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Novel Carbon Materials and Composites

Synthesis, Properties and Applications

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Series Preface

Carbon, the sixth element in the Periodic Table, is extraordinary. It forms a variety of materials because of its ability to bond covalently with different orbital hybridizations. For millennia, there were only two known substances of pure carbon atoms: graphite and diamond. In the mid-1980s, a soccer-ball-shaped buckminsterfullerene, namely a new carbon allotrope C₆₀, was discovered. Together with other fullerene-structures (C₇₀, C₈₄), the nanocarbon researcher was spawned. In the early 1990s, carbon nanotubes were discovered. They are direct descendants of fullerenes, and capped structures composed of 5- and 6-membered rings. This was the next major advance in nanocarbon research. Due to their groundbreaking work on these fullerene materials, Curl, Kroto and Smalley were awarded the 1996 Nobel Prize in Chemistry. In the beginning of the 2000s, graphene was prepared using Scotch tape. It is a single sheet of carbon atoms packed into a hexagonal lattice with a bond distance of 0.142 nm. For their seminal work with this new nanocarbon material, Geim and Novoselov were awarded the 2010 Nobel Prize in Physics. New members, carbon nanoparticles, such as diamond nanoparticles, carbon dots, and graphene (quantum) dots, have emerged in the family of nanocarbon materials. Although all these materials only consist of the same carbon atoms, their physical, chemical, and engineering features are different, and fully dependent on their structures and surface functional groups.

The purpose of this series is to bring together up-to-date accounts of recent developments and new findings in the field of nanocarbon chemistry and interfaces, one of the most important aspects of nanocarbon research. The carbon materials covered in this series include diamond, diamond nanoparticles, graphene, graphene-oxide, graphene (quantum) dots, carbon nanotubes, carbon fibers, fullerenes, carbon dots, carbon composites, and their hybrids. The formation, structure, properties, and applications of these carbon materials are summarized. Their relevant applications in the fields of electroanalysis, biosensing, catalysis, electrosynthesis, energy storage and conversion, environment sensing and protection, biology and medicine are highlighted in different books.

I wish to express my sincere thanks to Miss Sarah Higginbotham, Jenny Cossham, Emma Strickland, and Lesley Jebaraj from Wiley's Oxford office. Without their efficient help and valuable suggestions during this project, the publication of this book series would not be possible. Last, but not least, I want to thank my family, especially my

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February 2017

Nianjun Yang
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Preface

Novel carbons and carbon-related films are newly developed functional materials. Among them, carbon dots, silicon carbide, and carbon nitrides have been paid most attention. In recent years, the fabrication of novel carbon composites is also becoming a hot research topic because these composites address certain disadvantages of novel carbon materials, and further extend their potential applications. The synthesis, properties, and applications of novel carbon composites, such as diamond/SiC composites and diamond/graphite composites, have been widely reported and discussed. The object of this book is to provide an excellent entry into recent progress and achievements in these subjects, centered on novel carbon materials and their composites.

This book consists of two parts. In the first part, the synthesis, properties and applications of novel carbon materials, including silicon carbide, carbon nitrides, and nanocarbons are reviewed. Chapters 1 and 2 concentrate on silicon carbide films, where chemical vapor deposition of silicon carbide films and their electrochemical applications are presented. Chapter 3 is about synthesis and photocatalytic applications of silicon carbide powders featuring high surface areas. Chapter 4 discusses the fabrication of graphite carbon nitrides, summarizes their bandgap and nanostructure engineering, and highlights their water splitting applications. The applications of various novel carbon materials for the construction of supercapacitors are shown in Chapter 5.

The synthesis, properties and applications of novel carbon composites are summarized in the second part of this book. In Chapter 6, chemical vapor deposition of diamond/silicon carbide composite films is detailed, including applied instruments, conditions, properties, and growth mechanisms. Their mechanical, sensing, and biochemical applications are shown. Chapter 7 describes the related contents for diamond/graphite composite films. Their electrochemical applications are highlighted. In the last chapter of this book, carbon nanodot composites are shown, covering their fabrication processes and properties, and highlighting their use in catalytic applications, sensing and detection, environment, energy storage and conversion.

From our point of view, this book presents hot topics taking into account recent progress and achievements in the fields of novel carbon materials and composites. It is hoped that this book stimulates graduate students and young scientists, as well as experienced researchers, to explore these novel carbon materials and composites in their fundamental and practical aspects in future.

Finally, we thank all the scientists who contributed chapters to this book, as well as colleagues from Wiley who kindly devoted their time and efforts to allow this book to be smoothly published.

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1

Cubic Silicon Carbide: Growth, Properties, and Electrochemical Applications

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1.1 General Overview of Silicon Carbide

It is well known that carbon and silicon atoms form similar, covalently bonded and giant structures, as shown schematically in Figure 1.1a. They are thus called carbon diamond and silicon diamond. In both diamond structures, each atom is covalently bonded to four other atoms located at the corner of a tetrahedron. Another diamond-like compound is silicon carbide (SiC), building up with silicon and carbon atoms. In this crystal, each atom is sp^3 -hybridized and forms four bonds to four other atoms of the opposite kind. The tetrahedral arrangement of atoms encountered in the pure carbon and silicon diamond structures is preserved in SiC (Figure 1.1a).

The existence of a compound containing SiC bonds was proposed in 1824 for the first time by Jöns Jacob Berzelius, a Swedish chemist [1]. In 1905, Henri Moissan, a French chemist and the Nobel laureate, discovered SiC in nature [2]. In mineralogy, SiC is therefore known as moissanite [3]. In nature, moissanite SiC is very rare and only found in certain types of meteorite. The most commonly encountered SiC material is actually man-made.

SiC exists in about 250 crystalline forms, as variations of the same chemical compound that are identical in two dimensions but differ in the third. They can be viewed as layers stacked in a certain sequence. Different stacking sequences of C-Si double layers lead to different crystalline structures, or so-called polytypes [4]. Therefore, more than 250 polytypes have been predicted [4, 5]. Of these polytypes, only a few of them have been studied in detail. In principle, only three are of major importance: cubic (3C, or β)-SiC, 4H-SiC, and 6H(α)-SiC, which are shown schematically in Figure 1.1b–d, respectively. The most commonly encountered polymorph is 6H(α)-SiC, which forms at temperatures higher than 1700°C and has a hexagonal crystal structure (similar to wurtzite) (Figure 1.1c). Cubic 3C(β)-SiC (Figure 1. 1b) is formed at temperatures below 1700°C and has a zincblende (ZnS) crystal structure, similar to diamond [6].

1.1.1 SiC Properties

SiC is a fascinating material, although it has quite complicated polytypes. This is because the type of SiC polytype implies a corresponding set of relevant physical properties.

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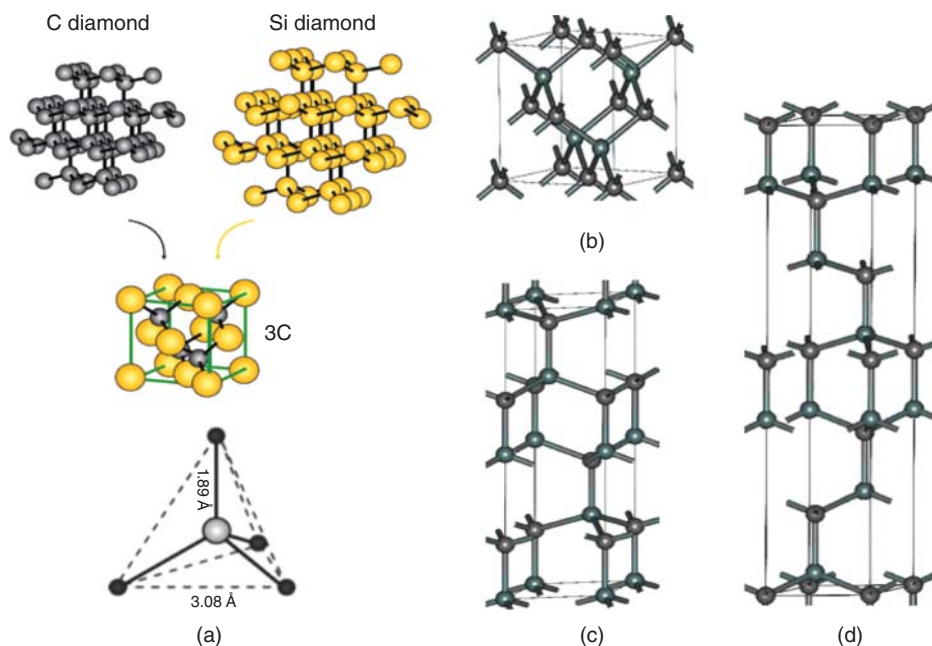


Figure 1.1 Chemical structures of carbon diamond, silicon diamond, SiC (a), 3C(β)-SiC (b), 4H-SiC (c), and 6H(α)-SiC (d) using ball-stick models.

As examples, some important physical properties of 4H-, 6H-, and 3C-SiC are listed in Table 1.1, compared with those of diamond and silicon.

SiC has been known for decades to be a semiconductor, based on the very first electroluminescence (yellowish light) from SiC crystals when subjected to electricity in 1907 [7]. More interestingly, its indirect bandgap is tunable in the range of 2.36–3.23 eV, determined by the polytype of SiC films. For instance, the bandgaps for 3C-, 4H-, and 6H-SiC are 2.36, 3.23, and 3.05 eV, respectively. However, SiC can be varied from insulating, semiconductive, to metallic-like in its properties when the dopants (n- or p-type) and the doping levels are altered. For example, SiC films can be doped with either n-type dopants (e.g. nitrogen, phosphorus) or p-type dopants (e.g. beryllium, boron, aluminum, gallium). Metallic conductivities of SiC films have been achieved by their heavy doping with boron, aluminum, or nitrogen. For example, at the same temperature of 1.5 K, superconductivity has been detected in 3C-SiC films doped with aluminum and boron as well as in 6H-SiC films doped with boron.

In comparison with Si, SiC has a higher thermal conductivity, electric field breakdown strength, and current density. It features a very low coefficient of thermal expansion ($4.0 \times 10^{-6} \text{ K}^{-1}$) and experiences no phase transitions that cause discontinuities in thermal expansion. The sublimation temperature of SiC is very high (approximately 2700°C), which makes it useful for bearings and furnace parts. SiC does not melt at any known temperature.

SiC is transparent to visible light. Pure SiC is colorless. The brown to black color of industrial SiC products results from iron impurities. The rainbow-like lusters of SiC crystals are caused by the passivation layers of SiO_2 that form on the SiC surface.

Table 1.1 Basic properties of three kinds of SiC, Si, and diamond.

Property	4H-SiC	6H-SiC	3C-SiC	Si	Diamond
Energy bandgap at 300 K (eV)	3.20	3.00	2.29	1.12	5.45
Intrinsic carrier concentration at 300 K (cm^{-3})	5×10^{-9}	1.6×10^{-6}	1.5×10^{-1}	1×10^{10}	$\sim 10^{-27}$
Critical breakdown electric field (MV cm^{-1})	2.2	2.5	2.12	0.25	1–10
Saturated electron drift velocity ($\times 10^7 \text{ cm s}^{-1}$)	2.0	2.0	2.5	1.0	1.5
Electron mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	1000	600	800	1450	480
Electron mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	115	100	40	470	1600
Thermal conductivity at 300 K ($\text{W cm}^{-1} \text{ K}^{-1}$)	3.7	3.6	3.6	1.49	6–20
Coefficient of thermal expansion at 300 K (10^{-6} K^{-1})	4.3 4.7	4.3 4.7	3.2	3.0	1.0
Lattice coefficient (a, c in Å)	a = 3.073 c = 10.053	a = 3.081 c = 15.117	a = 4.360	a = 5.430	a = 3.567
Calculated elastic coefficient (GPa)	$C_{44} = 600$	$C_{11} = 500$ $C_{12} = 92$ $C_{44} = 168$	$C_{11} = 352$ $C_{12} = 12$ $C_{44} = 233$	$C_{11} = 167$ $C_{12} = 65$ $C_{44} = 80$	$C_{11} = 1079$ $C_{12} = 124$ $C_{44} = 578$

SiC is a very hard material. Taking Mohs hardness scale as an example, the value of talc is given by 1 and diamond is given by 10: SiC has the value of 9.3 [8].

SiC is chemically inert. For example, it is resistive to radiation and many chemicals. This is because the electron bonds between the silicon and carbon atoms inside SiC are extremely strong. More importantly, SiC has shown superior biocompatibility and is non-toxic in both *in vitro* and *in vivo* tests. In addition, SiC is multifunctional, originating from the possibility of adopting both silicon and carbon chemistry on its surface.

