF can be seen in Figure 8.3a. The estimated length of these fibers was  $\sim 30\text{--}40\text{ }\mu\text{m}$  with diameter of about 533 nm. Wall thickness of the fibers was estimated around 100 nm with inner diameter of 333 nm (Figure 8.3b). The outer surface profile of fiber shown in the inset of Figure 8.3b suggests that the fibers have a rough surface [33].

A microwave absorption curve for such CNF films studied in Ku-band of microwave is shown in Figure 8.4. The absorption for such CNF films was calculated using equation,

$$A = 1 - (R + T) \quad (8.18)$$

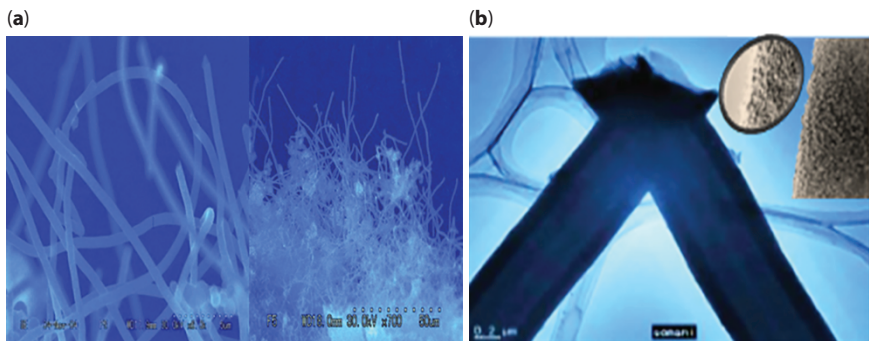
where  $A$  is absorption,  $R$  is reflectance  $= E_r/E_i$ ,  $T$  is transmittance  $= E_t/E_i$ . Here,  $E_i$  is incident energy,  $E_r$  is reflected energy and  $E_t$  is transmitted energy.

The reflection coefficient for CNF films was calculated using,

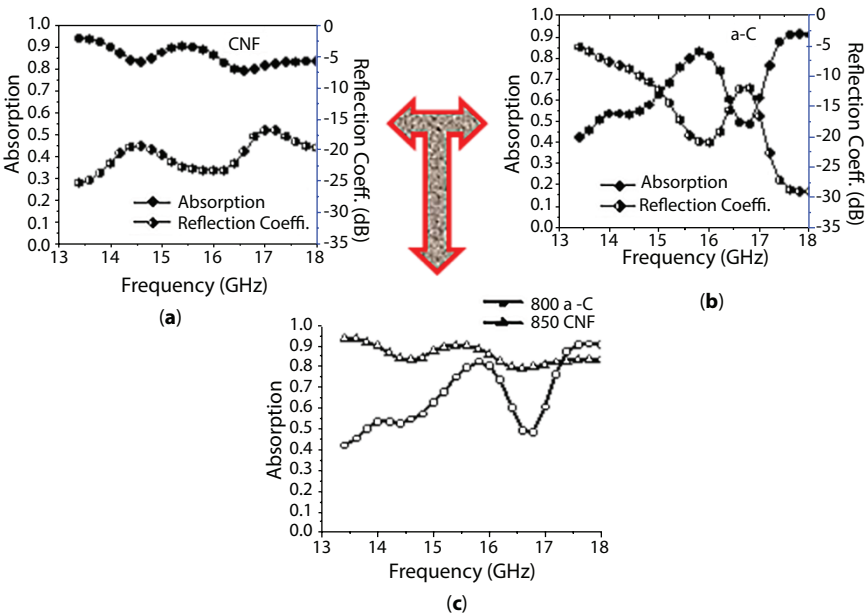
$$\text{Reflection coefficient} = -20\log(E_r/E_i) \quad (8.19)$$

The data of reflection coefficient and absorption is plotted against frequency, shown in Figure 8.4.

Relative curve for absorption by CNF and amorphous carbon shown in Figure 8.4 clearly indicates the higher absorption efficiency of CNF films.



**Figure 8.3** (a) SEM and (b) TEM of CNF synthesized from linseeds oil.



**Figure 8.4** Relative curves for an absorption and reflection coefficient as a function of frequency for CNF and amorphous carbon films.

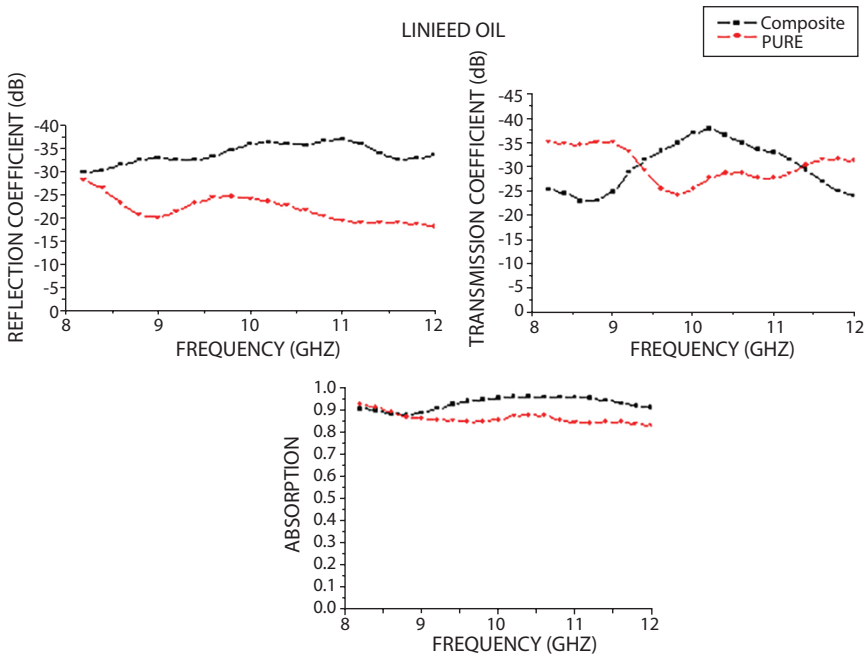
The percentage absorption for the films is found to be ~82–93% with maximum absorption bandwidth of 2.8 GHz in Ku band. Whereas, the amorphous carbon films show the percentage absorption between ~42–90% for the same frequency range with maximum absorption bandwidth of 0.6GHz.

## 8.6 Need for Fabricating a CNF and Polymer Composite

The stimulating result of CNF films has created interest in fabricating its polymer composites, which can be useful for various applications. Normally the use of polymer-based materials is popular due to their properties like light weight, flexibility, economy, etc. But the polymers are electrically insulating and transparent to electromagnetic radiation. Their inherent electromagnetic interference shielding effectiveness (EMI SE) is practically zero. However, both conductivity and EMI SE have been reported to be improved by the incorporation of electrically conductive fillers, including

carbon black, CNF fibers, metal fibers and metal particulate [18]. Also, it is well established that shielding effectiveness and absorption capability of a conductive composite is related to its conductivity. Here, the reflection and absorption coefficient of the dispersed filler and its size, shape and distribution in the matrix are equally important [13].

In CNF-polymer composite materials, mixing of CNF in acrylic as a polymer makes the material capacitive, where acrylic acts as a dielectric between the conducting materials (CNF). Here, CNF particles with acrylic as a mediator act as two plates of the capacitor. In such material, the microwave energy is dissipated by displacement current because of transfer of charge from one plate to another plate of the capacitor. Therefore, the greater the surface of the plate, the greater the accumulation of charge will be, which gives more displacement current and a greater loss of microwave energy. As the fiber (CNF) has longer length and diameter as compared to the CNB and MWCNT, the microwave energy loss inside the material is more. This is an indicative of more loss of microwaves in CNF composite, where displacement current is more effective than the conduction current.



**Figure 8.5** Variation of reflection coefficient, transmission coefficient and absorption in the case of CNF and CNF composite as a function of frequency in X-band. (Absorption by CNF is shown in red and CNF composite is shown in black.)

The study of absorption capability of CNF polymer composite in X-band shows an increase in absorption capability up to ~ 98% (Figure 8.5).

Here, the aspect ratio of CNF composite was 1.4 wt.%, which enhanced the percentage absorption.

## 8.7 Summary

Microwave absorbers are in use both in civil and military applications on account of their ability to eliminate electromagnetic wave pollution and to reduce RADAR signatures. They are categorized into various forms such as resonant absorber, broadband absorber, magnetic absorber, dielectric absorber and metal absorber. All these absorber materials should have dielectric, magnetic and conductive losses because the manner in which the properties change with frequency reflects the performance of the absorber. In general, absorbers work by allowing the wave to penetrate into a region where the electric and/or magnetic fields experience loss.

Absorber which requires a dielectric layer with phase thickness equal to a quarter wavelength ( $\lambda/4$ ) of incident wave (frequency as  $\lambda=1/f$ ) and is much thinner than other types are known as resonant absorbers. They are preferred for most applications where wide operational bandwidth is not a requirement.

- **Broadband absorbers** are designed by varying the impedance from that of free space at their incident surface to a low impedance, lossy material at their rear (back) surface. Good levels of reflectivity reduction (greater than 20 dB) can be achieved in materials with thickness less than  $1/3$  wavelength.
- **Magnetic absorbers** such as ferrites, iron and cobalt-nickel alloys alter the permeability for the absorption of microwave waves. The strong magnetism properties of magnetic absorber make them a good microwave absorber.
- **Dielectric absorber** is material in which the electrical and magnetic properties have been altered to allow absorption of microwave energy at discrete or broadband frequencies.

In dielectrics the variation of  $\tan \delta$  with frequency is more commonly used than that of dielectric constant  $\epsilon'$ . Here, the loss tangent  $\tan \delta = \epsilon''/\epsilon'$  is a good measure of microwave absorption materials with  $\tan \delta > 1$  considered as “lossy” materials. Loss tangents ( $\tan \delta$ ) of the order of 10 are considered to indicate strong absorption at a given frequency.

- In **metal absorbers**, the metal particles or the conducting material's particles are used as filler that alter the electrical properties such as permittivity and conductivity of the material.

The property of the metal to attenuate the fields is expressed in terms of a quantity defined as the depth of the penetration or skin depth. It is defined as the distance within the metal in which the amplitude of the traveling wave is attenuated to  $1/e$  or 36.8 percent of its value just above the metal surface.

Other than all these absorber materials, the nanostructured materials have attracted attention as an absorber in microwave frequency region due to their unique chemical and physical properties.

Therefore, the nano-size ferromagnetic particles having properties different than bulk materials or large particles are selected as microwave absorber. Unfortunately, these materials need a thick coating to meet practical demands.

In microwave absorbers, volume-to-weight ratio of absorber material is very important for lightweight and strong absorption properties that can be achieved using carbon nano absorber such as carbon nanofiber.

- **Radar** is a detection system that uses radio waves to determine the range, angle, or velocity of objects. It can be used to detect aircraft, ships, spacecraft, guided missiles, motor vehicles, weather formations, and terrain.
- **Multiband 3D imaging radar** requires the capacity to measure the range to the first scatter within every pixel, which needs an array of range counters. This technology is normally coupled with highly sensitive detectors of eye-safe wavelengths.
- **Quantum radar** is an emerging remote-sensing technology based on input quantum correlations and output quantum detections.
- **LIDAR** (Light Imaging Detection & Ranging) is a surveying method that measures distance to a target by illuminating the target with pulsed laser light and measuring the reflected pulses with a sensor.

Fortunately, we have an abundance of cheap low-conducting carbon materials. It is possible to construct synthetic materials from such carbon



that can have tailored conductivity, from very poor (insulated grains of carbon black) to very high (connected chains of graphite). Therefore, the carbon-based absorbers essentially follow the electric field loss mechanism. Also, the stimulating result of CNF suggests fabricating its polymer composites, which can be useful for various applications, as it is well established that shielding effectiveness and absorption capability of a conductive composite is related to its conductivity.

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# Carbon Nanofiber for Removal of Dye from Aqueous Medium

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*Likewise, nanotechnology will, once it gets under way, depend on the tools we have then and our ability to use them, and not on the steps that got us there.*

K. Eric Drexler

## 9.1 Introduction

The family of carbon nanomaterials though dominated by carbon nanotubes (CNTs) and fullerenes has evolved greatly with the growing demand for newer and better materials. Considered to be a close cousin of the carbon nanotube, carbon nanofibers (CNF) hold their own in this application-driven scientific world hungry for the new super material.

CNFs are not new materials. In 1889, before the advent of electron microscopes, Hughes and Chambers filed a patent for synthesizing “hair-like carbon filaments” by pyrolyzing hydrogen and methane in an iron crucible [1]. They felt it would be useful as filaments in electric glass bulbs. Though lack of technology hindered a closer look into the morphology of the material, it is the first reported synthesis of CNFs.

Thereafter, CNFs continued to be synthesized by pyrolyzing various hydrocarbons like methane, propane, ethylene and n-heptane at various temperatures ranging from 700–1200 °C.

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The traditional method of synthesis of CNFs is by electrical arc discharge, chemical vapor deposition of carbon on metal catalyst or by plasma-enhanced chemical vapor deposition technique.

The characterization of CNFs took place with the aid of the new age of microscopy techniques, such as SEM, TEM and X-ray diffraction analyses, giving us an insight into the structure and properties of these materials.

The CNFs have been classified into two major types, namely, stacked or bamboo-like and herringbone, which is in reference to the arrangement of the graphene layers with respect to the filament axis. A detailed analysis of these structures will be dealt with later.

The defining property of CNFs is its mesoporous structure, which governs all potential applications of this material. According to IUPAC nomenclature, a mesoporous material is a material containing pores with diameters between 2 and 50 nm. Microporous materials have diameters less than 2 nm while macroporous materials have diameters greater than 50 nm.

The mesoporous structure of CNFs leads to a vastly increased specific surface area which is a joy for researchers working on applications ranging from energy storage devices to carriers for targeted drug delivery, water purification, scaffolding and reinforcing materials and so on.

This chapter focuses on the application of CNF for adsorbing dyes from aqueous medium. During this study it has been noted that CNF synthesized from biogenic materials offer unique morphologies with very high surface area.

## **9.2 Morphology of Biogenic and Chemically Synthesized CNFs from Different Precursors**

Carbon nanofibers (CNFs) are the new wonder material with excellent field emission characteristics, chemical inertness, high aspect ratio, ability to adsorb dyes, heavy metals and gases. These properties rival that of the more researched CNTs. Yet for too long now, their versatility has not been thoroughly investigated. Let us look into the varied structure of these materials as well as the different methods of synthesis to see whether the methods influence the structure.

The CNFs are considered to be different from CNTs with respect to the alignment of the graphene sheets to the filament axis. Carbon nanotubes (CNTs) have their graphene layers aligned parallel to the filament axis. The stacked CNFs have parallel graphene layers aligned perpendicular to the filament axis, while the herringbone CNFs have their graphene layers

stacked at an angle to the filament axis, much like stacked cones, but with a hollow inside [2–6].

It has been observed that the structure of carbon depends on the precursor and the fabrication process that decides the layer planes in carbon fiber, which can be either turbostratic, graphitic or a hybrid. The turbostratic crystalline structure of carbon is a more porous intermediate stage between amorphous carbon and graphitic layers.

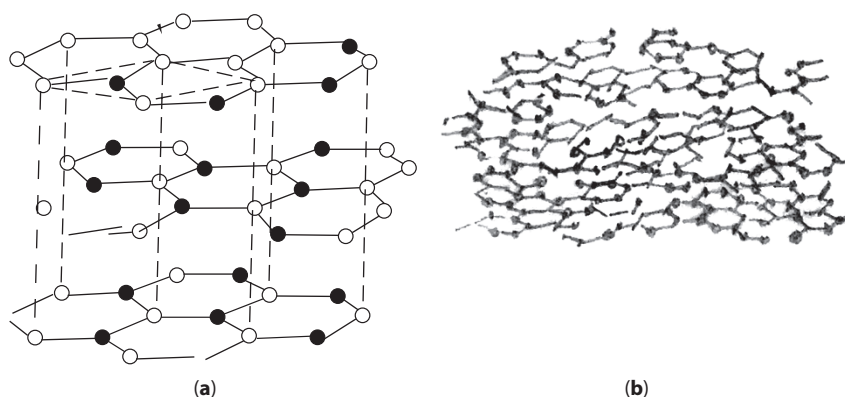
As can be seen in Figure 9.1, in graphitic crystalline regions the layer planes are stacked parallel to one another in a regular fashion. Carbon fiber produced from polyacrylonitrile (PAN) is turbostratic [7], while carbon fibers obtained from coal tar (after receiving a heat treatment of over 2200 °C) form the mesophase are graphitic. Turbostratic CNF usually shows higher elastic modulus but lower tensile strength than graphitic CNF.

Usually CNFs are synthesized by three methods, each having an impact on the morphology, properties and hence applicability.

### 9.2.1 Chemical Vapor Deposition Method (CVD)

The CVD method involves decomposition/pyrolysis of a predetermined precursor, i.e., a hydrocarbon and/or carbon monoxide vapors when passed over metal catalysts in nanoforms. The decomposition of the hydrocarbons takes place at elevated temperatures along some faces of the metal catalyst to release hydrogen and carbon. This is followed by diffusion of the carbon vapors through the catalyst and subsequent growth of the nanofiber along other faces of the metal catalyst [6].

The decomposition reaction of hydrocarbons is an exothermic reaction and hence a temperature gradient is established across the metal catalyst.



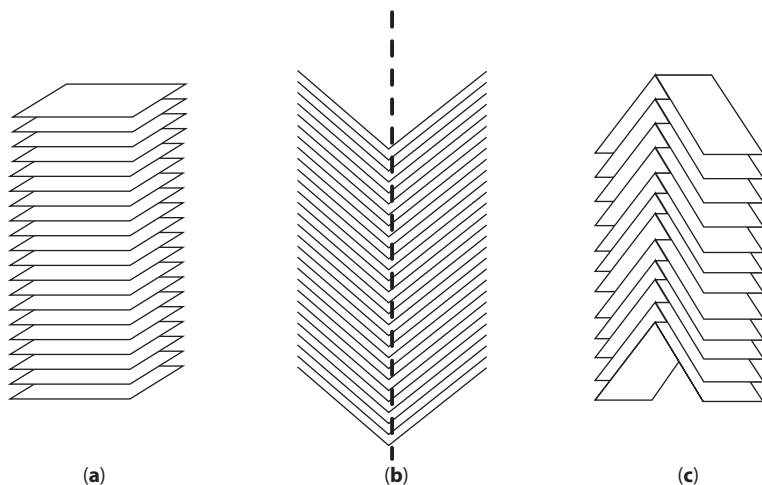
**Figure 9.1** (a) Structure of graphite; (b) Turbostratic carbon.

The carbon thus diffuses through the hotter zone of the metal catalyst and deposits as filamentous growth on the cooler parts. The diffusion of carbon through the catalyst particles is considered to be the rate-limiting step of the reaction. But let us also understand that since the size of the catalyst is in the nanoscale range, the existence of temperature gradient across the catalyst surface is a rather theoretical concept.

The nature and size of the metal catalyst plays a definitive role in the formation and morphology of carbon nanofiber, although temperature and type of precursor are also important. Unlike CNTs, the CNFs have successive graphene layers aligned either perpendicular or at an angle to the filament axis. Hence, the size and shape of the catalyst material determines the type of CNF formed. Hence, they are “multifaceted” with respect to catalyst surface, which is found to be conducive to the growth of CNFs [6, 8, 9].

It has been found that herringbone CNFs are formed when the catalyst is an alloy or a mixed metal catalyst, whereas stacked CNFs are formed when the catalyst is only iron based with CO-H<sub>2</sub> gas mixture as precursor. The typical lengths of CNFs produced by these methods vary from 5–100  $\mu\text{m}$  and widths between 5–500 nm. The role of hydrogen in formation of CNFs was explored. The hydrogen vapors are credited with terminating the many dangling bonds at the edges of the stacked graphite platelets (Figure 9.2).

But is the mere production and/or presence of CNFs conducive to their applicability in various fields? The answer is no. Loose CNFs, much like



**Figure 9.2** Types of carbon nanofibers: (a) Stacked CNF, (b & c) Herringbone CNF.

CNTs, are difficult to control and a hazardous substance. Immobilization or anchoring of the CNFs on a support helps to attain a greater exposed surface area and effectivity of application. This has led to use of CNFs instead of activated carbon (AC) as an adsorbent for both gas and liquid. Activated carbon is an excellent adsorbent for pollutants in water and air. Hence, they act as excellent scaffolding for growing nanofibers. The principle followed is to create micro- and mesopores in the activated carbon structure by catalytic carbonization and allowing the growth of pores in the CNFs, which would be excellent for adsorption and catalytic applications.

The chemical precursors used in this process include hydrocarbons with or without hydrogen. Most studies in this respect have been conducted with ethylene and hydrogen. The presence of hydrogen along with hydrocarbon has been found to be essential for the growth of CNFs, though decomposition of hydrocarbon also produces hydrogen.

The CNFs produced have diameters in the range of 20–400 nm, which may increase up to 1000 nm depending on the hydrocarbon: hydrogen ratio. The greater the ratio, the smaller is the diameter of the CNF.

Temperature plays an important part in the morphology of the CNFs. Higher temperatures imply greater rate of diffusion and greater solubility of carbon in the catalyst surface. Hence, it has been observed that the length of CNFs increases substantially as temperatures rise from 500 to 800 °C. It was found through BET analyses that surface area was greatest for CNF with smaller diameter and greater microporosity.

Let us now look at a few examples of CNFs derived from various precursors by CVD method. Most of the CNFs synthesized are grown on catalyst particles impregnated onto activated carbon fibers. This kind of tethering helps to gain better control of the CNF and its properties.

A study by Jahangiri *et al.* (2013) [10] using walnut shells to prepare activated carbon (AC) that was impregnated with nickel catalyst shows the effect of growing CNFs on the surface which were activated by CO<sub>2</sub>. The CNFs grew from methane pyrolyzed at 550 °C for one hour and were further activated by heating in CO<sub>2</sub>. Extremely thin CNFs are obtained with diameter of 10–20 nm and micropores of dimension less than 1 nm. The area of micropores decreases on the AC with growth of CNFs. But with activation by CO<sub>2</sub> there is an increase of micropores with smaller radii and CNF with greater surface area.

A somewhat similar study involves AC derived from palm kernel and nickel impregnated, and the subsequent growth of CNFs from benzene and hydrogen mixture, is also an excellent case study [11]. The average diameter of the CNFs is observed to be 100–200 nm. The CNF microstructure possesses defective platelets and more graphitic platelets. The CNF



surface area is found to be almost eight times greater than that of AC. Using the CVD method, the synthesis of CNFs using a combination of catalysts, Co-Cu [12] showed some interesting results. Upon varying the ratio of catalyst particles, it was found that there was an optimum concentration ratio of catalyst, which gave CNFs with the most uniform surface and a diameter of 27 nm having a surface area of 292 m<sup>2</sup>/g.

A series of experiments on immobilized CNFs on activated carbon (AC) show the effect of hydrocarbon and hydrogen ratio on the yield of CNFs. In one such experiment using iron as the catalyst, the AC is calcined in air at 400 °C before the growth of CNFs by CVD method. A mixture of ethylene and hydrogen is used as precursor for preparing the CNFs by varying the temperature between 500–800 °C. Though higher ratio of C<sub>2</sub>H<sub>4</sub>:H<sub>2</sub> gives smaller diameter of CNFs, it does not lead to higher productivity of CNFs. Optimum ratio for production and diameter of CNFs is found to be 5:5.

Some studies indicate that activated carbon (activated bamboo charcoal) impregnated with CNFs by CVD method show a decrease in the number of active pores on the AC, indicating that the CNFs grow on the pores of the AC, thus effectively blocking it [13]. The CNFs formed are found to be herringbone type with dangling bonds from the edges of the CNF structure, which are conducive for various applications. Also, such growth of CNFs can be tuned to modify their structure and hence properties. This study was conducted on activated bamboo charcoal with impregnated CNF using ferrocene as catalyst.

### 9.2.2 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

The plasma-enhanced CVD (PECVD) method can also be tuned to produce CNFs at low temperatures. PECVD is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of plasma of the reacting gases. The plasma is generally created by radio frequency (RF), alternating current frequency (AC) or direct current (DC) discharge between two electrodes, the space between them filled with the reacting gases.

The presence of ionized gases, especially dc plasma, is easy to operate and gives excellent results with respect to formation of herringbone CNFs. Though DC plasma is most preferred, CNFs have been produced with hot filament-assisted PECVD, microwave PECVD, dc glow discharge PECVD, inductively coupled PECVD, and RF PECVD.

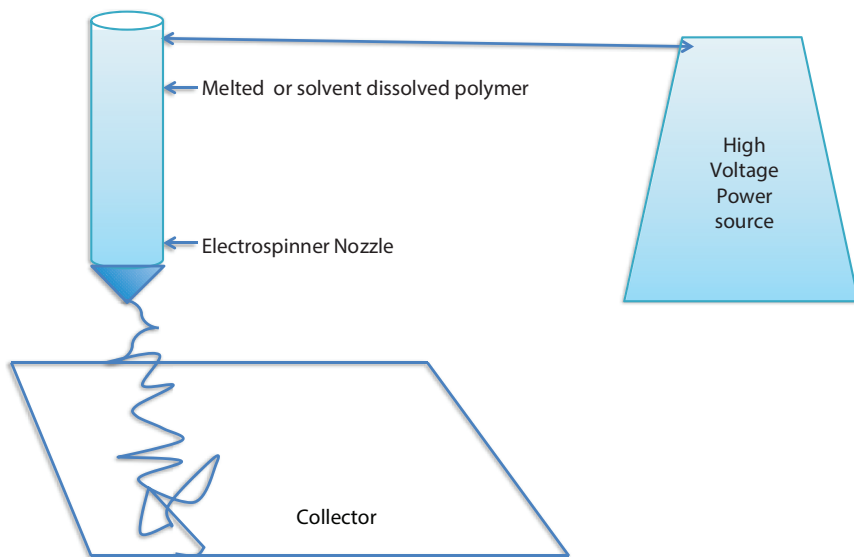
The plasma-induced depositions are extremely stable, low temperature syntheses. The CNFs grown in this manner can be controlled and reproduced easily. The steps in this synthesis involve adsorption and subsequent dissociation of the reactant species on the catalyst particle followed by diffusion of these species through the catalyst and subsequent formation of the CNF on the opposite face of the catalyst. Aligned CNFs can be produced by dc-induced PECVD.

There have been varying theories regarding the formation of CNFs by this method. Initially it was proposed that diffusion of the carbon vapors through the catalyst bulk was the rate defining step. Later, with greater experimentation and inputs from various researchers, it was stated that the carbon vapors diffused through the surface and not the bulk of the catalyst and formed platelet-like structures which were parallel to the catalyst surface but aligned at an angle to the filament or fiber axis. It was construed that diffusion through the surface was more rapid and hence the CNFs are formed at the bottom of the catalyst particle. Generally, CNFs synthesized at lower temperatures (below 400 °C) are found to have different structures, namely fishbone, herringbone, stacked cone or stacked cup. A variety of hydrocarbons have been used as precursors to prepare CNFs.

### 9.2.3 Electrospinning of Polymer Fibers

Electrospinning of polymer is becoming a more popular and controllable method of synthesis of CNFs. Electrospinning is a voltage-driven process wherein controlled flow of molten polymer through a syringe leads to the formation of nanofibers which are obtained on a collector (Figure 9.3). The voltage is applied across the syringe tip and collector and the spinning starts as the polymer melt starts flowing out of the syringe tip in a controlled manner. In some cases, the nanofibers are reinforced with CNTs to enhance surface area and storage capacity for various applications. This process enables the production of CNFs with 10–400 nm diameter and length running into kilometers. The fiber properties depend on the polymer viscosity, uniformity, strength of applied electric field, and distance between the syringe tip and collector.

The porosity of the CNFs can be controlled by careful carbonization after electrospinning process, where temperature plays a pivotal role. Carbonization of CNF at higher temperatures of 700–1400 °C in inert atmosphere leads to formation of micro- and mesopores, effectively increasing the surface area. This step may be followed by disorganized etching of carbon on the CNF structure using CO<sub>2</sub> to further increase the surface area.



**Figure 9.3** Schematic representation of electrospinning process.

SEM, TEM, and XRD analyses have shown that CNFs produced by electrospinning show a wide range of structures and porosities. Use of different polymers, viz. starch, polyacrylonitrile, polylactide, polyamide, polyimide and polyvinyl alcohol, as the precursors for the production of CNFs using the same electrospinning conditions lead to differing morphologies [13–16].

The electrospun CNFs can be further activated by physical or chemical processes to enhance their properties like adsorption and thermal and chemical stabilities.

Post synthesis the electrospun CNFs are subjected to stabilization by heating in air atmosphere around 200–300 °C, which leads to chemical and physical changes like cyclization, dehydrogenation, etc. This effectively converts the linear electrospun CNFs to an infusible ladderlike structure which is more capable of withstanding higher temperatures during the next step, carbonization. Carbonization of the stabilized CNFs in inert atmosphere at temperatures ranging from 800–3000 °C helps to convert the turbostratic, disordered structure to more graphitic structure with larger graphite crystals, more ordered arrangement and greater connection between the CNFs.

Chapter 2 of this book dealt with various aspects of CNF synthesized from biological precursors, such as plant parts, plant extracts and plant metabolites, and their impact on the morphology and properties, which helps in deciding the suitability of CNF for different applications.

### 9.3 Novel Dye Removal Properties of CNF

The structure of CNFs is more conducive than many other nanoforms of carbon in aiding the removal of various species from different effluents by adsorption. We have already discussed the structure of CNFs in Chapter 1. We are aware that CNFs generally have a mesoporous structure with pore diameters between 2–50 nm.

The CNFs consist of graphitic platelets which are arranged either parallel to the fiber axis or perpendicular to it. The perpendicular arrangement is of two types: one where the platelets are stacked one on top of the other and another where the platelets are aligned at an angle to the fiber axis (herringbone). The presence of pores as well as their alignment appears to impart CNFs with a selectivity that is rarely observed in other adsorbents. According to Anderson *et al.* (2000 [17]), the narrow space between two layers of graphitic platelets can allow the selective adsorption of flat, linear molecules which can slide in between them, in contrast to larger molecules which would be prevented from doing so. Hence, CNFs which were earlier considered to be undesirable during synthesis of nanomaterials gain a huge importance as an adsorbent. This ability of CNFs to adsorb small molecules through the platelet-like graphitic structure, wherein each plate is approximately 0.35 nm apart, is different from activated carbon (AC).

Activated carbon (AC), with micropores in a range less than 1 nm appear to be less selective than CNFs in adsorption characteristics of contaminants in solvent. While AC is good in adsorbing gases, it adsorbs both the solute and the solvent without preference with the result that its pores become rapidly saturated, and hence the effectivity of removing the small molecules of solute goes down.

It has been found that whereas the adsorption capacity of activated carbon fibers reduces drastically after the first two to three minutes of action, the CNFs continue to be active beyond this period up to ten minutes due to their selectiveness, which ensures that their active sites are still not fully saturated.

Apart from the structural advantage, the surface chemistry of CNFs enhances their ability to be used as adsorbents. The surface charge, hydrophobicity and chemical reactivity of CNFs can be modified, which is a boon to researchers working on the selectivity of adsorbents. The above properties can be modified either by choosing a particular method of synthesis or by post-synthesis processes like carbonization, graphitization, etc.

The surface of CNFs can be manipulated to increase the number of anchoring sites, selectivity, specificity or just maintain stability of the surface.

A comparison of the surface structures of untreated bamboo-like and herringbone CNFs (Ros *et al.* 2009) [18] has led to the conclusion that herringbone CNFs are more prone to surface oxidation than the bamboo-like CNFs. The herringbone CNFs have a greater number of reactive graphitic edges along the sidewalls, which are more prone to oxidation than in the case of bamboo-like CNFs.

Comparison of spectra from before and after processing treatments show that surface of CNFs can be oxidized to form carboxylic acid sites. Usually treatment of CNFs with concentrated  $\text{H}_2\text{SO}_4$  or a mixture of  $\text{C HNO}_3$  and  $\text{H}_2\text{SO}_4$  enable the creation of oxygen-carrying surface groups [19]. The total oxygen content and number of acidic groups are a function of the oxidizing agent used and the time period of treatment.

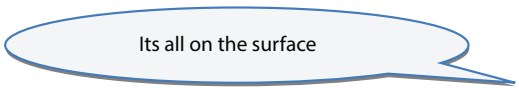
This treatment enables the CNFs to be selective in their adsorptive functions by attracting and adsorbing cationic dyes.

Researchers have observed that acid oxidation leads to the opening of an inner tubular channel along the length of the fibers which enhances the adsorptive capacity as it is directly linked to porosity [20]. Thus, surface chemistry of CNFs is critical to their use as adsorbents.

Carbon nanofiber is declared to be unique adsorption material due to the following properties:

- High surface area
- High aspect ratio
- High temperature stability
- Chemical inertness
- High tensile strength
- Unique pores and channels
- Insoluble in water
- Good adsorbent of dye, salt, heavy metal, gas and organic compounds

### *What Is Adsorption?*



Its all on the surface

Let us first discuss the factors that affect the adsorption capacities of adsorbents. Adsorption is a surface phenomenon where the adsorbate attaches itself to the adsorbent surface through physical (physisorption) or chemical (chemisorption) forces. The adsorption of solute particles is

due to surface chelation as well as diffusion through the micropores into the subsurface layer. The extent of adhesion depends upon several factors, most importantly surface area, and initial adsorbate concentration. Temperature, pH and contact time also play a role in determining the efficiency of adsorption.

Surface area is the key to a good adsorbent and CNFs with their unique mesoporous structure are thus extremely relevant. The presence of pores which are aligned according to the general shape of the CNF add to the versatility of CNFs.

## 9.4 Absorption of Different Dyes

A multitude of slit-shaped nanopores impart CNFs with selectivity in adsorption. The study of adsorption of dyes in electrospun Polyamide 6 CNFs [21] shows an increase in adsorption capacity with increase in concentration of adsorbate, due to greater mass transfer effects. Also, dynamic sorption processes showed that these CNFs have superior dye removal properties compared to conventional fibers. The hormone ( $17\beta$ -Estradiol) was taken as the dye to be removed. Dye removal capacity of nanofibers increased while the diameter decreased due to the specific surface area increasing. The factors, such as areal density, influent solution concentration, and fibers quantity, were considered for the dye removal rate of polyamide 6 nanofibers. And it showed a positive relation with fiber mats specific surface area and quantity.

Increase in porosity can be obtained if CNFs are impregnated with materials having charged surface area, even though pore diameters can reduce in size due to these substances. In fact, reduction in pore diameter and increase in porosity enhance the adsorption properties. This has been observed in a comparison of the adsorption properties of electrospun poly-acrylonitrile yarn and PAN yarn waste impregnated with graphene oxide (GO) [22]. Graphene oxide is prepared from graphite and is an excellent adsorbent for cationic species since it has hydroxyl, carboxyl and carbonyl groups on its surface. These negative functional groups exert an effective capacity to bond with cationic species in basic medium.

The electrospun PAN yarn waste and graphene oxide (GO) composite combined in different weight percentage of GO was tested as an adsorbent mat. The SEM analysis results showed a decrease in diameter of the PAN nanofibers upon increasing the GO concentration. Also, FTIR results showed no apparent bonding between PAN and GO. There is an increase in amorphous matter content with increase in GO percentage, which is

beneficial in dye removal. In keeping with the chemical characteristic of GO, it is observed that methylene blue dye adsorption increases in basic medium in comparison to acidic medium. The efficiency of adsorption increases with increase in weight percentage composition of GO in the nanofibrous mat of PAN. GO provides greater amorphous character and better adhesion by increasing the surface roughness.

The adsorption of  $\text{Cu}^{2+}$  ions by CNFs [23], though not a dye, can be taken as a case to illustrate the efficiency of this particular adsorbent. The analysis has been done with herringbone CNFs and showed excellent  $\text{Cu}^{2+}$  adsorption at higher pH, high temperature and lower contact time.

The isoelectric point (IEP) of the CNFs is found to be at pH 1.9, where the surface charge is zero. When pH values are lower than 1.9, the surface is positively charged, while at higher pH values, the surface is negatively charged. Hence, it has been observed that the adsorption of  $\text{Cu}^{2+}$  is lowest around lower pH while it reaches highest value around pH 10. This clearly shows the effect of surface charges on the adsorption efficiency.

The effect of activated CNF on adsorption efficiency was studied by [24]. Activation of the CNF prepared from PAN at 280 °C leads to shrinking of CNF diameter from 315 nm to 250 nm. This has been stated to be due to formation of ladder-like structure by cyclization. It has been assumed that upon heating, the PAN nanofibers undergo microcombustion and pyrolysis. In this case also experimental results showed greater adsorption rates at alkaline pH due to the inherent negative surface charge of the CNFs. Thus, strong interaction with the positively charged methylene blue (MB) leads to greater adsorption rates. Also, greater concentration of CNFs was observed to lead to greater efficiency of removal of MB dye, though, as expected, the initial rate of removal was far greater. The rate of removal up to 15 minutes is very high due to available vacant sites, which reduce after this, and complete removal is attained within 60 minutes. The bonding mechanism proposed by the researchers from FTIR studies is the  $\pi$ - $\pi$  stacking interactions between aromatic rings of the activated CNF and MB dye.