In conclusion, SiC is a material with exceptional physical properties (e.g. a low density, a high strength, a high thermal conductivity, high stability at high temperatures, a high resistance to shocks, low thermal expansion, a high refractive index, a wide but tunable bandgap) and chemical features. They present multiple options for smart devices through their electrical, chemical, and optical properties [5, 9–15].

1.1.2 SiC Applications

Thanks to its unique physical properties (e.g. electrical, thermal properties), SiC has found wide and varied applications where high blocking voltages or high switching frequencies are required [5, 9–15]. Shockley thus predicted in the 1950s that SiC would quickly replace Si. SiC-based power electronics can greatly reduce the power losses of electrical energy in most generators and distribution systems. The higher frequency,

smaller dimensions, reduced cooling requirements, and greater efficiency obtained with SiC power electronics will give more efficient systems in any application where AC-DC, DC-AC, or DC-DC conversion is required. One example application of SiC is for compact power supply units with extremely low losses, which also keep the power supply network free of electric smog (the unwanted interference frequencies resulting from the use of computers) [5, 15].

SiC is also suited for space-saving control units and for variable-speed drives, which are generally mounted directly on the mortars. For these applications, homoepitaxial SiC films are generally required. However, the typical growth rate for homoepitaxial SiC layers is $5\text{--}10\text{ }\mu\text{m h}^{-1}$. Thus, the epitaxial growth of SiC layers is very time-consuming, making them very expensive for most devices. The long production time and high cost of these epitaxial SiC layers are thus the main obstacles to overcome, in order to make SiC power devices more available to market [5, 11, 15]. In contrast, the latest discovery of new forms of SiC (e.g. nanoporous structures, superlattices) has triggered the development of SiC electronics, and in particular thin-film technologies [11].

Bulk SiC has become a more important compound in materials science, such as a support for loading heterogeneous catalysts, for hard coating (e.g. for cutting), for implantable sensors, and for protein separation and micro-fluidic systems where a porous SiC film is needed. Especially in recent years there has been increased attention to employing SiC as a valuable material for biomedical applications and as a transducer for biosensors. This is because SiC has the advantages of its chemical, tribological, and electrical properties. In addition, it can easily be integrated on a chip into a system. For example, SiC has been employed as an active material for micro-device fabrication [13, 14]. In addition, SiC offers an ideal surface to grow graphene, another important material with superior physical, chemical and electrical properties [16].

1.1.3 Scope of this Chapter

Since the physical and mechanical properties of SiC films and their related nanostructures (e.g. particles, wires, pores, etc.) as well as their applications in the fields of electronics, power devices, and biomedical applications have been widely reviewed and discussed [5, 9–15], we focus in this chapter only on the growth, interfacial properties, and electrochemical applications of 3C-SiC. The growth of 3C-SiC using various chemical vapor deposition (CVD) techniques is summarized. After the description of the interfacial properties (e.g. surface morphology, surface chemistry, and electrochemical properties) of 3C-SiC, the electrochemical applications of 3C-SiC films in the fields of electrochemical and biochemical sensing, energy storage and conversion are highlighted. Finally, we close this chapter with concluding remarks as well as discussion about the future research directions of 3C-SiC.

1.2 Synthesis of Silicon Carbide

1.2.1 Acheson Process

SiC is traditionally produced through the so-called Acheson process, where an Acheson graphite electric resistance furnace is required. At very high temperatures ($>2500^{\circ}\text{C}$), a solid-state reaction occurs between two precursors, namely silica sand and petroleum coke, leading to the formation of SiC [15]. Crystalline SiC synthesized by the Acheson

process features different polytypes and varies in its purity. The common impurities are nitrogen and aluminum. By altering the heating processes and/or the distances of the graphite resistor heat source of the Acheson furnace, colorless, transparent, or variously color SiC films have been synthesized [17]. These manufactured SiC films have large grain sizes and are invariably contaminated with oxygen. Such an Acheson process is still used for the production of polycrystalline SiC films, which are often known by the name carborundum. The as-obtained SiC ceramic is quite suitable for grinding and cutting applications, such as abrasive and cutting tools. However, the Acheson process requires excessive energy input during SiC synthesis, and the quality of the synthesized SiC is rather poor.

1.2.2 Physical Vapor Transport

Several alternative methods have since been developed for the synthesis of pure SiC films. Physical vapor transport (PVT) is the most popular and successful method for growing large single SiC crystals [18, 19]. As the first method of the sublimation technique (also known as the Lely method) [20], the synthesis of SiC with limited crystal sizes was carried out under argon ambient at about 2500°C in a graphite container. The formed SiC crystals (or Lely platelets) presented good quality (e.g. micropipe densities of $1\text{--}3\text{ cm}^{-2}$, dislocation densities of $10^2\text{--}10^3\text{ cm}^{-2}$). Unfortunately, this technique has several major shortcomings, such as uncontrollable nucleation rates and dendrite-like growth processes. Later, a modified PVT method (also called the modified-Lelly method or seed sublimation method) was proposed. Such a method controlled SiC growth and improved the limited adjustment of the gas phase composition between the concentrations of dopant species and the complements of C and Si [21]. The sources and the seeds of SiC were placed perfectly in close proximity to each other, where a gradient of temperatures was established. In such a way, the transport of the material vapor above the seeds became possible at a low argon pressure. The conventional PVT method was further refined through a gas pipe between the source and the crucible into the growth chamber (M-PVT setup) [22, 23]. By use of such a M-PVT setup, high-quality 4H- and 6H-SiC wafers have been grown, with diameters up to 100 mm. An additional gas pipe was used to introduce dopant gases and/or small amounts of C- and Si-bearing gases ($\text{SiH}_4:\text{H}_2 = 1:10$, propane). Namely, the gas phase composition was further controlled. By use of such a modified M-PVT setup, 15R-SiC and 3C-SiC have been also synthesized [23].

1.2.3 Chemical Vapor Deposition

The CVD technique is another suitable and widely investigated method to produce SiC samples in various forms (e.g. thin films, powders, whiskers, and nanorods, etc.) [16, 24–57]. For example, amorphous SiC powders have been prepared by a CVD method, where SiH_4 and C_2H_2 acted as the precursors and nitrogen as the carrying gas [24, 25].

Atmospheric pressure chemical vapor deposition (APCVD) is one of the first CVD techniques developed to deposit SiC [25]. During deposition, a carbonization process is initially applied to a clean Si surface, followed by SiC growth using Si- and C-containing precursors [26–28]. SiC growth rates of up to several $\mu\text{m h}^{-1}$ have been achieved, with the potential to be doped into n- and p- type materials. An APCVD system is a relatively

simple and easy setup due to the incorporation of few temperature sensitive components. Both epitaxial and polycrystalline 3C-SiC films have been deposited by APCVD. It is particularly advantageous for SiC epitaxy, where higher temperatures (1300°C) are typically required for the growth of single crystals of SiC on Si substrates.

Low-pressure chemical vapor deposition (LPCVD) is the second CVD system utilized for the growth of SiC films. Although the growth rates of SiC films during LPCVD processes are much lower than those in APCVD processes, generally more substrates can be accommodated in LPCVD systems, especially when resistive heating is used. Due to the vacuum system involved for a LPCVD system, it has much lower chamber pressure in comparison with an APCVD system. Therefore, a LPCVD reactor allows the exploitation of more varieties of precursors, as well as reducing impurity incorporation in the deposited films. In short, the LPCVD process generates generally higher quality SiC films with much better uniformity across large substrate areas. By means of LPCVD techniques, epitaxial 3C-SiC films have been grown on Si wafers [29]. In recent years, LPCVD has actually become a leading technique for the growth of polycrystalline 3C-SiC films on various substrates including SiO₂ and Si₃N₄. Doping can also be achieved during LPCVD processes, conducted by simply adding dopants (e.g. 1,3-disilabutane, nitrogen, etc.) into the feed gases [30–35]. For example, controlled nitrogen doping has been demonstrated by adding nitrogen or NH₃ as the precursor into the feed gases. By varying the fractions of dichlorosilane and 1,3-disilabutane in the gas mixtures, the residual stress and strain gradient of polycrystalline SiC films has been tuned [36].

The third CVD technique applied for the synthesis of SiC films is metal organic chemical vapor deposition (MOCVD), which is especially useful for the growth of thick SiC films on sapphire (001) and silicon (111) substrates. Diethylmethylsilane (DEMS) containing both Si and C atoms was used as an individual precursor. No gas carrier or bubbler was thus applied. The films grown at low temperatures (850 and 900°C) on both substrates showed crystalline 3C-SiC in the (111) orientation [37].

Plasma enhanced chemical vapor deposition (PECVD) has been employed to deposit SiC films at low temperatures. Due to the use of low temperatures during PECVD processes, it is feasible to deposit SiC on a variety of materials (e.g. aluminum) that are not possible during APCVD and LPCVD processes. Commercially available PECVD systems can thus be utilized for processes that benefit from future mass production of SiC. The low deposition temperatures also confirm its potential suitability for related processing. To grow SiC by means of PECVD, gas precursors such as SiH₄ and CH₄ [38, 39] as well as liquid sources such as C₆H₁₈Si₂ (hexamethyldisilane) [40] have been used. The as-deposited SiC films are amorphous, and thus post-deposition annealing is required for crystallization. Altering deposition parameters such as pressure and gas flow ratios resulted in the control of the stress in the deposited films during these PECVD processes [39]. Moreover, both doped and undoped SiC can be synthesized by PECVD [41–47]. We have employed microwave plasma chemical vapor deposition (MWCVD) techniques to grow three different kinds of 3C-SiC films, namely nanocrystalline, microcrystalline and epitaxial (001) 3C-SiC films [16]. Table 1.2 lists the depositional conditions we applied for the growth of these 3C-SiC films by means of MWCVD.

Figure 1.2 shows scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of three 3C-SiC films [16]. The nanocrystalline 3C-SiC film possesses a crystal size smaller than 50 nm (Figure 1.2a). Its surface is relatively smooth and

Table 1.2 Depositional parameters for the MWCVD growth of three 3C-SiC films [16].

Film type	Microwave power (W)	Gas pressure (Torr)	T_s ($^{\circ}\text{C}$)	TMS content (ppm)
Nanocrystalline	700	20	~ 800	290
Microcrystalline	1800	45	~ 700	290
Epitaxial	2200	55	~ 850	140

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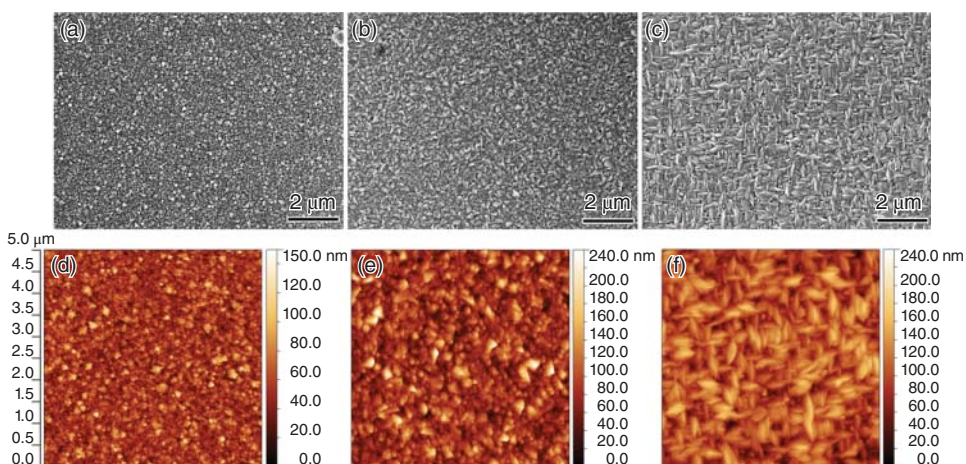


Figure 1.2 SEM (a–c) and AFM non-contact mode (d–f) images of a nanocrystalline (a, d), a microcrystalline (b, e), and an epitaxial (c, f) 3C-SiC film. The sizes of the AFM images are $5 \times 5 \mu\text{m}^2$ [16]. Source: Reprinted with permission from ACS publisher, Copyright 2015.

has a root-mean-square (RMS) roughness of only 12.6 nm, as estimated from its AFM non-contact mode image shown in Figure 1.2d. The average crystal size of the microcrystalline 3C-SiC film is ~ 200 nm (Figure 1.2b). Its larger crystal size results in its higher surface roughness, which is measured to be 22.9 nm from the AFM image (Figure 1.2e). The SEM image of the epitaxial 3C-SiC film (Figure 1.2c) shows densely packed 3C-SiC crystals lying along the $\{110\}$ directions of the Si wafer, presenting the very typical nature of heteroepitaxially grown 3C-SiC crystals on (001) Si [16, 48]. Its surface roughness is comparable to that of the microcrystalline 3C-SiC film, which is 20.6 nm determined by the AFM measurement (Figure 1.2f).