The novelty of this adsorbate is the easy desorption, which allows the ACNF to be reused after drying and treating with dilute HCl. So, such CNFs would be reusable, thus increasing their value.

Keeping in mind sustainability and environmental concerns, there have been studies on naturally derived CNFs which are biodegradable and retain their structure in different mediums. Zein, a biopolymer derived from corn, has been found to be nontoxic and biodegradable, but its structure collapses in aqueous medium. Hence, a study was conducted [16] by combining zein nanofibers with nylon-6. Both the constituents were



electrospun to produce a composite CNF material which overcomes the stability and strength challenges of zein nanofiber. The average diameter of the composite CNF was found to be 150 nm. FTIR studies indicate a downward shift of amide-I (CO stretching vibrations) and amide-II (N-H bending vibrations) peaks compared to pure zein and pure nylon-6 spectra, indicating a high degree of coupling of the two constituents. The removal efficiency of the Reactive Blue 19 dye by this CNF in aqueous solution was tested. It was found that almost 85% of the dye was removed in one minute while it took 10 minutes for complete removal of the dye. The removal efficiency was also affected by pH. Higher rate of removal was observed at lower pH as due to protonation of the CNF surface there was greater electrostatic interaction between the anionic RB19 dye and the surface of adsorbent. Conversely, at higher pH the adsorption efficiency of zein/nylon CNF composite went down with the surface charge turning negative and repelling the dye molecules. The researchers have also proposed an interaction of the  $-NH_2$  group of the zein/nylon composite with the dye and sulphonate group of dye interacting with the CNF composite. Hence, bonding between the adsorbent and dye is both chemical and physical.

Due to its easy accessibility and solubility, Methylene blue (MB) has been a topic of a flurry of research activities. Another study on oxidized and carbonized electrospun CNF from PAN [25], analyzes MB adsorption characteristics. Electrospun PAN CNFs are stabilized in air by heating at 280 °C and then carbonized by heating at 900 °C in argon atmosphere, giving the ECNFs. Another set of electrospun PAN CNFs are oxidized by treating with a mixture of concentrated  $HNO_3$  and concentrated  $H_2SO_4$  for 5 hours to give the O-ECNF. The SEM and TEM data show a decrease in pore diameter for O-ECNF compared to the normal ECNF, as well as an increase in surface roughness in O-ECNF due to the etching of the acids on the walls of the CNFs. We have already observed in the cases discussed above that pH greatly affects the rate of adsorption of the dye molecules. It was observed that adsorption rates increased from 9.45 to 21.77 and 88 to 98 mg/g for ECNF and O-ECNF for MB adsorption when pH varied from 2.5 to 9. This indicates the presence of electrostatic force of attraction between MB and the oxidized ECNF due to ionization of the carboxylic groups to carboxylate anions. The efficient removal of MB by ECNF is attributed to  $\pi$ - $\pi$  stacking interactions between aromatic rings of the activated CNF and MB dye. Increase in temperature and increase in adsorbent concentration all lead to an increase in rate of adsorption of MB. Hence, the oxidized ECNFs are considered to be an excellent adsorbent for removal of MB cationic dye.



## 9.5 Summary

The story of carbon nanofibers is one which is brimming with infinite possibilities for the future. It began as a slow starter in comparison to the carbon nanotubes but has in the past decade been rediscovered for the myriad applications it provides researchers. To begin with, it can be designed in different structural forms, such as platelet or bamboo-like, wherein the graphitic plates are arranged parallel or perpendicular to the fiber axis. As another form of CNFs, the graphitic plates are arranged at an angle to the fiber axis, giving the fishbone, herringbone, stacked-cup or stacked-cone structure. CNFs are also characterized by the presence of pores in the mesoporous range, i.e., between 2–50 nm.

The different types of CNFs can be synthesized by a variety of ways, including the catalyzed CVD method, the low-temperature plasma-enhanced CVD method, and the electrospinning method. The last method mentioned is slowly gaining more importance as it is more versatile in terms of fiber length and diameter of the CNFs. All the guiding parameters, like stability of the spinning process, average length of the polymer chain, concentration of the polymer solution, distance between the charged metal nozzle and earthed collector, can be controlled to produce CNFs of desired length and diameter.

Furthermore, these CNFs can be tuned or manipulated to suit the desired applications by post-synthesis processing like stabilization, carbonization, graphitization, etc. The herringbone CNFs with dangling bonds provide a greater number of reactive sites which are more prone to oxidation than the platelet-like CNFs. Hence, surface modifications leading to increase of surface area and change in surface morphology lead to improved adsorption capabilities and the ability to function as biosensors, electrochemical probes, storage devices, etc.

The ability of CNFs to function as extremely selective and specific adsorbents is of utmost importance. The alignment of the graphitic platelets enables small, flat, linear molecules to slide in between them and get selectively adsorbed. Also, post-synthesis processes which increase the surface area while decreasing the diameter of CNFs, lead to better adsorption capabilities. Greater experimentation done with dyes as modification of surface morphology as per requirement has led to better results of dye removal with CNFs.

There lies an ocean of further research which can be done with CNFs by modification of their structure and properties, both physical and chemical, leading to greater and better applications in adsorption of pollutants and significant chemicals.

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# Carbon Nanofiber to Remove Heavy Metals from Aqueous Medium

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*Pollution of water is killing more children today than malaria or AIDS or even war themselves.*

Tony Clarke

## 10.1 Introduction

This chapter focuses especially on those heavy metals that are the cause of water pollution, mainly due to their use in industrial production. With the advent of nanotechnology, efforts have been diverted to the use of nano-materials for removal of heavy metal pollutants. One of them is carbon nanofiber (CNF).

### 10.1.1 What Are Heavy Metals?

The term “heavy metal” was coined by the German chemist Leopold Gmelin [1]. He divided the elements into nonmetals, light metals and heavy metals. Heavy metals have relatively high densities, atomic weights and atomic numbers. Light metals had densities of 0.860–5.0 g/cm<sup>3</sup> and heavy metals 5.308–22.000. The term later became associated with elements of high atomic weight or high atomic number.

In metallurgy, heavy metals are defined on the basis of density, in physics the distinguishing criterion is atomic number, in chemistry it is the chemical behavior, and in biochemistry heavy metals are defined on the

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basis of the Lewis acid (electronic pair acceptor) behavior of their ions in aqueous solutions as class A, B and borderline metals.

- **Class A** metal ions prefer oxygen donors. Class A metals, which tend to low electro-negativity and form bonds with large ionic character, are the alkali metals and alkaline earths, aluminum the group 3 metals, and the lanthanides and actinides.
- **Class B** ions prefer nitrogen or sulfur donors. Class B metals, which tend to have higher electro-negativity and form bonds with considerable covalent character are mainly the heavier transition and post-transition metals.
- **Borderline or Ambivalent** ions show either class A or B characteristics, depending on the circumstances. Borderline metals largely consist of the lighter transition and post-transition metals (plus arsenic and antimony).

### 10.1.2 List of Heavy Metals

If one goes by the definition of a heavy metal as a metallic element with a density greater than 5, then the list of heavy metals consists of: Actinium, Americium, Arsenic, Astatine, Berkelium, Bismuth, Bohrium, Cadmium, Californium, Cerium, Chromium, Cobalt, Copernicium, Copper, Curium, Darmstadt, Dubnium, Dysprosium, Einsteinium, Erbium, Europium, Fermium, Gadolinium, Gallium, Germanium, Gold; and Hafnium, Hassium, Holmium, Indium, Iridium, Iron, Lanthanum, Lawrencium, Lead, Lutetium, Manganese, Meitnerium, Mercury, Molybdenum, Neodymium, Neptunium, Nickel, Niobium, Nobelium, Osmium, Palladium, Platinum, Plutonium, Polonium, Praseodymium, Promethium, Protactinium; and Radium, Rhenium, Rhodium, Roentgenium, Ruthenium, Rutherfordium, Samarium, Silver, Tantalum, Technetium, Tellurium, Terbium, Thallium, Thorium, Thulium, Tin, Titanium, Tungsten, Uranium, Vanadium, Ytterbium, Zinc, Zirconium.

### 10.1.3 Sources of Heavy Metals

Sources of heavy metals are geogenic, industrial (refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high-tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants), agricultural, pharmaceutical, domestic effluents,

and atmospheric. Environmental pollution is mainly due to mining, foundries, smelters, and other metal-based industrial operations. They are present throughout the Earth's crust, hence, natural phenomena such as weathering and volcanic eruptions have also been significantly contributing to heavy metal pollution.

## 10.2 Are Heavy Metals Essential for Living Beings?

Trace amount of some heavy metals are required for certain biological processes. These are iron and copper used for electron transfer, cobalt for synthesis and cell metabolism, zinc used for hydroxylation, vanadium and manganese for enzyme regulation, chromium for glucose utilization; nickel for cell growth; arsenic for metabolic growth in some animals; selenium as antioxidant and for hormone production; molybdenum for the catalysis of redox reactions; cadmium is used by some marine diatoms for the same purpose; tin may be required for growth in a few species; and tungsten is required by some archaea and bacteria for metabolic processes. A deficiency of any of these periods 4–6 essential heavy metals may increase susceptibility to heavy metal poisoning (conversely, an excess may also have adverse biological effects).

A few non-essential heavy metals have been observed to have biological effects, such as gallium, germanium, indium and most lanthanides, which can stimulate metabolism, whereas titanium promotes growth in plants.

### 10.2.1 Damaging Effect of Heavy Metals on Biosystem

Heavy metals can degrade air, water, and soil quality, and subsequently cause health issues in plants and animals. Chromium, arsenic, cadmium, mercury, and lead have a strong affinity for sulfur and usually bind via thiol groups (–SH) containing enzymes (responsible for controlling the speed of metabolic reactions), resulting in inhibition of proper functioning of the enzymes.

Other heavy metals noted for their potentially hazardous nature, usually as toxic environmental pollutants, include manganese (central nervous system damage); cobalt and nickel (carcinogens); copper, zinc, selenium and silver (endocrine disruption, congenital disorders, or general toxic effects in fish, plants, birds, or other aquatic organisms); tin, as organotin (central nervous system damage); antimony (a suspected carcinogen) and thallium (central nervous system damage).

#### 10.2.1.1 *Arsenic*

The inorganic forms of arsenic include the trivalent arsenite and the pentavalent arsenate and organic forms are the methylated metabolites: monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide.

##### 10.2.1.1.1 Hazards of Human Exposure to Arsenic

Arsenic is a carcinogen plus it has systemic health effects. It is estimated that several million people are exposed to arsenic chronically throughout the world, especially in countries like Bangladesh, India, Chile, Uruguay, Mexico and Taiwan, where the groundwater is contaminated with high concentrations of arsenic. Exposure to arsenic occurs via the oral route (ingestion), inhalation, dermal contact, and the parenteral route to some extent. Workers who produce or use arsenic compounds in such occupations as vineyards, ceramics, glass-making, smelting, refining of metallic ores, pesticide manufacturing and application, wood preservation and semiconductor manufacturing can be exposed to substantially higher levels of arsenic. People who have been exposed to high concentrations of arsenic in their drinking water display various clinico-pathological conditions, including cardiovascular and peripheral vascular disease, developmental anomalies, neurologic and neurobehavioral disorders, diabetes, hearing loss, portal fibrosis, hematologic disorders (anemia, leukopenia and eosinophilia) and carcinoma. Research has also pointed to significantly higher standardized mortality rates for cancers of the bladder, kidney, skin, and liver in many areas with arsenic pollution.

#### 10.2.1.2 *Cadmium*

Cadmium is a heavy metal of considerable environmental and occupational concern. Cadmium is frequently used in various industrial activities such as production of alloys, pigments, and batteries.

##### 10.2.1.2.1 Hazards of Human Exposure to Cadmium

Cadmium is known to cause a degenerative bone disease, e.g., decreases in bone mineral density and osteoporosis.

The main routes of exposure to cadmium are via inhalation or cigarette smoke and ingestion of food. Skin absorption is rare. Other sources of cadmium include emissions from industrial activities, including mining, smelting, and manufacturing of batteries, pigments, stabilizers, and alloys.

Cadmium is also present in trace amounts in certain foods such as leafy vegetables, potatoes, grains, mushrooms, shellfish, mussels, cocoa powder, dried seaweed, crustaceans and mollusks; it can greatly increase the cadmium concentration in human body especially in liver and kidney.

An important distribution route is the circulatory system whereas blood vessels are the mainstream organs of cadmium toxicity. Chronic inhalation exposure to cadmium particulates is generally associated with changes in pulmonary function and chest radiographs that are consistent with emphysema. Workplace exposure to airborne cadmium particulates has been associated with decreases in olfactory function. Cadmium compounds are also classified as human carcinogens by several regulatory agencies. The lung is the most definitively established site of human carcinogenesis from cadmium exposure. Other target tissues of cadmium carcinogenesis in animals include injection sites, adrenals, testes, and the hemopoietic system.

### 10.2.1.3 *Chromium*

Chromium in its hexavalent form is a carcinogen. The hexavalent [Cr(VI)] form is the second most stable state. Chromium is widely used in numerous industrial processes, e.g., welding, chrome plating, dyes and pigments, leather tanning, as anticorrosive in cooking systems and boilers and wood preservation; and, as a result, is a contaminant of many environmental systems.

#### 10.2.1.3.1 Hazards of Human Exposure to Chromium

In humans and animals, [Cr(III)] is an essential nutrient that plays a role in glucose, fat and protein metabolism by potentiating the action of insulin. However, exposure to high doses causes risk of Cr-induced diseases. Even though the principal route of human exposure to chromium is through inhalation, and the lung is the primary target organ, significant human exposure to chromium has also been reported to take place through the skin, causing dermatitis. It also causes multi-organ toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract in humans. Breathing high levels of chromium (VI) can cause irritation to the lining of the nose, and nose ulcers. The main health problems seen in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine, anemia, sperm damage and male reproductive system damage. Ingestion of extremely high doses of chromium (VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological



effects as part of the sequelae leading to death or in patients who survived because of medical treatment.

#### 10.2.1.4 *Lead*

Lead is a naturally occurring bluish-gray metal present in small amounts in the Earth's crust. Anthropogenic activities, such as fossil fuel burning, mining, and manufacturing, contribute to the release of high concentrations. Lead is currently used in the production of lead-acid batteries, ammunitions, metal products (solder and pipes), and devices to shield X-rays, lead oxides for paint, glass, pigments and chemicals. Lead in dust and soil often recontaminates cleaned houses and contributes to elevating blood lead concentrations in children who play on bare, contaminated soil.

##### 10.2.1.4.1 Hazards of Human Exposure to Lead

Lead damages the central nervous system. Exposure to lead occurs mainly via inhalation of lead-contaminated dust particles or aerosols, and ingestion of lead-contaminated food, water, and paints. In the human body, the greatest percentage of lead is taken into the kidney, followed by the liver and the other soft tissues such as heart and brain; however, the lead in the skeleton represents the major body fraction. The nervous system is the most vulnerable target of lead poisoning. Headache, poor attention span, irritability, loss of memory and dullness are the early symptoms of the effects of lead exposure on the central nervous system.

Lead is the most systemic toxicant that affects several organs in the body, including the kidneys, liver, central nervous system, hematopoietic system, endocrine system, and reproductive system.

Lead absorbed by the pregnant mother is readily transferred to the developing fetus, causing reduced birth weight, preterm delivery and neurodevelopmental abnormalities.

A large body of research has indicated that lead acts by interfering with calcium-dependent processes related to neuronal signaling and intracellular signal transduction. Lead perturbs intracellular calcium cycling, altering releasability of organelle stores, such as endoplasmic reticulum and mitochondria.

#### 10.2.1.5 *Mercury*

Mercury is found in nature in three forms (elemental, inorganic, and organic), with each having its own profile of toxicity. At room temperature,

elemental mercury exists as a liquid which has a high vapor pressure and is released into the environment as mercury vapor. Mercury also exists as a cation with oxidation states of +1 (mercurous) or +2 (mercuric). Methylmercury is the most frequently encountered compound of the organic form found in the environment and is formed as a result of the methylation of inorganic (mercuric) forms of mercury by microorganisms found in soil and water.

Mercury is a widespread environmental toxicant and pollutant which induces severe alterations in the body tissues and causes a wide range of adverse health effects. Because mercury is ubiquitous in the environment, humans, plants and animals are all unable to avoid exposure to some form of mercury.

#### 10.2.1.5.1 Hazards of Human Exposure to Mercury

Recent examples of heavy metal contamination and health risks include the occurrence of Minamata disease in Japan (1932–1968) due to mercury poisoning, contamination due to the Bento Rodrigues dam disaster in Brazil, and high levels of lead in drinking water supplied to the residents of Flint, Michigan, in the northeast region of the United States. Mercury damages the central nervous system. Humans are exposed to mercury through environmental pollution, food contamination, fish consumption, dental care, preventive medical practices, industrial and agricultural operations, and occupational operations. The elemental vapor is highly lipophilic and is effectively absorbed through the lungs and tissues lining the mouth. After  $\text{Hg}^0$  enters the blood, it rapidly passes through cell membranes, which include both the blood-brain barrier and the placental barrier. Once it enters the cell,  $\text{Hg}^0$  is oxidized and becomes highly reactive  $\text{Hg}^{2+}$ . A major proportion of what is absorbed accumulates in the kidneys, neurological tissue and the liver. All forms of mercury are toxic.

### 10.2.2 Heavy Metal and Soil Toxicity

Heavy metals are one of the major sources of soil pollution and are toxic to soil, plants, aquatic life and human health if their concentration is high. In soil heavy metals exhibit toxic effects towards biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Elevated Pb in soils may decrease soil productivity and a very low Pb concentration may inhibit some vital plant processes, i.e., photosynthesis, mitosis and water absorption, with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short leaves, stunted foliage and brown short roots.

### 10.2.3 Heavy Metal and Plant Toxicity

Some of the heavy metals like As, Cd, Hg, Pb or Se are not essential for plant growth. Others, like Co, Cu, Fe, Mn, Mo, Ni and Zn, are essential elements required for normal growth and metabolism of plants; but these elements can easily lead to poisoning when their concentration is greater than optimal values. Heavy metal accumulation in plants depends upon plant species and the efficiency of different plants to absorb metals. Elevated Pb in soils may decrease soil productivity, and a very low Pb concentration may inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption, with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short roots. Heavy metals are potentially toxic to plants, resulting in chlorosis, weak plant growth, yield depression, reduced nutrient uptake, disorders in plant metabolism and reduced ability to fixate molecular nitrogen in leguminous plants. Seed germination is delayed in the presence of increasing concentration of lead.

### 10.2.4 Toxic Effects of Heavy Metals on Aquatic Environment

Heavy metals are highly persistent, toxic in trace amounts, and can potentially induce severe oxidative stress in aquatic organisms. Metals are not subject to bacterial degradation and hence remain permanently in the marine environment. Heavy metals released into aquatic systems are generally bound to particulate matter, which eventually settle down and become incorporated into sediments. Surface sediment therefore is the most important reservoir or sink of metals and other pollutants in aquatic environments. Therefore, organisms in or near the sediments are adversely affected. Once heavy metals are accumulated in an aquatic organism, they can be transferred through the upper classes of the food chain. Contaminants in aquatic systems, including heavy metals, stimulate the production of reactive oxygen species (ROS) that can damage fishes and other aquatic organisms. Mercury is one of the most important pollutants for marine organisms Methylmercury, which is formed in aquatic sediments through the bacterial methylation of organic mercury, is a toxic chemical compound of mercury; in fact, nearly all the mercury in fish muscles occurs as methylmercury.

## 10.3 Methods Used for Removal of Heavy Metals

Since heavy metals are very toxic it is necessary to treat metal-contaminated wastewater prior to its discharge into the environment. The various methods

of removal of heavy metals from industrial wastewater include filtration, chemical precipitation, adsorption, electrodeposition, membrane systems, and ion exchange process. Nowadays the eco-friendly methods like physicochemical process, electro-coagulation process, nanofiltration, etc., are being researched.

### 10.3.1 Adsorption

Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [2]. Adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. The search for low-cost adsorbents that have metal-binding capacities has intensified. The adsorbents may be of mineral, organic, biogenic, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials.

#### 10.3.1.1 Adsorption on New Adsorbents

Various low-cost adsorbents derived from agricultural waste, industrial by-product, natural material, or modified biopolymers have been developed and applied for the removal of heavy metals from metal-contaminated wastewater. There are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

#### 10.3.1.2 Adsorption on Modified Natural Materials

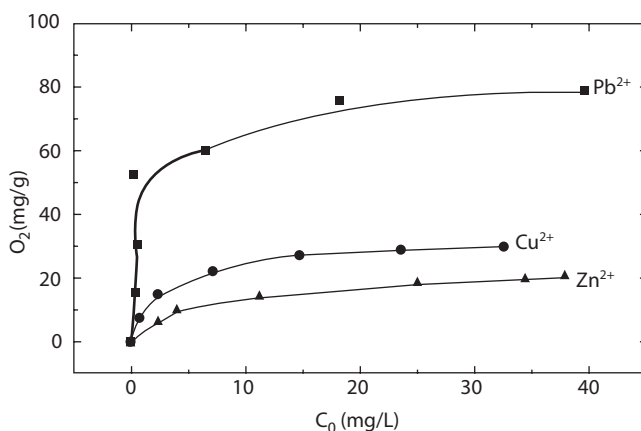
Natural zeolites gained significant interest, mainly due to their valuable property of ion-exchange capability. Among the most frequently studied natural zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II). It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pretreatment method and that conditioning improves its ion-exchange ability and removal efficiency [3, 4]. The role of pH is very important for the selective adsorption of different heavy metal ions [5–8]. The natural clay minerals can be modified with a polymeric material in a manner that significantly improves their capability to remove heavy metals from aqueous

solutions. These kinds of adsorbents are called clay-polymer composites [9–11]. Different phosphates, such as calcined phosphate, activated phosphate (with nitric acid), and zirconium phosphate, have been employed as new adsorbents for removal of heavy metals from aqueous solution [12–14]. Figure 10.1 shows the adsorption isotherm of Pb(II), Cu(II), and Zn(II) onto calcined phosphate at pH 5 [12]. Table 10.1 presents the highest reported metal adsorption capacities of low-cost adsorbents from various modified natural materials.

### 10.3.1.3 Adsorption on Industrial By-Products

Industrial by-products, such as fly ash, waste iron, iron slags, and hydrous titanium oxide, are chemically modified to enhance their metal removal performance from wastewater. Several studies have been conducted:

- Green sands, a by-product from the iron foundry industry, for Zn(II) removal [15].
- Iron slag was optimized for removal of Cu(II) and Pb(II) I using pH ranges from 3.5 to 8.5 [for Cu(II)] and from 5.2 to 8.5 [for Pb(II)] [16].
- Fly ashes from different sources were investigated as adsorbents for removal of toxic metals, e.g., bagasse fly ash, a solid waste from the sugar industry, for Cd(II) and Ni(II) removal from synthetic solution at pH ranging from 6.0 to 6.5 [17];



**Figure 10.1** Adsorption isotherm of Pb(II), Cu(II), and Zn(II) onto calcined phosphate. (Source: Aklil *et al.* 2004) [12].

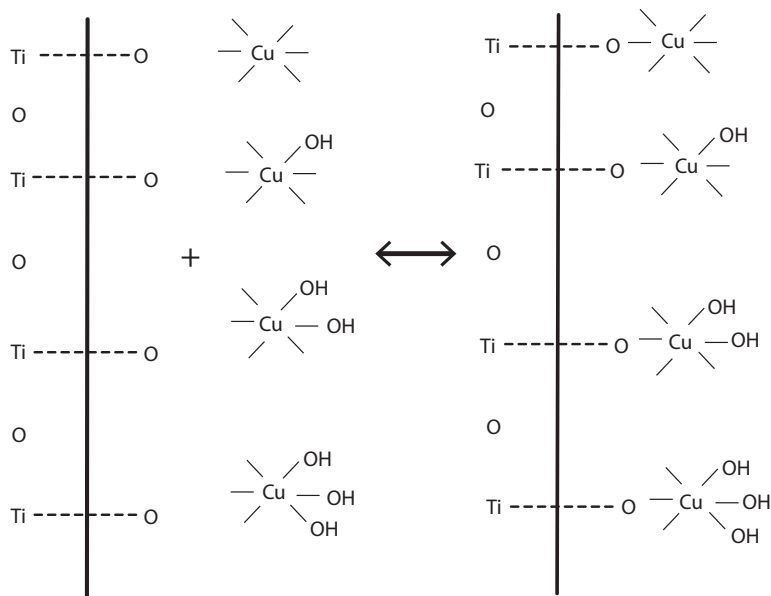
Table 10.1 Heavy metal adsorption capacities of modified natural materials.

| Adsorbent                         | Adsorption capacity (mg/g) |                  |                  |                  |                  |                  | References                    |
|-----------------------------------|----------------------------|------------------|------------------|------------------|------------------|------------------|-------------------------------|
|                                   | Pb <sup>2+</sup>           | Cd <sup>2+</sup> | Zn <sup>2+</sup> | Cu <sup>2+</sup> | Cr <sup>6+</sup> | Ni <sup>2+</sup> |                               |
| Zeolite, clinoptilolite           | 1.6                        | 2.4              | 0.5              | 1.64             |                  | 0.4              | Babel & Kurniawan (2003)      |
| Modified zeolite, MMZ             | 123                        |                  |                  |                  |                  | 8                | Nah <i>et al.</i> (2006)      |
| HCl-treated clay                  |                            |                  | 63.2             | 83.3             |                  |                  | Vengris <i>et al.</i> (2001)  |
| Clay/poly(methoxyethyl)acrylamide | 81.02                      |                  | 20.6             | 29.8             |                  | 80.9             | Sölenera <i>et al.</i> (2008) |
|                                   | 85.6                       |                  |                  |                  |                  |                  | Aklil <i>et al.</i> (2004)    |
| Calcined phosphate                | 155.0                      |                  |                  |                  |                  |                  | Moufliha <i>et al.</i> (2005) |
| Activated phosphate               | 4                          |                  |                  |                  |                  |                  | Pan <i>et al.</i> (2007)      |
| Zirconium phosphate               | 398                        |                  |                  |                  |                  |                  |                               |

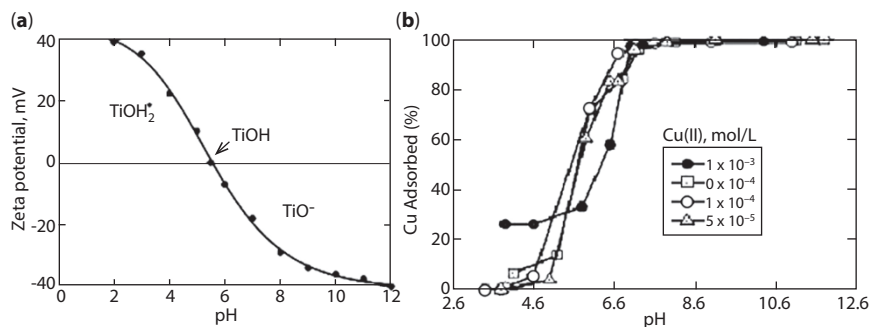
fly ash from coal-burning for removal of Cu(II) and Pb(II) ions [18].

- Sawdust treated with 1,5-disodium hydrogen phosphate was used for adsorption of Cr(VI) at pH 2 [19].
- Iron-based sorbents such as FerroSorp Plus [20] and synthetic nanocrystalline akaganeite were recently used for simultaneous removal of heavy metals [21].
- Hydrous titanium oxide for adsorption of Cr(VI) and Cu(II) [22, 23]. Barakat reported that the adsorbed Cu(II) aqueous species can undergo surface hydrolysis reaction as pH rises. This yields a series of surface Cu(II) complexes such as  $\text{TiO}-\text{CuOH}^+$ ,  $\text{TiO}-\text{Cu}(\text{OH})_2$ , and  $\text{TiO}-\text{Cu}(\text{OH})_3^-$  species. The formation of surface metal complexes can also be depicted conceptually by the following scheme (Figure 10.2).

Zeta potential of  $\text{TiO}_2$  and its adsorption behavior to Cu(II) in aqueous solution are shown in Figure 10.3a,b [23].  $\text{TiO}_2$  particles are negatively charged at  $\text{pH} \geq 6$ , and so complete Cu(II) adsorption was achieved at such pH range.



**Figure 10.2** The adsorption mechanism of Cu(II) on hydrous  $\text{TiO}_2$ . (Source: Barakat, 2005) [23].



**Figure 10.3** (a) Zeta potential of  $\text{TiO}_2$  in aqueous solution; (b) Adsorption of  $\text{Cu(II)}$  on  $\text{TiO}_2$ .

#### 10.3.1.4 Adsorption on Modified Agricultural and Biological Wastes (Biosorption)

The use of agricultural by-products in bioremediation of heavy metal ions is known as biosorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physicochemical pathways of mainly chelation and adsorption [24]. Resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk, have been used as adsorbents for heavy metal uptake after chemical modification or conversion by heating them into activated carbon. Some examples are presented in Table 10.2.

#### 10.3.1.5 Adsorption on Modified Biopolymers and Hydrogels

Biopolymers are capable of lowering transition metal ion concentrations to sub-part per billion concentrations. They are widely available, environmentally safe, and possess several different functional groups (such as hydroxyls and amines), which increase the efficiency of metal ion uptake and the maximum chemical loading possibility.

New polysaccharide-based materials are modified biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from the wastewater (Table 10.3).

Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells. Chitosan, which can be formed by deacetylation of chitin, is the most important derivative of chitin. Chitosan in partially converted crab shell waste is a powerful chelating agent and interacts very efficiently with transition metal ions [25]. Recently other modified



**Table 10.2** Heavy metal adsorption capacity of some agricultural and biological wastes.

| Adsorbent                          | Adsorption capacity (mg/g) |                  |                  |                  |                  |                  | References                      |
|------------------------------------|----------------------------|------------------|------------------|------------------|------------------|------------------|---------------------------------|
|                                    | Pb <sup>2+</sup>           | Cd <sup>2+</sup> | Zn <sup>2+</sup> | Cu <sup>2+</sup> | Cr <sup>6+</sup> | Ni <sup>2+</sup> |                                 |
| Maize cob & husk                   | 456                        | 43.7             | 495.9            |                  |                  |                  | Igwe <i>et al.</i> (2005)       |
| Orange peel                        |                            |                  |                  |                  |                  | 158              | Ajmal <i>et al.</i> (2000)      |
| Coconut shell-charcoal             |                            |                  |                  |                  | 3.65             |                  | Babel & Kurniawan (2004)        |
| Pecan shells activated C           |                            |                  | 13.9             | 31.7             |                  |                  | Bansode <i>et al.</i> (2003)    |
| Rice husk                          |                            | 2                |                  |                  |                  |                  | Bishnoi <i>et al.</i> (2003)    |
|                                    |                            | 0                |                  |                  | 79               |                  |                                 |
| Modified rice hull                 |                            |                  |                  |                  | 23.4             |                  | Tang <i>et al.</i> (2003)       |
| <i>Spirogyra</i> (green alga)      |                            |                  |                  | 133              |                  |                  | Gupta <i>et al.</i> (2006)      |
| <i>Ecklonia maxima</i> marine alga | 235                        |                  |                  | 90               |                  |                  | Fenga & Aldrich (2004)          |
| <i>Ulva lactuca</i>                |                            |                  |                  |                  |                  |                  | El-Sikaily <i>et al.</i> (2007) |
| <i>Oedogonium</i> sp.              | 145                        |                  |                  |                  |                  |                  | Gupta & Rastogi (2008)          |
| <i>Nostoc</i> species              | 93.5                       |                  |                  |                  |                  |                  | Gupta & Rastogi (2008)          |
| <i>Bacillus</i> biomass            | 467                        | 85.3             | 418              | 381              | 39.9             |                  | Ahluwalia & Goyal (2006)        |

**Table 10.3** Heavy metals adsorption capacity of modified biopolymers. (Source: Crini 2005) [27].

| Adsorbent                  | Adsorption Capacity (mg/g) |                  |                  |                  |                  |                  |
|----------------------------|----------------------------|------------------|------------------|------------------|------------------|------------------|
|                            | Pb <sup>2+</sup>           | Cd <sup>2+</sup> | Zn <sup>2+</sup> | Cu <sup>2+</sup> | Cr <sup>6+</sup> | As <sup>5+</sup> |
| Crosslinked chitosan       |                            | 150              |                  | 164              |                  | 230              |
| Crosslinked starch gel     | 433                        |                  |                  | 135              |                  |                  |
| Alumina/chitosan composite |                            |                  |                  | 200              |                  |                  |

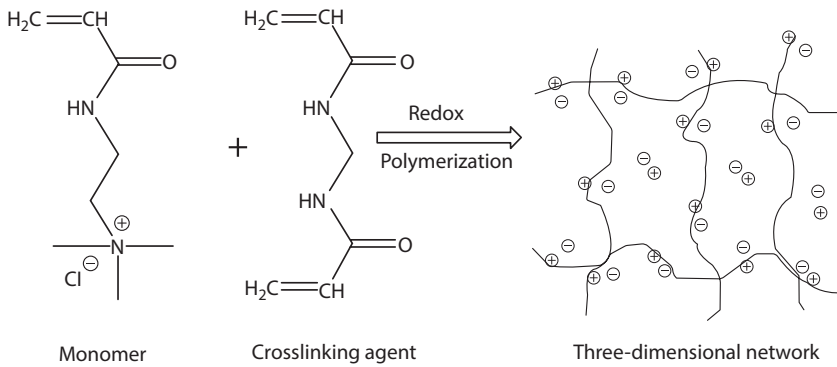
chitosan beads were proposed for diffusion of metal ions through cross-linked chitosan membranes (Liu *et al.* 2004). The excellent saturation sorption capacity for Cu(II) with the crosslinked chitosan beads was achieved at pH 5. [26] prepared new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of nonporous glass beads.

The sorption mechanism of polysaccharide-based materials is different from those of other conventional adsorbents. These mechanisms are complicated because they implicate the presence of different interactions. Metal complexation by chitosan may thus involve two different mechanisms (chelation versus ion exchange) depending on the pH, since this parameter may affect the protonation of the macromolecule [27].

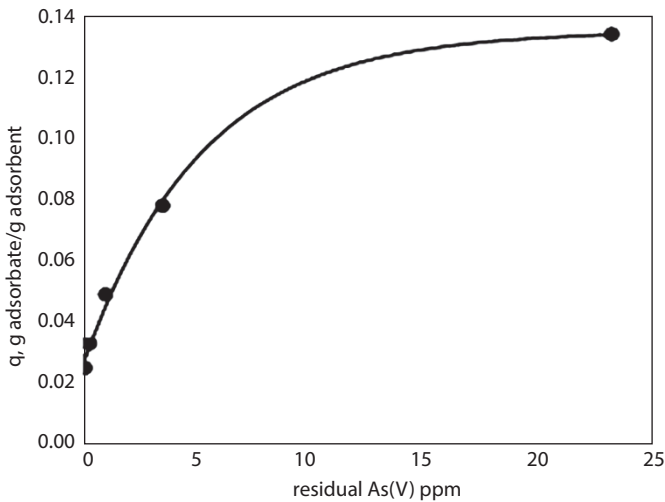
*Hydrogels* are crosslinked hydrophilic polymers capable of expanding their volumes due to their high swelling in water. They are widely used in the purification of wastewater by adsorbing heavy metals [28], e.g., poly(ethyleneglycol dimethacrylate-co-acrylamide) hydrogel beads; poly(vinylpyrrolidone-co-methylacrylate) hydrogel [29]; and poly(3-acrylamidopropyl) trimethyl ammonium chloride hydrogels [30]. The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metals inside. Figure 10.4 shows the schematic representation of polymerization/crosslinking reaction that results in three-dimensional network formation of cationic hydrogel, and the adsorption isotherm of As(V) onto the hydrogel is shown in Figure 10.5.

### 10.3.2 Membrane Separation/Filtration

Membrane separation is used for the treatment of inorganic effluent. It is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. There are three different



**Figure 10.4** Three-dimensional network formation of cationic hydrogel. (Source: Barakat and Sahiner 2008) [30].



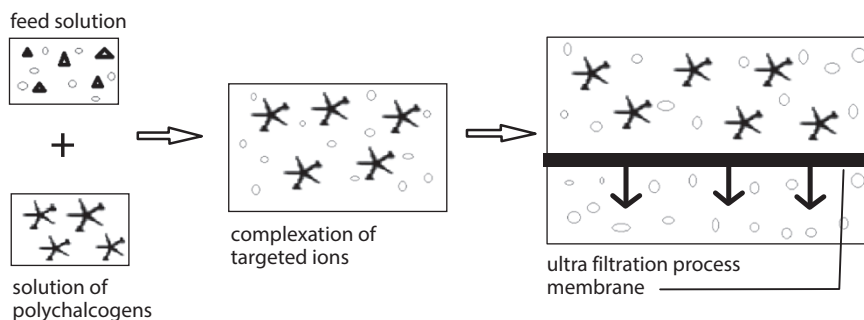
**Figure 10.5** Adsorption isotherm of As(V) onto the hydrogel. (Source: Barakat and Sahiner 2008) [30].

types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

- **Ultrafiltration (UF)** utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da). These unique specialties enable UF to

allow the passage of water and low-molecular-weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane [31].

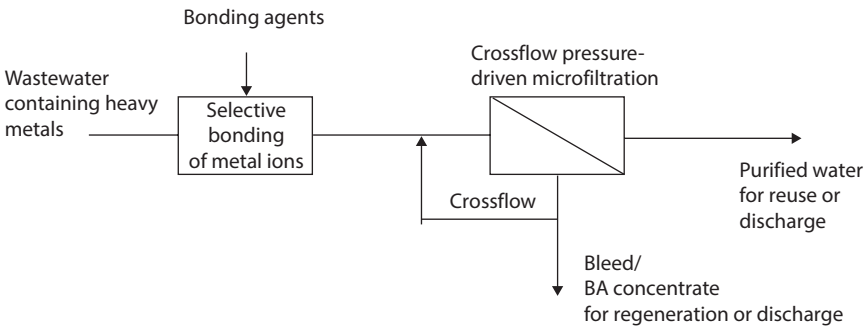
- **Complexation-Ultrafiltration** is a similar technique based on precipitation and ion exchange. The use of water-soluble metal-binding polymers in combination with ultrafiltration (UF) is a hybrid approach to concentrate selectively and to recover valuable elements as heavy metals. In the complexation-UF process, cationic forms of heavy metals are first complexed by a macroligand in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained; permeate water is then purified from the heavy metals [8, 32, 33]. The advantages of the complexation-filtration process is the high separation selectivity due to the use of a selective binding and low-energy requirements involved in these processes.
- **Polymer-Supported Ultrafiltration (PSU)** is another modification of UF [34]. It employs proprietary water-soluble polymeric ligands to bind metal ions of interest, and the ultrafiltration technique to concentrate the formed macromolecular complexes and produce an effluent that is essentially free of the targeted metal ions (Figure 10.6).
- **Surfactants-Enhanced Ultrafiltration** has been used for removal of lead and arsenic by using cationic (dodecylamine) and anionic (dodecylbenzenesulfonic acid) surfactants [35].
- **Reverse Osmosis (RO)** and **Nanofiltration (NF)** are technologies that remove copper and cadmium ions from



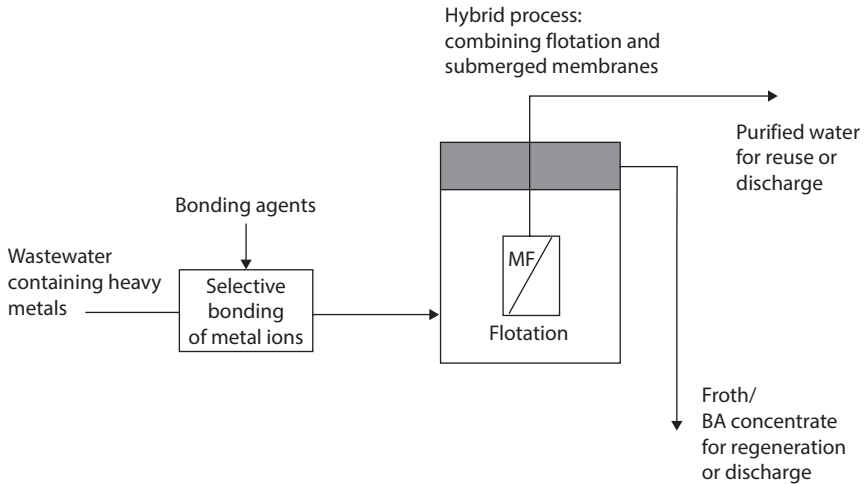
**Figure 10.6** Principles of polymer-supported ultrafiltration technique. (Rether & Schuster 2003) [34].

wastewater [36]. The removal efficiency of the heavy metals by RO process was 98% and 99% for copper and cadmium, respectively. Whereas NF was capable of removing 90% of the copper ions.

A new integrated process combining adsorption, membrane separation and flotation was developed for the selective separation of heavy metals from wastewater [37]. The process is diagrammatically explained in Figures 10.7 and 10.8. Moreover, many hybrid processes are also being developed.



**Figure 10.7** The integrated processes combining metal bonding and separation by crossflow membrane filtration (for low-contaminated wastewater). (Source: Mavrov *et al.* 2003) [37].



**Figure 10.8** The integrated processes combining metal bonding and separation by a new hybrid process (for highly contaminated wastewater). (Source: Mavrov *et al.* 2003).

### 10.3.3 Electrodialysis and Photocatalysis

Electrodialysis has also contributed to heavy metal removal. The photocatalytic process is an innovative and promising technique for efficient removal of heavy metal pollutants from water. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL) standards established.

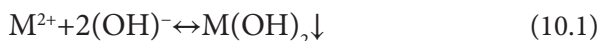
### 10.3.4 Chemical Oxidation and Advanced Oxidation

Chemical oxidation involves the introduction of an oxidizing agent to the polluted water, causing electrons to move from the oxidant to the pollutants, which undergo structural modification and become less destructive. However, chemical oxidation may produce toxic by-products.

Advanced oxidation through processes such as steam stripping, air stripping, or activated carbon adsorption, can help in removing any toxic by-products of chemical oxidation. Chemical oxidation and advanced oxidation are always used for the pretreatment of heavy metal wastewater containing organic compounds.

### 10.3.5 Chemical Precipitation

Chemical precipitation involves adding a precipitation reagent to the polluted water, resulting in a chemical reaction that converts the dissolved metals into solid particles. The particles can then be aggregated by chemical coagulation and removed by filtration or sedimentation. Chemical precipitation is the most common method for removing dissolved heavy metals from polluted water. It is also among the least expensive technologies and is always combined with chemical coagulation for heavy metal wastewater treatment. However, it is not effective for treating polluted water with high acid content, as in acidic water it produces a large quantity of toxic sludge that needs to be treated with chemical stabilization and disposed of properly. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation 10.1.

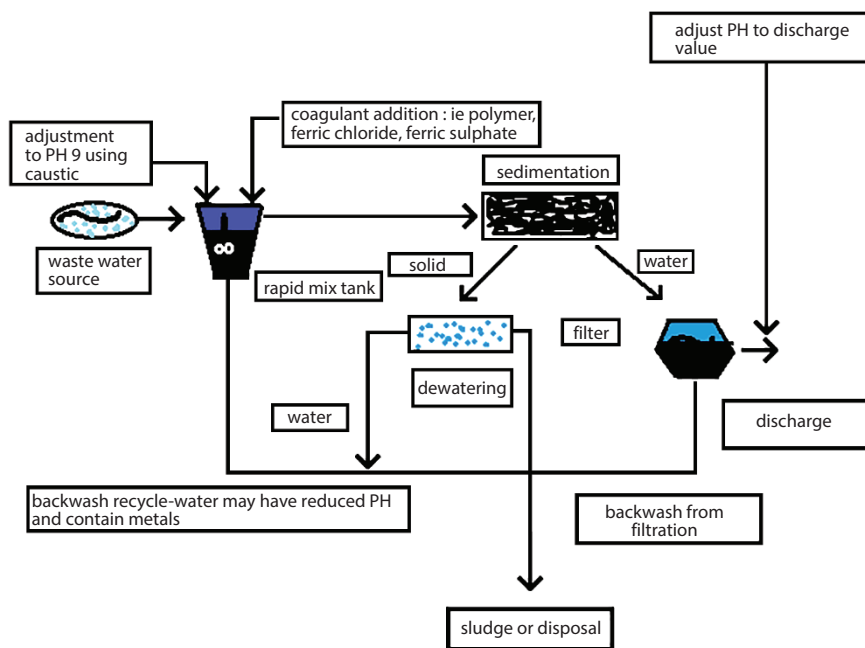


where  $M^{2+}$  and  $OH^{-}$  represent the dissolved metal ions and the precipitant, respectively, while  $M(OH)_2$  is the insoluble metal hydroxide. Adjustment

of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation (Figure 10.9). Lime and limestone are the most commonly employed precipitant agents due to their availability and low cost. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal.

### 10.3.6 Chemical Coagulation

Chemical coagulation is always used following chemical precipitation; it destabilizes fine solid particles so that they aggregate during chemical flocculation. The particles are normally negatively charged, preventing them from forming larger groups and settling. Chemical coagulation introduces positively charged coagulants that reduce the negatively charged particles, enabling them to form larger groups. An anionic flocculant introduced to



**Figure 10.9** Processes of a conventional metals precipitation treatment plant. (Source: Wang *et al.* 2004) [38].

the mixture reacts against the positively charged mixture to bind the particles into larger groups and can be removed by filtration or sedimentation. It is not acid-resistant, so it is not appropriate for treating polluted water with high acid content. The sediment also contains heavy metals that must be treated by extra processes such as neutralization or dehydration.

### **10.3.7 Chemical Stabilization**

Chemical stabilization involves treating sludge, a by-product of chemical precipitation and chemical coagulation, with an oxidant which decreases the rate of toxic growth within the sludge. The sludge is either incinerated or solidified and then disposed of in landfills.

### **10.3.8 Ion Exchange**

Ion exchange method is used successfully in the industry for the removal of heavy metals from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion-exchange resins. An ion exchange is a chemical reaction in which heavy metal ions are exchanged for a similarly charged ion attached to a solid particle. The solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The reusability of the adsorbed metal is high with ion exchange. However, ion exchange is the most expensive technology and is also limited by the matrix of the polluted water with high acid levels and high concentration of heavy metal ions, thus requiring pretreatment before the process.

### **10.3.9 Waste LCD Panel Glass**

Waste LCD panel glass is a kind of alkaline earth boro-aluminosilicate with stable composition and high purity. Every year, about 600 metric tons of LCD panels are discarded. The waste LCD panels are buried in landfills, creating an enormous burden on the environment. A unique technique to transform it into a novel type of heavy metal adsorbent (green glass adsorbent) has increased its reuse value. The production process to create green glass adsorbent from waste LCD panel glass involves crushing, extraction, blending, purification, reusing, leaching, concentration, and transformation. Due to the large amount of microporous material, high surface area and asymmetric charges and reactive sites, the green glass adsorbent is able to adsorb heavy metal by specific mechanisms such as nanometer porous absorption, ion



exchange and electrostatic charge attraction. The glass structure is retained on purpose during the transformation process, so the green glass adsorbent can work with acids and chemicals even in very low pH medium (equating to 0). As a result, the use criteria are wider, and the scope is broader for the green glass adsorbent. Waste LCD panel glass as a raw material is low cost and the transformation process cost is also low. Furthermore, the green glass adsorbent can adsorb heavy metal without pretreatment, produces no toxic by-products, and is easily regenerated for reuse.

#### **10.3.10 Electrolytic Recovery or Electrowinning**

Electrolytic recovery or electrowinning process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage is that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced.

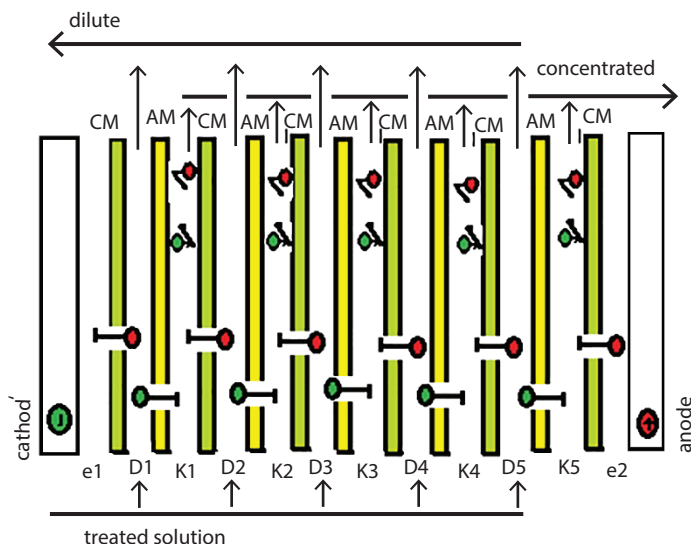
#### **10.3.11 Electrodialysis**

Electrodialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membranes [39]. Figure 10.10 shows the principles of electrodialysis.

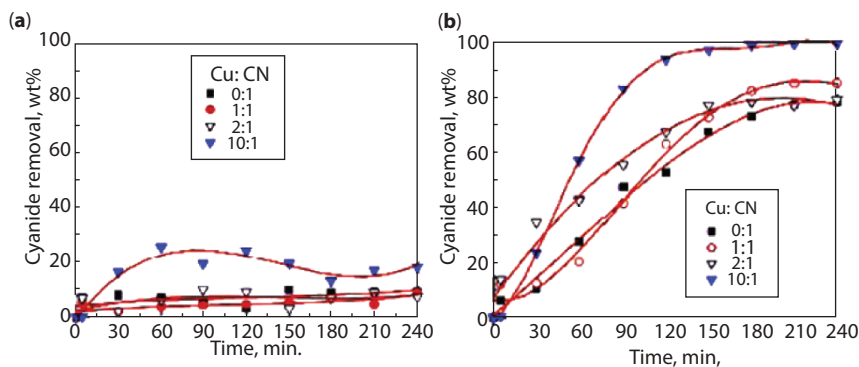
The ED process offers advantages for the treatment of wastewater laden with heavy metals. Moreover, valuable metals such as Cr and Cu can be recovered by this method. Since ED is a membrane process, it requires clean feed, careful operation, and periodic maintenance to prevent any stack damages.

#### **10.3.12 Photocatalysis**

Photocatalytic process in aqueous suspension of semiconductor using solar energy or UV radiation [40] has received considerable attention for rapid and efficient destruction of environmental pollutants (Figure 10.11). Upon illumination of semiconductor-electrolyte interface with light energy greater than the semiconductor band gap, electron-hole pairs ( $e^-/h^+$ )

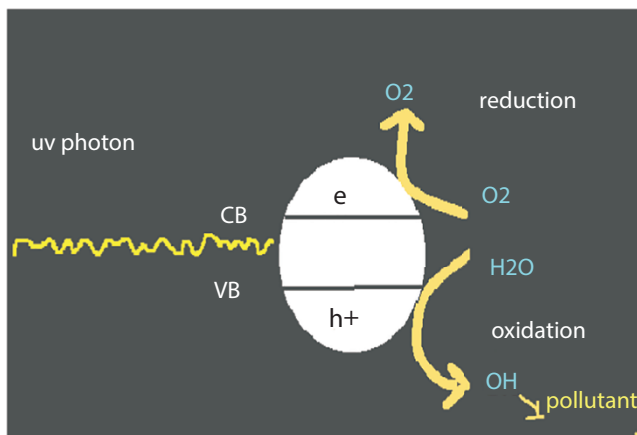


**Figure 10.10** Electrodialysis principles: CM – cation-exchange membrane, D – dilute chamber, e1 and e2 – electrode chambers, AM – anion exchange membrane, and K – concentrate chamber. (Source: Chen, 2004) [39].



**Figure 10.11** Cu(II) removal by UV illuminated TiO<sub>2</sub> at various Cu(II)/CN<sup>-</sup> ratios: (a) without UV light and (b) with UV light. (Source: Barakat *et al.* 2004) [40].

are formed in the conduction and the valence band of the semiconductor, respectively [41]. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Various semiconductors have been used: TiO<sub>2</sub>, ZnO, CeO<sub>2</sub>, CdS, ZnS, etc. As generally observed, the best photocatalytic performances with maximum quantum yields are always obtained



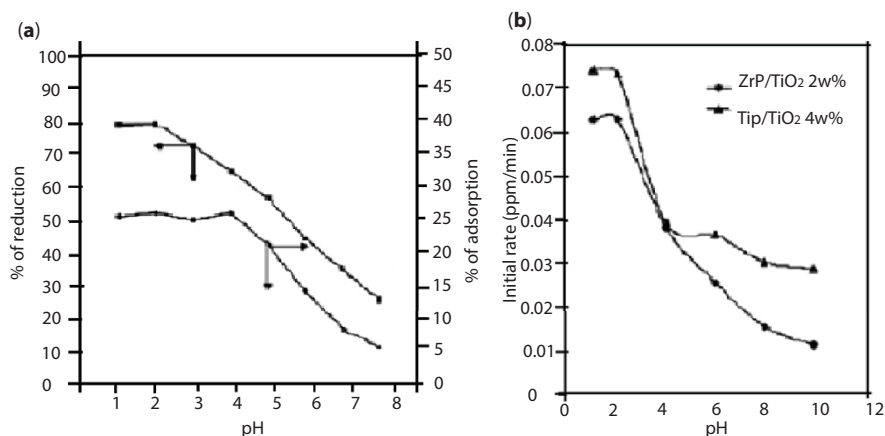
**Figure 10.12** The conceptual reaction path of photocatalysis over  $\text{TiO}_2$ . (Source: Herrmann 1999) [41].

with titanium dioxide. Figure 10.12 shows the conceptual reaction path of photocatalysis over titanium dioxide particle.

$\text{TiO}_2$  thin films immobilized on glass plates and prepared by sol-gel technique were investigated [42] for successful photocatalytic reduction of  $\text{Cr(VI)}$ . To enhance efficiency of  $\text{TiO}_2$ , its modification with sulphate [43]; loading  $\text{TiO}_2$  on zirconium phosphate (ZrP) and titanium phosphate [44] (Dasa *et al.* 2006); presence of organic compounds [45, 46] and the impact of pH have all been investigated (Figure 10.13).

## 10.4 Evaluation of Heavy Metals Removal Processes

In general, physicochemical treatments offer various advantages such as their rapid process, ease of operation and control, and flexibility to change of temperature. Unlike in biological system, physicochemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Whenever it is required, chemical plants can be modified. In addition, the treatment system requires less space and installation cost. Their benefits, however, are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high energy consumption and handling costs for sludge disposal. However, with reduced chemical costs (such as utilizing low-cost adsorbents) and a feasible sludge disposal, physicochemical treatments have been found to be one of the most suitable treatments for inorganic effluent [48].



**Figure 10.13** Effect of pH of the solution on the photocatalytic reduction of Cr(VI) over (a)  $\text{TiO}_2$  modified with sulphate. (Source: Lv *et al.* 2008) [47]. (b)  $\text{TiO}_2$  loading on zirconium phosphate (ZrP) and titanium phosphate (Source: Dasa *et al.* 2006) [44].

In water containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds, and a pretreatment step to remove or destroy organics is generally required. Pyrometallurgy, which is able to decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The most promising methods to treat such complex systems are the photocatalytic ones which consume cheap photons from the near-UV region. These photocatalysts serve as electron relays from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds (less than ppm). Table 10.4 summarizes the main advantages and disadvantages of the various physicochemical treatments.

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent.

## 10.5 Role of CNF in Removing Heavy Metals

Because of the many broken graphene sheets on its surface, CNF has very high specific surface area with more sites for adsorption of heavy metals.

**Table 10.4** Advantages and disadvantages of the various physicochemical methods for removal of heavy metal from wastewater.

| # | Treatment                      | Advantages                                                                      | Disadvantages                                                        | References                                                                     |
|---|--------------------------------|---------------------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------------|
| 1 | Chemical precipitation         | Low capital cost, simple operation                                              | Sludge generation, Extra operational cost for sludge disposal        | Kurniawan <i>et al.</i> (2006) [48]                                            |
| 2 | Adsorption with new adsorbents | Low cost, Easy operation, Works at wide pH range, High metal-binding capacities | Low selectivity, Production of waste products                        | Babel & Kurniawan (2003) [3]; Akil <i>et al.</i> (2004) [12]                   |
| 3 | Membrane filtration            | Small space requirement, Low pressure, High separation selectivity              | High operational cost due to membrane fouling                        | Kurniawan <i>et al.</i> (2006) [48]                                            |
| 4 | Electrodialysis                | High Separation selectivity                                                     | High operational cost due to membrane fouling and energy consumption | Mohammadi <i>et al.</i> (2005) [49]                                            |
| 5 | Photocatalysis                 | Removes metals and organic pollutant simultaneously; Less harmful by-products   | Long duration time, Limited applications                             | Barakat <i>et al.</i> (2004) [40]; Kajitvichyanukula <i>et al.</i> (2005) [42] |

Moreover, addition of appropriate functional groups also plays an important role in removal of heavy metal.

### 10.5.1 Suitability of Chemically Synthesized CNF for Heavy Metal Removal

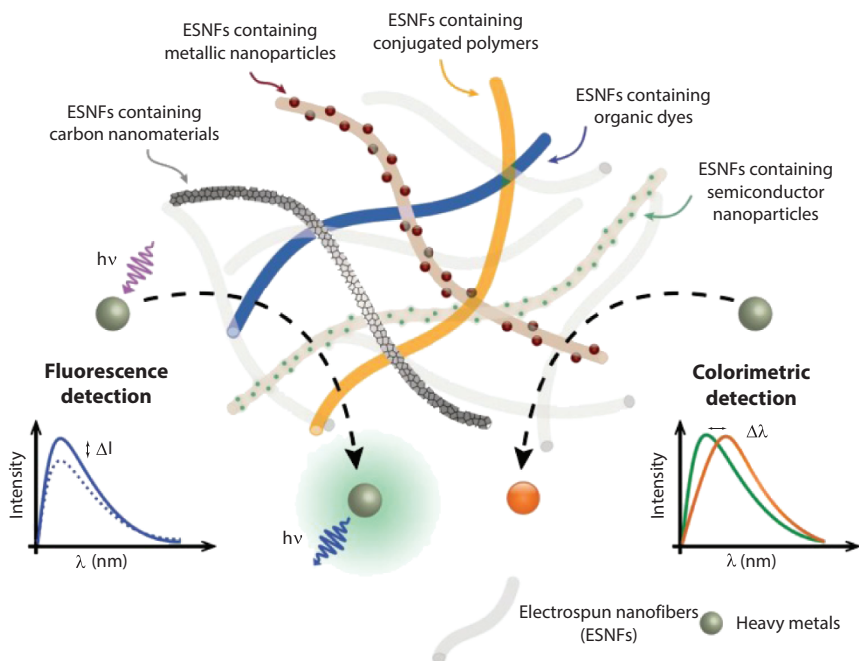
One of the popular examples of chemically synthesizing CNF is by using electrospun PAN (Poly-acrylo-nitrile) plastic as the precursor (See Chapter 1 of this book) in the presence of a catalyst at high temperature. Electrospinning is a technique that allows the fabrication of continuous fibers with diameters down to a few nanometers. It has been studied and used for its adsorption capacity, and it is found that the nitrile group from PAN nanofibers gets converted to amine group, which is highly active in forming strong complexes with metal ions. pH is one of several key parameters that provides pertinent information on the adsorption of heavy metals from aquatic systems. However, since the surface area of the particle size increases as the size of the particle decreases, there is an increase in cytotoxicity. Fibers of poly-L-lactide (PLLA) were tested for removal of Cu(II) and As(II). The results suggested that maximum percent removals (95%) for all metals tested were reached within 5 minutes. PVA: PAA nanofibers are one of the best for adsorption.

Nanofibrous mats based on chitosan have also been used for removal of copper (II) ions and other heavy metal ions from the aqueous medium. There is the possibility of building up multifunctional nanostructures by functionalizing the nanofibers with a wide range of optically active materials, as illustrated in Figure 10.14.

### 10.5.2 Suitability of Biogenic CNF

The removal efficiency of adsorbent is mainly related to the pore-size distribution, size of the adsorbent molecule, surface properties, chemical structure and solution pH of adsorbate. These physicochemical properties are very important because they have an influence on the interactions between the surface of adsorbent and adsorbed molecules [50]. Various carbon-based fibrous materials have been used as biosorbent for removal of heavy metals from aqueous medium, for example:

- ***Keratin protein fiber*** (AKF™) is a structured protein microfibril, consisting of numerous nano-sized pores. The mechanism of heavy metal uptake onto keratin protein involves a combination of several steps such as adsorption,



**Figure 10.14** Scheme of electrospun nanofibers (ESNFs) modified by distinct nanomaterials for applications in optical sensors for heavy-metal detection. The lower part of the figure provides a schematic showing the principles of optical detection by fluorescence quenching (left) or by the color change (right) of the ESNFs in the presence of the heavy metal ion.

precipitation, and ion exchange. Keratin protein has good tensile strength and is stable over a wide pH range.

- **Bio-waste-derived nanofibers** are an economically feasible, industrially scalable material having mechanical and adhesion characteristics that are appropriate for removing heavy metal. These carbon nanofibers (CNFs) can be fabricated from a wide range of plants and hold great promise as adsorbents for removal of heavy metal ions from polluted water. Mechanical properties of mats created from such nanofibers were also bonded both chemically (using aldehyde and ionic crosslinkers) and physically (by means of wet and thermal treatment) to increase the tensile strength to widen their range of applications.
- **Other carbon-based materials**, such as charcoal, mesoporous carbons [51, 52] and coal-based mesoporous

activated carbon [53], have been investigated for the removal of contamination from water systems. However, these adsorbents have relatively small adsorption capacity, less physical stability and slow process kinetics.

- **Activated carbon** is characterized by their highly developed internal surface area and porosity. The development of micro- and mesoporosity is of great importance because it allows the carbons to absorb large amounts and various types of chemicals from gases or liquids [54]. Activated carbon is a form of amorphous carbon which is a highly porous material with a broad pore size distribution. The large surface area of activated carbons is responsible for the adsorption of metal ions.
- **Carbon nanomaterials**, such as carbon nanotubes (CNTs), carbon spheres [55], carbon nanobeads (REF) and carbon nanofibers (CNFs) have also been developed as an adsorbent and thin film membrane [52]. The nanomaterials exhibited higher surface area compared with that of the conventionally available macromaterials as a function of mass.

## 10.6 CNF to Remove Heavy Metals

Carbon-based nonmaterials are a class of significant and widely used engineering adsorbent. As a relatively newer member of the carbon family, CNTs and carbon nanofibers (CNFs) have exhibited great potentials as an attractive adsorbent in wastewater treatment. Li *et al.* reported that CNTs with more defects and poor quality possess higher surface area and exhibit better lead sorption capacity compared to aligned CNTs [56]. As compared to CNTs, CNFs have significantly higher surface-to-volume ratio, exposed edges and chemical reactivity, hence show excellent adsorption capacity for various heavy metal contaminants. Moreover, CNF has higher pore volume than CNTs. Thus, the CNFs have great potential applications in comparison with CNTs [57, 58] towards removal of heavy metal. In a nutshell, the key properties required for the use of any engineered nanomaterial for *in-situ* remediation of polluted groundwater are:

- (i) chemical reactivity,
- (ii) enough mobility within porous media,
- (iii) suitable substrate with high reusability, and
- (iv) high adsorption capacity.



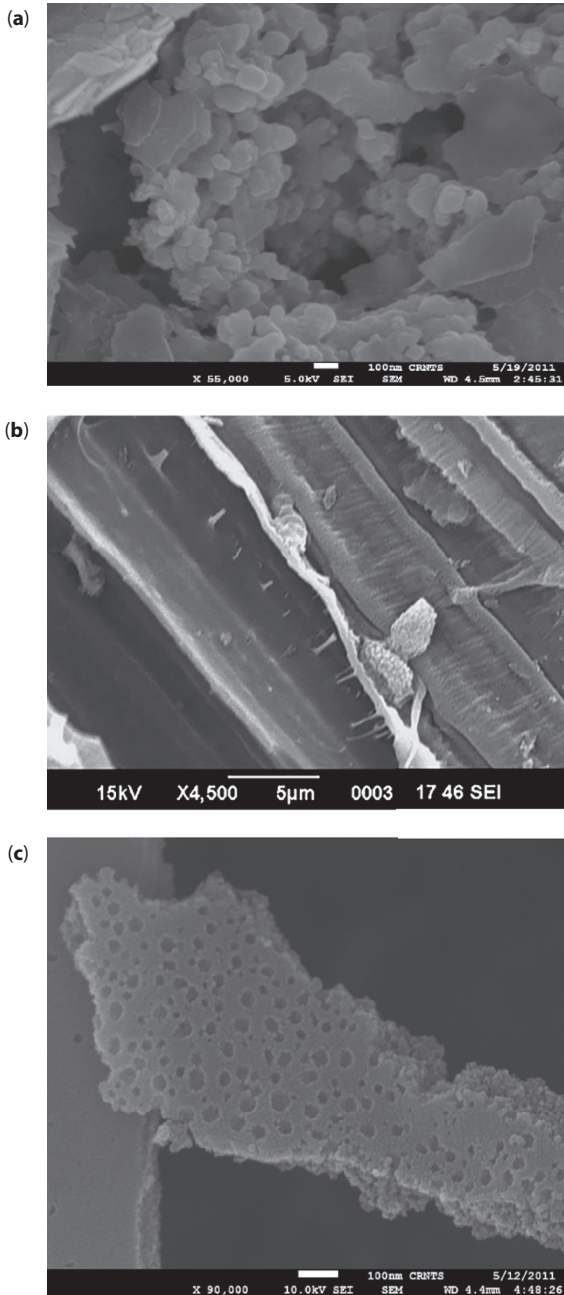
Surface functionalization plays a very important role in the adsorption properties of CNTs and CNFs. Both possibly contain functional groups such as -OH, -C=O, and -COOH depending on the synthetic procedure and purification process. Functional groups of materials can also be intentionally added by oxidation. Different kinds of acids, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$ , are used for surface oxidation to introduce -COOH on the surface of CNTs. These methods have been widely used for enhancing the adsorption properties of materials [59, 60].

Using CNFs-decorated beads for adsorption materials compared with conventional sorbents for removing pollutants from solution, such as commercial activated carbons and synthetic ion-exchange resins, are that the sorption using CNFs-decorated carbon beads-based materials as sorbents offer several advantages:

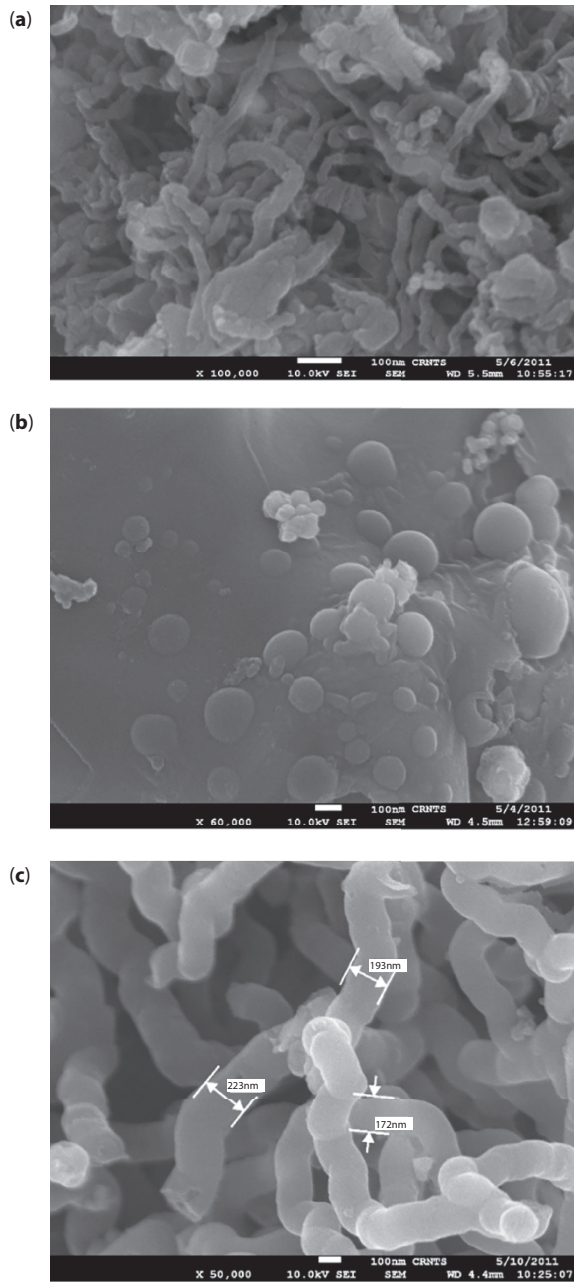
- They are economically viable.
- They have low operating cost.
- Volume of sorbent used is less than the conventional sorbents since they are more efficient.
- The materials are versatile.
- They possess a high capacity and high rate of adsorption, high efficiency and selectivity in detoxifying dilute or concentrated solutions.
- With repetitive functional groups, CNFs also provide excellent complexion materials for a wide variety of pollutants including dyes, heavy metals and pharmaceutical compounds.

Experiments done by our group on synthesis of CNF from (i) different parts (stem, calyx and cob hair) of the maize plant [62] and (ii) oils of different plants (Neem, Castor, Karanja) using different catalysts [63, 64], yield morphologically different types of CNF (Figures 10.15 and 10.16). The XRD analysis of CNF synthesized from all three oils showed a graphitic carbon crystalline nature. Raman analysis of CNF synthesized from all three parts of maize showed the presence of CNF.

It was observed that the morphology as well as surface area of CNMs are important factors for the adsorption of arsenic over the surface of CNM. From the three tried oils, CNMs obtained from Karanja oil show highest surface area ( $192.41\text{m}^2/\text{gm}$ ) with maximum adsorption of arsenic, i.e., 86%, followed by the Neem oil with surface area ( $97.39\text{m}^2/\text{gm}$ ) having 63% adsorption of arsenic (presented in Table 10.5).



**Figure 10.15** Different forms of CNF obtained from different parts of maize: (a) Beaded CNF from Cob Hair, (b) CNF showing channels and pores from Calyx, (c) CNF wall plate with many pores from Stem. (Source: Jayashri Shuklam, PhD Thesis, Solapur University) [61].



**Figure 10.16** Different forms of CNF obtained from oil of different plants: (a) CNF from Neem oil, (b) CNB from Castor oil, (c) CNF from Karanjia oil. (Source: Suman Tripathi, PhD Thesis, Solapur University) [65].

**Table 10.5** Comparative data (Yield, Morphology, Diameter, Surface area) of different CNMs obtained using nano-metal as catalyst and their Arsenic Adsorption capacity.

| Precursors  | Catalysts | Temperature<br>°C | Yield (g) | CNM Morphology | Diameter in<br>nm | Surface area<br>(m <sup>2</sup> /gm) | % Arsenic<br>Adsorption |
|-------------|-----------|-------------------|-----------|----------------|-------------------|--------------------------------------|-------------------------|
| Neem oil    | Co        | 500               | 0.325     | CNB            | 500 to 1000       | 78.39                                | 53                      |
|             | Zn        | 700               | 0.605     | CNB            | 250 to 1100       | 7.126                                | 00                      |
|             | Ni        | 900               | 3.108     | MWCNT          | 57 to 67          | 97.39                                | 63                      |
| Castor oil  | Zn        | 500               | 1.263     | CNS            | 100 to 200        | 11.87                                | 00                      |
|             | Ni        | 700               | 0.741     | CNS            | 150 to 250        | 30.88                                | 43                      |
|             | Co        | 900               | 3.436     | MWCNT          | 34 to 37          | 30.88                                | 49                      |
| Karanja oil | Ni        | 500               | 0.826     | MWCNT          | 50 to 100         | 26.13                                | 9.0                     |
|             | Co        | 700               | 1.625     | CNT            | 40 to 60          | 52.26                                | 40                      |
|             | Zn        | 900               | 1.177     | CNT            | 100 to 120        | 192.41                               | 86                      |

Similar results were obtained with CNF obtained from different parts of maize showing that the percentage adsorption is surface area dependent and it is maximum for the CNFs having largest surface area.

## 10.7 Summary

A comprehensive analysis indicates that heavy metals such as arsenic cadmium, chromium, lead, and mercury, occur naturally. However, anthropogenic activities contribute significantly to environmental contamination. These metals are systemic toxicants known to induce adverse health effects in humans, plants, soil and aquatic environment. Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent. In recent years, a wide range of treatment technologies, such as chemical precipitation, adsorption, membrane filtration, electrodialysis, and photocatalysis, have been developed for heavy metal removal from contaminated wastewater. Although many techniques can be employed for the treatment of wastewater laden with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economic parameters such as the capital investment and operational costs. Finally, technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for inorganic effluent. All the factors mentioned above should be taken into consideration in selecting the most effective and inexpensive treatment in order to protect the environment. In this chapter, the possibility of using CNF synthesized from agro-waste and plant-derived metabolite to adsorb as well as act as filtration base has been touched upon.

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# Carbon Nanofiber as Electrode in Li-Ion Battery

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*A battery by definition is a collection of cells. So the cell is a little can of chemicals. And the challenge is taking a very high-energy cell, and a large number of them, and combining them safely into a large battery.*

Elon Musk

## 11.1 Introduction

The demand for sustainable energy resources has urged researchers worldwide to explore alternatives for clean and green technology to harvest energy from renewable energy resources. The recent developments in the field of nanotechnology have proved to be a boon to cater to these demands for sustainable energy resources in terms of economy and efficiency combined with modern age technology. A rechargeable lithium-ion battery used in modern electronic gadgets like mobile phones, laptops, video cameras, etc., is a revolutionary example of such a technological reform.