Remote microwave hydrogen plasma chemical vapor deposition (RPCVD) has been applied to grow amorphous hydrogenated SiC (a-SiC:H) films. Dimethylsilane (DMS) or tetramethylsilane (TMS) was used as a single-source precursor [49]. The Arrhenius plots of substrate temperature dependencies of the thickness-based film growth rate implied that the investigated RPCVD for DMS precursor is a non-thermally activated process, whereas for TMS precursor it is an adsorption-controlled one. An increase in the substrate temperature from 30 to 400°C caused the elimination of organic moieties from the films and the formation of SiC networks. These a-SiC:H films proved to be

useful as scratch-resistant protective coatings for optical glass elements and various metal surfaces [49].

Some other CVD techniques have been employed to grow 3C-SiC films. For example, the halide CVD process was applied to fabricate oriented stoichiometric 3C-SiC films in a rapid way. During such a process, the flow rates of precursors (SiCl_4 and CH_4) were controlled [54]. The (110)-oriented stoichiometric 3C-SiC films with lower densities of defects were obtained when the molar ratios of C precursor to Si precursor were in the range of 0.86–1.00. The maximum deposition rate was $883 \mu\text{m h}^{-1}$ when the molar ratio of C precursor to Si precursor reached 1.00, leading to a thickness of 1.7 mm in a deposition time of two hours. A twin plane propagation model has been proposed to explain the formation of ridge-like morphologies of SiC films. Another example, the low pressure hot-wall CVD technique, has been used for the growth of 3C-SiC films on Si (100) substrates [55]. The C/Si ratio played an important role in the crystalline quality and surface morphology of 3C-SiC films. Comparisons indicate that the optimal C/Si ratio for high crystalline quality of 3C-SiC films is 4.5. Noticeably, the polycrystalline grains of 3C-SiC films exhibited an epitaxial nature with irregular shapes and random distribution. Pyramid-like shapes and regular distribution were found along the {110} directions, dependent on the C/Si ratios. The changes in crystalline quality with increasing C/Si ratios were attributed to the competition of the formation of defects by excess carbon species with the etching of the atomic hydrogen. Meanwhile, the changes of surface morphology were due to the changes in secondary nucleation rates.

In past decades, more efforts have contributed to achieving homoepitaxial CVD growth of 3C-SiC films. Typically, it was done using silane (SiH_4) as the silicon precursor, and light hydrocarbons (e.g. ethylene or propane) as the carbon precursor. In some cases, only TMS was used as the precursor. Hydrogen gas, sometimes mixed with some argon, was used as carrier gas. The growth temperature and pressure were usually between 1500 and 1650°C and 100–1000 mbar, respectively. For example, the laser CVD technique has been applied for the epitaxial growth of 3C-SiC thin films on Si(001) substrates [50]. The epitaxial relationship was 3C-SiC(001){111}//Si(001){111} and multiple twins {111} planes were identified. The maximum deposition rate was $23.6 \mu\text{m h}^{-1}$, which is about 5–200 times higher than that of conventional CVD methods. The density of twins increased with an increase in the thickness of 3C-SiC films. The cross-section of the films exhibited a columnar structure, containing twins at {111} planes that were angled at 15.8° to the surface of Si(001) substrates [50].

Conventional CVD equipment (c-CVD) was also employed for the growth of epi-SiC/Si-wafer/epi-SiC [51]. The Si wafer was double-side polished and mounted with a suspension mode in the c-CVD chamber. Homogeneous 3C-SiC (100) films were heteroepitaxially grown simultaneously on both surfaces of the suspended Si (100) wafer. Each film was uniform and continuous, with same trend of slight degradation from the inner to the outer region of the wafer. This technique offered a possible way to mass-produce high-quality 3C-SiC films on Si wafers in one run. The potential applications of 3C-SiC films (e.g. sensors, etc.) were thus also expanded.

Using PECVD techniques, the epitaxial deposition of 3C-SiC films has been achieved on (100) Si substrates [52]. A high density of defects (e.g. misfit dislocations, stacking faults, and twin boundaries) was generated in the film. Defect-induced strain distribution in the 3C-SiC film was analyzed by the geometric phase analysis method combined with X-ray diffraction (XRD) and Raman spectroscopy. The strain analysis at an atomic level revealed that periodic misfit dislocations at the interface generate high local

compressive strain ($>20\%$) around the core of the dislocations in the SiC film, relaxing a major part of the intrinsic strain. A highly compressive interfacial layer was found to form between the SiC film and Si substrate, regardless of the carbonization temperature. This interfacial layer was linked with the carbonization step of the film growth process. In addition, twins and stacking faults provided a complementary route for strain relaxation during the film growth process. More strain was accommodated at the matrix/twin interface during twin nucleation rather than that at the growth stage.

The controlled growth of heteroepitaxial 3C-SiC films was achieved by use of a 915 MHz MWCVD reactor [53]. TMS and hydrogen were used as the resource gases. With an increase in MW power, the morphology of the SiC crystals evolved from randomly oriented nanocrystals to well-oriented pyramid-shaped crystals. Suggested from the rocking curves, the 3C-SiC film deposited at a MW power of 9 kW and a gas pressure of 50 mbar remained epitaxial in nature. An increase in TMS gas flow rates did not affect such an epitaxial feature. Uniform heteroepitaxial deposition of 3C-SiC film on 4-in. silicon wafer was then realized at a low deposition temperature ($\sim 860^\circ\text{C}$).

Various SiC nanostructures have been grown using CVD techniques [56, 57]. For example, the morphology control of one-dimensional (1D) SiC nanostructures was achieved by manipulating the composition of the catalysts (e.g. Fe_5Si_3 , Fe_3Si) during MWCVD processes. Iron silicide was found to be the main catalyst to initiate the growth of 1D SiC nanostructures. As confirmed by high-resolution transmission electron microscopy (HRTEM), the stoichiometry of iron silicide governed the final morphology of 1D SiC nanowires (NWs). For the growth of SiC NWs, the catalyst is Fe_5Si_3 , while it is Fe_3Si for the growth of SiC nanoneedles. A special orientation match between iron silicide catalyst and SiC NWs was observed during the growth of 1D SiC nanostructures, due to different etching resistivities of the catalyst particles under H_2 plasma [56]. Direct synthesis of ordered 3C-SiC nanosheet arrays has been also realized in a MWCVD reactor through utilizing planar defects formed during hetero-epitaxial growth of crystals with close-packed lattices [57]. TMS was used as a single source precursor and diluted in hydrogen gas. The plasma with a high MW power (e.g. 2500 W) was applied to activate the gas phase reaction. With a very low concentration of TMS (e.g. 140 ppm), the growth of the 3C-SiC epitaxial layer was achieved at a low growth rate ($\sim 50 \text{ nm h}^{-1}$). The grown 3C-SiC nanosheet arrays are well oriented on (001) and (111) Si substrates. The planar defects and the plasma environment were identified as key factors to determine the resulting 2D nanosheet arrays. Consequently, a “planar defect induced selective growth” effect was proposed to elucidate the corresponding growth mechanism [57].

In summary, various 3C-SiC films and nanostructures have been grown at different sizes ($>3 \text{ in.}$) by altering CVD techniques, substrates, and growth parameters (e.g. power density, gas pressure, type and concentration of precursors, and growth temperature, etc.).

1.3 Properties of Cubic Silicon Carbide

1.3.1 Surface Morphology

From further analysis of growth conditions summarized in Table 1.2, one can see that the changes in morphology of three 3C-SiC films are possible by controlling the MW

powers, gas pressures, and the concentrations of TMS precursors during MWCVD deposition [52]. For example, at low MW powers and high TMS concentrations, nanocrystalline 3C-SiC films are grown. This is because of high secondary nucleation rates under these conditions. An increase in the MW power enhances the concentration of atomic hydrogen, which is an important species in determining the crystallinity of a 3C-SiC film during MWCVD deposition [52, 58]. It removes the defects and amorphous phase in a 3C-SiC film through a continuous etching process [52, 58]. The higher the concentration of atomic hydrogen, the stronger the etching will be. Since the defects and amorphous phase can serve as sites for secondary nucleation, their effective removal will improve in turn the crystallinity of the 3C-SiC films [52, 58]. As a result, microcrystalline 3C-SiC films with larger crystal sizes and higher crystal quality are formed at high MW powers. Further increase in MW power or reduction of TMS concentrations led to the epitaxial growth of 3C-SiC films on the (001) Si wafer [52].

More detailed information about the composition of nanocrystalline, microcrystalline, and epitaxial 3C-SiC films has been revealed by XRD measurements. Peaks positioning at 35.6° , 41.4° , 60.0° , and 90.0° are indexed to the (111), (200), (220), and (400) reflexes of 3C-SiC, respectively. However, certain differences are observable. For both nanocrystalline and microcrystalline 3C-SiC films, strong (111) reflex exists. Weak (220) reflex is only observed for the microcrystalline 3C-SiC film: an indication of its polycrystalline nature. The intensity of the (220) reflex is much weaker in the nanocrystalline 3C-SiC film. For the epitaxial 3C-SiC film, only (200) and (400) reflexes are present, indicating its perfect (001) orientation [16].

Except for the 3C-SiC crystals, it is well understood that amorphous phases normally form at the grain boundaries during the CVD growth of 3C-SiC films [52]. Such information for these three 3C-SiC films was confirmed using micro-Raman measurements [16]. For all 3C-SiC films, the characteristic Raman peak at $\sim 800\text{ cm}^{-1}$ is observable, corresponding to the transverse optical (TO) phonon of SiC. The full width at half maximum (FWHM) of this SiC TO peak for nanocrystalline, microcrystalline, and epitaxial 3C-SiC films is >40 , 17, and 24 cm^{-1} , respectively. In comparison with that for a nanocrystalline 3C-SiC film, the SiC TO peaks for both microcrystalline and epitaxial 3C-SiC films are sharper, indicating their better crystallinity. In addition to the SiC TO band, peaks corresponding to the existence of an amorphous carbon phase are also observable at $\sim 1320\text{ cm}^{-1}$ (D band) and $\sim 1600\text{ cm}^{-1}$ (G band) for both nanocrystalline and microcrystalline 3C-SiC films. Nevertheless, since the Raman efficiency of SiC is only a tenth of that of the amorphous carbon [59], the strong D and G bands do not imply an extremely large amount of amorphous carbon phase in the 3C-SiC films. A broad peak positioning at $\sim 900\text{ cm}^{-1}$ is attributed to the Si-C rocking in Si-CH₃ [60–63]. The existence of the C-H bonding has been further confirmed by the secondary ion mass spectrometry (SIMS) measurements [64]. Such an observation indicates the presence of the amorphous SiC phase in both 3C-SiC films [60–63]. However, these three peaks completely disappear in the epitaxial 3C-SiC film. This result indicates strongly that no amorphous phase is incorporated into the epitaxial 3C-SiC film. In other words, the epitaxial 3C-SiC film is composed solely of 3C-SiC crystal. Furthermore, a shift in the position of this SiC TO peak is observed. For the microcrystalline and nanocrystalline 3C-SiC films, it shifts to lower wavenumbers in comparison with that of the epitaxial 3C-SiC film, indicating reduced crystallinity for both microcrystalline and nanocrystalline 3C-SiC films. However, a slight upshift

of this SiC TO peak for a nanocrystalline SiC film in comparison with that of a microcrystalline SiC film is reasonable. This is because the nanocrystalline 3C-SiC film contains more amorphous phase, whose thermal expansion coefficient is different from that of a microcrystalline 3C-SiC film. Moreover, the thickness of the nanocrystalline 3C-SiC film is different from that of the microcrystalline 3C-SiC film. These factors lead to the different stress levels in the nanocrystalline 3C-SiC film, resulting in the upshift of its Raman peak in comparison with that of the microcrystalline 3C-SiC film.