Another important impetus for technological development in the field of battery is introduction of hybrid electric vehicles, reducing fuel consumption and gas emissions significantly. These batteries have rapidly replaced the less energetic and less environmentally friendly Ni-Cd batteries, as well as the bulkier Ni-MH cells, in portable devices. However, in large-scale batteries where cost is the key issue, the older battery types

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are still prominent. In 1958 a new metal was proposed to be used in non-rechargeable battery.

11.1.1 Why Lithium?

Lithium has the lightest weight, highest voltage and greatest energy density of all metals. The theoretical specific capacity of lithium is 3860 mAh/g and the redox potential is -3.01 V versus standard hydrogen electrode. These features attracted battery investigators and the idea of using lithium has now been in use for more than six decades in primary (non-rechargeable) batteries.

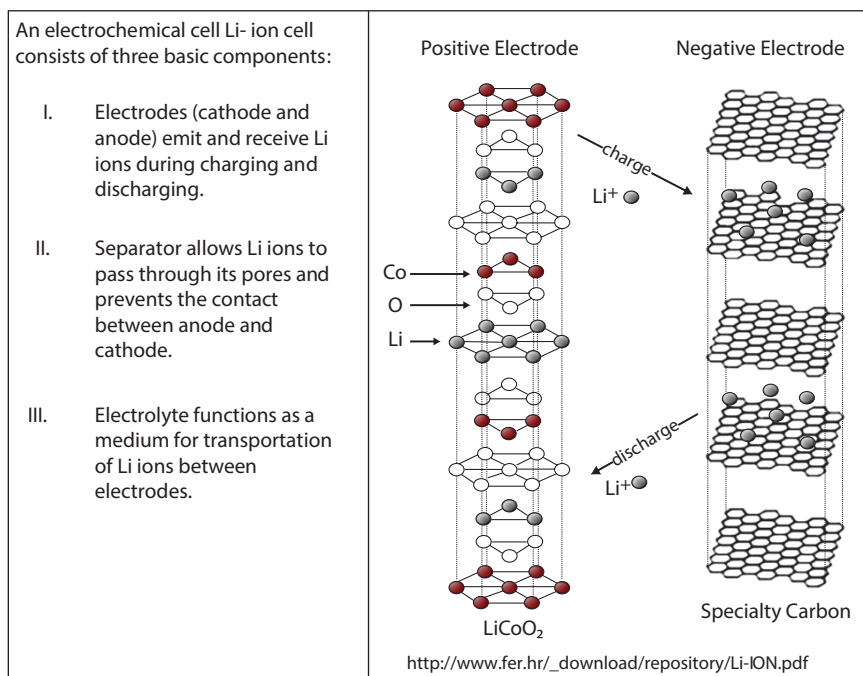
Rechargeable lithium-ion battery (LIB) was commercialized by Sony in 1991, realizing that the battery was a key technology, making their consumer products competitive. Till 1990, the lack of safe anode material was the main reason for non-commercialization of LIB. Besenhard and Eichinger (1976), Yazami and Touzain (1989), and Basu *et al.* (1979) [1–3] suggested that since graphite has a layered structure, it could be used to reversibly store Li through the process called intercalation and de-intercalation in the early 1980s. This idea was utilized by Yoshino *et al.* in 1987 [4] and he carried out the first safety test on LIB having graphite anode. However, maximum theoretical capacity of carbon-based anodes is 372mAh/g, hence some composite oxides of Sn and Si and other nano-forms of carbon are also being explored as alternate anode materials to enhance the energy density of LIB.

Accordingly, there are two types of lithium batteries:

| Lithium-metal battery                                                                                                                                                                                                                                                                                                                                                                     | Lithium-ion battery                                                                                                                                                                                                                                                                                                                                      |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"><li>• It is primary non-rechargeable type of battery.</li><li>• Anode is made up of pure lithium metal.</li><li>• It has high energy density (theoretical energy density 3862 mAh/g).</li><li>• Self-discharge rate is 10% in 5 years giving it longer shelf life.</li><li>• Poor rechargeabilty and susceptible to catch fire and explosion.</li></ul> | <ul style="list-style-type: none"><li>• It is secondary rechargeable type of battery.</li><li>• Anode is mainly graphite or carbon-based material.</li><li>• It has low energy density (graphite 372 mAh/g).</li><li>• Self-discharge rate is 5% in 24 h, then 1–2%/month (plus 3% for safety circuit).</li><li>• Good charging rate and safe.</li></ul> |

Carbon-based nanomaterials like carbon nanofiber (CNF) have attracted the interest of researchers in the field of rechargeable batteries as an option to graphite electrode and also as potential candidates for hydrogen storage in fuel cells because of a combination of adsorption ability, high specific surface, pore microstructure and low mass density. Use of CNF is supposed to enhance the performance and safety of LIB.

A typical Lithium-Ion battery is composed of electrodes (anode and cathode), a separator with pores and an electrolyte (Figure 11.1). The lithium-ion (Li-ion) battery fulfils many of the demands made within the areas of portable electronics and electric vehicles (hybrid electric vehicles), and is superior in many ways to the more common nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) batteries. Its superiority lies in the use of lithium with its large negative electrode potential (-3.04 V vs. SHE) and high energy density, and in the development of intercalation electrodes that can repeatedly accept and release  $\text{Li}^+$  ions on charge and discharge. Battery development is a major task for both industry and academic research, hence the effort to develop powerful, cheap and reliable



**Figure 11.1** Details of a typical Lithium-ion cell.

rechargeable batteries continues. The battery technology dominating the market today is the lithium-ion (Li-ion) battery.

The demand for Li-ion batteries had rapidly increased by the end of the 20th century due to the large interest in wireless devices, leading to the production of several million batteries per month today.

Increasing the energy density of Li-ion batteries has become an important focus of material research due to the urgent needs of energy storage for vehicles and grid-scale applications. To establish the improvement in performance of Li-ion batteries, since 1990 the most important factors under consideration are improvement in specific energy and volumetric energy density, cyclability, charging rates, stability and safety.

Improving the performance of a Li-ion battery puts an important emphasis on understanding of construction, working and some important concepts related to it.

A wide range of applications and vast commercial demand of LIB has led to extensive material research to reduce the cost, and improve the energy density, cycle life and safety aspects. The material choice of cathode, anode and electrolyte changes the overall chemistry and performance of LIB.

## **11.2 Types of Lithium-Ion Batteries**

There are five types of Li-ion batteries, which are briefly described below.

### **11.2.1 Lithium Nickel Manganese Cobalt Oxide Battery**

It is used in power tools such as e-bikes and electric powered trains, because it has advantages such as being less prone to heating, and has lower energy density (95–130) Wh/kg. But the cobalt is scarce and expensive.

### **11.2.2 Lithium Cobalt Oxide Battery**

This is used mostly in handled electronics, e.g., cell phones, laptops and cameras. Here also the cobalt is scarce and expensive, it is risky when damaged and has low discharge rate. Moreover, it has higher energy density.

### **11.2.3 Lithium Manganese Oxide Battery**

Apart from cell phones and laptops it is also used in hybrid vehicles. It has longer life, is inherently safe, low cost, less prone to heating and has lower energy density (110–120)Wh/kg.

#### 11.2.4 Lithium-Titanate Battery

It is specifically used in Mitsubishi MiEV electric vehicles. It can operate at very low temperature ( $-40^{\circ}\text{C}$ ), can be rapidly charged and discharged, has lower inherent voltage 2.4 V compared to 3.7 V, and has lower energy density (30–110)Wh/kg.

#### 11.2.5 Lithium Iron Phosphate Battery

It is used in medical equipment and in power tools. It dramatically reduces the risk of overheating. Moreover, it offers less volumetric capacity, has longer life, is inherently safe and has lower energy density (95–140)Wh/kg.

### 11.3 Theory of Generation of Power in Lithium Battery

According to Deng (2015) [5], “Lithium-ion cells are supplied in the form of battery pack composed of hundreds of cells that are connected through electrical connections and electronics. Individual cells can be connected in series to increase the voltage or parallel to increase the current or the combination of both. Multiple battery cells can be integrated into a module. Multiple modules can be integrated into a battery pack. For example, the 85 kWh battery pack in a typical Tesla car contains 7104 cells. A 400 V battery used in electrical equipment or vehicles may consist of a number of cells.”

The chemistry of LIB has been continuously changing due to the fusion of research in the field of material science and nanotechnology. However, the most commonly used materials in the construction of LIB are discussed below.

#### 11.3.1 Positive Electrode or Cathode

It consists of electroactive transition metal oxides of lithium which can liberate Li ions. Lithium cobalt oxide ( $\text{LiCoO}_2$ ) is most widely used in the batteries due to its high structural stability during electrochemical cycling, high energy density and ease of preparation in bulk quantities. Cobalt is toxic and being a rare element makes LCO batteries costly.

Spinel-shaped lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) and lithium nickel oxide ( $\text{LiNiO}_2$ ) are other potential candidates used as cathode materials having more safety but comparatively less energy density. Moreover, LNO is not easy to prepare on a large scale because of the difficult oxidation of



$\text{Ni}^{+2}$  to  $\text{Ni}^{+3}$  and the easy decomposition of  $\text{LiNiO}_2$  into Li-efficient compounds during a high-temperature synthesis.  $\text{LiMn}_2\text{O}_4$  has good thermal behavior and does not require expensive safety devices but it suffers from capacity fading due to Mn dissolution at high temperature. Recently, a comparatively cheaper lithium iron phosphate has also been used as cathode material in production of LIB for electrical vehicles.

### 11.3.2 Negative Electrode Anode

The most commercially popular negative electrode is graphite/carbon-based materials. Carbon-based materials have good electronic conductivity due to their layered structure and wide operating voltage from 0 to 3 V. The light weight and low cost are the other advantages that make carbon electrodes a better choice.

In graphitic carbons, lithium forms graphite intercalation compounds (GICs) at the highest level, which corresponds to an insertion of one lithium per 6 carbon atoms ( $x = 1$  in  $\text{Li}_x\text{C}_6$ ), and has a theoretical capacity of 372 mAh/g. This kind of structure can prevent the production of lithium dendrites and the problems associated with lithium metal electrode can be avoided to greater extent.

When the SEI film is sufficiently thick to prevent electron tunneling, the electrolyte reduction is suppressed and the electrode can be cycled reversibly. The capacity on the second and subsequent cycles is about the same, and lithium intercalation during charge and discharge is nearly 100% reversible.

### 11.3.3 Electrolyte

Aqueous electrolyte cannot be used in lithium-ion batteries as lithium metal reacts vigorously with water to form lithium hydroxide ( $\text{LiOH}$ ) and hydrogen gas. The battery pack is sealed properly to protect it from moisture.

The electrolyte in lithium rechargeable batteries falls into one of the following categories: non aqueous liquid electrolyte, a polymer electrolyte, a solid fast ionic conductor, or a combination of one or more of the above. Due to the low conductivity of solid electrolytes, particularly dry polymers, liquid electrolytes dominate in most electrochemical systems.

The solvents should be aprotic to be stable at negative potentials and should have high polarity to dissolve lithium salts and yield high ionic conductivity. The dielectric constant and viscosity of the solvents are the most important properties that determine the ionic conductance of the electrolyte solution.

The non-aqueous electrolyte used in battery should possess the following properties:

1. High ionic conductivity to minimize cell resistance and resistive heating of the device.
2. Good electrochemical stability to withstand the high voltage difference ( $>4$  V).
3. High chemical stability to prevent decomposition of electrolyte.
4. Low reactivity toward the components of the battery such as the electrodes, current collectors, and separators.
5. Non-toxicity to be accepted environmentally for ease of handling, mass production, and waste treatment.
6. Low melting point to provide good conductivity at low temperatures.
7. High boiling point to avoid explosions resulting from high pressure buildup in the cell.
8. Low cost to compete with existing power sources using aqueous electrolytes.

Alkyl carbonates have widely been used as excellent solvents in lithium batteries. Cyclic esters like propylene carbonate (PC) and ethylene carbonate (EC) have high viscosity. These solvents are mixed with low-viscosity solvents like dimethyl carbonate (DMC) or diethyl carbonate (DEC) to compensate for the viscosity.

Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is a common salt for application in rechargeable lithium-ion batteries. In spite of its high-ionic conductivity,  $\text{LiPF}_6$  electrolyte has distinctive disadvantages such as limited thermal stability and hydrolytic instability. Upon contact with water,  $\text{LiPF}_6$  decomposes to generate toxic gaseous products, most notably hydrofluoric (HF). Hydrofluoric reacts with the electrodes and increases the electrodes impedance.

Other salts used are lithium hexafluoro arsenate monohydrate ( $\text{LiAsF}_6$ ), lithium perchlorate ( $\text{LiClO}_4$ ), lithium tetrafluoro borate ( $\text{LiBF}_4$ ), and lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ).

## 11.4 Role of Carbon, Lithium and Cobalt in Li-Battery

The structure of  $\text{LiCoO}_2$  is layered, which provides 2D channels for lithium ion diffusion. In lithium-ion battery the Li ions move between the two

electrodes through a reversible process called intercalation (insertion) and deintercalation (removal). This kind of mechanism is also known as shuttle mechanism.

During the charging process, the two electrodes are connected externally to an external electrical supply. The electrons are forced to be released at the cathode and move externally to the anode. Simultaneously the lithium ions move in the same direction, but internally, from cathode to anode via the electrolyte. In this way the external energy is electrochemically stored in the battery in the form of chemical energy in the anode and cathode materials with different chemical potentials.

During the discharging process, a reverse process takes place, resulting in electrons moving from anode to the cathode through the external circuit, whereas the Li ions simultaneously move from anode to the cathode through the electrolyte. This results in release of stored chemical energy [6].

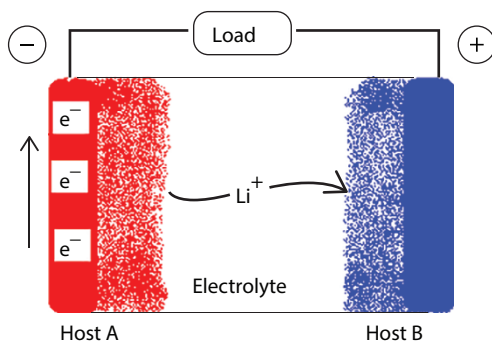
This can be explained in general as follows:



where Host A represents the negative electrode (Figure 11.2) and is generally based on a carbon material, e.g., graphite, whereas host B, the positive electrode, is typically based on a lithiated metal oxide such as  $LiCoO_2$ . The electrode materials determine the battery voltage and energy density. The high voltage of Li-ion batteries (4 V) is one major advantage; another is the low weight of the materials.

The gravimetric energy density (GED) of a battery in mWh/g is given as:

$$GED = E \times GC \quad (11.2)$$



**Figure 11.2** Schematic diagram of Li-ion battery showing movement of Li ions towards the electrodes.

Where E is the operating voltage (in V) and GC is the gravimetric capacity (in mAh/g). The latter indicates the total quantity of charge involved in the cell reaction. A reaction of compound 'A' with 'n' number of lithium ions and the corresponding number of electrons can be represented as:



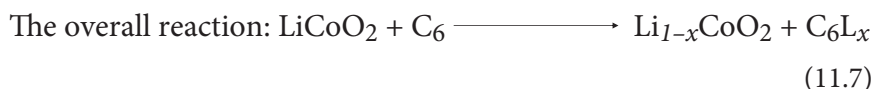
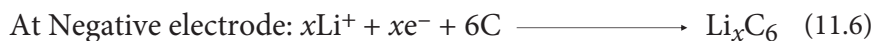
The theoretical gravimetric capacity, GC (in mAh/g), for compound A is given by:

$$GC = \frac{\left(\frac{1}{M}\right) \times nF}{3.6} \quad (11.4)$$

Where M is the molar mass of A and F is Faraday's constant. These factors are all influenced by the chemistry of the system, thus making the choice of battery materials crucial in designing a battery.

Thus, when  $LiCoO_2$  is used as cathode material and graphite is used as anode material, the transportation of Li ions between the two electrodes involves the redox reaction where the *Co is oxidized from  $Co^{3+}$  to  $Co^{4+}$  during the discharge process and the reverse process (reduction) occurs when the battery is being charged.* The electrochemical reactions taking place during discharge process can be represented as:

Chemical reaction (discharge):



In the above reaction x can be 1 or 0.

Thus, theoretical gravimetric capacity (mAh/g) of graphite anode will be

$$GC = xF/nM = 1 \times (96485 \text{ C/mol}) / 6 \times (12 \text{ g/mol}) = 372 \text{ mAh/g} \quad (11.8)$$

where  $x$  is number of electrons transferred in reaction,  $F = 96485$ , C/mol is Faraday's constant,  $n$  is number of moles of a chosen electroactive component that takes place in the reaction, and  $M$  is the molecular weight of the same electroactive component.

The electrochemical studies of cobalt cathode indicate that if all the  $\text{Li}^+/\text{Co}$  could be removed ( $x = 1$ ) then the specific capacity of cell will be  $280 \text{ mAhg}^{-1}$ . But the lithium ion cell which was commercialized by Sony in 1990 showed that the value of  $x$  in the above reaction is  $x < 5$  in the voltage range of 3–4.2 V.

Hence, if we take 0.5 as the practical number of electrons transferred, the theoretical gravimetric capacity will be  $\sim 140 \text{ mAhg}^{-1}$  as follows:

$$\text{GC} = xF/nM = 0.5 \times (96485 \text{ C/mol})/1 \times (98 \text{ g/mol}) = 137 \text{ mAh/g} \quad (11.9)$$

This limits the depth of allowable discharge voltage and it is recommended that lithium-ion cells should not be discharged below 2.50 V/cell. If the cell voltage falls below 2.5 V, the protection circuit turns off and a “boost” program is required to wake up the protection circuit.

Ideally a Li-ion cell is put to sleep when discharging below 2.50 V/cell. Copper dendrites grow if the cell is allowed to dwell in a low-voltage state for longer than a week. This results in elevated self-discharge, which could compromise safety.

Charging of LIB to higher voltage of 5.2 V and above results in the formation of cobalt (IV) oxide and finally evolution of oxygen due to peroxide formation, causing safety concerns [7].

### 11.4.1 Advantages of LIB

Rechargeable lithium-ion batteries offer significant advantages compared to Ni-Cd and Ni-MH cells. Some of the advantages are listed here:

- **Portability:** Li-ion batteries are lighter, about half the weight of Ni-Cd batteries and 30–50% smaller in volume, yet have a life span and energy density nearly twice that of Ni-Cd batteries. In cylindrical shape lithium ion batteries, the 18650 is an extremely popular size which means diameter 18 mm and length 65 mm. This battery can be easily used in all electronic equipment from laptops to cars.
- **Self-discharge:** All the batteries have the characteristic self-discharge depending upon type and chemistry of

battery. It is a permanent process and increases with aging and cycling. Increase in temperature also increases the self-discharge and it almost doubles with every 10 °C rise in temperature. Ni-Cd batteries show a self-discharge (capacity loss during storage due to internal leakage between the positive and negative cell plates) of 20–30% over a month, compared to the 5% of a Li-ion battery. The self-discharge of LIB is also supposed to be dependent on state of charge. Studies have shown that self-discharge increase with full state of charge (SOC) and there is minimum self-discharge at 40–60% SOC.

- **Rate of charge:** The rate of charge or discharge is also an important factor which indicates how frequently and how long one needs to charge the battery and is called the C-rate. If the battery is fully discharged in 1 h, releasing maximum capacity, it is rated as 1C. Most of the commonly used Li-ion batteries in portable devices take 1–4 h to return to the fully charged state and can typically be discharged at rates up to 1.5C continuously. Even though lithium batteries recharge more quickly, with an 80% charge in an hour and full charge within 2.5 hours, Li-ion batteries used in heavy electric vehicles require overnight charging. Some special devices with high current circuits can be used for fast charging but they reduce the battery life due to heating effect.
- **Environmentally benign:** Lithium-ion cells also do not present environmental hazards (i.e., those with lithium manganese oxide cathodes), especially compared with Ni-Cd batteries, because they contain no poisonous metals like lead, cadmium or mercury.
- **Memory effect:** Most importantly, Li-ion batteries have no memory effect; memory effect refers to a change in crystalline formation from the desirable small size to a large size which leads to reversible capacity loss, which happens because of earlier incomplete charge/recharge cycles. For Ni-Cd batteries, memory effect is a serious issue.
- **Gravimetric energy density (GED):** The gravimetric energy density of a battery is based on weight and expressed as mWh/g. Lithium-ion batteries store three times the voltage of competing cells, so that a single 3.7 V Li-ion battery can replace three Ni-Cd or Ni-MH cells. By weight, Li-ion batteries provide roughly twice the energy density (~150

Wh/Kg) of Ni-Cd cells. Consequently, to provide the same output as a Ni-Cd or Ni-MH battery, a Li-ion battery will weigh about half as much, an important factor in portable equipment. By volume, Li-ion cells provide about 25% and 40% more energy ( $\sim 400$  Wh/L) than Ni-MH or Ni-Cd cells, respectively. Greater energy in a small volume is an important factor in some of the most critical applications for batteries: laptop computers and cellular phones.

- **Wide temperature operating range:** Li-ion batteries also have a wide temperature operating range. The lithium-ion cell can be charged between 0 and 45 °C and discharged between -20 and 65 °C.
- **Specific capacity:** Specific capacity of  $\text{LiCoO}_2$  should be around  $140 \text{ mAhg}^{-1}$  in the voltage range of 3–4.2 V. High capacity, higher drain multi-cell packs are achieved by connecting multiple cells in parallel—something which is not easily achieved when using Ni-Cd or Ni-MH cells.
- **Cycle life:** Lithium-ion batteries offer long cycle life (greater than 1000 cycles).

#### 11.4.2 Disadvantages of LIB

Although Li-ion batteries have lots of advantages over Ni-Cd or Ni-MH cells, there are still a number of problems associated with metallic lithium used as anode, a few of them are:

- Li metal is highly reactive and can react with the aqueous electrolyte. While the thermal stability of lithium metal foil in many organic electrolytes is good, with minimal exothermic reactions occurring up to temperature near the melting point of lithium (181 °C), the large surface area of dendrites increases lithium reactivity, thereby lowering the thermal stability of the system.
- Another problem is the failure of attaining 100% lithium cycling efficiency. This occurs because lithium is not thermodynamically stable in the organic electrolytes and the surface of lithium is covered with a film of reaction products between the lithium and electrolyte.
- After repetitive charge/discharge cycling, its surface morphology changes. This makes cells become increasingly sensitive to abuse as they are cycled. In addition, the fine

metallic lithium can easily penetrate into the separator, which can cause an internal short circuit, resulting in heat generation and ignition.

- Every time lithium is stripped off and replaced during discharge and charge, a new lithium surface is exposed and then passivated with a new film, which means more lithium is consumed.
- Because of the mossy deposit, some lithium becomes electrochemically inactive on repeated cycling. In order to obtain a reasonable cycle life, a 3- to 5-fold excess of lithium is required.
- The failure to control the surface area of the lithium anode remains a problem, limiting the commercialization of lithium anode cells with liquid organic electrolytes.
- After several discharge and charge cycles, lithium dendrites grow at the surface of lithium metal or its alloys, which can penetrate through the separator and cause the direct contact between anode and cathode. Consequently, a short-circuit appears and large amounts of heat and gases are produced, leading to severe problems such as burning or explosion [8].
- For secondary batteries, the use of metallic lithium as negative electrode is unfortunately not possible due to an important lack of safety.

## 11.5 Role of CNF in Lithium Battery and Possibility of Increasing Its Efficiency

Research areas in the field of LIB are mainly contributing in the search for advanced materials for electrodes and electrolytes to improve the rate performance of lithium-ion batteries. Lithium-ion batteries with reduced time of charging are in great demand in the electric vehicles market [9, 10].

The ultimate negative electrode material in terms of energy density and voltage is lithium metal (theoretical energy density 3862 mAh/g). Application of pure lithium was tested commercially during the '80s but the poor surface properties of the material caused dendrites to grow during charging, eventually short circuiting the cell internally, causing an explosion and/or fire. The carbon-based materials used today have poorer energy densities (graphite 372 mAh/g), approximately the same voltage, but are safer. A variety of metal oxides are presently used and all result



in fairly high battery voltages (3–5 V). However, as a consequence of the poorer energy density of these materials (around 150 mAh/g) they generally limit the overall energy density of the battery.

Compounds that accommodate Li-ions ( $\text{Li}^+$ ) either in vacant sites or having open channels (1-, 2- or 3-dimensional) for Li-ion migration are capable of reversible lithium insertion. At present, carbon-based materials are the best choice for electrode material due to their characteristic good electronic conductivity and wide range of operating potential of 0–3 V and reversibility. They are cheap and nontoxic.

The power of a battery depends on the amount of active material taking part in the chemical reaction, i.e., Li in lithium-ion cells. Lithium-ion cells based on graphite-based electrodes have maximum capacity of 372 mAh  $\text{g}^{-1}$  and poor energy density (1–10 W h  $\text{kg}^{-1}$ ) [9, 10]. Thus, to improve energy density other materials need to be explored which can accommodate higher amounts of active electrode material lithium and provide energy equivalent to lithium metal electrode, i.e., capacity of 3861 mAh.g<sup>-1</sup>. Therefore, other types of carbon materials are widely studied as candidates to improve the energy density and long cycle performance in LIBs [11].

The newly developed carbon nanomaterials, such as carbon nanofibers (CNFs) [12], carbon nanotubes (CNTs), graphene [13, 14], mesoporous carbon spheres [15], and even some carbon nanocomposites [16, 17], have been explored to replace the traditional carbon materials for electrode materials, due to their excellent electronic conductivity and abundant porosity.

Carbon nanofibers (CNFs) belong to a class of one-dimensional (1D) carbonaceous materials with excellent electronic conductivity, leading to their use as conductive additives in electrode materials for lithium-ion batteries (LIBs). Additionally, CNFs show excellent lithium storage performance when used directly as anode materials via template and activation strategies to produce numerous intercalation sites. In the case of the non-carbon electrodes for LIBs, CNFs are capable of functioning as electron-conducting and porous substrates to enhance the overall electronic and ionic conductivity and stabilizing the structures of electrodes during cycling, facilitating the improvement of the electrochemical performance of non-carbon anode and cathode materials.

The diameter of CNF is very small compared to graphite. CNF has a similar layered structure to graphite. Three distinct structure types of CNF have been identified based on the angle of graphene layers with respect to the filament axis: coin-stacked, cup-stacked, and tubular. CNF has

remarkable electronic properties and many other unique characteristics. For this reason, CNF has received much attention. Therefore, in this study [18], investigated that coin-stacked CNF (CSCNF) was synthesized by the chemical vapor deposition (CVD) method, and CSCNF negative electrode for LIBs was evaluated.

## 11.6 Recent Advances in Lithium Battery Utilizing Carbon Nanomaterial and CNF

Rate capability of carbon-based anodes is improved by using materials like meso-carbon microbeads (MCMB) and micro-carbon fiber (MCF) with perfectly ordered structure and morphology. Still, the first-cycle irreversibility associated with SEI formation is high for these carbons. Other carbon-based materials with special structures, like fullerenes, CNT, graphene, and graphene-based composites, have also been studied as anodes [9]. They showed improved capacity but with more first-cycle irreversibility and hence do not have many implications.

Pyrolytic carbon consists of disordered carbon in the form of CNTs and CNF, having planar hexagonal network lagging in long-range order. It consists of a mixture of crystalline and amorphous carbon. This pyrolytic carbon has exhibited high specific capacity ( $x > 1$  in  $\text{Li}_x\text{C}_6$ ) but it suffers from huge capacity loss after the first cycle, resulting in irreversibility and fading [19]. This irreversibility is mainly attributed to two factors:

- Decomposition of electrolyte on the carbon surface resulting in SEI, which grows with time and prevents the insertion of lithium ion into the electrode. This leads to an increase in internal resistance of cell and irreversibility with cycling.
- Intercalation of certain organic solvent molecules along with lithium ions in the graphite matrix leading to expansion of anode material. This causes distortion in graphite structure and its capacity is reduced [20].

The increasing demand for higher capacity lithium-ion batteries for their potential use in electric vehicles has compelled researchers worldwide to focus on disordered carbon allotropes, which were easily synthesized using organic precursors and also by pyrolysis of waste biomass [21–23]. Performance of CNF synthesized from various precursors is discussed in brief below.

### 11.6.1 Polyacrylonitrile (PAN)

Kim and coworkers prepared CNFs from PAN and applied them as electrode materials for LIBs, demonstrating a high initial storage capacity of  $450 \text{ mA h g}^{-1}$  at  $0.03 \text{ A g}^{-1}$  but with a very unstable performance [24]. After that, Ji *et al.* prepared composite CNFs from PAN/PPy (polypyrrole), which exhibited a large reversible storage capacity of  $556 \text{ mA h g}^{-1}$  at  $0.05 \text{ A g}^{-1}$  and superior stability [25].

### 11.6.2 Walnut Shell

Tao *et al.* (2018) prepared CNF [26] from walnut shells for flexible anode materials for lithium-ion batteries and observed excellent cycling performance having specific capacity above  $200 \text{ mAhg}^{-1}$  after 200 cycles at  $100 \text{ mAhg}^{-1}$ .

### 11.6.3 FeOx-CNT/CNF Composite

Joshi *et al.* (2017) [27] prepared lightweight, flexible composite anode material consisting of CNF loaded with CNT and iron oxide nanoparticles. The FeOx-CNT/CNF electrode maintained a capacity of  $1008 \text{ mAhg}^{-1}$  at a current density of  $100 \text{ mA g}^{-1}$  after 100 cycles.

### 11.6.4 Carbon Nanobeads (CNB) from Camphor

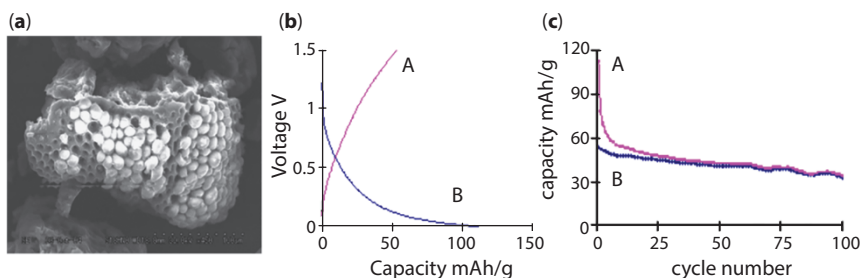
Sharon *et al.* (1998) [28] have been making efforts to find suitable plant-derived precursors to synthesize carbon nanomaterials. Camphor was a very successful precursor during this course of study. They have synthesized carbon nanobeads (CNB) from camphor and have also studied the intercalation of lithium with carbon [29–33]. It was found that almost 65% of the theoretical value could be obtained by carbon nanobeads. The intercalation of Li-ion with carbon depends upon various factors such as pore size (either the size of the diameter of the CNT or pore size of channels present in fibrous carbon materials), density, surface area, activation of CNM, etc. As discussed earlier, examination of the literature suggests that the capacity and reversibility of lithium interaction depends largely on the surface area, pore size and morphology of carbon nanomaterials. Because the structure of carbon fibers obtained by pyrolysis of plant precursors depends upon the structure of seeds and stems, researchers came up with the idea of pyrolyzing various different plant parts, like seeds, stems and fibers, to examine which part of the plant and its pyrolysis conditions gives

a better lithium intercalation. Moreover, for such precursors no catalyst is needed for the formation of CNM. It is also expected that carbon obtained from the pyrolysis of seeds or stems of plants would produce a type of porous fibers difficult to produce otherwise. Thus, it would be interesting to examine the role of such natural porous materials as the anode in lithium battery.

### 11.6.5 Tea Leaves

Sharon's group [34] used highly porous fibrous carbon fibers and carbon nanobeads (Figure 11.3a) synthesized by pyrolyzing tea leaves (*Ehretia microphylla*). These porous carbon and carbon beads were used as the anode in Li secondary batteries. Results of charging/discharging up to 1.5 V and number of reversible cycle are shown in Figure 11.3b, c. In the first cycle of discharging the carbon trend showed lower value of capacity ( $\sim 100$  mAh/g). Carbon showed slow a decrease in capacitance with the number of cycles, though its capacitance at 100th cycles was 63.31 mAh/gm. Efficiency of charging and discharging was more than 96%; exhibiting relatively high reversibility in charging-discharging profiles and good cycle stability.

Similar studies were performed by the same group using fibrous carbon materials prepared from soapnut seeds (*Sapindus mukorossi*), jackfruit seeds (*Artocarpus heterophyllus*), date seeds (*Phoenix dactylifera*), neem seeds (*Azadirachta indica*), tea leaves (*Ehretia microphylla*), bamboo stem (*Bambusa bambos*) and coconut fiber (*Cocos nucifera*) by pyrolysis. The analysis of size of nanopores and capacity of battery suggested that carbon materials should possess a certain specific pore size in order to give



**Figure 11.3** (a) SEM micrograph of carbon nanomaterials obtained from tea leaf, (b) represents charge curve and (c) represents discharge curve and capacity of Li-ion cell. (Source: Bhardwaj *et al.*, *Asian J. Exp. Sci.* 22(2), 89-93, 2008) [34].

optimum capacitance for a lithium battery. Moreover, carbon [35, 36] materials should possess more graphitic structure and less D-band to give optimum capacitance. Soap-nut seeds gave the best capacitance value of 130 mAh/g even after the 100th cycle of charging/discharging and maintained the capacitance throughout.

### 11.6.6 Various Carbon Materials

Other carbon-based materials that have been extensively studied are fullerene, carbon nanotubes, and graphene. Carbon nanotubes in particular can be a good lithium host on the grounds of their excellent electronic conductivity and other properties associated with their linear dimensionality [35]. Current interest has been diverted to CNT- and graphene-based composites instead of pristine CNTs or graphene to achieve much higher capacity than that of pristine carbon [37, 38].

Li-air ( $\text{Li-O}_2$ ) and Li-sulfur ( $\text{Li-S}$ ) batteries have also been hot areas of research to obtain batteries with high energy density to provide longer mileage to electric vehicles.

Zheng *et al.* (2011) [39] have reported a hollow CNF-encapsulated sulfur cathode for effective trapping of polysulfides and demonstrated experimentally high specific capacity and excellent electrochemical cycling of the cells. They reported that high specific capacity of about 730 mAh/g was observed at C/5 rate after 150 cycles of charge/discharge. They also observed that introduction of  $\text{LiNO}_3$  additive to the electrolyte was shown to improve the Coulombic efficiency to over 99% at C/5.

Robert Mitchell, a graduate student in MIT's Department of Materials Science and Engineering (DMSE) and co-author of a paper in the *Journal Energy and Environmental Science* describing the new findings, reported a way to improve the energy density of lithium-air (or lithium-oxygen) batteries. They produced a novel carpet-like material composed of more than 90 percent void space that could potentially pack several times more energy per pound than the conventional lithium-ion batteries being used presently. A group of these MIT researchers produced carbon-fiber-based electrodes that are substantially more porous than other carbon electrodes and therefore can more efficiently store the solid oxidized lithium that fills the pores as the battery discharges [40]. A lot of studies related to various parameters, including the Li-electrolyte interface chemistry and safety of the battery, need to be carried out before commercialization of all these high-performance Li-O<sub>2</sub> or -S batteries.

For better performance of LIB, researchers are also focusing on developing new electrolytes and trying to replace alkyl carbonate with other solvents. Trans butylene carbonate was found to be a suitable solvent in which graphite electrodes behave highly reversibly [41]. Chlorinated and fluorinated alkyl carbonate were also found to be very suitable for graphite anodes. The major importance of these solvents is their use as a replacement for EC, whose freezing point is too high. There are studies of pyrocarbonate and bicarbonate as co-solvents. Their major advantage relates to modification of surface chemistry of both anodes and cathodes and an improvement of the high-temperature performance.

## 11.7 Summary

Demand-oriented research in the field of LIB has resulted in considerable changes in the chemistry of LIB, thereby continuously improving their performance, safety and cost. In the future, the technically advanced Li-ion batteries will not only be employed in conventional electronic equipment and vehicles but also will be employed to buffer the intermittent and fluctuating green energy supply from renewable non-conventional energy resources, such as solar and wind, to smooth the difference between energy supply and demand. For example, extra solar energy generated during the daytime can be stored in Li-ion batteries that will supply energy at night when sunlight is not available.

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# Carbon Nanofiber and Photovoltaic Solar Cell

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*Solar power is a safe form of nuclear energy. We are using fusion reactions that are 93 million miles away to make light that we then convert to electricity with photovoltaic modules.*

Sean White

## 12.1 Introduction

A device which directly converts the energy of light into electrical energy through the process of photovoltaics is called a solar cell. This concept has been evolving since 1839, when the development of solar cell technology began with the research of Alexandre-Edmond Becquerel. He observed the photovoltaic effect via an electrode in a conductive solution exposed to light [1]. Since then, many scientists have worked on this idea and improvised on it. In 1877, Adams and Day [2] observed the photovoltaic effect in solidified selenium. In 1904, Wilhelm Hallwachs made a semiconductor-junction solar cell from copper and copper oxide, a prototype of thin-film Schottky barrier devices. This barrier layer at the semiconductor-metal interface was confirmed by Goldmann and Brodsky in 1914 and later studied in more detail by Walter Schottky, Nevill Mott and others in the 1930s [3–5]. Between 1950 and 1959, work leading to the practical silicon

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single-crystal photovoltaic device emerged. The key events were Bell Labs announcement of the silicon solar cell in 1954 with the Pearson, Chapin, and Fuller patent in 1957 for the 8% efficient silicon solar cell [6, 7]. However, this period was just a discovery period without any real understanding of the science behind the operation of these first photovoltaic devices. A theoretical foundation for photovoltaic device operation and potential improvements was formulated in the second phase of the history of photovoltaics in the period from 1905 to 1950. Key events in this period were Einstein's photon theory [8], the adaptation of the Czochralski crystal growth method for single-crystal silicon and germanium growth and the development of band theory for high purity single-crystal semiconductors [9, 10]. In 1956, Loferski reported [11] that the optimum band gap for photovoltaic solar energy conversion is 1.5 eV. However, the research in 1960 resulted in the discovery of other photovoltaic materials, like GaAs (suitable even for high temperature), CdSe, CuInSe<sub>2</sub>, etc. Neither GaAs nor CdSe nor CuInSe<sub>2</sub> could be used for terrestrial applications because Ga is not available in plenty and Cd is toxic. Silicon solar cell is also not economical for general purpose use, though its cost has come down to below Rs 50 peak watt due to large-scale production. Carbon, on the other hand, having similar chemistry as that of silicon, is being considered to develop carbon solar cell. Sharon *et al.* were the first group [12–15] to have developed homojunction solar cell of configuration Au/n-C/p-C/Au with an efficiency of 2.1%, and they have predicted its cost to be around Rs. 20 per peak watt.

Before discussing the principle of photovoltaic solar cell, it is imperative to briefly discuss and become familiar with certain basic properties and the theory of semiconductor. Finally, the role that carbon materials play in photovoltaic cells are discussed in detail.

## 12.2 Formation of a Semiconducting Material

In a single isolated atom, energy levels of electrons are discrete. For hydrogen atom, the Bohr's model gives:

$$E_H = -\frac{m_0 q^4}{8\epsilon_0 h^2} \left( \frac{1}{n^2} \right) \quad (12.1)$$

where  $m_0$  is the free electron mass and  $q$  its charge,  $\epsilon_0$  is the free space permittivity and  $n$  is a positive integer known as the principal quantum number. The fundamental level corresponds to  $n = 1$  and the related energy is  $E_{H(n=1)} = -13.6 \text{ eV}$ .

If  $N$  atoms interact (for example in a crystal),  $N$  outer levels have energy that is only slightly different and thermal energy allows electrons to pass from one level to another (the energy corresponding to  $T = 300\text{ K}$  is  $kT \approx 0.026\text{ eV}$ ). Resulting energy levels are grouped into bands. Two main bands are recognizable: conduction band and valence band. These two bands are separated by a forbidden region that is characterized by an energy value  $E_g$ . This value makes the difference among insulators, conductors, and semiconductors.

In a conductor the conduction band is partially superimposed on the valence band. As a consequence, there are many electrons available for conduction and an electric field can give them sufficient energy to perform conduction. In an insulator, the forbidden band has a wide energy (for diamond,  $E_g = 5.5\text{ eV}$ ), and neither thermal energy nor an electric field is able to raise the energy of an electron to send it into the conduction band. Due to the absence of free electrons for conduction, the material behaves as an insulator. In a semiconductor, the two bands are separated but the energy of the forbidden band is low ( $E_g = 1.12\text{ eV}$  for Si at  $T = 300\text{ K}$ ) and it is easy to give energy to an electron to go into the conduction band. In this case, the hole in the valence band contributes to the conduction as well as the electron in the conduction band.

The semiconductors of electronic grade are very pure crystalline materials. The crystalline nature means that their atoms are aligned in a regular periodic array. This periodicity, coupled with the atomic properties of the component elements, is what gives semiconductors their very useful electronic properties. An abbreviated periodic table of the elements is given in Table 12.1.

Silicon, a column IV element, has four valence electrons—that is, four electrons that can be shared with neighboring atoms to form covalent bonds with those neighbors. In crystalline silicon, the atoms are arranged in a *diamond lattice* (carbon is also a column IV element) with tetrahedral

**Table 12.1** Abbreviated periodic table of the elements.

| I  | II | III | IV | V  | VI |
|----|----|-----|----|----|----|
|    |    | B   | C  | N  | O  |
|    |    | Al  | Si | P  | S  |
| Cu | Zn | Ga  | Ge | As | Se |
| Ag | Cd | In  | Sn | Sb | Te |

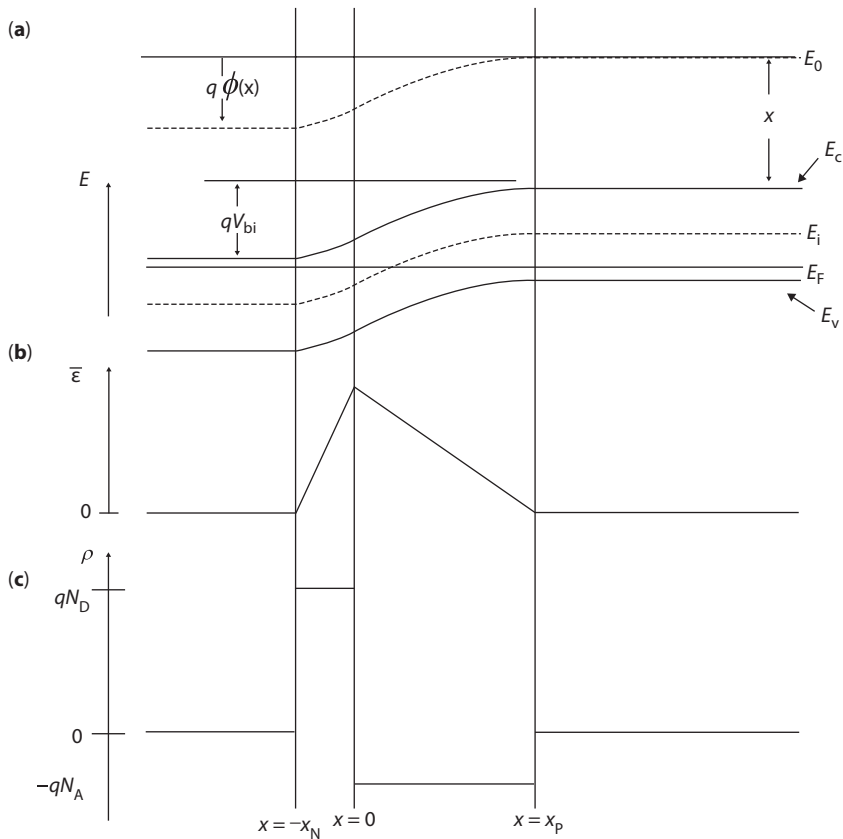
bonding—four bonds from each atom where the angle between any two bonds is  $109.5^\circ$ . Perhaps, surprisingly, this arrangement can be represented by two interpenetrating face-centered cubic (*fcc*) unit cells where the second *fcc* unit cell is shifted one-fourth of the distance along the body diagonal of the first *fcc* unit cell. The lattice constant,  $a$ , is the length of the edges of the cubic unit cell. The entire lattice can be constructed by stacking these unit cells. A similar arrangement, the *zincblende* lattice, occurs in many binary III–V and II–VI semiconductors such as GaAs (III–V compound) and CdTe (II–VI compound). For example, in GaAs, one interpenetrating *fcc* unit cell is composed entirely of gallium atoms and the other entirely of arsenic atoms. Note that the average valency is four for each compound, so that there are four bonds to and from each atom with each covalent bond involving two valence electrons. Some properties of semiconductors are dependent on the orientation of the crystal lattice, and casting the crystal structure in terms of a cubic unit cell makes identifying the orientation easier by means of Miller indices.

### 12.2.1 Introduction to P-N Junction

It would be difficult to deal with p-n junction theory in detail in this chapter due to limitation of space. Hence, readers are requested to refer to the book, *An Introduction to the Physics and Electrochemistry of Semiconductors: Fundamentals and Applications*, by Maheshwar Sharon, published by Wiley-Scrivener Publishing in 2016 [16].

Semiconductor without doping is called intrinsic semiconductor. Semiconductor doped with donor impurity, resulting in an increase in number of electrons in the conduction band, is known as n-type semiconductor. Semiconductor doped with an acceptor impurity, leaving excess holes in the valence band, is known as p-type semiconductor. These semiconductors are known as extrinsic semiconductors. If these n-type and p-type semiconductors are joined then the Fermi level in the two regions should be at the same energy, which leads to an energy displacement configuration, as shown in Figure 12.1.

In thermal equilibrium there is no net current flow through the junction and so by definition the Fermi energy must be independent of position. As there is a concentration difference of holes and electrons between the two types of semiconductors, holes diffuse from the p-type region into the n-type region and similarly electrons from the n-type material diffuse into the p-type region. As the carriers diffuse, the charged impurities (ionized acceptors in the p-type material and ionized donors in the n-type material) are uncovered, i.e., they are no longer screened by the majority carrier. As these impurity



**Figure 12.1** At equilibrium (a) energy bands, (b) electric field, and (c) charge density for a simple abrupt p-n junction silicon diode in the vicinity of the depletion region.

charges are uncovered, an electric field (or electrostatic potential difference) is produced, which counteracts the diffusion of the holes and electrons. In thermal equilibrium, the diffusion and drift currents for each carrier type exactly balance, so there is no net current flow. The transition region between the n-type and the p-type semiconductors is called the *space-charge region*. It is also often called the *depletion region*, since it is effectively depleted of both holes and electrons. Assuming that the p-type and the n-type regions are sufficiently thick, the regions on either side of the depletion region are essentially charge-neutral (often termed quasi-neutral). The electrostatic potential difference resulting from the junction formation is called the built-in voltage,  $V_{bi}$ . It arises from the electric field created by the exposure of the positive and the negative space charge in the depletion region.

The electrostatics of this situation (assuming a single acceptor and a single donor level) are governed by Poisson's equation

$$\nabla^2 \varphi = \frac{q}{\epsilon} (n_o - p_o + N_A^- - N_D^+) \quad (12.2)$$

where  $\varphi$  is the electrostatic potential,  $q$  is magnitude of the electron charge,  $\epsilon$  is the electric permittivity of the semiconductor,  $p_o$  is the equilibrium hole concentration,  $n_o$  is the equilibrium electron concentration,  $N_A^-$  is the ionized acceptor concentration, and  $N_D^+$  is the ionized donor concentration.

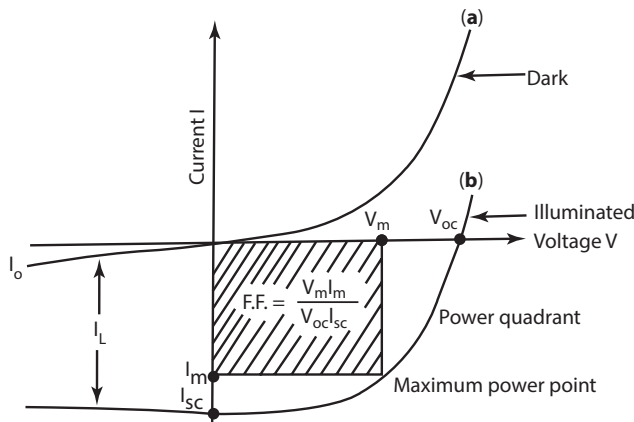
The built-in voltage  $V_{bi}$  is obtained as,

$$V_{bi} = \frac{kT}{q} \ln \left[ \frac{N_D N_A}{n_i^2} \right] \quad (12.3)$$

where  $n_i$  is intrinsic density.

Figure 12.2 shows at equilibrium (a) energy bands, (b) electric field, and (c) charge density for a simple abrupt p-n junction silicon diode in the vicinity of the depletion region.

Now, if p-n junction is connected in reverse bias condition, the motion of electrons and holes will make the inherent electric field even stronger, resulting in no flow of current. The small current which will flow through the p-n junction is due to minority charge carriers, i.e., the flow of electrons from the p-side and hole from n-side. If the junction is connected



**Figure 12.2** Current-voltage characteristics of solar cell showing two curves (a) when junction is not illuminated and (b) when it is illuminated.

in forward bias, the width of depletion region or internal energy barrier is reduced and the current is obtained due to majority charge carries.

In absence of light, the relation between the flow of junction current  $I_j$  and applied voltage  $V$  in p-n junction is given by,

$$I_j = I_o \left[ e^{\frac{qV}{kT}} - 1 \right] \quad (12.4)$$

where  $q$  is the electronic charge,  $I_o$  is the saturation current, also called dark current, as shown in Figure 12.2. This saturation current is obtained when large negative voltage is applied across the diode. When light (photons) is incident on the junction, the electron-hole pairs are generated and electric current is the difference between the light generated current  $I_L$  and the normal diode current  $I_j$ .

$$I = I_L - I_j \quad (12.5)$$

Figure 12.2 show two curves, one when junction is not illuminated (curve a) and the other when it is illuminated (curve b).

The solar cell is characterized using three parameters, the open circuit voltage  $V_{oc}$ , the short circuit current  $I_{sc}$  and the fill factor FF. The fill factor is the ratio of maximum power a photovoltaic cell can produce to the theoretical limit if both voltage and current are simultaneously at the maximum.

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (12.6)$$

The most important figure of merit for a solar cell is its power conversion efficiency  $\eta$ , which is defined as

$$\eta = \frac{P_o}{P_{in}} = FF \cdot \frac{V_{oc} I_{sc}}{P_{in}} \quad (12.7)$$

The incident power  $P_{in}$  is determined by the properties of the light spectrum incident upon the solar cell.

In order to design an efficient solar cell, the following important points should be considered:

1. Selection of a semiconductor material with a band gap well-matched to the solar spectrum.
2. Minimizing optical losses such as grid shadowing, reflectance and absorption in the optical components, as well as maximizing the optical thickness of the solar cell.



3. Minimizing series and shunt resistances in the cell and its connections, thereby maximizing the fill factor.
4. Minimizing the bulk and surface recombination rates, maximizing  $\eta V$  and hence the open circuit voltage.
5. Minimizing the bulk and surface recombination rates will also maximize the internal collection efficiency and hence the short-circuit current.

Simultaneous achievement of all of these goals will result in a very efficient solar cell. For a silicon solar cell with  $V_{oc} = 0.72$  V, the predicted efficiency under AM1.5 global illumination is 26.2%—just slightly higher than the best reported silicon solar cells [17].

### 12.3 Semiconductors for Solar Cell

Solar cell materials are chosen largely on the basis of how well their absorption characteristics match the solar spectrum and upon their cost of fabrication. Silicon has been a common choice due to the fact that its absorption characteristics are a fairly good match to the solar spectrum, and silicon fabrication technology is well developed as a result of its pervasiveness in the semiconductor electronics industry. However, silicon cells have a theoretical maximum power conversion capacity of less than 26.2% [17].

Alternate forms of cells are thus being heavily researched, particularly those using nanomaterials, due to the favorably small amount of material needed and the likely associated decrease in cost per watt. Currently, silicon crystalline solar cells still dominate the industry due to their cell efficiency. Table 12.2 shows some conventionally used materials for photovoltaic applications [18].

### 12.4 Attempts Made in Making Carbon-Based Solar Cell

In the search for alternative materials, carbon is highly attractive because it is expected to have similar properties as silicon and would be highly stable. Carbon is a remarkable element existing in a variety of stable forms. It ranges from insulator/semiconducting diamond/diamond-like amorphous film to metallic/semi-metallic graphite (or graphene, conducting/semiconducting fullerenes (e.g.,  $C_{60}$ ) and carbon nanotubes (CNTs). They also show many interesting physical and chemical properties.

Table 12.3 shows the allotropes of carbon having different band gaps which can be controlled in the wide range of 0.2–3 eV by controlling the dose of dopants or structures (e.g.,  $sp^3/sp^2$  ratio, cluster size).

**Table 12.2** Energy gap (eV) of some materials used for photovoltaic cells.

| Material            | Energy gap (eV) | Material                        | Energy gap (eV) |
|---------------------|-----------------|---------------------------------|-----------------|
| Si                  | 1.11            | InP                             | 1.27            |
| SiC                 | 2.60            | In <sub>2</sub> Te <sub>3</sub> | 1.20            |
| CdTe                | 1.44            | In <sub>2</sub> O <sub>3</sub>  | 2.80            |
| CdSe                | 1.74            | ZnO                             | 3.30            |
| CdS                 | 2.42            | Zn <sub>3</sub> P <sub>2</sub>  | 1.60            |
| CdSnO <sub>4</sub>  | 2.90            | ZnTe                            | 2.20            |
| GaAs                | 1.40            | ZnSe                            | 2.60            |
| GaP                 | 2.24            | AlP                             | 2.43            |
| CuO                 | 2.00            | AlSb                            | 1.63            |
| Cu <sub>2</sub> S   | 1.80            | SnO <sub>2</sub>                | 3.80            |
| Cu <sub>2</sub> Se  | 1.40            | CdAs <sub>2</sub>               | 1.00            |
| CuInSe <sub>2</sub> | 1.01            | As <sub>2</sub> Se <sub>3</sub> | 1.60            |
| CuInS <sub>2</sub>  | 1.50            | Ge                              | 0.67            |
| CuInTe <sub>2</sub> | 0.90            | Se                              | 1.60            |

Sharon's group first attempted a semi-conducting grade carbon at lower temperature in the range of 600–800 °C as compared to 1700 °C needed for silicon [12, 19, 20]. The main problem with carbon material is in finding the exact condition to get carbon with a desired band gap of 1.4 eV. The other problem associated with carbon is its low mobility of carriers. Most of the carbon materials show p-type character even without any external doping. Hence, preparation of an intrinsic semiconducting carbon is a challenge. Several groups have reported the performance of carbon-based photovoltaic cells as listed in Table 12.4 [21].

## 12.5 Is CNF a Suitable Material for Solar Cell?

Since if the solar cells developed using carbon materials are listed in Table 12.4, which suggests that most of the solar cells using carbon (Figure 12.3)

Table 12.3 Properties of carbon allotropes [21].

| Allotropes of carbon   | Crystal structure | Hybridization | Conduction type              | Band gap (eV) |
|------------------------|-------------------|---------------|------------------------------|---------------|
| Amorphous carbon       | –                 | $sp^3 + sp^2$ | Semiconductor                | 0.2–3.0       |
| Diamond                | Cubic             | $sp^3$        | Insulator                    | 5.5           |
| Graphite               | Hexagonal         | $sp^2$        | Conductor                    | 0.25          |
| Fullerene ( $C_{60}$ ) | Cubic             | $sp^2 + sp^3$ | Semiconductor                | 1.6           |
| Carbon Nanotube        | Cylindrical       | $sp^2 + sp^3$ | Metallic/Semi-conducting     | 0.3–2.0       |
| Graphene               | –                 | $sp^2$        | Semi-metallic/Semiconducting | 0–0.3         |

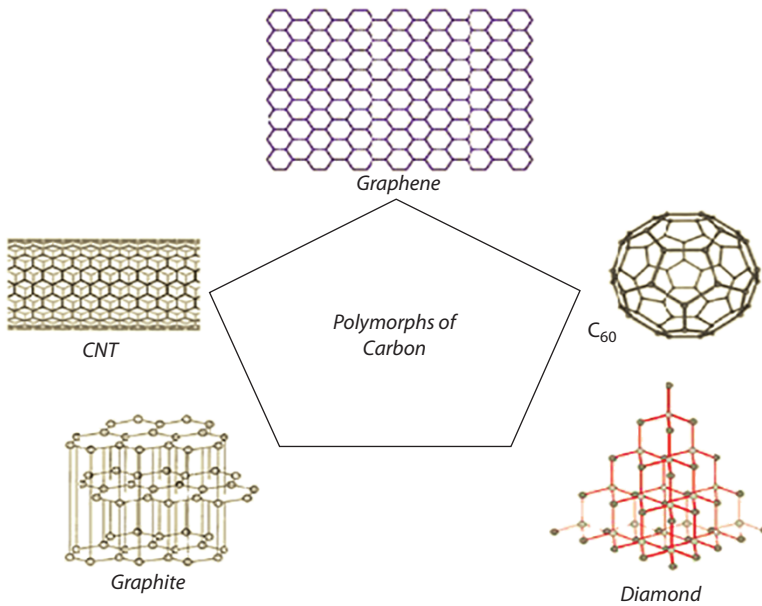
Table 12.4 Performance of various carbon-based photovoltaic cells.

| Photovoltaic cells                                 | $J_{sc}$ (mA/cm <sup>2</sup> ) | $V_{oc}$ (V) | FF   | $\eta$ (%) | Ref. |
|----------------------------------------------------|--------------------------------|--------------|------|------------|------|
| p-C/n-Si                                           | 3.71                           | 0.42         | 0.63 | 6.45       | [23] |
| p-C/p-SiC/n-Si                                     | 16                             | 0.85         | 0.71 | 8.8        | [24] |
| n-C/p-C/p-Si                                       | 17.1                           | 0.34         | 0.42 | 1.82       | [25] |
| p-C/n-Si                                           | 32.5                           | 0.58         | 0.42 | 7.9        | [26] |
| a-C:H/p-Si                                         | 15                             | 0.4          | 0.38 | 2.1        | [27] |
| n-C/p-Si                                           | 10.5                           | 0.26         | 0.41 | 1.14       | [28] |
| p-C/p-i-n-aSi                                      | 17.6                           | 0.8          | 0.58 | 5.6        | [29] |
| CNTs/n-Si                                          | 26                             | 0.54         | .53  | 7.4        | [30] |
| P3HT/C60-CNTs                                      | 2.7                            | 0.54         | 0.49 | 0.75       | [31] |
| CNTs-P3OT/n-Si                                     | 2.9                            | 0.22         | 0.27 | 0.175      | [32] |
| Glass/SWCNT/PEDOT:PSS/P3HT:PCBM/Ga <sub>2</sub> In | 6.50                           | 0.50         | 0.30 | 0.99       | [33] |
| Glass/ITO/P3OT/P3OT:SWCNT/Al                       | 0.12                           | 0.75         | 0.40 | 0.04       | [34] |
| Glass/ITO/PEDOT:PSS/PTEBS:MWCNT/C60/Al             | 1.52                           | 0.57         | 0.62 | 0.55       | [35] |
| Glass/SWCNT/PEDOT:PSS/P3HT:PCBM/Ca/Al              | 13.78                          | 0.57         | 0.53 | 4.13       | [36] |
| Glass/SWCNT/P3HT:PCBM/Al                           | 4.46                           | 0.36         | 0.38 | 0.61       | [37] |

(Continued)

Table 12.4 Performance of various carbon-based photovoltaic cells. (Continued)

| Photovoltaic cells                                           | $J_{sc}$ (mA/cm <sup>2</sup> ) | $V_{oc}$ (V) | FF   | $\eta$ (%) | Ref. |
|--------------------------------------------------------------|--------------------------------|--------------|------|------------|------|
| Glass/SWCNT(H <sub>2</sub> O:SDS)/PEDOT:PSS/P3HT:PCBM/LiF/Al | 7.30                           | 0.59         | 0.46 | 2.2        | [38] |
| PET/SWCNT/PEDOT:PSS/P3HT:PCBM/Al                             | 7.80                           | 0.61         | 0.52 | 2.5        | [39] |
| Glass/ITO/MWCNT/P3HT:PCBM/LiF/Al                             | 4.00                           | 0.50         | 0.47 | 0.93       | [40] |
| Glass/ITO/PEDOT:PSS/P3HT:PCBM:MWCNT/LiF/Al                   | 9.33                           | 0.57         | 0.38 | 2.00       | [41] |
| Glass/ITO/PEDOT:PSS/P3HT:C60:SWCNT/LiF/Al                    | 2.69                           | 0.54         | 0.49 | 0.75       | [42] |
| Glass/ITO/PEDOT:PSS/P3HT:SWCNT/Al                            | 1.93                           | 0.58         | 0.42 | 0.52       | [43] |
| Glass/ITO/PEDOT:PSS/P3HT:PCBM:SWCNT/Al                       | 4.95                           | 0.55         | 0.52 | 1.40       | [44] |
| Glass/ITO/PEDOT:PSS/QTF12:PCBM:DWCNT/LiF/Al                  | 2.37                           | 0.56         | 0.37 | 0.50       | [45] |
| Glass/ITO/MWCNT/P3HT:PCBM/LiF/Al                             | 7.30                           | 0.61         | 0.62 | 2.70       | [46] |
| Glass/ITO/ODA-SWCNT:P3HT:PC70BM/BCP/Al                       | 7.66                           | 0.52         | 0.44 | 1.76       | [47] |
| Glass/FTO/MWCNTs/MoO <sub>3</sub> /P3HT:PCBM/Ca/Al           | 8.88                           | 0.51         | 0.46 | 2.1        | [48] |
| Glass/ITO P3HT:PCBM:SWCNTs/Al                                | 11.46                          | 0.57         | 0.46 | 3.02       | [49] |
| Glass/ITO/PEDOT:PSS/f-MWCNT/Al                               | 11.15                          | 0.50         | 0.30 | 1.65       | [50] |
| MWNTs/PEDOT-PSS (DSSC)                                       | 15.5                           | 0.66         | 0.63 | 6.5        | [51] |
| Graphene/PEDOT-PSS (DSSC)                                    | 13.0                           | 0.72         | 0.48 | 4.5        | [52] |
| Glass/ITO/HTM/PTM10:PTM21-CNT:PCBM/LiF/Al                    | 0.45                           | 0.88         | 0.38 | 0.15       | [53] |



**Figure 12.3** Different forms of carbon [21, 22].

have the configuration of carbon/silicon. In these cells it is not very clear whether carbon is used as a semiconducting carbon, or carbon fiber, or carbon behaving like metal. It can be assumed that these carbon solar cells are like Metal-Schottky type cell where carbon has acted like a metal. Therefore, it would be interesting to develop such carbon solar cell with semiconducting carbon nanofiber. Depending on its preparation and structure, CNF shows the property of metal or semiconductor. However, carbon solar cell of configuration "n-C/p-C/Si" is like a p-n junction photovoltaic cell. In this cell also it is not clearly explained whether the carbon was CNF or CNT or amorphous C doped to get n-C and p-C. Hence, there is a need to carry out more research on application of CNF to make Metal-Schottky type cell or p-n type photovoltaic cell. These are listed here:

- Use of CNF in development of carbon solar cell demands answers to a few important questions so that CNF solar cell with higher efficiency can be achieved. The structure of CNF contains carbon with configuration  $sp^3$  as well as  $sp^2$ . The ratio of these carbons decides whether CNF will behave like metal or a semiconductor. But under no condition will either of these two types of carbons ( $sp^3$  or  $sp^2$ ) be absent in a

CNF structure. If that is so then carbon of  $sp^2$  configuration in CNF will act like a trapping center for the photogenerated carriers (electrons or holes). Hence, the efficiency of solar cell developed will depend on whether these trapping centers have been neutralized by some external doping.

- Another problem with carbon material, irrespective of whether CNF or CNT, is that this material possesses both direct and indirect band gaps and invariably its indirect band gap possesses zero eV band gap. Hence, unless its indirect band gap is not increased to a certain suitable value, like 1.2 eV, the indirect band gap will also act like a trapping center and will also reduce the depletion region depth.
- The third factor to be considered is that carbon material without any doping, i.e., the intrinsic carbon material, shows p-type character. How can this effect be neutralized so that one could effectively dope CNF to get conventionally n- or p-type carbon?

These are some basic points which need to be carefully understood and remedies to problems found before it will be possible to make an effective carbon solar cell which could replace silicon solar cell. These points are not an impossible task, but they are needed to be looked into before CNF can find its place in photovoltaic solar cell. Nevertheless, some efforts have been made to make carbon solar cell.

Metal wires and glass fibers have poor flexibility, and conductive performance of polymer fibers is not good. So, Chen *et al.* (2011) [54] and Luo *et al.* (2012) [55] used flexible, lightweight, ultrastrong, and semiconductive CNT fibers to develop a novel solar cell. The high alignment of building nanotubes in the fiber allows charges to separate and transport along the fibers efficiently, which provides a fiber solar cell with high performance. They used CNT/N719 composite fibers to fabricate the organic solar cells on fluorine-doped tin oxide, and the power conversion efficiencies can reach 2.6%.

Grynko *et al.* [56] were the first to structure nanoscale hybrid solar cells in the form of a brush of radially oriented CdS nanowire crystals around a single carbon fiber. A solar cell was assembled on a carbon fiber with a diameter of  $\sim 5\text{--}10\text{ }\mu\text{m}$  which served as a core electrode; inorganic CdS nanowire crystals and organic dye or polymer layers were successively deposited on the carbon fiber as active components resulting in a core-shell photovoltaic structure. The development in this technology may lead to a major step towards “photovoltaics on curtains” [57].

## 12.6 Summary

In this chapter an effort was made to explain some basic points that need to be considered before making any carbon solar cells. Some of the experimental efforts made to develop carbon solar cells were also discussed. Finally, a few basic points which need to be considered before using CNF as a carbon material for developing carbon solar cell were discussed.

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# Application of Carbon Nanofiber in Antenna

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*Science is a beautiful gift to humanity; we should not distort it.*

**A. P. J. Abdul Kalam**

## 13.1 Introduction

This chapter is devoted to the application of carbon nanofiber as a material for various applications, one of which is its use in antenna. However, before we can examine the application of CNF as suitable material for antenna, it is necessary to discuss the specific theory of antenna and properties of material which could be useful in making an antenna. Nevertheless, considering the constraints imposed by the number of pages allotted for this chapter, it is not possible to have an in-depth discussion of the theory of antenna and the materials used for antenna. Therefore, efforts have been made to present some salient features of antenna.

An antenna is a device that is used to transfer guided electromagnetic waves into electrical signals and vice versa (i.e., either in transmitting mode or in receiving mode of operation) (Figure 13.1). Antennas are frequency needy devices. Each antenna is designed for a certain frequency band and outside of this band the antenna rejects the signal. Therefore, we can say antenna is a bandpass filter and transducer. Antennas are an essential part in communication systems, therefore understanding their basics are

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**Figure 13.1** Schematic of antenna.

important. With the advances in telecommunication, the requirement for compact antenna has increased significantly. In mobile communication, the requirement for smaller antennas is quite large, so significant developments are carried out to design compact, minimal weight, low-profile antennas for both academic and industrial communities of telecommunication.

For wireless communication systems, the antenna is one of the most critical components. A good antenna design can relax system requirements and improve overall system performance. A typical example is a TV, for which the overall broadcast reception can be improved by utilizing a high-performance antenna. An antenna is the system component that is designed to radiate or receive electromagnetic waves. In other words, the antenna is the electromagnetic transducer which is used to convert, in the transmitting mode, guided waves within a transmission line to radiated free-space waves or to convert, in the receiving mode, free-space waves to guided waves. In a modern wireless system, the antenna must also act as a directional device to optimize or accentuate the transmitted or received energy in some directions while suppressing it in others [1]. The purpose that an antenna serves in a communication system equates with the purpose of eyes and eyeglasses for people.

The history of antennas [2, 3] dates back to James Clerk Maxwell, who unified the theories of electricity and magnetism and eloquently represented their relations through a set of profound equations, best known as Maxwell's equations. His work was first published in 1873. He also showed that light was electromagnetic and that both light and electromagnetic waves travel by wave disturbances at the same speed. In 1886, Professor

Heinrich Rudolph Hertz demonstrated the first wireless electromagnetic system.

From Marconi's inception through the 1940s, antenna technology was primarily centered on wire-related radiating elements and frequencies up to about UHF. It was not until World War II that modern antenna technology was launched and new elements (such as waveguide apertures, horns, reflectors, etc.) were primarily introduced. Much of this work is captured in the book by Samuel Silver (1949) [4]. A contributing factor to this new era was the invention of microwave sources (such as the klystron and magnetron) with frequencies of 1 GHz and above.

While World War II launched a new era in antennas, advances made in computer architecture and technology during the 1960s through the 1980s have had a major impact on the advance of modern antenna technology; and, as expected, have continued to have an even greater influence on antenna engineering in the 1990s and beyond. Beginning primarily in the early 1960s, numerical methods were introduced that allowed previously intractable complex antenna system configurations to be analyzed and designed very accurately. In addition, asymptotic methods for both low frequencies (e.g., moment method (MM), finite-difference, finite-element) and high frequencies (e.g., geometrical and physical theories of diffraction) were introduced, contributing significantly to the maturity of the antenna field. While in the past antenna design may have been considered a secondary issue in overall system design, today it plays a critical role. In fact, many system successes rely on the design and performance of the antenna. Also, while in the first half of this century antenna technology may have been considered almost a "cut-and-try" operation, today it is truly an engineering art. Analysis and design methods are such that antenna system performance can be predicted with remarkable accuracy. In fact, many antenna designs proceed directly from the initial design stage to the prototype without intermediate testing. The level of confidence has increased tremendously.

## 13.2 Radiation Types and Characteristics of Antenna

As mentioned in the introduction, antennas have the function of converting one type of wave into another. The direction of energy conversion is of no importance for the operational principle or ease of understanding. The transmitting and the receiving antenna can therefore be looked at in the same way (reciprocity principle), and the parameters described in this chapter are equally valid for transmission and reception. This even applies

if the parameters are in some cases measurable only for transmission or for reception or if their specification appears to be meaningful only for one of these modes. Active antennas are the only exception: being pure receiving antennas, they are non-reciprocal. Apart from that, a clear distinction between transmitting and receiving antennas must be made if, for example, the maximum transmitter power is to be taken into account. However, this is irrelevant to the characteristics and the principle of operation.

The parameters to assess radiation are *radiation density* and *radiation pattern*.

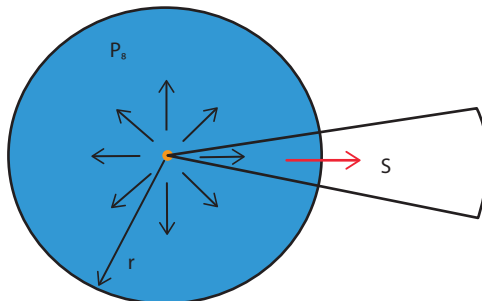
### 13.2.1 Radiation Density

The simplest imaginable antenna is the isotropic radiator, which does not exist in practice, but makes an excellent theoretical model. An isotropic radiator (Figure 13.2) is a dimensionless point in space which generates waves with spherical wave fronts that are radiated uniformly in all directions. When the ideally matched transmitter power  $P_s$  is applied to it, then at distance  $r$  this gives rise to the radiation density:

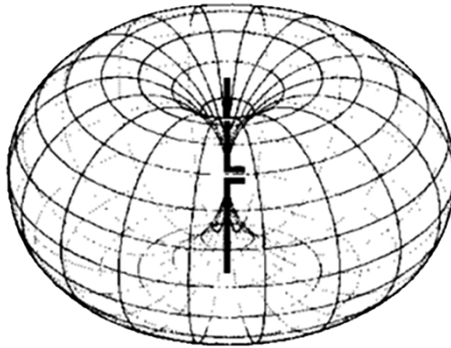
$$S = \frac{P_s}{4\pi r^2} \quad (13.1)$$

### 13.2.2 Radiation Pattern

The three-dimensional radiation behavior of antennas is described by their radiation pattern (normally in the far field). As explained before, only an isotropic radiator would exhibit the same radiation in every spatial



**Figure 13.2** The isotropic radiator in homogeneous space.



**Figure 13.3** Three-dimensional radiation.

direction, but this radiator cannot be implemented for any specified polarization and is therefore mainly suitable as a model and comparison standard. Dipoles and monopoles possess directivity. An electrically short dipole in free space has a three-dimensional radiation pattern shown in Figure 13.3, with nulls in the direction of the antenna's axis.

### 13.2.3 Directivity

The directivity factor  $D$  is defined as the ratio of the radiation intensity  $F_{max}$  obtained in the main direction of radiation to the radiation intensity  $F_i$  that would be generated by a loss-free isotropic radiator with the same radiated power  $P_t$ . The radiation intensity can be replaced by the power density represented by the Poynting vector as shown below:

$$S = E^{\rightarrow} \times H^{\rightarrow} \quad (13.2)$$

with  $S$  perpendicular to  $E^{\rightarrow}$  and  $S$  and  $E^{\rightarrow}$  perpendicular to  $H^{\rightarrow}$  in the far field.