To get deep insight into the microscopic structures of nanocrystalline, microcrystalline, and epitaxial 3C-SiC films, their transmission electron microscopy (TEM) images were recorded. As shown in Figure 1.3, the difference in crystal sizes of these 3C-SiC films is clearly seen even from their low magnification TEM images. For the nanocrystalline 3C-SiC film, two kinds of crystals are present but with significant difference in their sizes, as indicated in Figure 1.3a with arrows. The small crystals are about ~ 5 nm in size, whereas the large ones are tens of nanometers in size. They were confirmed to be 3C-SiC crystals by HRTEM measurements. As shown in Figure 1.3d, the typical lattice fringes of these 3C-SiC crystals feature an interplanar spacing of 0.252 nm for their $\{111\}$ planes. Moreover, a certain amount of planar defects (twins and stacking faults) is found in these crystals. Those twins and stacking faults lie parallel to the $\{111\}$ planes, as denoted by the circles in Figure 1.3d. Regardless of their higher crystallinity,

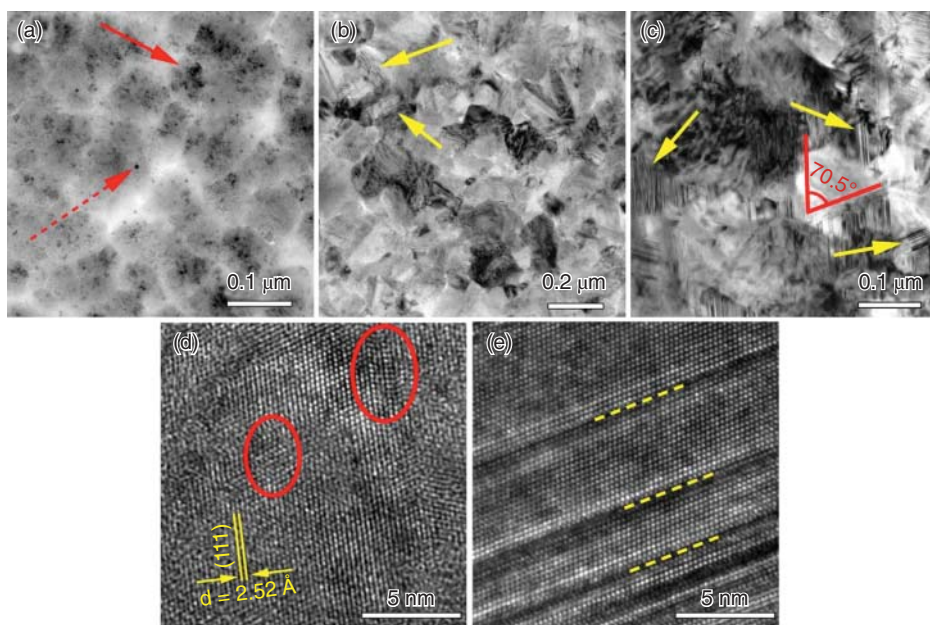


Figure 1.3 Low magnification TEM images of a nanocrystalline (a), a microcrystalline (b), and an epitaxial (c) 3C-SiC film; HRTEM images of one typical 3C-SiC crystal in the nanocrystalline (d) and microcrystalline (e) 3C-SiC film. The arrows in (a) indicate the 3C-SiC crystals with different sizes in the nanocrystalline 3C-SiC film. The arrows in (b) and (c) indicate the existence of planar defects in the microcrystalline and epitaxial 3C-SiC films. The circles in (d) denote the existence of planar defects, of which positions are indicated with dashed lines in (e) [16]. Source: Reprinted with permission from ACS publisher, Copyright 2015.

planar defects (arrows) are also observed in the microcrystalline (Figure 1.3b) and epitaxial (Figure 1.3c) 3C-SiC films. Figure 1.3e shows the HRTEM image of one typical 3C-SiC microcrystal with planar defects indicated by the dashed lines. The formation of planar defects is difficult to avoid. It is a very common phenomenon during the growth of various SiC structures [56, 64]. This is because the formation energies of these planar defects are low. During MWCVD processes, the energy generated by the mismatches (e.g. lattice mismatch, thermal expansion coefficient mismatch, etc.) between the SiC film and the substrate is sufficient to trigger the formation of these phase defects, leading to their high concentration in the crystals. Even though the existence of the planar defects is clearly observable throughout the whole film, no small angle grain boundaries exist in the epitaxial 3C-SiC film. This indicates such an epitaxial 3C-SiC film can be viewed as a single 3C-SiC crystal but with a high density of planar defects. This result is in good accordance with the Raman observation, where the epitaxial 3C-SiC film is found to be composed solely of the 3C-SiC crystal without any amorphous phase.

Therefore, there are significant differences in the compositions of the nanocrystalline, microcrystalline, and epitaxial 3C-SiC films. Both nanocrystalline and microcrystalline 3C-SiC films consist of amorphous carbon, amorphous SiC, and 3C-SiC crystals, while the epitaxial 3C-SiC film is composed solely of 3C-SiC crystals. Moreover, there are big differences in the crystal sizes of the nanocrystalline and microcrystalline 3C-SiC films. Furthermore, both nanocrystalline and microcrystalline 3C-SiC films are polycrystalline, while the epitaxial 3C-SiC film shows perfect (001) orientation. In addition, a large number of planar defects are incorporated in the 3C-SiC crystals for the nanocrystalline, microcrystalline, and epitaxial 3C-SiC films [16].

1.3.2 Electrochemical Properties

Understanding the mechanisms of charge transfer across the interfaces of various SiC films and the electrolytes is of importance and significance. It is a basic prerequisite for exploring the practical applications of these SiC films [65].

SiC has been tried more than 70 years ago as an electrode. Single crystalline SiC film behaved in a similar way to a noble electrode [66]. Single SiC films were used to construct impedance and temperature sensors. SiC based biomedical needles were used for open-heart surgery monitoring and graft monitoring of organs during transportation and transplantation [67]. However, it was troublesome to get the right contacts due to low conductivities of these films. Later, the nanocrystalline 3C-SiC film was found to exhibit much higher electron mobility than a single crystalline SiC film [68, 69]. It was thus employed as a novel electrode material for electrochemical applications (e.g. for electrochemical sensing applications) [55, 70]. Moreover, the properties of 3C-SiC films, especially their electrochemical properties, were found to be tunable through controlling the microstructures of 3C-SiC films (e.g. crystallinity, crystal sizes, defects, and composition, etc.) [16]. For example, by manipulating the deposition conditions (e.g. power density, growth temperature, etc.) during MWCVD processes, the nanocrystalline, microcrystalline, and epitaxial (001) 3C-SiC films have been grown with altered electrochemical properties [16].

First, these 3C-SiC films exhibited different electrical conductivities, as measured by a four-point-probe technique. Both nanocrystalline and microcrystalline 3C-SiC films possess a sheet resistance of $\sim 3300 \Omega \text{ cm}^{-2}$, whereas the epitaxial 3C-SiC film only

shows a sheet resistance of $86 \Omega \text{ cm}^{-2}$. Their conductivities result from the existence of defects in the 3C-SiC films (e.g. planar defects, grain boundaries, and the amorphous phases). The average oxygen concentration of the nanocrystalline 3C-SiC film was enhanced, and then the oxygen accumulated at crystal defects, resulting in much better conductivity [68, 69]. According to experimental investigation [71] and theoretical simulation [72], the planar defects in 3C-SiC films have high electrical conductivities, which are even higher than those of heavily nitrogen doped ($5 \times 10^{18} \text{ cm}^{-3}$) 3C-SiC films. In contrast, the amorphous phases show low electrical activities [73, 74]. Even though the nanocrystalline and microcrystalline 3C-SiC films contain significant amounts of planar defects, the existence of amorphous phases at the grain boundaries might resist the passage of the electric current between the SiC crystals, resulting in increased resistivity. For the epitaxial 3C-SiC film, it is free of the amorphous phases. In addition, anti-phase boundaries normally exist at the boundaries between the (001)-oriented SiC crystals, which give a further rise in its electrical conductivity, making the film even metallically conductive [75]. In this context, the epitaxial 3C-SiC film presents a higher electrical conductivity in comparison with the nanocrystalline and microcrystalline 3C-SiC films. Note that those 3C-SiC films were undoped. However, according to the values of their electrical conductivities, these 3C-SiC films could be applied as electrodes.

Prior to examining electrochemical properties of the nanocrystalline, microcrystalline, and epitaxial (001) 3C-SiC films, they were carefully cleaned to remove inorganic and organic contamination. After that, the films were treated in a hydrofluoric acid (HF) solution, resulting in OH-terminated surfaces [76, 77]. The double layer capacitive behavior of these 3C-SiC films was investigated using cyclic voltammetry in both aqueous (0.1 M H_2SO_4) and non-aqueous (0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile) solutions (Figure 1.4). The calculated double layer capacitances of the epitaxial 3C-SiC film were 6.3 and $5.2 \mu\text{F cm}^{-2}$ in aqueous and non-aqueous solutions, respectively. Higher capacitances of $14.2 \mu\text{F cm}^{-2}$ in the aqueous solution and $10.9 \mu\text{F cm}^{-2}$ in the non-aqueous solution were obtained for the microcrystalline 3C-SiC film. Taking into consideration the surface roughness of a microcrystalline

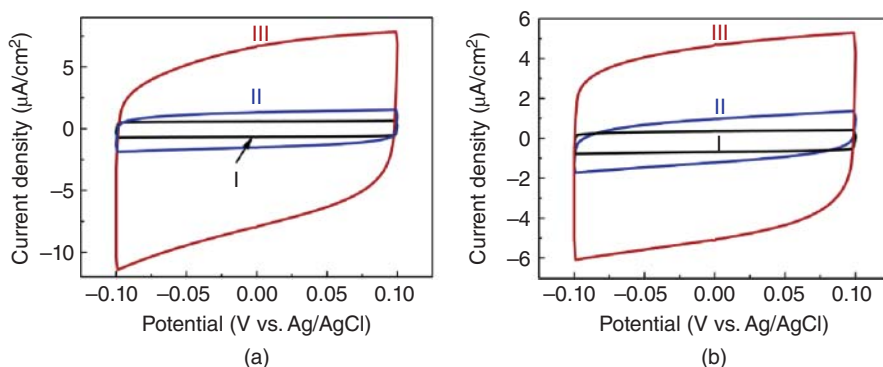


Figure 1.4 Cyclic voltammograms of an epitaxial (I), a microcrystalline (II), and a nanocrystalline (III) 3C-SiC film at a scan rate of 100 mV s^{-1} in 0.1 M H_2SO_4 (a) and in 0.1 M tetrabutylammonium tetrafluoroborate dissolved in acetonitrile (b). The currents were normalized with the geometric areas of the 3C-SiC films [16]. Source: Reprinted with permission from ACS publisher, Copyright 2015.

3C-SiC film, its specific capacitances were double those of an epitaxial 3C-SiC film. The nanocrystalline 3C-SiC film possessed the highest double layer capacitances (e.g. $72.7 \mu\text{F cm}^{-2}$ in aqueous solutions and $48.5 \mu\text{F cm}^{-2}$ in non-aqueous solutions, respectively). Once the real surface area of this nanocrystalline 3C-SiC film was taken into account, the corresponding capacitances were 56.8 and $37.9 \mu\text{F cm}^{-2}$, respectively. Depending upon MWCVD deposition conditions for the nanocrystalline 3C-SiC films, their double layer capacitances varied in the range from ~ 40 to $\sim 100 \mu\text{F cm}^{-2}$. In contrast to the nanocrystalline 3C-SiC film, the double layer capacitances of the microcrystalline and epitaxial 3C-SiC films exhibited much narrower distributions [16].

The electrochemical activity of the nanocrystalline, microcrystalline, and epitaxial (001) 3C-SiC films was examined in water-soluble redox probe (e.g. $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$) contained aqueous solutions as well as in organic solvent-soluble redox probes (e.g. ferrocene and quinone) contained non-aqueous solutions [78]. Figure 1.5 shows cyclic voltammograms of four redox probes on the nanocrystalline 3C-SiC film. Well-defined redox waves are seen for all cases. The values of ΔE_p (the difference of the anodic peak potential from the cathodic peak potential) and $I_p^{\text{ox}}/I_p^{\text{red}}$ (the ratio of the anodic peak current, I_p^{ox} , to the cathodic peak current, I_p^{red}) are 130 mV, 1.0 for $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox couple (Figure 1.5a); 120 mV, 1.0 for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple (Figure 1.5b); 150 mV, 1.0 for quinone (Figure 1.5c); and 140 mV, 1.0 for ferrocene (Figure 1.5d), respectively. Both I_p^{ox} and I_p^{red} are proportional to the square roots of scan rates from 10–200 mV s^{-1} . These results indicate that on the nanocrystalline 3C-SiC film these four faradaic reactions are quasi-reversible and controlled by the diffusion of those redox probes. Consequently, the nanocrystalline 3C-SiC film can be applied as a novel electrode material.