### 13.2.4 Gain

Corresponding to the directivity factor, the gain  $G$  is the ratio of the radiation intensity  $F_{max}$  obtained in the main direction of radiation to the radiation intensity  $F_{i0}$ , that would be generated by a loss-free isotropic radiator with the same input power  $P_{t0}$ .

$$G = F_{max} / F_{i0} \text{ where } F_{i0} = P_{t0} / 4\pi \quad (13.3)$$



### 13.2.5 Effective Area

The effective area  $A_w$  of an antenna is a parameter specially defined for receiving antennas. It is a measure for the maximum received power  $Pr$  that an antenna can pick up from a plane wave of the power density  $S$ :

$$Pr_{max} = S \cdot A_w \quad (13.4)$$

### 13.2.6 Input Impedance

One of the most significant parameters of an antenna is its input impedance:

$$Z_{in} = R_{in} + jX_{in} \quad (13.5)$$

This is the impedance present at the antenna feed point. Its real part  $R_{in}$  can be split up into the radiation resistance  $R_R$  and the loss resistance  $R_L$ ,

$$R_{in} = R_R + R_L \quad (13.6)$$

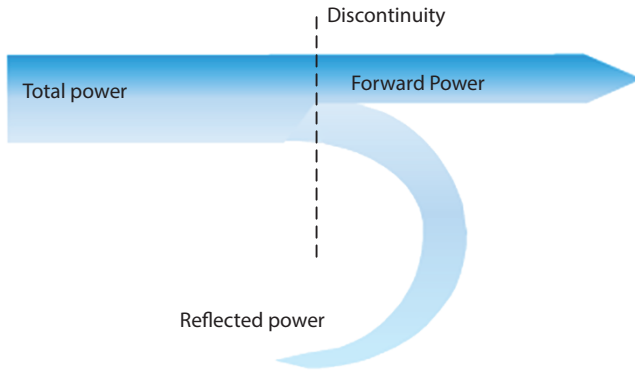
It should be noted, however, that the radiation resistance, being the quotient of the radiated power and the square of the RMS value of the antenna current, is spatially dependent. This applies also to the antenna current itself. Consequently, when specifying the radiation resistance, its location on the antenna needs to be indicated.

### 13.2.7 Impedance Matching

If the impedance of an antenna is not equal to the impedance of the cable and/or the impedance of the transmitter, a certain discontinuity occurs. The effect of this discontinuity is best described for the transmit case, where a part of the power is reflected and consequently does not reach the antenna (Figure 13.4). However, the same will happen with the received power from the antenna that does not fully reach the receiver due to mismatch caused by the same discontinuity.

### 13.2.8 Return Loss and Voltage Standing Wave Ratio (VSWR)

The reflection coefficient at the antenna input is the ratio of the reflected voltage to the incident voltage and is the same as the  $S_{11}$  when the antenna is connected at the port 1 of the network analyzer. It is the measure of the impedance mismatch between the antenna and the source line. The degree of mismatch is usually described in terms of return loss or VSWR. Return loss is the ratio of the reflected power to the incident power, expressed in  $dB$  as



**Figure 13.4** Forward and reflected power due to mismatch.

$$RL = -20\log(|\Gamma|) = -20\log(|S_{11}|) = -|S_{11}|(dB) \quad (13.7)$$

The frequency corresponding to return loss minimum is taken as resonant frequency of the antenna. The range of frequencies for which the return loss value is less than  $-10\text{ dB}$  points is usually treated as bandwidth of the antenna. The bandwidth of the antenna can be expressed as percent of bandwidth:

$$\% \text{ Bandwidth} = (\text{Bandwidth}/\text{Center frequency})100 \quad (13.8)$$

The VSWR is the ratio of the voltage maximum to the minimum of the standing wave existing on the antenna input terminals. VSWR equal to 2 gives a return loss that approximately equals  $10\text{ dB}$  and is set as the reasonable limits for a matched antenna.

### 13.3 Carbon Nanomaterial

Carbon nanomaterials, such as graphene, carbon nanotubes (CNTs), crystalline diamond, and diamond-like carbon, all display exceptional electrochemical properties which has resulted in their widespread application. The potential of these materials is unquestionable in sensing applications, as the novel carbon-derived nanomaterials possess properties that are unfathomable in bulk materials. This results in their capability to operate with not only a higher sensitivity and selectivity in harsh environments but also over greater temperature and dynamic ranges. Historically, a number of materials, including platinum, gold, and various forms of carbon, have been exploited

as electrode materials for electrochemical detection [5–9]. Graphene, CNTs, and diamond are the polymorphs of carbon that have been widely employed as electrode materials for electrochemical sensing in recent years. Consequently, this review focuses on the recent (<5 years) incorporation and use of carbon-derived nanomaterials for electrochemical sensing applications and their potential implications. Moreover, excellent properties of carbon nanomaterials, such as large surface-to-volume ratio, high conductivity, and electron mobility at room temperature, have led to numerous advances in electrochemical sensors. This review aims to highlight the application of carbon-based sensors in multiple fields such as electrochemical sensors for DNA, proteins, pollutants, metal ions, gases, and immunosensors.

### 13.4 Application of Carbon Nanofibers in Antenna

Carbon has a high level of chemical bonding flexibility, which lends itself to the formation of a number of stable organic and inorganic molecules. Elemental carbon has a number of allotropes (variants), including diamond, graphite, and fullerenes [9]. Though they all consist of elemental carbon, their properties vary widely. This underscores the versatility of CNFs, which are notable for their thermal, electrical, electromagnetic shielding, and mechanical property enhancements [10]. As carbon is readily available at low cost, CNFs are popular additives to composite materials [7]. CNFs are very small, existing at the nanometer scale. An atom is between 0.1–0.5 nm, thus specialized microscopic techniques such as scanning tunneling microscopy and atomic force microscopy are required to examine the properties of CNFs. Both CNT and CNF are like hollow cylinder. But the outer layer of CNT is made up of unbroken graphene sheet whereas CNFs are made up of broken graphene sheet. CNFs are made from camphor by CVD process [11]. Depending on the raw material for synthesis of CNM and nanocatalyst used for the process, different types and shapes of CNFs are formed [6, 12–14].

Wang *et al.* (2004) [15] have clearly shown that an array of aligned carbon nanotubes can behave as an electromagnetic antenna. The response of the material used for the antenna depends upon the polarization of the incoming radiation, i.e., the electric field of the radiation to be absorbed has a particular orientation. Transmission of radiation is weakest if the plane of polarization is at 90° to the antenna's long axis. This means that the response depends upon length of the material used to make the antenna. Carbon nanofibers have their longer length along the ab-axis as compared to the c-axis. Hence, it is expected that CNF may be a useful material for developing antenna. Another property of material for antenna depends on

whether the impedance of the CNF is the same as the co-axial cable used for transmission of the radiation. Because if both are the same then there would be no resistance for the transmission of signal. Moreover, excellent properties of carbon nanomaterials, such as large surface-to-volume ratio, high conductivity, and electron mobility at room temperature, are useful properties for use as an antenna. The use of carbon fiber composite (CFC) materials has been investigated for building antennas and microwave circuits, by replacing the metal with CFC. Two kinds of composite materials were investigated, namely reinforced continuous carbon-fiber (RCCF) composite and carbon nanotube (CNT) composite. The RCCF composite is used to build ultra-wideband antennas. Various types of SWCNT antennas are fabricated for different wireless antenna applications [8] (Mehdipour *et al.* 2012). The use of carbon fiber composite (CFC) materials has been investigated for building antennas and microwave circuits, by replacing the metal with CFC. As one of the most highly conductive composites, single-wall carbon nanotube (SWCNT) buckypapers are used to build composite antennas. A new fabrication method is proposed to print arbitrarily shaped full-composite SWCNT antenna on any type of substrate. As compared to the normal nanoparticles used in antenna, the use of carbon nanofibers in an antenna can absorb the electromagnetic waves.

### 13.5 Summary

This chapter summarized antennas. In radio engineering, an antenna is the interface between radio waves propagating through space and electric currents moving in metal conductors, used with a transmitter or receiver. In transmission, a radio transmitter supplies an electric current to the antenna's terminals, and the antenna radiates the energy from the current as electromagnetic waves (radio waves). In reception, an antenna intercepts some of the power of a radio wave in order to produce an electric current at its terminals, which is applied to a receiver to be amplified. Antennas are essential components of all radio equipment. An antenna is an array of conductors (elements), electrically connected to the receiver or transmitter. Antennas can be designed to transmit and receive radio waves in all horizontal directions equally (omnidirectional antennas), or preferentially in a particular direction (directional or high-gain antennas). An antenna may include parasitic elements, parabolic reflectors or horns, which serve to direct the radio waves into a beam or other desired radiation pattern. Using the normal nanoparticles in an antenna, carbon nanofibers are more effective for modern applications.

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## Carbon Nanofiber in Cosmetics

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*The capacity to learn is a gift;  
The ability to learn is a skill;  
The willingness to learn is a choice.*

Brian Herbert

### 14.1 Introduction

*Nanoscience, nanotechnology, nanomaterials and nanostructure* have drawn much attention in the last few decades due to their wide range of applications. These words are not only restricted to research and publications, but have also become common in our day-to-day life. Nanoscience is an innovative science which encompasses the study of the design, characterization, production, applications of structure, devices and systems by controlling shape and size at the nanometer scale (measuring 1–100 nm).

Since the last decade, nanotechnology has acquired prominence in several scientific fields. It is a powerful emerging technology which involves the manipulation of materials and the creation of structures and systems that exist at the atomic and molecular level. At this level the properties differ significantly from those at larger scale. These are the promising materials that bring changes to every industry, from aerospace to agriculture. Nanotechnology is potentially beneficial and expanding rapidly with tremendous implications for society, medicine and cosmetic industries.

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Enhancements in the physicochemical properties of nanotechnology-based products, like color, transparency, solubility and chemical reactivity, are leading to nanomaterials becoming more attractive and hence have opened up a new prospective to the personal care products and cosmetics industries (Figure 14.1). Due to the unique properties of matter at the nanoscale, nanomaterials have been incorporated into a number of skin care products. The widespread use of these engineered nanoscale materials is commercially used in cosmetics and personal care products, including sunscreen, soap, shampoo, foundation, anti-wrinkle cream, perfume, after-shave lotion, etc.

Cosmetics are designed to cleanse, protect and change the appearance of external parts of our bodies. The key ingredients of cosmetics are naturally occurring or artificial water, emulsifiers, preservatives, thickeners, moisturizers, colors and fragrances. Humans have used cosmetics to alter their appearance or accentuate their features for more than approximately 10,000 years. Today, cosmetics are big business.

## **14.2 What Is a Nanocosmetic**

The cosmetic industry was among the first to implement nanotechnological principles in product development. Nanomaterials are being used in cosmetic products for various effects. Fronza has (2007) defined a nanocosmetic as “a cosmetic formulation that carries active or other nanostructured ingredients, which has superior properties regarding its performance if compared with conventional products” [1]. The different types of nanomaterials employed in cosmetics are nanosomes, liposomes, fullerenes, solid lipid nanoparticles, etc.

## **14.3 Cosmetics with Nanoparticles in Today's Market**

Nanotechnology has played an important role in the cosmeceutical arena. In the coming years cosmeceutical products will continue to have strong growth prospects in the market. In Asian countries the global cosmetic market offers huge potential in the future. Nanotechnology is the way of the future for cosmetic companies and is considered to be the hottest emerging technology available.

Almost all the major cosmetic manufacturers have started using nanoscale versions of ingredients in their products to manipulate matter at an atomic

or molecular level so as to provide better UV protection, deeper skin penetration, long-lasting effects, increased color, finish quality, etc.

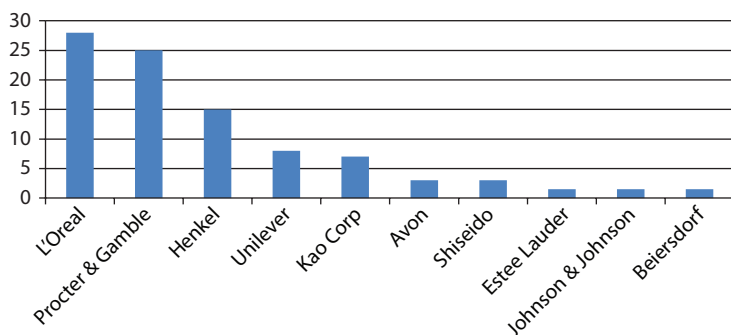
The cosmetic industry is always looking to improve the properties of its products and hence is making more and more use of the developments in nanotechnology (Figure 14.1). From different surveys it has been found that almost all front-running brands of cosmetic manufacturers worldwide use this technology in their various products (Figure 14.2). Using nanotechnology, the cosmeceutical sector is expanding at an annual growth rate of 7.7%, and the global market of cosmetics is projected to impact the overall economy.

The use of engineered nanomaterials has risen in today's world. They have also captured the hearts of the cosmetic industry with their enhanced



**Figure 14.1** Some commercially available nanocosmetics from: (a) Vegan and kosher certified Fine French Press Zinc Oxide Powder (cosmetic grade size 325 nm) sunscreen, also a safe sunblock for infants, (b) Amavara mineral sunscreen (transparent zinc oxide, SPF 30), (c) Neutrogena sunblock, SPF 50, (d) Sunscreen by Shade, (e) Fujifilm skincare products.





**Figure 14.2** The ten top-ranking cosmetic companies in terms of number of nano-related patents. (Source: Raj *et al.* Review article, Nanotechnology in cosmetics: Opportunities and challenges, *Pharm. Bioallied Sci.* 4(3), 186–193, 2012) [2].

properties and are shifting their focus from cosmeceuticals to nanocosmeceuticals by incorporating nanotechnology into most of their manufacturing processes.

## 14.4 Nanoparticles Used in Cosmetics

Nanomaterials are used in the manufacture of cosmetics as encapsulation or carrier system to transport agents into deeper skin layers where they activate skin metabolism, improve skin appearance, and act as an optimal UV protective filter in sunscreen. Nanoscale materials can also be found in different cosmetic products such as nanoparticles of silver and gold, ceramic nanoparticles, pigments, minerals, and fullerenes.

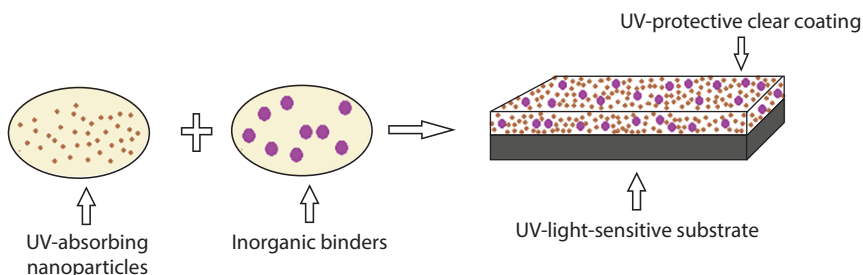
The two main uses for nanoparticles in cosmetic products are UV filtering and delivery of active ingredients. Nanometer-scale materials in these cosmetics provide greater clarity, coverage, cleansing or absorption. The cosmetics industry uses nanomaterials to provide better UV protection, deeper skin penetration and long-lasting effects and better finishing quality. Some of the nanoparticles that are extensively used in enhancing the efficiency of cosmetics are discussed below.

### 14.4.1 Titanium Dioxide ( $\text{TiO}_2$ )

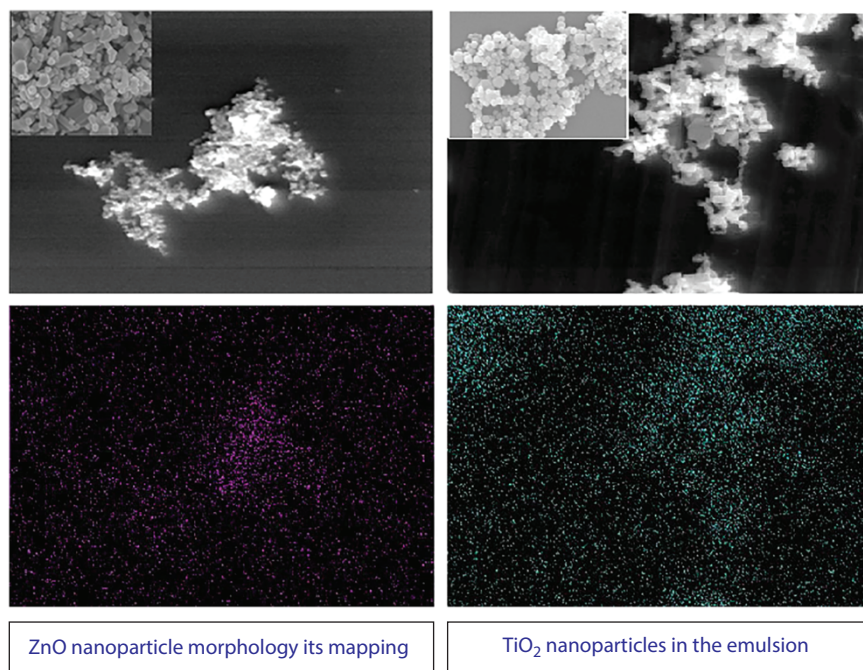
Titanium dioxide is one of the top chemicals produced worldwide and is safely used in many products from paint to food to drugs and cosmetics.  $\text{TiO}_2$  possesses a higher refractive index than diamond, does not absorb visible rays, and is highly chemically stable. Therefore, it is widely used in paints and cosmetics as a white pigment and ultraviolet (UV) absorbing agent.

It's an opaque mineral pigment that is mainly used in sunscreen and color cosmetics. It is used as colorant to make cosmetics and personal care products which are applied to the skin (including the eye area), nails and lips, which is white in color. Because of its white color, opaqueness and ability to refract light, the ingredient is often used as a pigment, brightener and opacifier.

The nanoparticles used in sunscreen (Titanium dioxide and zinc oxide) provide extensive protection from harmful UV radiations. The nano formulations (Figure 14.3) of these materials have been repeatedly shown to give much better results than larger particles, reflecting visible light and absorbing UV light with very high efficiency [3]. Titanium dioxide particles (particle size of 20–40 nm) are primarily used in sunscreen lotion because of their resistance to discoloration under UV light and high refractive index ( $n = 2.6142$  in comparison to water  $n=1.33$  at 20 °C). Nanoparticles of  $\text{TiO}_2$  scatter visible light much less than titanium dioxide pigments and can give UV protection (wave length from 315–340 nm). The range of scattered light depends on the particle size. Nano-sized titanium dioxide particles which are used in sunscreens and other cosmetic products do not cross the stratum corneum and block both UV-A (315–400 nm) and UV-B (280–315 nm), causing less skin irritation. Because nano titanium dioxide ( $\text{TiO}_2$ ) is nontoxic, chemically stable at high temperature and has permanent stability under UV exposure, it has good ultra-blocking UV blocking power. Nano titanium dioxide is present in large clusters with a size much greater than 100 nm, which further increases UV absorption in sunscreen lotions and reduces its photoprotection efficacy. Being chemically inert, semiconducting material, nanoparticles of  $\text{TiO}_2$  exhibit photocatalytic activity in the presence of light with energy equal to or higher than its band gap energy. An electron is promoted from the valence band to the conduction band, leaving behind a positive hole. The photocatalytic activity results in the formation of highly reactive radicals that are capable



**Figure 14.3** Preparation of a UV-protective clear coating of inorganic nanoparticles. (Source: Faure *et al.*, *Sci. Technol. Adv. Mater.* 14(2), 2013) [4].



**Figure 14.4** Field emission scanning electron microscopy (FESEM) of nano-sized TiO<sub>2</sub> and ZnO in formulations. (Source: Fathi-Azazarbyjan *et al.*, *Sci. Pharm.* 81(4), 1141–1150, 2013) [5].

of reacting with most of the surrounding organic substances. They can also combine with other organic sunscreens and do not react with other ingredients present in the compound.

Field emission scanning electron microscopy (FESEM) was used to view the shape, size, and distribution of nano-sized TiO<sub>2</sub> and ZnO in formulations. From Figure 14.4 it is evident that the particles have agglomerated in the emulsion. Zinc oxide consisted of rod-like (80 nm in diameter and 250 nm in length) and spherical particles (with an average diameter of 90 nm). Titanium dioxide nanoparticle used in SPF 50/PA<sup>+++</sup> (Figure 14.5) mainly of spherical shape with an average diameter of 80 nm.

#### 14.4.2 Zinc Oxide (ZnO)

Besides the authorized use of ZnO nanoparticles in all cosmetics as a cosmetic colorant, zinc oxide has widespread use in cosmetic products as bulking agent and as a UV absorber for skin protection due to its high photocatalytic behavior. ZnO minerals are frequently used in sunscreens as



**Figure 14.5** Colorescience Sunforgettable total protection face shield with SPF 50/PA+++ containing  $\text{TiO}_2$  NPs for complete protection from harmful environmental aggressors.

inorganic physical sun blockers. In addition to appearance enhancement, face powders including zinc oxide can also provide sunscreen protection with strong scattering components such as ZnO. The particle size distribution of ZnO also affects appearance, stability and sunscreen protection.

The ZnO nanoparticles are photoactive and UV absorbing due to their electronic structures, characterized by a filled valence band and an empty conduction band. The concentration of ZnO as UV filter used in sunscreens is approximately up to 25%. The size of ZnO particles employed in sunscreens is in the range of 20 to 60 nm. In the visible range of the light spectrum, zinc oxide nanoparticles are transparent and act as a physical filter in sunscreens against the UV-A and UV-B rays of the sun. In sunscreens with sun protection factor above 25, physical UV filters are mainly used.

Nano-sized ZnO raw material in the form of both coated and uncoated nanomaterials in cosmetic products are used by various leading manufacturers because cosmetic products using nanosized ZnO show more vibrant color, improved texture, and greater skin penetration.

As per the reports of the Scientific Committee on Consumer Products [6]: Clarification on Opinion, examples of some final cosmetic products containing nano-sized ZnO raw material are:

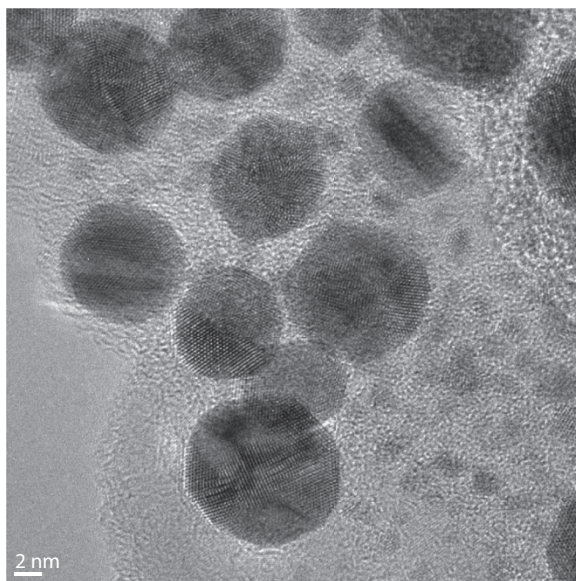
- W/O emulsion, uncoated ZnO (Sun defense SPF 30/PA++, Ponds, 8.4% ZnO) Unilever
- O/W emulsion, coated ZnO (all day moisture lotion, SPF 15, Olay) Procter and Gamble
- W/O emulsion, coated ZnO (20% ZnO) Umicore

### 14.4.3 Gold Nanoparticles

Gold has been used throughout history, with Cleopatra being framed for sleeping in a gold mask. Alchemists referred to gold as the “elixir of life.” In India, colloidal red gold was used in the form of Ayurvedic medicine for rejuvenation and revitalization during old age and was called Swarna Bhasma. Gold in cosmetics is used in two different forms: an ingredient of topical skin care (mask or cream) and as gold foil for direct application to skin.

Gold nanoparticles (AuNPs) have been widely employed in bionanotechnology for centuries as organic photovoltaics, sensory probes, therapeutic agents, and drug delivery in medical and biological applications based on their unique optoelectronic properties and multiple surface functionalities. The optical and electronic properties of AuNPs can be tuned for different applications by altering the shape, size, aggregation or surface chemistry. Due to the vibrant colors produced by their interaction with visible light, colloidal gold nanoparticles have been utilized for centuries by artists. Gold nanoparticles are available in a variety of solvent compositions in sizes ranging from 5 nm to 400 nm in diameter (Figure 14.6) with various surface functionalities.

Nanogold particles are applied/used in cosmetic products as an anti-aging material, as gold becomes a catalyst in the formation of collagen.



**Figure 14.6** TEM image of gold nanoparticles.

AuNPs act as a cofactor of enzymes, which helps in the formation of collagen in other tissues. For maintaining youthful skin, regular regeneration of collagen is an important process. A recent development in research of anti-aging cosmetics has obtained optimum catalytic effect by using AuNPs. Gold is an effective catalyst for the formation of C-O, C-H, C=O, C-C and N-H bonds. It is the basis of the existing bond with the exception of the membrane proteins collagen, which is the main and largest constituent of skin layers. Whenever there is damage to skin cells new skin will be formed immediately so that skin becomes firmer, more elastic and younger looking. Naturally occurring damage to collagen can be inhibited by continuous regeneration of collagen by employing gold nanoparticles as an important material in modern anti-aging cosmetics. Nanoscale forms provide a catalytic effect 20–200 times faster as compared to its micrometer size. The presence of nanogold particles is not harmful to the human body, as AuNPs do not show denaturation of proteins that exist in the skin collagen.

The nanoparticles penetrate deep into the skin and focalize on the outer layer of the skin as well as within. These golden antioxidants increase the flow of blood to the skin. This regenerates the flow of oxygen and skin cells of the face by reducing fine lines and wrinkles. The mineral rich and formulated skin care products with AuNPs vitalize the skin metabolism and detoxify the skin, making it feel younger and replenished. These minerals send essential nano atoms and exfoliants to revitalize cellular production. Another way this latest technology works is by delaying the aging process and maintaining the youthful appearance of skin.

#### 14.4.4 Silver Nanoparticles

Silver nanoparticles have received attention due to their physical, chemical, and biological properties that are attributed to their catalytic activity and bactericidal effects, which have found application in nanobiotechnological research. AgNPs are being used in numerous technologies and incorporated in a wide array of consumer products that take advantage of their desirable optical, conductive, and antibacterial properties. Due to the antibacterial properties of AgNPs, they can be used as a preservative in cosmetics. They were found to be very stable and showed sufficient efficacy against mixed bacteria and fungi and did not penetrate normal human skin. The antibacterial effect of AgNPs is due to the sustained release of Ag ions from the nanoparticles, which serve as a vehicle for silver ions. The antibacterial effects of AgNPs have been used to control bacteria growth in a variety of applications, including dental work, surgery applications,





**Figure 14.7** Pure silver 35,000 ppm skin cream containing 3,500 times more silver than 10 ppm colloidal silver gels.

wound and burn treatment, and other biomedical devices. Soap cleanser containing nanosilver was claimed to have bactericidal and fungicidal properties and was found useful in treatment of acne and sun-damaged skin. Silver nanoparticles have been used for cosmetic material ingredients and have no toxic effect on human cells, especially facial cells.

High efficacy within a short time span is an important parameter to prevent transmission of infectious diseases. Handwash containing 15 mg per liter nanosilver was found to satisfy both parameters very effectively.

Silver nanoparticle is a potent broad-spectrum antimicrobial agent and can protect against skin diseases like atopic dermatitis. AgNPs are also being incorporated into toothpastes and shampoos as preservatives. AgNPs had no effect on HaCaT keratinocytes and did not enhance UV-B-induced cell death at concentration of 0.002–0.02 parts per million.

These results suggest that AgNPs have potential for use as a preservative in cosmetics [7–9].

Nanosilver particles are employed in soaps, wet wipes, deodorants, lip products as well as body and face cream (Figure 14.7) and foams. Silver nanoparticle are also used in day and night creams to give the skin a fresher appearance, e.g., GNS Nanogistnanover™ Premium range of makeup contains nano silver.

#### 14.4.5 Selenium Nanoparticles

Selenium (Se) is a trace element that is essential for the body to carry out health maintenance and disease prevention. It exists in the human body



**Figure 14.8** Abbott Selsun S anti-dandruff shampoo for scaly scalp.

in the form of selenoprotein. Selenium has much potential to influence the immune system. An adequate supply of Se is crucial to sustain various cerebral functions. It is believed to support the healthy environment of the body and brings other numerous health benefits depending on multiple regulative effects. SeNPs promote development of Se-based nanomedicine, which refers to the medical application of nanotechnology involving nano-biosensors and biological nanodevices. The SeNPs possess many therapeutic advantages and are extensively utilized to deal with anti-diabetic efficacy, oxidative stress injury, inflammatory diseases, Se-related thyroid dysfunction, etc., and other biomedical applications. SeNPs have also been used to increase the sensitivity of chemotherapy by co-administration with a chemotherapeutic drug. Nanoscale Se has a very wide range of biomedical applications. Besides its use as an antioxidant, nano-Se also possesses potential as a chemopreventive and chemotherapeutic agent. When used in conjunction with antibiotics its anticancer efficacy is enhanced [10].

Selenium sulfide is a chemical agent commonly used for treating dandruff (Figure 14.8). It is an antifungal agent that also relieves itching, flaking, scaling, and dry skin on the scalp due to dandruff. Selenium sulfide is also used for treating seborrhea and tinea versicolor, which are fungal infections of the skin. Therefore, selenium nanoparticles are being included in many shampoos and skin care lotions.

## 14.5 Nano-Compositions Used for Loading and Delivery of Nanoparticle

For the purpose of delivery of required nanoparticles from the cosmetics compositions it is imperative that they are formulated in composite forms.

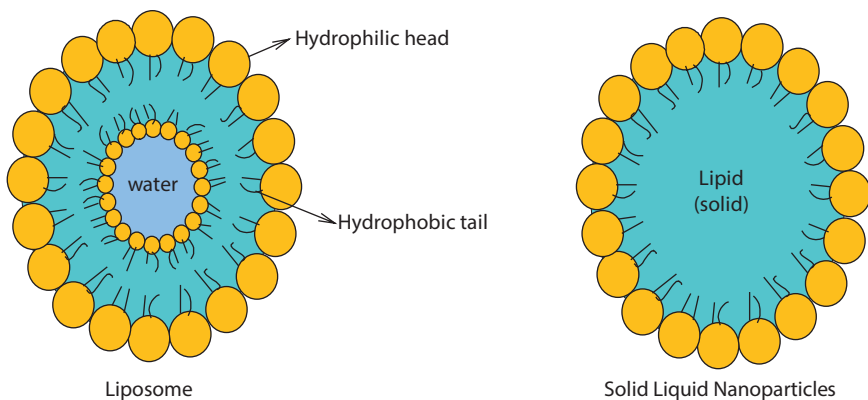


Composites are combinations of two or more components with varied physical and chemical properties which result in the formation of a new material with characteristics different from the individual composite.

### 14.5.1 Nanoliposomes

Liposomes are employed in a wide range of cosmeceuticals as they are nontoxic, biocompatible, biodegradable, and flexible vesicles and have the capacity to encapsulate active ingredients easily. Liposomes are concentric bilayered vesicles of hydrophobic and hydrophilic molecules. Nanoliposomes are used as vesicular delivery systems. The size of the liposomes typically varies between 20 nm to a few hundred micrometers. Liposomes are contained within a shell of one or more bilayer membranes of the lipid phosphatidylcholine (lecithin) (Figure 14.9), which are GRAS (generally regarded as safe) products.

The lipid bilayers of liposomes can fuse with other bilayer, such as cell membrane, which promotes the release of its contents, making them useful for cosmetic delivery applications. They are suitable for cosmetic application due to ease of their preparation, enhanced absorption of active ingredients by skin and continuous supply of agents into the cells over a sustained period of time. They are vesicular structures composed of a phospholipid bilayer and a hydrophilic core. Liposomes are suitable for delivery of hydrophobic and hydrophilic compounds as they have an ability to protect the encapsulated drug from the external environment.



**Figure 14.9** Schematic diagram of liposome having lipid bilayer enclosing an aqueous core (left) and solid lipid nanoparticle showing lipid monolayer enclosing a solid lipid core (right).

The first anti-aging liposomal cosmetic was Dior's *Capture* in 1986. Today nanoliposomes are used in a wide range of cosmetics in various forms like gels, creams and moisturizers. Nanoliposomes are an excellent choice for cosmetic formulations designed for dry skin because the lipid used for nanoliposome contains moisture; therefore, as the liposomal vesicle ruptures, moisture adheres to the skin surface and provides hydration. Liposome also creates a barrier over the surface of the skin. Liposomal vesicles form an occlusive adhering to the surface of skin which promotes the penetration of encapsulated active ingredients in the skin by protecting the cell from sunlight and sweat. This facilitates delivery of the active ingredients to the deeper skin layers, which is desirable for cosmetic products; for example, aqueous sun care products containing nanoliposome-encapsulated UV filters are water resistant. Moisturizer containing aloe vera leaf gel extract encapsulated nanoliposomes having anti-wrinkle qualities are far more effective than gel application alone.

Based on composition and indications, cosmetic nanoliposomes are divided into different types. Depending upon the features of the cosmetic products they are transferosomes, nanosomes, glycerosomes, oleosomes, niosomes, etc.

### 14.5.2 Solid Liquid Nanoparticles (SLN)

Due to the diminishing ozone layer, there is a need for effective UV protection systems with minimal side effects. Solid liquid nanoparticles have been reported to be an attractive carrier for various cosmetics, especially in sunscreens agents [11, 12]. Solid nanoparticles (SLNs) have the ability to reflect and scatter UV radiation on their own, leading to photoprotection. These structures are more stable than liposomes.

SLNs are nano-sized particles with a solid lipid matrix. They are composed of oily droplets that are embedded in a solid lipid matrix, which are solid at body temperature, and coated with surfactant acting as stabilizer. They contain a hydrophobic solid matrix core with a phospholipid coating. The hydrophobic tail regions of the phospholipid are embedded into the core matrix. These are the new group of lipid emulsions carriers, where solid lipid is being utilized instead of liquid lipid (Figure 14.9). SLNs have a higher efficiency of entrapment for hydrophobic drugs. Due to this, nano-sized solid lipid particles offer an advantage in sunscreen formulations by virtue of the high efficiency of lipophilic sunscreens and proper size for both coetaneous performance and minimal skin absorption [13, 14]. The size of SLN particle ranges from 50 to 1000 nm.

Since they have the capacity to protect the encapsulated ingredients from degradation, SLNs are useful for various cosmetic products. They exhibit many features for topical treatment of cosmetics, i.e., controlled release of actives, chemical and physical stability of active ingredients, drug targeting, and occlusion along with enhanced penetration and increased skin hydration. *In-vivo* studies have shown that an SLN-containing formulation is more efficient in hydration of skin. SLNs can be used for the controlled delivery of cosmetic agents over a prolonged period of time and have been found to improve the penetration of active compounds into the stratum corneum.

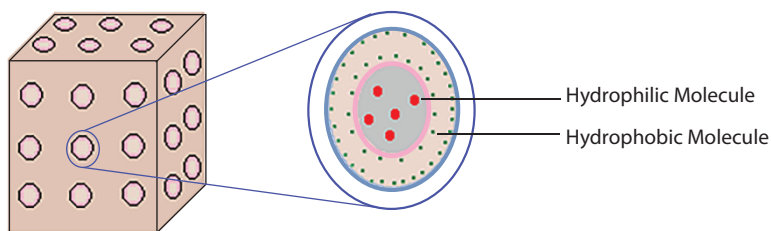
SLNs are composed of solid lipids or mixtures at a concentration of 0.1% (w/w) to 30% (w/w) in an aqueous dispersion. They are also tested in perfume formulations. Chanel's *Allure* perfume is incorporated into SLN nano-formulation.

Toxicity associated with the polymeric nanoparticles is minimized by utilizing biodegradable, biocompatible, physiological lipids to prepare these SLNs. These are extensively used for topical treatment of acne.

### 14.5.3 Cubosomes

Cubosomes are aggregates consisting of a few hundred to tens of thousands of atoms that combine in a cluster. They are nanostructured discrete submicron particles of bicontinuous cubic liquid crystalline phase, comprised of curved lipid bilayers organized into three-dimensional honeycomb-like structures separating two internal aqueous channels and large interfacial area with distinct amphiphilic, hydrophilic and hydrophobic regions. Cubic phases are viscous and crystalline with cubic crystallographic symmetry [15]. These are aggregates consisting of several hundred to thousands of atoms that combine in clusters. Cubosomes are composed of hydrophobic and hydrophilic molecules arranged in a cuboidal structure. Nanocrystals of cubosomes have been used in the cosmetics industry for the delivery of poorly soluble actives. They allow safe and effective passage of these actives through skin. Cubosomes are nanostructured particles of discontinuous cubic liquid crystalline phase stability. They serve as a carrier in drug delivery [16] for various bioactive molecules like drugs, peptides, and proteins to protect them from hydrolysis, oxidation or any other methods of degradation.

Nanocrystals of cubosomes have been used in the cosmetics industry for the delivery of poorly soluble actives. Discontinuous cubic liquid crystalline phase, either in bulk or cubosome form, offer properties of particular interest to the personal care product industry. Cubic phase materials can be formed by a simple combination of biologically compatible lipids and water



**Figure 14.10** Schematic diagram of cubosome. (Source: Ribier and Biatry, Cosmetic compositions comprising a stable aqueous dispersion of phytantriol-based gel particles containing a long chain surfactant as dispersant and stabilizer. *Eur. Pat. Appl.* 1995) [20].

and are thus well-suited for use in treatments of skin, hair, and other body tissues. They allow safe and effective passage of these actives through skin.

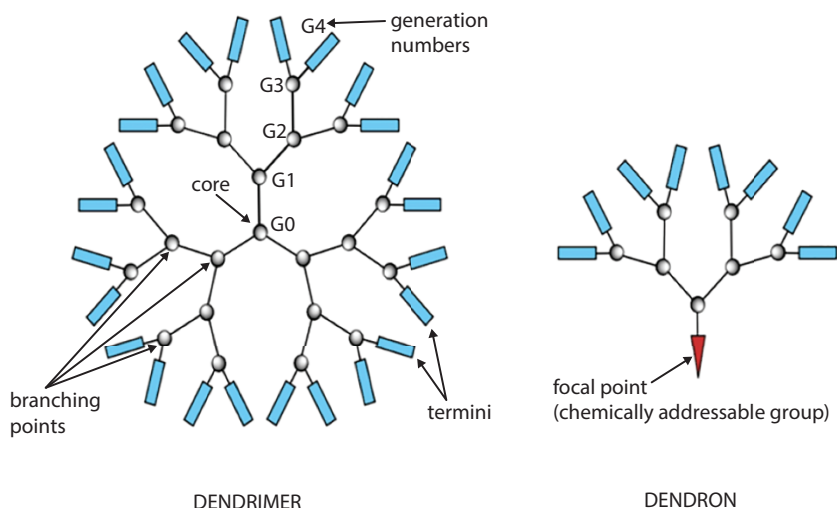
Cubosomes are curved bicontinuous lipid bilayers which are organized in three-dimensional structures resembling honeycomb-like structure with distinct amphiphilic, hydrophilic and hydrophobic regions (Figure 14.10). They serve as a carrier in drug delivery for various bioactive molecules such as chemicals, drugs, peptides, and proteins to protect them from hydrolysis, oxidation or any other method of degradation. Furthermore, several studies have demonstrated the benefits of cubosomes in nanoparticle drug delivery, sustained release, controlled release, and also to provide improved bioavailability.

L'Oréal, Nivea, and Procter & Gamble are investigating cubosomes for cosmetic applications. The use of cubosomal particle as oil-in-water emulsion stabilizers and pollutant absorbents in cosmetics is incorporated under modern development by L'Oréal. The latest patent activity by Nivea shows use of cubosome in personal care products like skin care, hair care, cosmetic products and antiperspirants [17–19].

#### 14.5.4 Dendrimers

Dendrimers are unimolecular monodispersed, micellar nanostructures (around 20 nm in size) with a well-defined, regularly branched symmetrical structure and a high density of functional end groups at the periphery (Figure 14.11). Dendrimers and hyperbranched polymers have also been considered for use in the cosmetics industry.

Dendrimers are known to be robust, covalently fixed, three-dimensional structures possessing both a solvent-filled interior core (nanoscale container) as well as a homogeneous, mathematically defined exterior surface functionality (nano-scaffold) [21]. They are prepared in a step-wise fashion, with architecture like a tree branching out from a central point. Hyperbranched polymers are effectively disorganized, unsymmetrical



**Figure 14.11** Schematic diagram of dendrimer and dendron.

dendrimers that are prepared in a single synthetic polymerization step, making them much more cost-effective than dendrimers. The large number of external groups are suitable for multi-functionalization, which is a requirement for their use as a cosmetic agent carrier. L'Oréal has a patent for a formulation containing hyperbranched polymers or dendrimers which form a thin film when deposited on a substrate. This formulation could be used for a wide variety of cosmetics, e.g., mascara or nail polish. A problem with current polymers is that films are formed too soon after deposition. The new formulations will form highly adherent, water washable films only upon oxidation, usually by exposure to air. It is also possible to incorporate cosmetic agents into the medium to help form films for different applications. They have also developed a formulation consisting of a tanning agent and dendrimers for artificial skin tanning. Unilever has a patent for hydroxyl-functionalized dendrimers from polyester units to create formulations for use in sprays, gels or lotions [23]. Several patents have been filed for the application of dendrimers in hair care, skin care and nail care products [24].

### 14.5.5 Nanocrystals

Nanocrystals are aggregates of hundreds to tens of thousands of atoms combined to form a cluster. Typical sizes of these aggregates are between 10–400 nm, and they exhibit optical, electrical and chemical properties that are not found in their bulk counterparts. Their properties, such as

crystalline structure, band gap, charge conductivity and melting temperature, can be altered by controlling the size and surface area. To prevent larger aggregate forms the crystals must be stabilized. This allows safe and effective passage to a molecule through skin. Nanocrystals have been used in the pharmaceutical industry for the delivery of poorly soluble actives.

Rutin and hesperidin are two poorly soluble plant glycoside antioxidants that previously could not be used dermally. Once formulated as nanocrystals they became dermally available as measured by their antioxidant effect. The dermal use of nanocrystals is protected by patents [24].

Incorporation of nanocrystals into cosmetic products is a straightforward process. Nanocrystals dispersed in water (nanosuspension) is admixed with a cosmetic product (typical dilution factor; 50). For cosmetic applications, nanocrystals are commercially available.

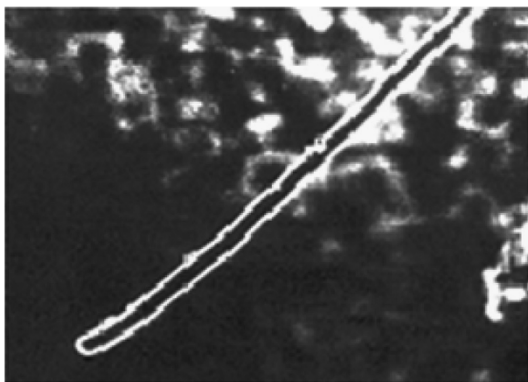
## 14.6 Cosmetics Containing Carbon Nanomaterials

Carbon nanomaterials, including carbon nanotubes, nanofluids, fullerenes, carbon nanoemulsions, nanocapsules, etc., are increasingly being used in the field of cosmetics owing to their unique size-dependent functions and physiochemical properties. These materials are considered to be safe for humans as well as for the environment because of their toxicological potencies.

### 14.6.1 Nanoforms of Carbon for Cosmetics Used in Ancient India that Still Prevail Today: Herbal Kajal/Kohl

Kajal and kohl are a black color cosmetic used for decorating eyes. India has an age-old tradition of preparing *kaajal* at home from the soot collected on a plate from burning herbal extract-soaked cotton in the presence of vegetable oil (mustard oil, coconut oil, and ghee) and camphor. Synthesis of *kaajal* is mentioned in epics like the Ramayana and the Mahabharata. Prof. Sharon of IIT Bombay produced *kaajal* by burning mustard oil (soaked in cotton piece) and, using a scanning electron microscope, showed that the raw soot has an extensive network of CNTs. He suggested that being a tubular structure, the carbon nanotubes do not pierce or irritate the eyes. The FESEM image of the sample prepared exhibits carbon nanoparticles of size less than 50 nm. Among his personal communications, Prof. Maheshwar Sharon has also shown that the soot is actually carbon nanotubes (Figure 14.12).

It has been found that the carbon-based nanoparticles (CNTs, graphitic CNF, fullerenes, graphene) have gained great importance in the field of cosmetics, because when the size of carbon particles decreases into nanoscale



**Figure 14.12** SEM image of carbon soot showing CNT. (Courtesy: Prof. Maheshwar Sharon from his personal collection).

range the antibacterial action increases due to the large surface area and the presence of a number of atoms near the surface. Carbon nanoparticles damage the membranes in bacteria due to photo-oxidation [25]. The use of nanoparticles in cosmetics is not new. Black soot and mineral powders have been used as cosmetics for thousands of years in ancient India. The properties of nanoparticles, such as easy release into skin, antibacterial property, and optical properties, make them ideal for use in various cosmetic preparations.

#### 14.6.2 Carbon-Based Cosmetics

Carbon black has been used as a temporary hair dye in hair coloring compositions and as a pigment in cosmetic formulations such as eye shadow, eye liner and mascara. The peptide-based carbon nanotube colorants provide significant advantages for high-performance hair coloring without damaging the hair. Its nano size provides a thin coating resulting in a smooth texture and volumizing effect to the hair. In addition to this, the strong affinity of the hair-binding peptide for hair results in a long-lasting coloring effect.

#### 14.6.3 Contemporary Cosmetics Using Carbon

- **Carbonates:** Incorporation of carbonates has been found to significantly control the grease of hair [26].
- **Activated Carbon:** Patanjali has come up with a product called Activated Carbon Facial Foam which they claim

absorbs and removes dirt and oil from the face, keeps pores clean and reduces blackheads. Apart from activated carbon it also contains *Aloe vera*, lemon and mint to provide a cooling wash and pleasant smell.

- **Carbon Black:** It is used as a pigment in many cosmetic formulations for dying white/grey hair black. However, it has some limitations because it has weak interaction with hair, ultimately staining other contacting surfaces such as clothes, combs, brushes and even the scalp. Moreover, Sugar and Kobermick (1966) [27] have shown that the use of eye cosmetics containing carbon black is linked to increased subconjunctival pigmentation and incidence of cancer. Nowadays many cosmetics, such as eyeliner, mascara, nail polish, eye shadow, brush-on-brow, lipstick, blushers, rouge, makeup, and foundation, contain carbon black. A list of big companies and their cosmetic products is given in Table 14.1.
- **CNTs:** To combat the various side effects of carbon black, CNTs are now being added to carbon black to enhance the affinity of carbon black for hair fibers. A patent by Huang *et al.* (2007) [28] provide new hair colorant and cosmetic compositions consisting of carbon nanotubes that have either been chemically functionalized or physically modified to increase their affinity for hair. The small size and increased surface-area-to-volume ratio of carbon nanotubes result in enhanced affinity and interaction with hair fibers for a lasting effect. Hiroyuki Muto *et al.* of Japan's Toyohashi University of Technology have developed a low-cost efficient method for producing electrically conducting composites based on electrostatic adsorption of CNTs onto resin and ceramic particles for applications including enzymes and cosmetics [29]. These CNTs are for cosmetics and enzymes.

## 14.7 Can Activated Carbon, Carbon Black and Carbon Nanotubes Be Replaced with CNF for Use in Cosmetics?

More than any other components, CNM and CNF are both ideal for oily, combination and acne-prone skin for absorbing oiliness and controlling oil production. It is no wonder that now the latest in the cosmetics



**Table 14.1** Cosmetics incorporating carbon-based products.

| Sr. no. | Company                | Cosmetic product                                                                             |
|---------|------------------------|----------------------------------------------------------------------------------------------|
| 1       | A! Absolute!           | Magnetic Nail Lacquer                                                                        |
| 2       | Boots                  | No7 Stay Perfect Eye Shadow                                                                  |
| 3       | Bourjois               | Liner Feutre Eyeliner                                                                        |
| 4       | butter London          | Nail Polish                                                                                  |
| 5       | butter London          | Patent Shine Nail Lacquer                                                                    |
| 6       | CoverGirl              | Intensify Me Liquid Eyeliner                                                                 |
| 7       | Jesse's Girl Cosmetics | Liquid Eyeliner                                                                              |
| 8       | L'Oréal Paris          | Infallible Never Fail Liquid Eyeliner                                                        |
| 9       | Max Factor             | False Lash Effect 24 Hour Bold Volume Mascara<br>Masterpiece Glide & Define Liquid Eye Liner |
| 10      | OPI Brazil             | Nail Lacquer Collection                                                                      |
| 11      | Prestige               | My Biggest Lashes Mascara                                                                    |
| 12      | RevitaLash             | Volumizing Mascara                                                                           |
| 13      | Revlon                 | ColorStay Liquid Eye Pen.                                                                    |
| 14      | SensatioNail           | Gel Nail Polish                                                                              |
| 15      | Surya Brasil           | Natural Nail Polish                                                                          |

industry world has been the use of CNM for whiter teeth and clearer skin. The idea behind this new trend of adding CNF to just about everything is based on the same idea of how activated charcoal works in filters. It removes contaminants and toxins from whatever it is in contact with due to its large surface area on a microscopic level, causing it to have important absorption properties. Therefore, the idea is that it traps impurities before or while they are in the body before causing unwanted damage such as acne or other skin health issues. As CNF is becoming more and more popular amongst cosmetics products, it is important to ask what impacts it will have on your body in the long run, or rather, does it have a dark side? However, several studies have concluded that it is safe for

external use but inhaling it is not safe and digesting it is fine in small quantities; and the FDA has also deemed it harmless due to its mineral-like qualities.

Although CNF is not metabolized, adsorbed or absorbed by the body, it can be used to treat some poisonous bites and disinfect some wounds. When used in a face mask, activated carbon binds to dirt and helps pull it out of our pores, making them less visible (it's the oil and dirt that makes them appear bigger). So, a face mask is great for all skin types to help control oil and acne problems. CNF can be used in shampoo for oil-free hair that is soft without turning the hair black. It is also incorporated into formulas for shampoos, fighting the oiliness of the scalp. CNFs are ideal for oily, combination and acne-prone skin since it absorbs oiliness more than any other component and controls the production of oil.

Like charcoal, which is still used in villages in India for cleaning teeth, CNF is also pretty safe for teeth. It's not acidic, and is quite soft. It is a passive agent and it isn't harmful to teeth. An attempt has been made to add CNF to toothpaste that is pH balanced and is sulfate free; and it was found to makes teeth pearly white as well as help maintain healthy gums.

## 14.8 Summary

This chapter gave a glimpse of the application of nanotechnology in personal care and cosmetics products, and the possibility of the entry of carbon black fiber (CBF) in many cosmetic products. The majority of cosmetic manufacturers around the world have started using nanoscale versions of ingredients in their products to manipulate matter at an atomic or molecular level so as to provide better protection from UV rays and other pollutants. Skin care and hair care products have received maximum attention because of the deeper skin penetration, delivery of active ingredients, and long-lasting effects of the nanomaterials. Some of the important nanoparticles that are extensively used in enhancing the efficiency of cosmetics include titanium dioxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), gold, silver, and selenium. Moreover, the role of the silent features and advantages of using these materials are discussed in this chapter. There are various nanocompositions, also known as composites, that are used for loading and delivering nanoparticles to the different layers of skin, such as nanoliposomes, cubosomes, dendrimers, and nanocrystals, which are also discussed along with their compositions, necessity, roles and characteristics to throw light on their importance in cosmetic products.

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# Carbon Nanofiber in Regenerative Medicine

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*The regenerative medicine revolution is upon us. Like iron and steel to the industrial revolution, like the microchip to the tech revolution, stem cells will be the driving force of this next revolution.*

Cade Hildreth

## 15.1 Introduction

### 15.1.1 Tissue Engineering – Concept in a Nutshell

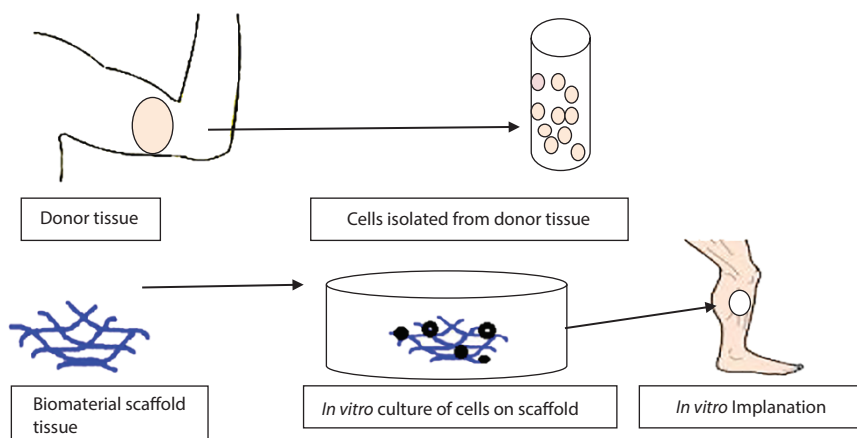
Tissue engineering is a discipline which is still in its infancy, but is rapidly emerging and receiving extensive attention [1, 2]. It involves replacement of the anatomic structure of damaged, injured or missing tissue or organs by agglomerating biomaterials, cells and biologically active molecules [3, 4]. Biomaterials are three-dimensional scaffolds which provide mechanical support to the growing cells or tissue, guiding them in a microenvironment mimicking the biological system. These can then be transplanted into the system. The schematic in Figure 15.1 illustrates that one approach to tissue engineering is to use a biomaterial scaffold to direct growth of the body's own cells in a lab and then implant the cells back into the body. The principal function of a scaffold is to direct cell behavior, such as migration,

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**Figure 15.1** Schematic representation of the use of tissue engineering on a scaffold and then implanting it in the desired organ of the body.

proliferation, differentiation, maintenance of phenotype and apoptosis, by facilitating sensing and responding to the environment via cell matrix communications and cell-cell communications [2, 5]. Such scaffold should have the capacity to give highly porous surfaces allowing seeding of cells at high densities as well as facilitating proper cell-cell interaction through a regulated molecular myriad [6, 7]. In addition, it also provides spatial signals to actuate the organization of the cell as well as that of the extracellular matrix derived from them.

The extracellular matrix (ECM) secreted by cells is responsible for supporting the tissue development and providing the microenvironment needed for cellular growth. ECM consists of an array of proteinaceous nanofibers conferring physical and chemical homeostasis of the tissue. For example, collagen is a natural extracellular matrix molecule having a fibrillar structure found in many tissues such as bone, skin, tendons, ligaments and other connective tissues. Earlier tissue engineers were mostly focused on investigations of macro-level structures. However, the present-day need is to engineer functional units of the subcellular scale structures and nanostructures to control cell molecular and cell-cell interactions [8]. Thus, engineering tissue for miniaturization at the nano level to precisely design mimicry of the native tissue structures is one of the most promising directions for the tissue fabricators.

There are four basic components in tissue engineering, i.e., biomaterial scaffold, functional cells, biomolecules (e.g., growth factors, ECM, other

functional molecules) and dynamic forces. This chapter deals with the most ambidextrous biomaterial scaffold, i.e., carbon nanotubes (CNT).

### 15.1.2 Why Carbon Nanotubes Are Versatile Scaffolds

This chapter demands focus on the use of carbon nanofibers in regenerative medicine. However, its cousin carbon nanotube (CNT) has received more attention from scientists in this direction. Therefore, it is imperative that we first look at the contribution of CNT and then look at the possibility of CNF's use.

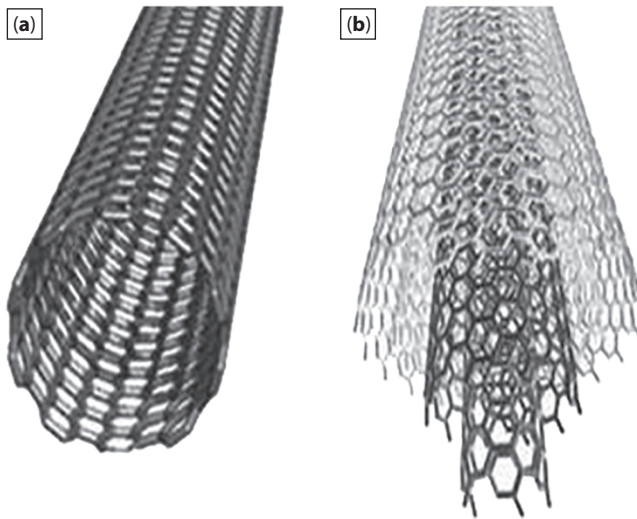
It has been clear till now that tissue engineering needs the design of smart biomaterials which can support cell growth without altering the biological functions required for growth of the tissue. Marriage between nanotechnology and microengineering can be the best option for designing biomaterials to generate scaffolds for tissue engineering.

Nanotechnology, the science which deals with material properties at nanoscale (1–100 nm), focuses on constructing designs either by bottom-up or top-down approach. The ability of nanotechnology to form materials which can act as biological machines, such as molecular motors, actuators and optical tweezers, has made it a reliable methodology for tissue engineering. Interestingly, nanomaterials can also be multifunctional, capable of both targeting and imaging [9].

One nanomaterial that has the potential for multiple uses in tissue engineering is carbon nanotube [10]. The field of biomaterial fabrication was revolutionized soon after the discovery of carbon nanotubes by Ijima (1991) [11]. Carbon nanotubes are cylindrical tubes of 2 to 100 nm diameter, resulting in very large surface-to-volume ratio. They are made up of carbon atoms arranged in a series of condensed benzene rings rolled up into a tubular structure (Figure 15.2a).

This smart material belongs to the family of fullerenes, the third allotropic form of carbon along with graphite and diamond. Single-walled carbon nanotubes (SWCNT) are constructed from a single sheet of graphite while multi-walled carbon nanotubes (MWCNT) consist of multiple concentric cylinders of graphite (Figure 15.2b). Both SWCNT and MWCNT possess very interesting properties such as ordered structures with high aspect ratio, ultralight weight, high mechanical strength, high electrical and thermal conductivity, metallic or semi-metallic behavior and high surface area [12]. These properties have made CNTs the favorite material for nanofabrication of compatible biomaterials which can act as scaffold for engineering tissues [13].





**Figure 15.2** (a) Single-walled carbon nanotube and (b) Multi-walled carbon nanotube.

There are four areas where carbon nanotubes have significant relevance for tissue engineering:

- Cell tracking and labeling
- Monitoring cellular physiology
- Regulating cellular behavior
- Structural support for tissue engineering

## 15.2 Cell Tracking and Labeling

It is important to trace implanted cells and monitor the advancement of tissue formation *in vivo* in tissue-engineered fabrications of clinically relevant sizes. Tagging implanted cells would assess or evaluate the viability of engineered tissue and also help in understanding biodistribution and the migration pathway of transplanted cells. For tagging, contrasting agents *in vivo* need to have good biocompatibility and stability. The literature thus far has shown that CNTs are feasible as imaging contrast agents for optical labeling, magnetic resonance and radiotracer modality.

### 15.2.1 Optical Labeling

Optical detection can be a simple and direct diagnostic method for biomedical imaging. Carbon nanotubes reflect many characteristic properties

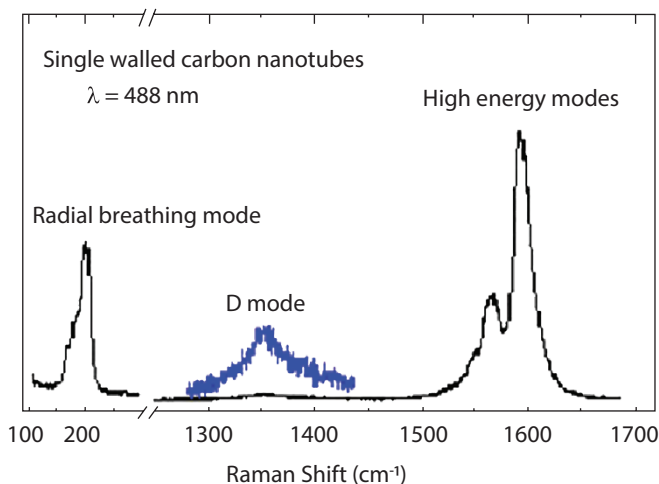
desirable for optical detection. They possess optical transitions in the near-infrared (NIR) region. The infrared spectrum between 900 and 1300 nm is an important optical window for biomedical applications because of the lower optical absorption (greater penetration depth of light) and smaller autofluorescent background [14]. In addition, carbon nanotubes display good photostability. Raman scattering and fluorescence spectroscopy may be promising methods for tracking carbon nanotubes in cells over long periods of time. For instance, SWCNTs dispersed in a Pluronic surfactant incubated with mouse peritoneal macrophage-like cells can be imaged using fluorescence techniques. Approximately 70,000 nanotubes were reported to be ingested per cell at the rate of one nanotube per second [15]. Excitation at 660 nm is the signature absorption of the single-walled carbon nanotube. SWCNTs are very stable when inside the biological cell. Nucleic-acid encapsulated SWNTs have been shown to be stable for weeks when ingested by 3T3 fibroblasts and murine myoblast stem cells [16]. The nanotubes remain in the cells during repeated cell divisions, suggesting that such probes could be used for studying cell proliferation and stem-cell differentiation.

Carbon nanotubes remain stable in the cell because of their hydrophobic nature. They are internalized by a myoblast stem cell. The concentration of such CNTs within the cell can be determined using the signal intensity. Since Raman spectroscopy is very sensitive to functional groups in a molecule, it may provide useful information about the microenvironment of the cell. This is one of the most promising methods for using carbon nanotubes as optical biosensors *in vivo* and can serve as a cornerstone technique for more complicated techniques [16].

The problem associated with this method is tissue absorbing or scattering light, autofluorescence, and photobleaching. In many cases, the optical absorption bands are narrow and the resulting emissions are broad. This can limit the simultaneous detection of multiple fluorophores; hence, this aspect has to be looked into prior to using CNT for optical labeling [15].

### 15.2.2 Magnetic Resonance Imaging (MRI) Contrast Agent

Magnetic resonance imaging is a technique which involves proton relaxation associated with the water molecules interacting with coordinated paramagnetic ions. There has been a significant impact of MRI contrasting agents like gadolinium-based nanoparticles, iron oxide superparamagnetic nanoparticles and quantum dots [17–19]. Fullerenes such as Buckminsterfullerenes and carbon nanotubes are composed entirely of carbon, thus providing poor contrast in MRI. These require functionalization



**Figure 15.3** Standard Raman spectra of SWCNT showing RBM, D-Mode and HEM (Source: Thomsen and Reich, 2003; Ferrari and Robertson, 2004) [22, 23].

to make them more readily detectable, which is done by attaching a heavy metal such as gadolinium to the surface of the fullerene or caging the heavy atom [20, 21].

Raman spectrometry can be used to characterize CNTs. Each part of the Raman spectrum (Figure 15.3), the radial breathing mode (RBM), the disorder-inducing mode (D-mode) and the high-energy mode (HEM), can be used to access different properties of single-walled carbon nanotubes [22, 23]. Out of all the Raman modes, the radial breathing mode is unique to single-walled carbon nanotubes. In the high energy range of around  $1600\text{ cm}^{-1}$ , single-walled nanotube shows a characteristic double-peak structure.

There has been a demonstration of gadolinium loading into ultra-short (20–100 nm long) nanotubes through sidewall defects, which displays 40 times greater proton relaxivities than the standard gadolinium clinical contrast agent. With such a large contrasting capability such materials can be dispersed throughout an engineered tissue, allowing the complete process of its monitoring.

### 15.2.3 Radio Labeling

Radio labeling involves use of radioisotopes like  $^{111}\text{In}$ , whose radioactivity can be measured by scintillation counters. Carbon nanotubes are covalently bound to the radioisotope and are then administered into the biological system to measure the biodistribution of nanotubes. In a research

study with BALB/c mice, such functionalized SWCNTs were shown not to accumulate in any specific organ and are rapidly cleared from the blood system through the renal excretion route without any toxic side effects or mortality, and could be visually observed in the urine [24].

### 15.3 Sensing Cellular Behavior

Monitoring cellular physiology such as solute transport, enzyme/cofactor interactions, secretion of protein and metabolite and cellular behavior, such as matrix adhesion, assists in fabricating better engineered tissues. Continuous monitoring of the performance of the engineered tissues could be provided by biosensors. Already, tissue and cellular responses have been observed using other nanoparticle contrast agents such as inflammation of pancreatic islets [25], apoptosis and angiogenesis [26, 27]. One method of monitoring engineered tissues would be to use implantable sensors capable of relaying information extra corporeally. Such a sensor would offer real-time data related to the physiological relevant parameters such as pH,  $pO_2$ , and glucose levels.

There are several advantages in using nanosensors for evaluating engineered tissues *in vivo*. First, because the sensing element is nanosized, miniaturization of the probe and implanting throughout an engineered tissue would not adversely perturb the system. Second, due to their enormous surface area, the active area is large for immobilizing numerous biological and chemical compounds, including DNA [28] and proteins [29], for improved sensitivity. Biosensors are electrochemical devices which rely on the transduction of the molecular recognition event into an analytical output signal. Amongst many molecular recognition biomolecules, single-walled carbon nanotubes are one of the most promising candidates for the development of nanoscale biosensor, because of their capability to provide strong electrocatalytic activity and minimize surface fouling of the sensors [30]. SWCNTs were reported to have high ability to promote electron transfer reactions in electrochemical measurement [31]. They have a high aspect ratio so that the total surface for electrode becomes significantly large on the same site than the surface of the bare electrode. Electrochemical biosensors based on carbon nanotubes array (CNT) modified electrodes have been reported previously by Kerman *et al.* (2003) [32]. Amongst the plethora of biosensors, the ones which are responsible for electrochemically detecting total prostate-specific antigens with SWCNT modified platinum array microelectrode, were monitored using some linkers like dimethyl formamide solution. Label-free electrochemical

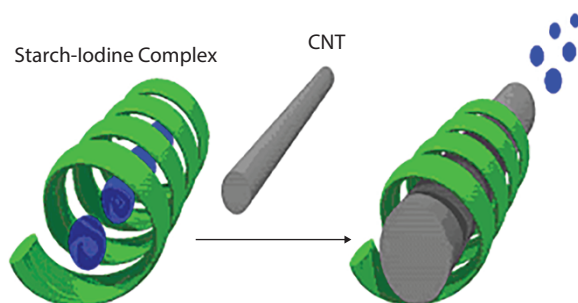
immunosensors in connection with a linker molecule that has a high affinity for graphite structure exhibited high selectivity with successful suppression of the non-specific adsorption [33].

Carbon nanotubes have very strong potential to address the needs of even label-free sensing for protein arrays [34]. They are functionalized and their conductance is modulated as the target molecules bind to the functionalized carbon nanotubes. This sensing technology has been used to detect the binding of small virus particles [35], small molecules binding to proteins [36] and streptavidin [37] and anti-biotin immunoglobulin binding to immobilized biotin [37].

Coupling carbon nanotubes with macromolecules has paved the way for various applications in fields like molecular electronics, drug delivery and pharmaceuticals. Because of their unique electronic structures, carbon nanotube electrochemical sensors can potentially simplify the analysis of redox-active proteins and amino acids, allowing cell monitoring in engineered tissues.

## 15.4 Augmenting Cellular Behavior

Carbon nanotubes can make an impact in tissue engineering in controlling the production or delivery of tissue-inducing substances such as growth factors. These are very well known for a number of cell-altering applications, including localized drug delivery [13] and transfection [28], and also as ion channel blockers. Many of these methods take advantage of the large aspect ratio and ease of functionalization of carbon nanotubes. Thus, carbon nanotubes could be components of drug delivery systems. A significant advantage of carbon nanotubes over spherical nanoparticles is that they can be heterogeneously functionalized. The ends and sidewalls of carbon nanotubes possess different chemical reactivities that can facilitate a dual-functionalized drug delivery platform. For instance, amine containing targeting agents such as antibodies could be attached to the ends of the nanotube. Drugs can then be linked with biodegradable linkers to the sidewall of the carbon nanotube and a targeting or imaging moiety can be attached to the ends. In another instance, experiments with starch8b have revealed that, although carbon nanotubes are not soluble in an aqueous solution of starch, they are soluble in an aqueous solution of the starch-iodine complex (Figure 15.4). The reversible water solubilization of SWCNTs in water using starch may provide the means for developing fully integrated biological nanotube devices. These observations suggest that iodine pre-organizes the backbone of the amylose in starch into a helical



**Figure 15.4** Starch-iodine complex with CNT.

conformation and makes its hydrophobic cavity accessible to a single carbon nanotube or bundles thereof. The formation of such starch-wrapped SWCNT complexes is driven by simultaneous enthalpic and entropic gains that result from creating favorable van der Waals interactions and from expelling the many small iodine molecules located inside the helix out into the solvent by a “pea-shooting” type of mechanism. This result has led to a simple protocol for the cleaning up of SWCNTs with starch.

Carbon nanotubes facilitate delivery of DNA or any bioactive agent to cells. They can be functionalized to attach either electrostatically or covalently to DNA and RNA, and the remaining unfunctionalized and hydrophobic portions of the nanotubes can be attracted to the hydrophobic regions of the cells. This hydrophobicity explains non-specific binding between nanotubes and proteins [29]. In addition, they can be functionalized with bioactive proteins to help cross the cellular membrane. For example, biotin-functionalized carbon nanotubes bound to fluorescent dyes were capable of intercellular transport of fluorescent streptavidin. Nanotubes can also be functionalized with cationic components capable of penetrating human and murine cell types. Such nanotubes can be complexed with plasmid DNA to facilitate transfection of cells [25]. In addition, DNA or siRNA can be bound to nanotubes with cleavable disulfide bonds and delivered to mammalian cells [14].

Besides heterogeneous functionalization, carbon nanotubes could provide localized delivery of therapeutic agents elicited by external sources. Previously, it was revealed that carbon nanotubes absorb NIR light at wavelengths that are optically transparent to native tissue. For example, irradiation with 880 nm laser pulses can induce local heating of SWNTs *in vitro*, thereby releasing its molecular cargo without harming cells, or can be internalized within a cancer cell and with sufficient heating kill the cell. This could allow selective delivery of drugs to certain

cell types, helping to control the distribution of such cells throughout the engineered tissue.

## 15.5 Carbon Nanotubes as Structural Support for Tissue Engineering

Carbon nanotube as structural support for tissue engineering of the growing tissue is a very pivotal role played by carbon nanotubes. Structural support or matrix defines the space for engineered tissue and helps in the process of tissue development. Synthetic polymers, such as PLGA and PLA, lack the required mechanical strength and such material cannot be easily functionalized. The best support for the growing tissue is provided by carbon nanotubes. CNTs have the potential for providing the needed structural and mechanical reinforcement for tissue scaffolding [38]. They can be grown on a patterned bed of catalysts, thus creating 3-dimensional arrays having complete control in size, shape and periodicity. This can be exemplified when L929 mouse fibroblasts and neurons have been grown on such scaffolds [39]. In a recent study, Ago *et al.* (2006) [40] have demonstrated mechanical immobilization of Hela cells on aligned carbon nanotube array through insertion of nanotube tips into the cell. This type of an array has proved to be successful in that it can fix a much larger number of cells compared with the flat surface of a Silicon substrate, which indicates strong binding force of the aligned nanotubes towards the cell. This has been considered to be the first avalanche of mechanical cell immobilization which offers future applications of the nanotube array for cell biology, tissue engineering and biomolecular devices. Since carbon nanotube is not biodegradable and is not readily dispersed in aqueous solutions, it is blended with polymers. For example, MWCNTs mixed with chitosan bring significant improvement in mechanical properties, Young's modulus and tensile strength compared to neat chitosan [41].

*In-vitro* study showed several different types of cells successfully grown on carbon nanotubes and nanocomposites. For example, natural scaffolding agent like collagen blends with SWNT, supporting smooth muscle cell growth [42]. Because of their diameter of approximately 100 nm, carbon nanotubes can possibly be used to mimic neural fibers for neuronal growth. Hippocampal neurons from 0- to 2-day-old Sprague-Dawley rats have been grown on carbon nanotubes coated with 4-hydroxylneonetal [43].

Nanotubes in an array can be used to construct neural networks. Cortical tissue from 1-day-old Charles River rats has been cultured on a nanopatterned substrate containing carbon nanotubes [44]. The dissociated



neuronal cells were self-organized into an ordered, compactly wired network on the three-dimensional array of CNT islands. Neuron deposited on CNTs showed a significant increase in the frequency of spontaneous post-synaptic currents. This significant difference is due to the electrical conductivity of the CNTs, a property which can be a useful tool for directed cell growth. For example, when an alternating current is applied to the substrate, nanocomposites of polylactic acid and MWCNTs have been shown to increase osteoblast proliferation, increase in calcium production and an upregulation of collagen I, osteonectin and osteocalcin. This has attracted researchers to use nanocomposites as stimulators of bone formation [45].

Carbon nanotubes can also be functionalized to release bioactive factors like glucose oxidase, which can be attached to nanotubes and still retain the enzymatic activity [46]. This has attracted researchers to use carbon nanotubes having inherent electrochemical properties coupled with enzymatic or protein functionalization as a paradigm scaffold providing mechanical integrity for cell growth and simultaneously monitoring the growth process.

## 15.6 Cytotoxicity of Carbon Nanofiber (CNF)

Carbon nanotubes (CNTs) are nanostructures derived from rolled graphene planes which possess various interesting chemical and physical properties. CNTs exist as single (SWNTs), and multi-walled (MWNTs) structures (Figure 15.2). The results of CNT toxicological assays found in the literature are contradictory. Some preliminary *in-vitro* tests have showed that CNTs are toxicologically benign to certain cells, while other further studies have indicated that CNTs, especially raw materials, are potentially dangerous to many living systems [47–49]. It is perceived that pharmacological activities of CNTs conjugated with therapeutic molecules are still not applied in men and consequently their clinical toxicity is also not evaluated.

The toxicity of CNTs has been an important issue in the scientific community because they have fiber-like characteristics in terms of their elongated shape, dimensions and aspect ratio. Thus, in many ways they resemble asbestos fibers. Considerable efforts have been made to investigate the toxicity and biocompatibility of CNTs both *in vitro* and *in vivo* [50–52]. CNTs have been tested *in vitro* in various cell types, e.g., lung epithelial cells, mesothelial cells, keratinocytes, and fibroblasts, and some authors have demonstrated that CNTs induce cytotoxicity and/or inflammatory responses [53–57], while others have found CNTs to be biocompatible when cultured with cells *in vitro* [58, 59]. The data concerning the



potential hazards related to CNT exposure to date is not conclusive. This apparent inconsistency in the literature might be due to the fact that different CNTs were used in these studies. It is known that (i) carbon nanotubes are synthesized and purified by different methods, (ii) they can be single- or multi-walled, (iii) they have various length and diameter distribution, and (iv) they can be subjected to numerous surface modifications. Furthermore, different cell lines and assays were often employed for the toxicological evaluation of these materials. These variations, not only for carbon nanotubes, but also for nanoparticles in general, present significant challenges in the assessment of their potential toxicity [60].