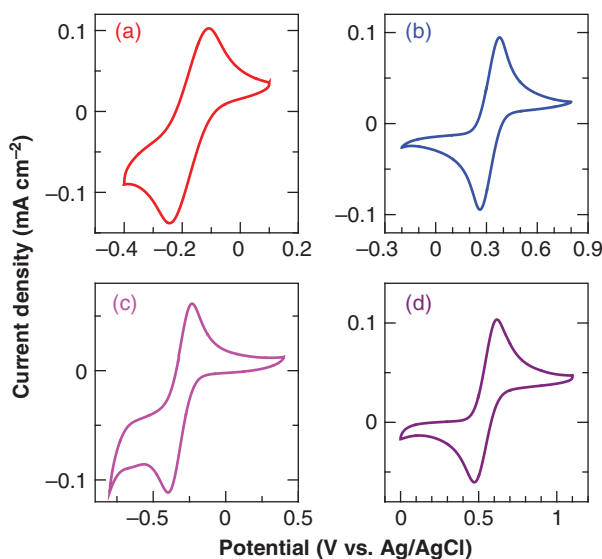
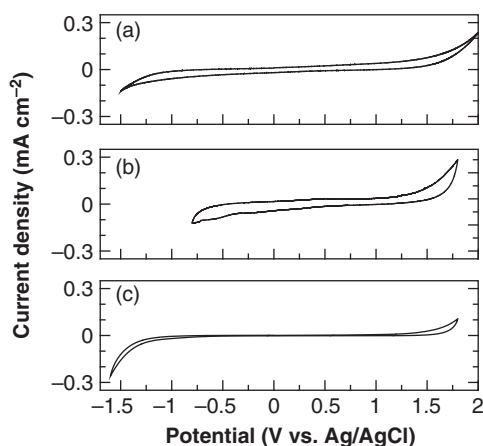


Figure 1.5 Cyclic voltammograms of a nanocrystalline 3C-SiC film at a scan rate of 10 mV s^{-1} in 1.0 mM $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ (a) and 1.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ dissolved in 0.1 M KCl solution (b), as well as in 1.0 mM quinone (c) and 1.0 mM ferrocene (d) dissolved in 0.1 tetrabutylammonium tetrafluoroborate solution [78] Source: Reprinted with permission from Wiley. Copyright 2012.

For the microcrystalline and epitaxial (001) 3C-SiC films, well-defined redox waves are also observed in water-soluble redox probes (e.g. $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$) containing aqueous solutions as well as in organic-solvent soluble redox probes (e.g. ferrocene and quinone) containing non-aqueous solutions [78]. The peak currents are proportional to the square roots of scan rates, indicating that the faradaic reactions of those redox probes are controlled by their diffusion. Moreover, the reversibility of the redox probes on all 3C-SiC films in aqueous solutions is better than that in the non-aqueous solutions, judging from their values of ΔE_p and $E_p - E_{p/2}$ (the difference of anodic/cathodic peak from its half-peak potential). Further comparison of ΔE_p and $E_p - E_{p/2}$ for the same redox probe on different 3C-SiC films leads to the conclusion that the best reversibility of redox probes is on the epitaxial 3C-SiC film, and the worst reversibility of redox probes is on the nanocrystalline 3C-SiC film. The difference in the reversibility of the redox probes originates from different charge transfer resistances of these 3C-SiC films. For example, the lowest charge transfer resistance is about $580\ \Omega$ for the epitaxial 3C-SiC film and the highest value is about $3300\ \Omega$ for the nanocrystalline 3C-SiC film [16]. In conclusion, the measurements of four different redox probes featuring varied electrode kinetics (e.g. the appearance of redox waves in different potential ranges) on three 3C-SiC films suggest that three 3C-SiC films can be applied in different media as well as in different potential ranges. However, the epitaxial 3C-SiC film presents the lowest double-layer capacitance and the highest reversibility of redox probes, because of its perfect (001) orientation and high phase purity. The highest double-layer capacitance and the lowest reversibility of redox probes have been realized on the nanocrystalline 3C-SiC film, due to its concentration of grain boundaries, amorphous phases, and high diversity in crystal sizes.

The electrochemical potential window of a nanocrystalline 3C-SiC film was further measured in an aqueous solution ($0.1\ \text{M}\ \text{H}_2\text{SO}_4$). The obtained cyclic voltammogram was featureless in the scanned potential range [70], indicating that the SiC/electrolyte interface is almost polarizable. The currents were stable with repeated sweeps and independent of the composition and pH value of the electrolytes. As shown in Figure 1.6, the capacitive current of the nanocrystalline 3C-SiC film is about 3–5 times smaller than that of a glassy carbon electrode, but 20–50 times larger than that of a boron-doped diamond electrode. Here, the boron concentration of this boron-doped diamond

Figure 1.6 Cyclic voltammograms of a nanocrystalline 3C-SiC film (a), a glassy carbon electrode (b), and a boron-doped diamond electrode (c) in $0.1\ \text{M}\ \text{H}_2\text{SO}_4$ at a scan rate of $100\ \text{mV}\ \text{s}^{-1}$. The boron concentration of the boron-doped diamond electrode is $5 \times 10^{20}\ \text{cm}^{-3}$ [70]. Source: Reprinted with permission from ACS. Copyright 2011.



electrode is $5 \times 10^{20} \text{ cm}^{-3}$. Moreover, the increase in anodic current on this heavily boron-doped diamond electrode is much faster than that on the nanocrystalline 3C-SiC film when the potential is higher than 1.2 V. The decrease in cathodic current on this heavily boron-doped diamond electrode is much faster than that on the nanocrystalline 3C-SiC film. Defined by a current density of 0.1 mA cm^{-2} as the threshold, the deduced potential window for a nanocrystalline 3C-SiC film SiC is about 3.0 V, which is slightly narrower than that of the boron-doped diamond electrode (3.2 V), but much wider than that of a glassy carbon electrode (2.2 V).

Fundamental electrochemical studies on n-type 6H-SiC and 4H-SiC electrodes have also studied the ferri-/ferrocyanide redox couple contained aqueous electrolytes [79]. To determine the energetic positions of the SiC band edges, as well as to investigate the electron-transfer kinetics between SiC and the ferricyanide molecules, cyclic voltammetry and impedance spectroscopy measurements were performed over a wide potential range. For both n-type 6H-SiC and 4H-SiC electrodes, a broad distribution of surface states with energy levels close to the conduction band was found to mediate electron transfer. This results in deviations of the observed charge transport characteristics from the predictions of well-established models. Detailed evaluation of the impedance data clarified further the correlation of the charge-transfer resistances of ferricyanide reduction reactions with the potential-dependent distribution of surface states [79]. The stability of n-type 6H-SiC photoelectrodes in buffered aqueous electrolytes was also investigated using cyclic voltammetry [80]. In pure Tris buffer, photogenerated holes accumulated at the interface under anodic polarization, resulting in the formation of a porous surface oxide layer. To significantly enhance the stability of the SiC photoelectrodes, two possibilities were then proposed. As the first approach, redox molecules were added to the buffer solution and then hole transfer to these molecules was kinetically facilitated. The second approach was to induce water oxidation through depositing a cobalt phosphate catalyst on the SiC surface. AFM and X-ray photoelectron spectroscopy (XPS) measurements confirmed that both approaches effectively suppressed photocorrosion of the SiC electrodes [80]. Furthermore, surface polishing of n-type polycrystalline 3C-SiC film was achieved by means of electrochemical etching, conducted in diluted HF solution under constant applied current density. No UV illumination was applied [81]. Such electropolishing led to a smooth 3C-SiC surface, which was flat and featureless. There was no sign of intergranular corrosion or other degradation phenomena related to the polycrystalline structure. After optimizing etching conditions (e.g. HF concentration, current density, and etching time), the roughness of this polycrystalline 3C-SiC film was reduced by more than half compared with its initial value [81].

1.3.3 Surface Chemistry

To expand the applications of SiC films, especially their electrochemical and biochemical applications, the surfaces of SiC films have been decorated with various terminations and/or organic molecules [82–88].

1.3.3.1 Surface Terminations

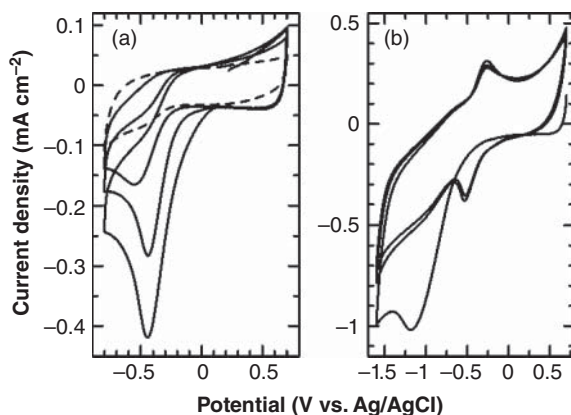
Since SiC possesses both silicon and carbon atoms, SiC films have different surface terminations. For example, cleaning (001) 3C-SiC films using HF as an oxide removal

The chamber was then heated up to 60°C for 10 minutes at 6 mbar and then further increased to 150°C for 1 hour. Prior to such functionalization, SiC substrates were cleaned in 50% HF solution with the intention of removing the native oxide on the SiC surface. Meanwhile the hydroxyl-terminated surface was obtained. The XPS of functionalized SiC films showed a prominent peak positioned at about 400 eV. This approach was also conducted on SiC epi-layers. Thermal grafting of both alkylated and fluorine-containing 1-alkynes and 1-alkenes onto SiC has been realized [93]. XPS, infrared reflection-absorption spectroscopy (IRRAS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements indicated that acetyl groups were presented at the organic-inorganic interfaces of alkyne-modified SiC surfaces. The static water contact angles measured on these interfaces were up to 120°. Using AFM, the tribological properties of these organic monolayers were also explored. The fluorinated monolayers exhibited significant reduction of adhesion forces, friction forces, and wear resistance compared with non-fluorinated molecular coatings, and especially bare SiC substrates. The successful combination of hydrophobicity and excellent tribological properties makes these strongly bound, fluorinated monolayers promising candidates for applications in high-performance microelectronic devices [93].

The wet-chemical functionalization of n-type (100) and (111)3C-SiC surfaces has been demonstrated with self-assembled monolayers (SAMs) of amino-propyldiethoxymethylsilane (APDEMS) and octadecyltrimethoxysilane (ODTMS) [94]. These organic layers were found to be smooth and densely packed on 3C-SiC surfaces. Confirmed from combined contact potential difference and surface photovoltage measurements, the heterostructure functionality and surface potential of these SAMs were found to be tunable once different organosilane precursors were utilized. Molecular dipoles significantly affected the work functions of the modified surfaces. The magnitude of the surface band bending was reduced on the hydroxylated surfaces with organosilanes, indicating that partial passivation of electrically active surface states is achieved. Self-assembly of APDEMS and ODTMS onto 6H-SiC films was also demonstrated [83]. The structural and chemical properties of these layers were studied by contact angle measurements, AFM, thermal desorption, and XPS. The organic layers were smooth and the wetting angles were up to 100°. Desorption temperatures in the range of 557°C proved the covalent bonding of the organic silane molecules to the SiC surface. The monolayers of 11-hydroxyundecylphosphonic acid and 9,10-diphenyl-2,6-diphosphonoanthracene have been self-assembled on 6H-SiC films [95]. Structural and chemical properties of these monolayers were investigated through contact angle measurements, AFM, XPS, and Fourier transformation infrared (FTIR) spectroscopy. Covalent bonding of the phosphates to both (0001)- and (000-1)-oriented 6H-SiC crystal faces was confirmed. Electrical characterization was achieved through contact potential difference and surface photovoltage measurements, which revealed significant changes in the work functions of the substrates by monolayer formation.