Upon the introduction of a foreign substance in the body, understanding the organism's response is a crucial step [38]. There is a dilemma in the literature concerning the cytotoxicity of fullerene nanomaterial such as buckyballs and carbon nanotubes. Without a discussion of the cytotoxicity of carbon nanotubes, this chapter will remain unjustified. Several *in-vitro* studies report that carbon nanotubes are cytotoxic when incubated for 6 h with alveolar macrophages [61]. It is worth noting that CNTs which are cytotoxic are 90% pure, the remaining balance being the amorphous carbon and residual catalyst. Interestingly, C60 was also analyzed and found to be relatively less toxic. Molecular characterization of the cytotoxic mechanism of MWCNT and multi-walled carbon nano-onions (MWNO) on human fibroblast indicates that the effect of gene expression is dose dependent [62]. At concentrations of 0.6 micro gram per ml, a serious impact on cellular functions in maintenance, growth, and differentiation occurs. The observed effects on the expression of P38/ERK and EGFR from fibroblast in contact with these fullerenes suggest that they may be useful nanomedicine for cancer therapy, especially those derived from epithelium. The reason for the observed cytotoxicity is oxidative stress and activation of nuclear transcription factor- $\kappa$ B in human keratinocytes [63] (Manna *et al.*, 2005). There are three important factors which decide the potential of a particle to be toxic [64, 65].

- The surface area/mass ratio of the particle – a large surface area provides the particle a greater area for interaction with the cellular membrane, as well as great capacity for absorption and transport of toxic material.
- The particle retention time – the longer the particle stage with the cellular membrane, the greater the chance of damage is.
- The reactivity or the inherent toxicity of the chemical content within the particle.

The following properties of carbon are particularly more hostile:

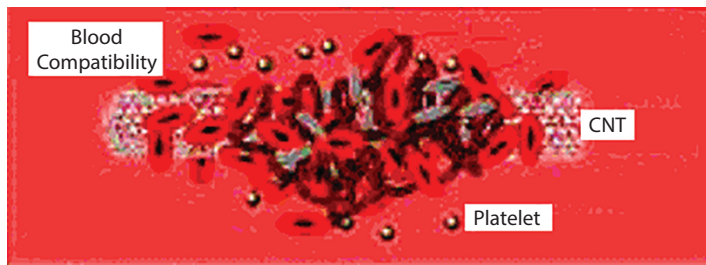
- Highly pure carbon black with an average particle diameter of 14 nm increases oxidative stress in human type II alveolar epithelial cells *in vitro* [66, 67] (Stone *et al.*, 1998; Barlow *et al.*, 2005).
- Long-term inhalation of carbon black with an average diameter of approximately 16 nm can lead to development of pulmonary tumors in rats [68].
- C60 fullerenes have not proved to have significant toxicity [69].

Shvedova *et al.* [57] reported the first cytotoxicity study on CNT in 2003. They investigated the effects of impure SWCNT on immortalized human epidermal keratinocyte (HaCaT). HaCaT cells were incubated up to 18 h in media containing unrefined SWCNT (0.062–0.024 mg/ml). Exposure to SWCNT resulted in accelerated oxidative stress, loss in cell viability and morphological alteration to cellular structure. It was concluded that these effects were the result of a high level of iron catalyst present in the unrefined SWCNT; dermal toxicity was also a consequence of handling unrefined CNT. Similar dermal toxicity was reported in a study which found that MWCNT initiated an irritation response in human epidermal keratinocytes [70]. Purified MWCNT (synthesized via CVD) incubated at the doses of 0.1–0.4 mg/ml with HEK cell for up to 48 h were observed to localize within the cells, eliciting the production of the pro-inflammatory cytokine (IL-8) release and decreasing cell viability in a time- and dose-dependent manner. Thus, lack of catalyst leads to a toxicological effect.

Jia *et al.* (2005) [61] investigated the effects of carbonaceous nanoparticles on the cytotoxicity of alveolar macrophages, which showed that SWCNT exhibited the most cytotoxic response compared to MWCNT. Cui *et al.* (2005) [37] investigated the cytotoxicity of SWCNT, showing that SWCNT inhibited human embryonic kidney (HEK293) cells by inducing apoptosis and decreasing cellular adhesion ability. Both cell proliferation and adhesion ability decreased in a dose- and time-dependent manner. Genes involved in apoptosis were unregulated, while genes associated with the G1 phase of the cell cycle were down-regulated along with the genes associated with adhesion.

## 15.7 Biocompatibility of Carbon Nanofibers

Biocompatibility is defined as “the ability of a material to perform with an appropriate host response in a specific application” [71]. As carbon



**Figure 15.5** Schematic illustrating the biocompatibility of platelets with carbon nanotubes.

nanotube finds its application in different facets of technology, it has become imperative that CNT biocompatibility be properly investigated before its widespread use. Pyrolytic carbons initially were considered to be excellently blood compatible. Heart valves made of pyrolytic carbon were highly compatible, with good adherence of endothelial cells and minimal adherence and activation of platelets. Recently, diamond-like carbon (DLC) has been demonstrated for use as coating for many orthopedic and cardiovascular applications [72, 73]. They have been found to be biocompatible in the way in which they can adhere to osteoblast and fibroblast cells and allow proliferation of these cells. DLC coatings on cardiovascular stents have also been found to reduce platelet (Figure 15.5) and macrophage activation [74, 75].

The above carbon-based biomaterials have been found to be biocompatible and hence CNTs are also considered to be the next probable candidate as a biomaterial. Various investigations dealing with the interaction between CNT-based materials and neural cells, osteoblasts, fibroblasts, antibodies and the immune system, ion channels and cellular membranes are discussed below.

### 15.7.1 CNTs with Neuronal Cells

Carbon nanotubes have been found to be biocompatible for neural applications [43, 44, 76]. The investigation done by McKenzie *et al.* (2004) [76] showed the effects of varying carbon nanofibers and surface energy on proliferation and function of astrocytes. It was found that astrocytes preferentially adhered to and proliferated on larger diameter and higher surface energy CNF. Webster *et al.* (2009) [77] investigated the interaction between nanocomposites (polyurethane/CNF) and astrocytes. But due to lack of dispersion, CNF has turned out to have poor mechanical

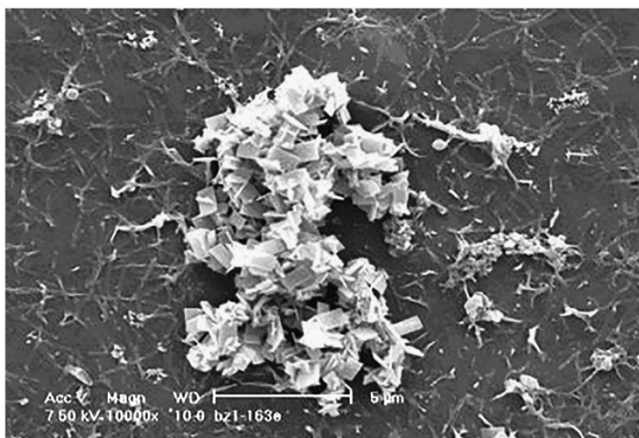
properties. This nanocomposite also exhibits decreased astrocyte adhesion and retarded neurite in rat pheochromocytoma cells.

Both pristine and chemically functionalized CNT have a positive impact on neuronal growth. Confluent layers of neurons were seeded onto lithographically patterned CNT surfaces and axons formed an interconnected network that replicated the pattern of CNT template. Similarly, purified MWCNTs that were chemically functionalized with carboxylic acid, ethylenediamine or poly-m-aminobenzene sulfonic acid were each observed to provide a substrate for neurite extension.

### 15.7.2 CNTs with Osteoblast Cell

Elias *et al.* (2002) [78] investigated the proliferation and function of osteoblast cells seeded onto four variants of compacted CNFs (of diameter >100 nm or <100 nm). They concluded that there was increased osteoblast proliferation on the nanophase (<100 nm) CNFs and increased alkaline phosphatase activity, intracellular protein synthesis and deposition.

Consequently, Zanello *et al.* (2006) [79] also examined osteoblast cells cultured on SWNTs that produced plate-shaped crystals (100–1000 nm in length, and approximately 20 nm thick) similar in shape to hydroxyapatite (HA) crystals, which aggregated in clusters outside the cells (Figure 15.6). Although plate-shaped crystals aggregated on the nanomaterials in a disordered fashion, results indicated that CNTs constitute a suitable substrate for deposition of a mineralized matrix.



**Figure 15.6** Osteoblast cells cultured on SWNTs (Source: Zanello *et al.*, 2006).

### 15.7.3 CNTs with Antibody Interactions

The generation of fullerene-specific antibody was first determined by Chen *et al.* (1998) [80], which were achieved by the immunization of BALB/c mice with a C60 fullerene-thyroglobulin conjugate, yielding a polyclonal IgG antibody that could bind to both C60 and C70 fullerene derivatives. In a similar study by Erlanger *et al.* (2001) [81], binding of C60-specific monoclonal antibodies to SWCNT was investigated. The study shows that the antibodies are bound to aqueous SWCNT ropes. Poly-L-lysine adsorbed onto CNT was shown to enhance antibody and protein binding. Similarly, binding of monoclonal antibody was influenced by the hydrophilicity and surface disorders of the fibers [82].

### 15.7.4 Ion Channel Interactions with CNTs

The interaction between SWCNT, MWCNT, fullerenes and ion channels were investigated. It was found that SWCNT blocked the channels formed from exp-2, kvs-1, and HERG-potassium channels. Fullerenes were discovered to be less effective channel blockers than CNT [83].

## 15.8 Dispersion of Carbon Nanofibers

The most oblivious question raised against carbon nanotube is its non-biodegradability and non-dispersibility, leading to its toxicity. The manipulation and characterization of a large number of individual CNTs is a difficult task because high molecular weights and strong intertubular forces (both van der Waals and electrostatic) promote the formation of bundles and ropes of CNTs [84]. Since many applications of CNT (biomedical or otherwise) require its dispersion in a variety of solvents, there has been much investigation done on improving CNT solubility. The most successful and popular methods are sonication, stabilization with surfactant, and covalent functionalization

### 15.8.1 Sonication

Sonication is the most efficient method for segregating CNT agglomerates in solution, thus leading to its dispersion. There are two main methods of sonication, the ultrasonic bath and the ultrasonic probe, and both are involved in bubble nucleation and collapse mechanism. Ultrasonic baths typically have higher operating frequencies (40–50 KHz) and no defined

cavitation zone, while ultrasonic probes operate at frequencies of around 25 KHz with a conical bubble nucleation zone extending from the probe tip [85, 86].

### 15.8.2 Stabilization with Surfactant

Surfactants are used to enhance CNT solubility in aqueous solution. Sodium dodecyl soleplates (SDS), Pluronic and Triton X-100 are three of the most popular surfactants [87, 88]. Likewise, biomolecules such as DNA [89], protein [90] and carbohydrates [91] are commonly studied surfactants to solubilize CNT in aqueous solutions. Unfortunately, some processing conditions have been found to cause surfactant dissociation from CNT.

### 15.8.3 Covalent Functionalization

Carbon nanotubes can be solubilized using various covalently attached molecules, such as peptides, acids, amines, and polymers, on the side walls of CNT. This is most commonly achieved by amidation or esterification of the carboxyl groups present after CNT purification by the reactive nature; many of these methods are associated with uneven surface coverage or inter-CNT coupling [87, 92, 93].

## 15.9 Summary

The principal task of a scaffold is to direct cell behavior, such as migration, proliferation, differentiation, maintenance of phenotype and apoptosis, by facilitating sensing and responding to the environment via cell matrix communications and cell-cell communications. Such scaffold should have the capacity to give highly porous surfaces, allowing seeding of cells at high densities, as well as provide spatial signals to actuate the organization of the cell as well as that of the extracellular matrix derived from them. Both SWCNT and MWCNT possess very fascinating properties as a scaffolding agent such as ordered structures with high aspect ratio, ultra-lightweight, high mechanical strength, high electrical and thermal conductivity, metallic or semi-metallic behavior and high surface area. These properties have made carbon nanotubes a favorite material for nanofabrication of compatible biomaterials which can act as scaffold for engineering tissues.

Carbon nanotubes have found importance in various aspects of tissue engineering, i.e., cell tracking and labeling, monitoring and regulating cellular behavior and acting as structural support for fabrication of a tissue.

All these applications will be rendered useless if carbon nanotubes are not safe and biocompatible. Hence it becomes imperative to check for their cytotoxicity. Dispersion of bare carbon nanotubes is also a matter of relevance, which requires their proper functionalization.

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# Carbon Nanofibers and Agro-Technology

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*The discovery of agriculture was the first big step toward a civilized life.*

Arthur Keith

## 16.1 Introduction

A brilliant vital thought that was envisioned by Richard Feynman was presented in 1959 in a lecture entitled “There’s Plenty of Room at the Bottom,” which eventually culminated in a new vista of Nanotechnology.

Nanotechnology promised us materials at 1–100 nm scale with new properties, various applications and new technologies with inputs from all the branches of science, be it chemistry, physics, biology, medicine, diagnostics or engineering. The uniqueness of Nanotechnology is described by the U.S. National Science and Technology Council in the statement: *The essence of Nanotechnology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supramolecular levels and to learn to efficiently manufacture and use these devices.*

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### 16.1.1 The Importance of Nanoscale

Nanotechnology is the ability to build micro and macro materials and products with atomic precision. The Greek word “Nano,” meaning “dwarf,” refers to a dimension which is one thousand times smaller than a micron. One nanometer (nm) is one billionth of a meter and it is also equivalent to ten Angstroms; 1 nm is 10,000 times smaller than the diameter of a human hair. Following are some reasons why at nanoscale materials exhibit magical properties that are so significant:

- Nanotechnology permits us to make new materials using the self-assembly features of nature, thus bridging the biology with material chemistry, and come out with new materials.
- Variations on the nanoscale are responsible for quantum mechanical wavelike properties of electron inside matter.
- The properties, such as charge capacity, magnetization and melting temperature of materials, can be changed by designing them at nanoscale without changing their chemical composition.
- Nanomaterials have very high surface-to-volume ratio, making them ideal for use in composite materials, reacting systems, drug delivery, and chemical energy storage such as hydrogen and natural gas.
- Nanomaterials have been shown to be better and improved conductors of electricity, which has resulted in new smaller, faster, more sophisticated electronic devices that consume less power.

### 16.1.2 Carbon Nanomaterials

A series of discoveries in a short span of less than two decades, i.e., fullerenes in 1985 [1], carbon nanotubes in 1991 [2], and graphene in 2004 [3], has led to Carbon Nanotechnology as an evolving tool to unravel as well as comprehend the appearance of strange, but useful structures such as fullerene, carbon nanotube (CNT), carbon nanobead (CNB), carbon nanofiber (CNF), carbon quantum dots; when it ventures into the kingdom of nanoscale (1–100 nm). Each of these structures have shown the emergence of unique physicochemical and optoelectronic properties. These novel properties are primarily due to the confinement of electrons within particles of dimensions smaller than the bulk electron delocalization length. This ability to tune the optical absorption or emission

properties (Quantum Dots) by simple variation in nanoparticle size is particularly attractive in the facile band-gap engineering of material and the growth of quantum dots. Carbon nanofibers (CNFs) are one of the allotropes of carbon, which consist of graphene layers arranged in the form of stacked cones or like a cup diameter in nanometer and several millimeters in length. CNFs have been applied in the field of medicine in some diagnostic methods, for drug delivery, tissue regeneration, biosensor, etc.

This chapter deals with one of the carbon nanomaterials, the carbon nanofibers (CNF), with special emphasis on their application in agriculture.

## 16.2 Carbon Nanofibers

Carbon nanofibers (CNF) are produced from the decomposition of both chemical and biogenic precursors rich in hydrocarbons. Commonly used hydrocarbons are acetylene, carbon monoxide, etc., using metal nanoparticles as catalyst. The development of high-resolution transmission electron microscopy has helped in observing the fine details of the morphology of CNF.

Carbon nanofibers consist of extremely small graphite platelets that are stacked at a distance of at least 0.335 nm. Arrangement of the graphene layers in CNF are (i) perpendicular to the fiber axis and resemble an infinite stack of cards, or (ii) the graphite layers are oriented parallel to the fiber axis and take the form of faceted tubes or ribbons. The spacing between the graphene layers is very narrow and this allows the entrance of most gas or liquid adsorbate. CNF does not have very high external surface area, but the void space between graphene platelets offers enormous surface area. Therefore, CNF is used as a very sophisticated type of molecular sieve, suitable for very refined separation processes. Because of these properties CNF is being tried as reinforcing agent in conjunction with polymers to form electrodes [4–6], for magnetic shielding [7], as selective adsorption agents and as a hydrogen storage agent [8].

## 16.3 Carbon Nanofiber and Agriculture

Along with an alarming increase in population, the demand for food to feed a population estimated to be up to 9 billion people by 2050 [9] is one of the big concerns. Challenges like unavailability of enough land space for cultivation, scarcity of water in many areas, decreasing soil fertility, impact of changing climate, demand for sustainable use of natural resources, accumulation of pesticides and fertilizers causing environmental concern, etc.,



have impelled us to look for a well-recognized multidirectional approach to increase agricultural production.

So far as the effect of carbon nanomaterials, especially CNTs, on plants is concerned, both positive (e.g., enhanced growth, anti-fungal and anti-microbial) and negative (cytotoxic) impacts have been reported.

One of the unique properties of CNF are that they are very good adsorbent because they have small cross-sectional area, combined with a multitude of slit-shaped nanopores. CNF can be used for selective adsorption of both inorganic and organic molecules. Hence, they can be used for the selective removal of organic impurities from aqueous solutions because the slit-shaped nanopores existing between the two adjacent graphene layers allow the interaction with nonpolar molecules, and the hydrophobic nature of the material prevents these regions from becoming saturated with water molecules.

At present, application of CNF in agriculture is in the nascent stage, but it is expected to contribute significantly to solving these problems through the application of CNF to plants as well as soil. Already efforts are underway to use carbon nanomaterials as tools in agriculture, for example:

- to improve precision farming,
- to maximize production,
- to reduce production cost,
- to reduce the spray drift with aerodynamic nanoparticles for optimized deposition,
- for controlled release for season-long treatment,
- for efficient formulations with reduction in dose,
- for advanced delivery systems of fertilizers, pesticides, herbicides and antimicrobials,
- for seed treatments to improve plant health and stress resistance,
- for encapsulation of toxic compounds,
- for photoprotection, and
- to reduce run-off.

Potential applications of carbon-based nanomaterials in agricultural sectors encompasses:

- As plant growth promoters and new fertilizers based on CNM to increase crop yield and to improve the soil quality such as killing pathogenic microbes or removing salty and toxic materials.
- A general reduction in application of agrochemicals can be achieved by using CNM for slow-release fertilizers and plant protection through slow release of pesticides, herbicides, insecticides, etc.

- As antimicrobial and antifungal agents to protect plants from disease as well as killing soil microbes.
- Removing pollutants from water, water filtration and soil remediation.
- In sensors for sensing soil condition, contaminant concentration, crop diagnostics for nutrient and moisture content, etc.
- Another possibility is optimization of agricultural practices by introducing precision farming.

According to Gogos *et al.* (2012) [10], in coming years carbon-based nanomaterials will be contributing about 40% of all of nanotechnology to agriculture either as additives or as active components. Scientists have already identified some principal properties of carbon nanomaterials that are relevant for their interactions with plants such as:

- Most carbon nanomaterials can be taken up by plants by internal translocation. They can enter a plant through endocytosis as well as through the roots.
- Though at higher concentration they may be detrimental to plant growth, this may be due to induction of oxidative stress by formation of ROS causing phytotoxicity.
- At lower absorbed concentrations carbon nanomaterials (<100 mg L<sup>-1</sup>) can induce physiological responses resulting in beneficial or no effects. It seems that the beneficial effects are due to hormesis, which is found during exposure to toxic agents at sub-toxic levels (e.g., glyphosate, Al<sup>3+</sup>, pathogens) by inducing and strengthening the stress defense systems [11, 12]. Moreover, it has been observed that CNM promotes seed germination by stimulating the water uptake.
- CNMs are easy to functionalize or can be modified with chemicals or by conformation (agglomeration), and thus can significantly influence their toxicity potential. Here also concentration remains the main factor that affects the phytotoxicity.

### 16.3.1 CNF for Plant Growth and Crop Yield

Prior to looking at the possibility of using CNF, which shows graphitic nature, it must be mentioned here that most of the work has been done on CNTs. The entry of CNF, especially plant-derived CNF, has been rather late and is still in the nascent stage of development, but with umpteen possibilities. This is due to the graphitic nature of CNF, which can be accepted as

the sister structure of CNTs, and which is expected to show a similar effect on plants as that of the CNTs.

Despite the fact that CNTs have large diameter and length, their uptake by the plant and internal translocation has been reported. They can penetrate not only cells of developing seedlings, but even rigid seed coats, by perforation and creation of new pores [13].

In the presence of some of the CNMs it was observed that there was a pronounced increase in the rate of germination of rice seeds [14], increased moisture content of seeds and enhanced water absorption machinery of root tissues resulting in a beneficial effect on the growth of *Brassica juncea* [15] and *Cicer arietinum* plants [16]. These observations as well as the high adsorption capacity of CNM are making it suitable material to be used for fertilizer application.

#### 16.3.1.1 Seed Germination

The interesting findings of Lahiani *et al.* (2013, 2015, 2016) [17–19] have shown that CNTs can penetrate tomato seed coat to enter the seed and affects the seed germination as well as plant growth by supporting water uptake by seeds. Later this group worked on the relationship between the morphology of different carbon-based nanomaterials (helical multi-walled carbon nanotubes (MWCNTs), few-layered graphene, long MWCNTs, and short MWCNT) and the specific response of plants as expressed by activated cell growth, germination, and plant growth. They found that helical MWCNTs affected the overexpression of water channel genes and a number of genes involved in cellular and metabolic processes and the response to stress factors. It was shown that the expression of the tomato water channel gene in tomato seeds exposed to helical MWCNTs was upregulated. Different types of carbon-based nanomaterials, such as nanohorns and helical carbon nanotubes [18–20], can also affect the water uptake.

Both CNTs as well as graphene have been effectively used in enhancing plant seed germination and growth. CNTs or graphene can be used as regulators of seed germination and plant growth. Moreover, both CNTs and graphene could significantly reduce symptoms of salt stress imposed by the addition of NaCl into the growth medium. Thus, it has been suggested that carbon-based nanomaterials can protect plants against salt stress by desalination of saline growth medium. This finding may open the door to carbon-based nanomaterials not only being beneficial as plant growth enhancers but also playing a positive role in the elimination of environmental stress symptoms of plants, as they can be used as a base for the development of new technologies to make salty water soil suitable for

agricultural practice. It is worth mentioning here that almost all the nano-forms of carbon exhibit graphene-like morphology, whether it is in the form of a tube, buckyballs, carbon dots or carbon nanofibers.

MWCNTs have been found to exhibit the ability to enhance the growth of tobacco cell culture by 55–64% when compared to control [21]. The impact is concentration dependent.

#### 16.3.1.2 CNF as Fertilizer

Controlled and slow release of fertilizers, pesticides, herbicides, plant growth regulators and other active substances, involves nanoscale systems like encapsulation and entrapment.  $\text{KNO}_3$  encapsulated by graphene oxide films by [22] Zhang *et al.* (2014) has exhibited slow release of fertilizer  $\text{KNO}_3$ . These nanoscale systems may be polymers, dendrimers, surface ionic attachments, etc. The use of nanoscale delivery vehicles not only minimizes the amount of agrochemical but also prevents runoff into the environment and increases effectiveness by binding firmly to the plant surface.

Due to the proprietary nature of the details of many of the CNM containing minerals and organic fertilizers, the information is not freely available. However, it can be said that compared to other nanoparticles ( $\text{TiO}_2$ , Ag, Al-/Al-nanoclays, ZnO, CuO,  $\text{SiO}_2$ , sulfur, etc.), there are more numbers of publications and patents filed for carbon nanomaterials used in plant protection and fertilizer.

The importance of a nanoscale delivery system in agriculture is because of its improved stability to degradation in the environment; and there are many reports that show the positive impact of CNM on plant growth. Earlier MWCNTs have been found to be able to penetrate into roots and accumulate there as well as be transported into leaves of *Onobrychis arenaria* seedlings [23]. However, recently the use of CNF as carrier and slow release of micro- and macronutrients has been tried [24, 25].

The Cu nanoparticle carrying CNF can effectively penetrate gram seeds and then translocate them into the plant and enhance the plant growth by increasing its water uptake and protein and chlorophyll contents [24].

It must be mentioned here that the toxicity of CNF remains a concern when used in living systems, which is due to its aggregation, agglomeration and solubility in dispersion medium. Moreover, the amount/dose of CNF used is another concern [25, 26]. The need for developing a soluble biodegradable coating or encapsulation has been thought of as an alternative to facilitate slow release. PVA blended with starch was used for slow release of the Cu–Zn micronutrients carrying CNFs in plants [27]. Upon dispersion of the PVA blend-dispersed micronutrients in soil, the blend dissolves

releasing the Cu and Zn NP carrying CNFs that have translocation ability and, as mentioned above, CNFs enhance water uptake capacity and germination rate, subsequently enhancing the growth of plants. Such efforts will cause a reduction in use of fertilizers and slow release will supply nutrients to plants for a prolonged period of time in order to be easily absorbed.

Fan *et al.* (2012) [28] have shown that for soda saline-alkali soil the utilization rate of nitrogen fertilizer can be increased after a combined application of nanocarbon, this can save N.

#### 16.3.1.3 CNF as Plant Growth Stimulator

There have been many reports on the stimulatory effects of CNM on plant growth, such as *Ficus carica* [28], *Zea mays*, *Solanum lycopersicum* seedlings [21], *Solanum macrosiphon*, *Capsicum annuum*, *Ficus carica* [29], *Ficus arundinacea* [30], *Rubus adenotrichos* [31], *Brassica oleracea*, *Daucus carota*, *Cucurbita sativus*, *Lactuca sativa*, *Allium cepa*, and *Solanum lycopersicum* [32].

Apart from being a good molecule carrier, CNMs also have a positive impact on plant growth. However, not all CNMs exhibit stimulatory effects on plant growth. Many times it was shown that concentration and morphology caused depended-negative impact also [33, 34]. Scientists have discovered that CNTs can boost plant growth if they are treated to be more soluble and are absorbed by plants. One of the problems with CNF is that unlike CNT, no water-soluble CNF has been created.

### 16.3.2 CNF for Plant Protection

Soil as well as plant-associated microbes are a big challenge in agriculture, as they directly impact the seed germination, plant growth, nutrient cycling, decomposition of organic matter, and symbiotic relationships with terrestrial plant species [35]. Wang *et al.* (2014) [36] have evaluated and shown the mechanism of antifungal effects of carbon nanomaterials (CNM) in controlling fungal pathogen of plants. According to them, CNM exhibits a tight contact with the fungal spores, which induces plasmolysis, associated with reduced water content and growth arrest. This has opened the way to develop CNM-based novel fungicides.

#### 16.3.2.1 CNF as Antimicrobial and Antifungal for Surface Coating

One of the challenges in seed germination is inherent or external fungal infection of seeds. Though there is limited information available on the

interaction between carbon nanomaterials (CNM) and the soil microbial community [37, 38], the well-known toxicity of CNM to microbes is seen as a possible solution to combat the negative impact of microbes on growing plants [38].

Joshi *et al.* (2015) [39] have studied the applications of functionalized CNFs in some fungal infected seeds of maize and barley, which show very poor germination and seedling growth. They have found that CNF could penetrate and germinate effectively inside the seeds. This property can be used as a smart delivery system for antimicrobial agrochemicals as well as organic nutrient molecules for the transport of DNA molecules and oligonucleotides into plant cells.

A possibility to deliver SWCNTs into isolated chloroplasts by passively penetrating through the chloroplast membrane via diffusion was able to influence photosynthetic activity by supplying electrons into the photosynthetic electron transport chain [40].

Another site where microbes and fungi have been found to be present and affect the plant growth is soil. Shrestha *et al.* (2013) [41] found that when when sandy loam soil microbes were exposed to higher concentrations (10,000 mg/kg) of MWCNT for 90 days, microbes like *Waddlia*, *Holophaga*, *Derxia*, and *Opitutus* showed a decrease in population; but the polycyclic aromatic hydrocarbon (PAH) degrading organisms, e.g., *Cellulomonas*, *Rhodococcus*, *Pseudomonas*, and *Nocardioideis*, showed a marked increase. However, the findings of proteins are too limited to be conclusive as CNM may have neutral or perhaps modestly beneficial effects on microbial communities. According to Sharon *et al.* [42], CNTs interact strongly with bacteria cell membranes by disrupting them due to strong electrostatic interactions and denaturing of membrane.

One of the CNMs—graphene—which is the base of all nanocarbon morphologies, exhibits broad-spectrum antimicrobial activity against bacterial phytopathogens and fungal conidia by intertwining and membrane perturbation [43] and electron transport [44] and oxidative stress by increased production of reactive oxygen species (ROS) [45, 46].

Hui *et al.* (2014) [45] found that the availability of the basal planes of graphene oxide determine whether it is antibacterial or not. CNF that has many broken graphene sheets on the surface needs to be assessed for broad-spectrum antimicrobial activity. Moreover, the masking of the basal plane by noncovalent protein adsorption with bovine serum albumin resulted in loss of antibacterial activity [47].

It can be said that at present a general lack of understanding of the impact of CNM in the living system persists and needs a lot of research.

### 16.3.2.2 CNF as Support for Pesticides, Herbicides and Insecticides

Minimum use of pesticides, herbicides and insecticides are the demand of the day for sustainable agriculture. This will not only protect the environment but also save the excess use of chemicals and reduce the phytotoxicity of herbicides on crops [48].

Efforts are being directed towards slow and targeted release of pesticides.

CNM-based plant protection products [10] include pesticides [49, 50] and herbicides [51]. Different forms of CNM are found to have a positive effect on reducing the accumulation of pesticides by select plant species. The parameters that affect the use of CNF as agrochemicals are plant species, nature of the growth medium, CNM type/concentration, and growth conditions. CNM-mediated alteration of pesticide uptake/toxicity in crop plants, such as zucchini, soybean, tomato, lettuce, etc., has been demonstrated by De La Torre-Roche *et al.* (2013) [25] and Hamdi *et al.* (2015) [52].

### 16.3.3 CNF for Soil Improvement

Soil is an integral part of agriculture and cultivation. Not only the composition but soil microbes are also a big consideration in agriculture. Tomato plants grown on soil supplemented with CNTs have exhibited the same amount of leaves but twice the number of flowers and fruits than control plants grown in regular soil [53]. Though this is not the work done with CNF, this observation also opens new perspectives on applications for the introduction of CNFs. While using CNF, size impact has to be seriously considered so as to penetrate root or seed easily. There are already many patents on CNM-based uses for soil improvement [54]. Since CNF has the very high absorbing property of both organic and inorganic materials, it will be a good idea to treat soil with CNF prior to sowing seeds, so as to remove harmful chemicals from soil that may affect plant growth.

Therefore, critical knowledge gaps regarding the use of CNF must be taken into consideration. Moreover, we need more soil-based investigations under environmentally relevant conditions and efforts need to be focused on a better understanding of the underlying mechanism of CNM-plant interactions.

### 16.3.4 CNF for Controlled Environment Agriculture

Controlled environment agriculture encompasses cultivation in green houses; where plants are maintained under defined environments where



care is taken to eliminate insects, pest control, controlled nutrient provision, reduced water and land use as well as runoff and top soil loss. Greenhouses built by applying Nanotechnology can provide pest protection, appropriate required nutrient amounts, controlled humidity, temperature, and air of particular composition.

One of the concerns in agriculture is contaminated water. Purification of water is needed not only for drinking purposes but also for agricultural use. The contaminants present in water could be heavy metals, phosphate, ammonium, nitrate, nitrite, organic pollutants, dyes, viruses, and also microbes and other parasites. CNF is proving to be very effective for water decontamination, purification and filtration. Carbon nanofibers have been exploited to build structures that have complete control over shapes, density as well as dimensions for specific filtration of water. Sharon's group [55] have designed a porous ceramic coated with vertically aligned multi-walled carbon nanotubes (MWCNTs) coated with  $\text{TiO}_2$  nanoparticles. This setup could successfully photocatalytically kill a most dreadful enterohemorrhagic pathogenic strain of *Escherichia coli* O157:H7. The photocatalytic killing rate constant under fluorescent light was found to be  $2.23 \times 10^{-2} \text{ min}^{-1}$ . Further trials using CNF are underway.

Moreover, various applications of CNF explained in previous paragraphs of this chapter such as seed germination, plant growth, crop yield, fertilizer, plant growth stimulator, for plant protection through antimicrobial and antifungal effects, for soil improvement and a support for pesticides; all these uses of CNF can be applied for controlled environment agricultural practices.

However, despite the fact that CNMs promote the agricultural progress, there are concerns about a potential release of CNMs into the environment and their interactions with biosystems leading to their incorporation into food chains with consequences that are to be discovered.

### 16.3.5 CNF for Precision Farming

The recent trends in development of Agrotechnology are application of nanotechnologies for optimization of agricultural practices by introducing precision farming [56] (Auernhammer, 2001).

*Precision farming is a marriage of management with new and emerging information and communication technologies consequently leading to the development of low cost and high yield farming [57].*

With the help of precision farming there is complete automation of farming. It helps in better quality control with low labor cost, can adjust to adverse climatic condition, quicker response time, systematic monitoring of cultivation variables, maximizes farm products and minimizes input



of fertilizers, pesticides, herbicides, etc. Precision farming is supported by high-tech gadgets, such as remote sensing devices, global satellite, computers, etc., to collect data related to plant growth and identify problems by determining the soil conditions [58]. The greatest impetus for precision farming is efficient exploitation of farming with agricultural waste minimization. Moreover, sensors, and especially nanosensors, are an important part of precision farming.

#### 16.3.5.1 *CNF and Nanosensors for Diagnostics in Agriculture*

Since CNMs offer novel chemical, physical and mechanical properties they are employed to develop highly sensitive sensors and diagnostic devices for agricultural applications. The operating principle of nanosensor is conversion of physicochemical properties into signals.

Sensors are used for:

- Sensing agricultural parameters.
- Identification of sensing location and data gathering.
- Transferring data from crop field to control station for decision-making.
- Actuation and control decision based on sensed data [59].

Small nanosensors attached to a GPS (global positioning satellite) system are used for real-time monitoring of the crop growth, soil conditions and transmit the signals to the main server. There is a plethora of nanodevices which can detect anomalies in the quality of soil milieu, leading to the alarming signal report given by the server. Such wireless sensors are already in use in countries like the USA and Australia; and one of the finest examples for employing such sensors are in the California vineyards.

Since they possess very high conductivity, surface-to-volume ratio, photocatalysis, tensile strength, etc., CNTs and other CNMs have been exploited in designing the most efficient and sensitive paraphernalia for augmenting the sensitivity of detection in various applications in agriculture.

Following are some examples of the use of nanosensors. Because CNT possesses very high surface area to capture very small molecules, such as individual proteins or even smaller metabolite, nanosensor using CNTs has been designed for the detection of an infecting pathogen by triggering an electrical or chemical signal [60].

Carbon has been used as an electrode for electrochemical analysis [61]. Sharon's group is working on selection of CNM synthesized from different raw materials for an electrochemical sensor to measure the electrochemical

properties in response to different pesticides in the plants. Preparation of electrochemical cell having CNM as an electrode is used in the electrochemical sensor to assign appropriate oxidation/reduction potential values of a particular analyte. Nanosensor devices that use carbon nanotubes or nanocantilevers are specially engineered and are small enough to trap and measure individual proteins or small molecules. A contaminant on the CNM surface triggers an electrical or chemical signal. Pathogen detection is also being considered as a possibility to offer increased sensitivity and decreased response time due to CNM nanosensor.

The large surface area of CNM provides large spaces for interactions with the sensed molecules. Various sensors that have been developed include CNF and SWCNT for *in-vivo* monitoring of ROS formation in plant tissues as stress indicators [62]; graphene for the detection of heavy metal cadmium contamination in water [63]; and graphene oxide for detection of pesticides and herbicides [64]. Other sensors are those using modified CNT for detection of nickel [65], for sensing ammonia [66], to detect pesticides, herbicides and their metabolites [67, 68]; and an electronic device for real-time sensing of toxic gases [69].

Currently, most of the CNF-based nanosensors are still in the product development stage. Major challenges still remain concerning the use of CNMs around the issues of their safety, health aspects and risk assessment.

## 16.4 Summary

In the present chapter, the unique properties of carbon nanomaterials have been discussed for their use in agriculture. It is established that the nanoscale material can be used for agro-equipment, viz. sensors, in creating controlled and precision farming, the durable slow release of pesticides, etc. In this chapter, a quick peek into the near future prospects of CNF have been envisaged and they are fairly bright, as it is a low-cost solution for a manifold increase in the crop production.

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