A short chain molecule of allylamine has been photochemically attached to 3C-SiC films, as confirmed by SIMS and XPS measurements [96]. The maximum coverage of allylamine on a 3C-SiC surface was achieved after four hours of UV illumination. With further UV illumination, allylamine cross-polymerized slightly with each other. The allylamine dense monolayer was formed under UV illumination for four

Figure 1.8 (a) Electrochemical grafting of a nanocrystalline 3C-SiC film with 1.0 mM 4-nitrobenzene diazonium tetrafluoroborate using cyclic voltammetry. The electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. The scan rate is 200 mV s^{-1} . (b) Electrochemical reduction of nitrophenyl film in 1 M KCl in a mixture of ethanol: water (V:V = 1:9) at a scan rate of 100 mV s^{-1} [70]. Source: Reprinted with permission from ACS publisher, Copyright 2011.



hours. From its XPS results, the maximum surface density was calculated to be $\sim 4 \times 10^{14} \text{ molecules cm}^{-2}$.

The nanocrystalline 3C-SiC film has been modified using an electrochemical approach, namely by means of electrochemical reduction of diazonium salts [70]. The attachment was confirmed by electrochemical, time-of-flight secondary ion mass spectrometry (ToF-SIMS), and XPS measurements. Figure 1.8a shows voltammograms for the reduction of 4-nitrobenzene diazonium salt on a nanocrystalline 3C-SiC film. An irreversible reduction peak centered around $-440 \pm 60 \text{ mV}$ (vs. Ag/AgCl) is detected during the first cycle. The cathodic peak potential shifts toward more negative potentials in subsequent cycles. The peak disappears after more than 10 cycles (dashed line). The peak arises by the reduction of diazonium salt cations, yielding radical species that covalently bind to the SiC surface. The decreased cathodic peak current and the negative shift of the cathodic peak potential indicate the formation of an insulating film, where either the reduction is halted or the electron transfer through the formed film is kinetically slowed down as a function of time [97–99]. Moreover, the redox currents of $\text{Fe}(\text{CN})_6^{3-/4-}$ on a nitrophenyl layer functionalized SiC surface was strongly suppressed. As shown in Figure 1.8b, such a functionalized surface exhibited in the first cycle a large irreversible reduction peak at $-1.10 \pm 0.05 \text{ V}$ (vs. Ag/AgCl) in the aqueous solution of ethanol: water (V:V = 1:9). This is due to the electrochemical reduction of nitrophenyl (Ar-NO_2) groups to amine (Ar-NH_2) or hydroxyaminophenyl (Ar-NHOH) groups [97–99]. In the second and subsequent cycles, this reduction peak was drastically diminished, indicating that nearly all electroactive nitrophenyl groups are reduced in the first scan. The reversible couple at $E_{1/2} = -350 \pm 30 \text{ mV}$ (vs. Ag/AgCl) appeared only after the first cycle, indicating an incomplete reduction process of $-\text{Ar-NO}_2$ to $-\text{Ar-NH}_2$ [97–99]. The density of nitrophenyl on the SiC surface, evaluated from the charge transferred for the wave at -1.10 V (vs. Ag/AgCl), was $3.1 \times 10^{15} \text{ cm}^{-2}$ or $5.1 \times 10^{-9} \text{ mol cm}^{-2}$. In SIMS, nitrogen-related characteristic peaks (CN^- , CNO^- , NO_2^- , $\text{C}_6\text{H}_4\text{NO}_2^-$, and $-\text{OC}_6\text{H}_4\text{NO}_2^-$) are clearly seen in the functionalized areas. The XPS of a nitrophenyl-grafted SiC surface did present a broad N peak where two sharp peaks at 399 and 406 eV were simulated [100], assigned to the NO_2 group and some reduced nitrogen-containing functionalities, respectively.

1.4 Electrochemical Applications of Cubic Silicon Carbide Films

3C-SiC films feature wide potential windows, stable capacitance currents, and good electrochemical response toward electroactive species. Therefore, they have been employed as the electrode materials for various electrochemical applications.

1.4.1 Electrochemical Sensors

3C-SiC thin films have been used to construct electrochemical sensors. As an environmentally friendly and alternative electrode material, nanocrystalline 3C-SiC film has been employed as an electrode for anodic stripping voltammetric detection of trace metal ions [101]. The obtained detection limits for Cu^{2+} and Ag^+ ions were as low as 6 and 4 ppb, respectively. In addition to the individual detection of these metal ions, the 3C-SiC electrode also showed good capability and good reproducibility for simultaneous detection of Cu^{2+} and Ag^+ ions [101].

An electrochemical dopamine sensor was fabricated using epitaxial 3C-SiC film [16]. This is because epitaxial 3C-SiC film shows a lower background current and better reversibility for the redox probes in aqueous solutions than a nanocrystalline SiC film [16]. In pH 7.4 phosphate buffer solution containing 100 μM dopamine, a well-defined oxidation peak appeared at 0.4 V. A small reduction peak was observable at ~ 0 V. An increase in the scan rates led to the proportional enhancement of the anodic peak current densities. These results implied that irreversible oxidation of dopamine on the epitaxial 3C-SiC film is a diffusion-controlled process, instead of an adsorption-controlled one. Differential pulse voltammetry was adopted for the monitoring of dopamine. The anodic peak current density was linearly enhanced with the concentration of dopamine in the concentration range of 2–200 μM . The detection limit was determined to be 0.7 μM or 0.1 mg l^{-1} [16]. Although the limit-of-detection of dopamine on the epitaxial 3C-SiC film was not as low as that obtained on other electrodes reported in the literature [102], the workable concentration range for dopamine detection on the epitaxial 3C-SiC film was still one to two orders lower than its concentration in tissue (4–10 mg l^{-1}) [103, 104]. Therefore, the epitaxial 3C-SiC film is a suitable and promising electrode material for electrochemical determination of dopamine.

1.4.2 Biosensors

Surface functionalized SiC films have been applied for biochemical applications. For example, by utilizing self-assembled layers with functional terminal groups, immobilization of proteins was demonstrated [83, 94, 95]. The bio-application of a nanocrystalline 3C-SiC film was also tested by attaching DNA [70]. The probe DNA was labeled with a redox center of ferrocene moiety. The complementary DNA was labeled with a red fluorescent marker of Cy5 dye. As shown in Figure 1.9a, the fluorescence image of a bare 3C-SiC film shows no emission of red light, indicating no adsorption of DNA on the surface of the film. After electrochemical grafting of a nitrophenyl layer and further hybridization of probe DNA with complementary DNA onto the nanocrystalline 3C-SiC surface, the functionalized area showed a high intensity of red fluorescence, indicating complementary DNA has been immobilized. The voltammogram of probe

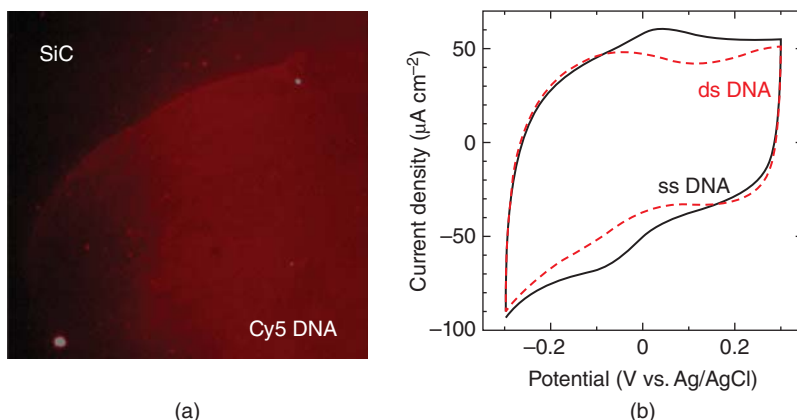


Figure 1.9 (a) Fluorescence microscopy image of a double-stranded DNA functionalized SiC electrode, and (b) cyclic voltammograms of single-stranded DNA (solid line) and double-stranded DNA (dashed line) modified 3C-SiC film in pH 7.4 phosphate buffer at a scan rate of 50 mV s^{-1} [70]. Source: Reprinted with permission from ACS Publisher, Copyright 2011.

DNA (single-stranded DNA) immobilized 3C-SiC film (Figure 1.9b) showed a couple of redox waves of ferrocene moiety centered at $E_{1/2} = 0 \pm 5 \text{ mV}$ (vs. Ag/AgCl) and with ΔE of $50 \pm 10 \text{ mV}$. These waves became smaller or even disappeared after hybridizing the probe DNA with complementary DNA (double-stranded DNA). A decrease in the redox current specifically indicates the presence of complementary DNA. Since the hybridized DNA has increased rigidity, the access of the terminal ferrocene moiety to the 3C-SiC surface is thus inhibited, leading to a reduced or absent redox current from the ferrocene moiety of probe DNA. This method was simple, since either labeling target DNAs or adding external electroactive species were needed.

The label-free electrical detection of DNA molecules has been reported using SiC nanowire based field effect transistors (NWFETs) [105]. Non-intentionally n-doped SiC NWs with a length of approximately $2 \mu\text{m}$ and a diameter ranging from 25 to 60 nm were grown using a bottom-up vapor–liquid–solid mechanism. The SiC NWFETs were fabricated and further functionalized with DNA molecules via covalent coupling of an amino-terminated organosilane. The drain current vs. drain voltage characteristics obtained after the DNA grafting and hybridization were measured and compared. As a representative result, the current was lowered by 22% after probe DNA grafting, and by 7% after target DNA hybridization. The current decrease confirmed the field effect induced by the negative charges of DNA molecules. Moreover, the selectivity, reproducibility, reversibility, and stability of the NWFET devices were studied by dehybridization, non-complementary hybridization, and rehybridization experiments. This first proof of concept opens the way for future developments using SiC-NW based sensors [105].

1.4.3 Energy Storage

SiC has been employed for the construction of supercapacitors and batteries as well as for the loading of catalysts. For example, an electrochemical capacitor was constructed using a nanocrystalline 3C-SiC film. This is because the nanocrystalline 3C-SiC film

shows not only a relatively high double layer capacitance ($40\text{--}100\text{ }\mu\text{F cm}^{-2}$, depending on the growth conditions), but also long-term stability of its capacitance. Moreover, SiC features high thermal and long-term chemical stability in harsh physicochemical environments [65, 106, 107]. Figure 1.10a depicts the cyclic voltammetric curves of nanocrystalline 3C-SiC film in $0.1\text{ M H}_2\text{SO}_4$ at different scan rates [16]. For all the scan rates considered, the quasi-rectangular shape of the curves is clearly observable in the potential range scanned. The curves are symmetric, as expected for a typical electrical double layer capacitor (EDLC). Its charging–discharging behavior at different current densities ($4\text{--}80\text{ }\mu\text{A cm}^{-2}$) is shown in Figure 1.10b. For all current densities tested, the anodic charging segment is symmetric to the cathodic discharging counterpart, indicating the high reversibility of this EDLC. Its specific capacitance was calculated to be $70\text{ }\mu\text{F cm}^{-2}$ at a scan rate of 10 mV s^{-1} . Nevertheless, only 34% reduction in its capacitance is observed, even with a 20-fold increase in the scan rate. As summarized in Figure 1.10c, the specific capacitance decreases by only 25% (from 65 to $43\text{ }\mu\text{F cm}^{-2}$) in the case of altering charging current density from 4 to $80\text{ }\mu\text{A cm}^{-2}$. Therefore, an

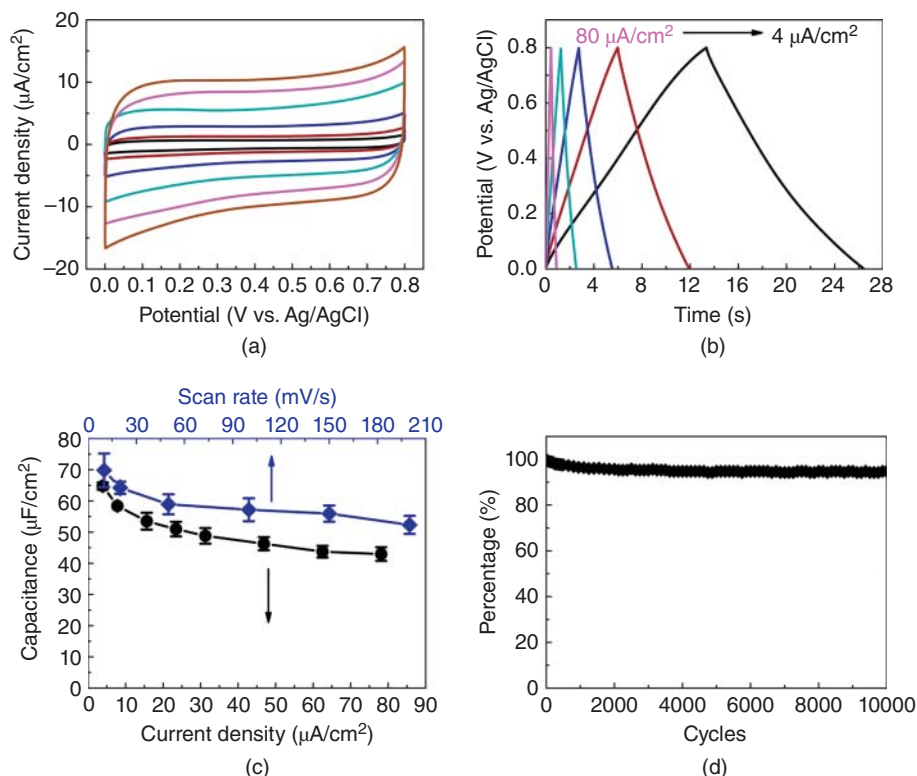


Figure 1.10 The performance of a nanocrystalline 3C-SiC film based EDLC in $0.1\text{ M H}_2\text{SO}_4$: (a) cyclic voltammetric curves at different scan rates, from inside to outside: $10\text{--}200\text{ mV s}^{-1}$; (b) charging–discharging curves with different current densities; (c) specific capacitance as a function of scan rates and charging current densities; (d) the variation of capacitance with charging–discharging cycles. The current densities were normalized with the real surface area of the nanocrystalline 3C-SiC film [16]. Source: Reprinted with permission from ACS Publisher, Copyright 2012.

excellent rate performance has been achieved on the nanocrystalline 3C-SiC film based EDLC. In addition to its high specific capacitance, the cyclic stability of the 3C-SiC film based EDLC was examined. As shown in Figure 1.10d, the nanocrystalline 3C-SiC retains 94.8% of its initial capacitance after 10 000 cycles. These results are comparable with those constructed using carbon materials (>80%) [108, 109], indicating a very high cyclic stability of the nanocrystalline 3C-SiC film based EDLC.

To further improve the capacitances of SiC-based supercapacitors, the usage of thin SiC films with high geometric areas or SiC nanostructures (e.g. wires, particles, etc.) has been proposed. For example, an activated carbon-derived SiC nanoparticle showed a specific capacitance of 114.7 F g^{-1} at a current density of 0.12 A g^{-1} [110]. A CVD-fabricated SiC NW showed an areal capacitance of $240 \mu\text{F cm}^{-2}$ at a scan rate of 100 mV s^{-1} [111]. In $0.1 \text{ M H}_2\text{SO}_4$ solution, a 3C-SiC NW synthesized on graphite paper (GP) by a carbothermal reduction method exhibited specific capacitances of 25.6, 37, 28, and 28 mF cm^{-2} at current densities of 0.2, 0.3, 0.5, and 2.0 A cm^{-2} , respectively. These values remained unchanged even after 2000 cycles, showing excellent capacitance retention [112]. A SiC nanocauliflower featured a specific capacitance of up to $\sim 300 \text{ F g}^{-1}$ at a scan rate of 5 mV s^{-1} . With a working voltage of 1.8 V, a fabricated symmetric supercapacitor device delivered a specific capacitance of 188 F g^{-1} at a scan rate of 5 mV s^{-1} , capacitance retention of 97.05% after 30 000 cycles, an energy density of $31.43 \text{ W h kg}^{-1}$, and a power density of $\sim 18.8 \text{ kW kg}^{-1}$ at $17.76 \text{ W h kg}^{-1}$ [113, 114]. However, it is still a great challenge to fully utilize active SiC electrode materials [114–116]. Further integrating SiC nanostructures with other metal oxides or conducting polymers is proving to be an alternative approach for further enhancement of the performance of SiC-based supercapacitors. For example, coating SiC NWs with Ni(OH)_2 and MnO_2 improved the specific capacitances up to 1724 and 273.2 F g^{-1} , respectively [117, 118].

Besides electrochemical capacitors, SiC films have been identified as possible anode materials for rechargeable lithium batteries [119–121]. Note that SiC bulk is generally regarded as electrochemically inactive in lithium-ion batteries (LIBs). However, very recently, a few reports revealed that SiC could serve as an anode material for LIBs. For example, a nanocrystalline SiC film grown on metallic current collector substrates by means of modified PECVD exhibited a reversible reaction with Li ions [119]. The CVD-grown SiC film consisted of nanocrystalline 4H-SiC surrounded by amorphous SiC networks. As the anode, such a film exhibited a specific discharging capacity of 309 mA h g^{-1} , which was stable over 60 cycles at different charging and discharging rates. The formation of Li_4C layers in lithiation was proposed. Cubic nano-SiC, prepared by a CVD method, has also been used as an anode for lithium insertion. A reversible lithium insertion was reported with a capacity of about 1200 mA h g^{-1} over 200 cycles [120]. Bead-curtain shaped, SiC-coated SiO_2 (by convention, SiC@SiO_2) core-shell nanowires (SiC@SiO_2 -CSNWs) have been synthesized on GP [121]. Bare SiC NWs (SiCNWs) were also fabricated on GP. These as-prepared SiCNWs and SiC@SiO_2 -CSNWs (without addition of binder or electron conductive materials) were directly used as working electrodes for lithium batteries. For example, SiCNWs exhibited high specific capacities and good cycling stabilities, ascribed to the unique NW structure, effectively buffering volume changes upon repeated alloying and de-alloying. Comparatively, SiC@SiO_2 -CSNWs presented much better electrochemical properties. The conducted intensive TEM and FTIR measurements revealed that the SiO_2 shell effectively separated the direct contact between active SiC and the electrolyte, thus

suppressing the rapid growth of solid electrolyte interface film in repeated cycling, and stabilized the structure of active material [121]. SiC@Si core-shell NWs have been synthesized on carbon paper via a two-step CVD method. Without any additional binder, they have been further employed as a hybrid anode for lithium-ion batteries [122]. Silicon was selected because it is considered one of the most promising anode materials for next-generation LIBs due to its high theoretical capacity. However, its large volume changes during electrochemical cycling limit its commercial application. The synthesized SiC@Si NWs exhibit high specific capacity, high coulombic efficiency, and good cycling stability. After 50 cycles, the discharge capacities remained 2837 and 1809 mAh g⁻¹ at rates of 0.1 and 0.5 C, respectively. The influence of the growth time of SiC NWs and the thickness of Si film on the performance of LIBs was also considered [122].

Combining these results with the high cyclic stability of SiC films and nanostructures, one can believe that they are very promising candidates for the construction of stable, reversible, and long lifetime capacitors and batteries. There is tremendous potential for SiC films and their nanostructures as electrodes in energy storage and conversion applications.

1.4.4 Other Applications

SiC films and their nanostructures have been used for electrocatalytic and related applications. For example, core-shell structured SiC@C (namely a nanoscale SiC core and a graphitic carbon shell) has been used as a support to load electrocatalysts for direct methanol fuel cells [123]. The SiC@C was prepared by graphitization of nano-SiC under a vacuum of 10⁻³ Pa at 1500°C. The epitaxially grown carbon layer had a high conductivity and an affinity for Pt metal catalysts, while the SiC core retained its high stability. Pt electrocatalysts supported on SiC@C (Pt/SiC@C) were prepared using a microwave heating method. The Pt/SiC@C electrocatalyst had much higher catalytic activities than the Pt/SiC electrocatalyst toward methanol electro-oxidation and oxygen reduction reactions. More significantly, the Pt/SiC@C electrocatalyst showed greater stability in comparison with the traditional Pt/C. The superior electrocatalytic performance of Pt/SiC@C has been ascribed to a high dispersion of Pt nanoparticles on the SiC@C support, and high stability of the SiC@C support in acid solutions.

Bio-inspired N-doped SiC/Mo composite has proved to be a green and cost-effective alternative for practical desulfurization of fuel [124]. This is because MoO₃, Mo₂C, and MoSi₂ particles dispersed well on the surface of N-doped SiC composite. It has shown superior catalytic properties in oxidative desulfurization of model fuel (99.6%).

1.5 Conclusions

By use of different techniques and under different growth conditions (e.g. growth temperature, power density, precursor, etc.), various 3C-SiC films and nanostructures have been grown. These materials feature changed properties, ranging from their morphology (e.g. crystallinity, defects, phase composition, roughness, etc.), conductivities, and interfacial properties (e.g. surface reactivity, capacitive and faradaic behavior, etc.). The structural heterogeneity of SiC films actually determines their properties. For example,

surface conditions of the SiC films (e.g. crystal orientation, composition, surface functional groups, etc.) drastically affect the formation of electrical double layers and charge transfer kinetics during electrochemical processes. Therefore, the performance of the applications (e.g. detection limits for electrochemical sensing, capacitances for electrochemical capacitors, etc.) of different SiC films and nanostructures is varied. For example, a high-performance supercapacitor and a sensitive dopamine electrochemical sensor were demonstrated using a nanocrystalline 3C-SiC film and an epitaxial 3C-SiC film, respectively.

However, more detailed and in-depth studies are still required in order to explore various SiC films and nanostructures for different applications. Regarding the growth of SiC films and their nanostructures, currently established methods always involve toxic reagents and solvents. Moreover, some byproducts always remain that might limit the overall performance of SiC materials, especially SiC nanomaterials. With respect to the characterization and property investigation of SiC films and their nanostructures, most of them are only qualitatively discussed. Quantitative studies are of course needed in some cases to distinguish clearly their property differences (e.g. crystallinity, crystal orientation, phase composition, defects, roughness, surface reactivity, surface functional groups, capacitive and faradaic behavior, etc.). For example, the sources of the conductivities of various SiC films, as well as how to further improve or tune their conductivities, have to be clarified. Doping of SiC films and their nanostructures with different dopants needs to be conducted, and their conductivities as well as electrochemistry (e.g. electrochemical potential window, double-layer capacitance, and redox activity, etc.) should be investigated. To compare with previously reported robust electrodes such as boron-doped diamond electrodes, the effects of surface termination, the conductivities (resulting from dopants and doping levels), and crystal structures/polytypes of SiC films on the electrochemical properties of SiC films and nanostructures need to be investigated. The stability of SiC films and their nanostructures at high positive potentials or with strong oxidative reactants (namely the oxidation of silicon atoms on the surface of SiC films and their nanostructures), various approaches to modify SiC films and their nanostructures by use of silicone and/or carbon chemistry (more exactly the reaction sites – carbon or silicon atoms during functionalization processes), and the employment of functionalized SiC surfaces for electrochemical and biochemical applications should be considered. As for the applications of SiC films and their nanostructures, more strategies are still needed. Taking the construction of SiC-based supercapacitors as an example, only the surfaces of active SiC materials contribute efficiently to the total capacitance, while most of SiC materials below the surface do not take part in the electrochemical processes, leading to lower specific capacitances than expected. For SiC-based lithium batteries, the interaction of lithium ions with active SiC materials has not been clarified. For the biosensors and biointerfaces based on SiC films and their nanostructures, more experiments are still required to evaluate their performance with respect to sensitivity, stability, and detection limits. In particular we require more knowledge of the reaction efficiency of SiC films and their nanostructures with biomolecules (e.g. DNA), investigation of the linker density, and the reaction conditions (e.g. reaction time, reaction temperature, the concentration and amount of biomolecules, etc.).

In summary, SiC films and their nanostructures are fantastic materials featuring many unique physical and chemical properties. More applications of SiC films and

their nanostructures in different fields are highly expected, such as in the fields of electrochemical and biochemical sensing as well as electrochemical energy storage and conversion.

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2

Application of Silicon Carbide in Photocatalysis

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Energy crisis and environmental pollution due to the extensive utilization of fossil fuels are the two major challenges facing the world in the twenty-first century. Among various technologies available today, heterogeneous photocatalysis based on semiconductors, plasmonic metals and non-plasmonic metals making use of renewable solar energy has been regarded as one of the most promising strategies for solving both the energy and environmental issues, and has thus received much attention during recent decades [1–5]. Particularly, since the discovery in the 1970s by Fujishima and Honda that splitting of water occurred over TiO_2 during UV light irradiation [6], there has been an increasing interest in the application of semiconductor photocatalysis in artificial photosynthetic systems, photocatalytic synthesis of organic compounds, and photodegradation of contaminants in water and air. Therefore, considerable efforts have been made toward developing efficient and stable semiconductor particle systems. However, most semiconductors are responsive only to UV light (less than 5% of solar radiation) due to their wide bandgap. For example, TiO_2 has turned out to be one of the most commonly investigated semiconductors because of its high efficiency, nontoxicity, high stability in aqueous solution, and low cost, but its bandgap is 3.0–3.2 eV and it requires UV light to operate, seriously restricting its solar efficiency [7]. Moreover, most semiconductors are unstable, leading to chemical or photochemical corrosion. Since visible light constitutes a large fraction of solar energy (about 43%), one of the great challenges for photocatalysis study is to develop visible light-driven photocatalysts through the modification of wide-bandgap semiconductors or finding new native visible light-responsive photocatalysts. Silicon carbide (SiC) is a semiconductor with excellent chemical stability. Moreover, it has a suitable bandgap (2.39–3.33 eV) that can strongly absorb visible light. Recently, it has attracted much more attention as a photocatalyst, and many related research works have also been published. In this chapter, we will briefly introduce the preparation of SiC, and introduce in detail its application in photocatalytic water-splitting to produce hydrogen, degradation of pollutants, photocatalytic organic synthesis, and CO_2 reduction.

2.1 Preparation of SiC with High Surface Area

SiC is a covalently bonded IV–IV compound that can be characterized by 1D pleomorphism. In SiC, each C (or Si) atom is surrounded by four Si (or C) atoms with strong tetrahedral sp^3 -hybridized bonds, leading to the fact that SiC has high strength, high thermal conductivity, good thermal shock resistance, low thermal expansion, and good chemical inertness [8]. Therefore, SiC is widely used in high-temperature and high-strength materials. Meanwhile, the unique electronic properties of SiC mean it is recognized as an ideal candidate for power electronics, hostile-environment electronics, blue light-emitting diodes, and sensors. However, there are few applications of SiC in the chemical field. As we know, about 90% of chemical processes employ catalysts, and most are heterogeneously catalytic processes, often performed under high temperatures and high pressures, and even in strongly acidic or alkaline environments. Many chemically stable materials, such as alumina, silica, and molecular sieves, are usually employed in heterogeneous catalysis [9].

For SiC, good chemical stability is conducive to maintaining the catalyst structure, thereby prolonging the life of the catalyst; the high mechanical strength and hardness of SiC are beneficial for the strength and wear resistance of the catalyst; the good thermal conductivity and electrical conductivity of favorable to the heat transfer of the catalyst during the reaction and electron transfer between active sites and supports; the suitable bandgap enables it to respond well to visible light; and therefore, SiC is a potentially excellent catalytic material. However, as yet there is no SiC-based catalyst in industrial applications. The main reason is that the specific surface area of SiC currently available on the market is very low, and it is difficult to meet the requirements of the catalysis material. Therefore, preparation of SiC with a high specific surface area that can be used as a catalysis support has attracted the attention of researchers, and related research has been increasing [10].

Herein, we introduce some general methods for preparing SiC with high specific surface area [10]. Here we generally refer to porous SiC with a specific surface area greater than $20 \text{ m}^2 \text{ g}^{-1}$; other morphologies, such as nanowires, nanoprisms and nanoneedles, will not be discussed in this section. For the preparation, properties, and applications of SiC with other nanostructures, please refer to the corresponding review articles [11–13].

Industrially, SiC is usually prepared by a carbon-thermal reduction method; that is, powdery carbon and silica are mixed directly, and then heated to above 2000°C to form SiC. The overall reaction equation is:



Due to the high temperature, both SiO_2 and carbon are in a mixed melting state. So the prepared SiC is a dense bulk solid with a very low specific surface area, which is α -SiC. Currently, researchers prepare SiC with high specific surface areas generally at a relatively low reaction temperature. Commonly used preparation methods include the carbon template method, the sol-gel method, and the polycarbosilane pyrolysis method, and all obtained products are β -SiC.

2.1.1 Carbon Template Method

Usually, the grain structure and morphology of SiC largely depend on the structure and morphology of the carbon particles of the original reactant in the carbothermal reduction process. Therefore, converting high specific surface area porous carbon into high specific surface area porous SiC through a carbon thermal reduction process is a common method. Among them, the most representative work is the shape memory synthesis (SMS) method proposed by Ledoux and coworkers [14–17]. This method consists of the attack of high-specific-surface activated carbon by SiO vapor generated by the high-temperature reaction of Si and SiO₂. The high specific surface is probably due both to the low temperature of the reaction between SiO and C and to the presence of a stable carbon skeleton. Before reaction, the carbon can be doped with different additives to improve the surface interaction between SiC and the impregnated active phase. Since the temperature of the process is low and the silicon atoms in the gas phase SiO displace the carbon atoms on the surface of the porous carbon, the formed SiC can maintain the skeleton structure of the porous carbon. On the other hand, CO formed by the reaction of oxygen atoms in SiO with carbon atoms escapes from the system, which is also favorable for the formation of pore structures of SiC and an increase in specific surface area. Using the SMS method, Ledoux and coworkers prepared a series of porous SiC with specific surface areas of 40–400 m² g⁻¹ (Figure 2.1a and b) [16]. If carbon nanotubes are used as templates, SiC nanotubes can also be prepared by the SMS method (Figure 2.1c and d) [16].

In addition to the gas–solid surface reaction of SiO with carbon template used to maintain the template morphology of SiC, the reaction of carbon template with liquid silicon or silicon dioxide can also be employed to get porous SiC. For example, Wu

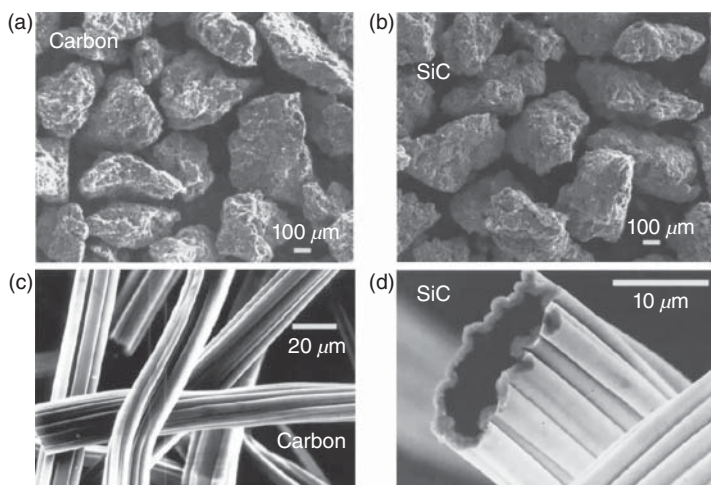


Figure 2.1 Scanning electron microscope (SEM) images of (a) starting activated charcoal and carbon microfibers (c), and equivalent final SiC with high surface area (b) and SiC microtubes (d) by SMS [16]. Source: Reprinted with permission from Elsevier, Copyright 2001.

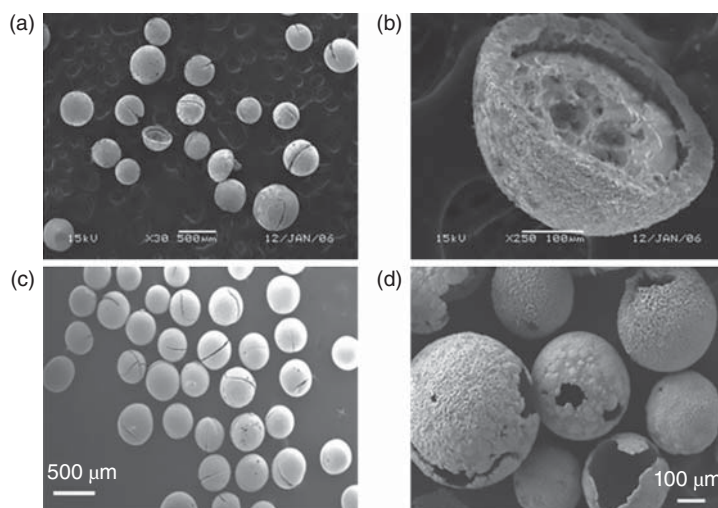


Figure 2.2 SEM images of $\alpha\text{-Fe}_2\text{O}_3/\text{SiC}$ composite spheres (a), a broken sphere with obvious core-shell structure (b), macroscopic hollow SiC spheres (c), and broken hollow spheres (d) [18]. Source: Reprinted with permission from Elsevier, Copyright 2006.

et al. utilized strongly acidic ion exchange resin spheres exchanged by Fe^{3+} cation as template, and then obtained core-shell structured $\alpha\text{-Fe}_2\text{O}_3/\text{SiC}$ composite spheres by carbothermal reduction of the resin spheres and commercial silica (Figure 2.2a and b) [18]. The composite spheres can be converted into porous SiC hollow spheres by etching in hydrochloric acid (HCl) and hydrofluoric acid (HF) mixture solution (Figure 2.2c and d) [18]. The resins exchanged with univalent cations cannot produce spherical composites because the resins will undergo a plastic phase-change during the carbonization. Those with cations of lanthanum, cerium or aluminum do not produce stable spherical composites, because the SiC catalytically produced by these metals mainly consists of nanowires that cannot form a stable shell-like framework.

Preparation of biomorphic porous materials by natural products has recently received particular attention. One of the main reasons is that biological structures usually exhibit some unique features of complex hierarchical cellular structures ranging from micro-(cell) to macro-scale (skeletons). These hierarchical structures offer a highly efficient system for transportation of biological matter. Therefore, it is interesting to prepare such materials, which have biomorphic porous structures similar to those of natural products, and may find widespread applications in catalysis, separation, and other industrial processes. On the other hand, most of the biological structures are characterized by indirect and open porous systems, which offer the possibility of using infiltration techniques to transform natural plants into porous ceramic materials. Wang et al. transformed biomass millet, broomcorn, and lotus root into carbon template by high-temperature pyrolysis (Figure 2.3) [19, 20]. The carbon templates were covered with silicon powder and heated at 1600°C for two hours in argon flow to obtain porous SiC having a similar morphology and structure as the biomass templates. The specific surface area is about $30\text{ m}^2\text{ g}^{-1}$, and the porosity is more than 60%. Figure 2.3 shows the obtained biomass SiC successfully replicate the microstructure and morphology of the carbon

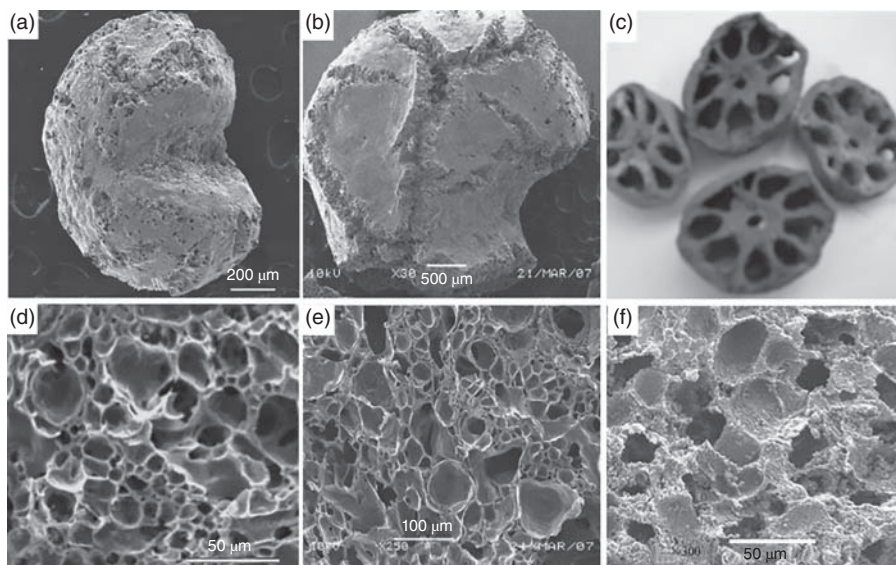


Figure 2.3 SEM images of biomorphic SiC materials and their inner structures: (a, d) millet-SiC, (b, e) broomcorn-SiC, and (c, f) lotus-root-SiC [19, 20].

template derived from millet, broomcorn, and lotus root, respectively. The small pores and large pores are combined organically in biomass SiC. The former can accommodate more active centers, while the latter are beneficial to the rapid diffusion of reactants and products. In addition, the biomass SiC produced from millet and broomcorn has a similar morphology and particle size as industrial catalysts, and does not require further shaping processes. The biomass SiC can potentially be applied in the special liquid waste treatment field due to its unique pore characteristics.

Different carbon templates are employed in the above methods to prepare porous SiC. Similarly, mesoporous material containing silicon can also be used as templates to react with carbon precursor to get SiC by carbothermal reduction reactions under high-temperature conditions. Parmentier et al. filled mesopores of MCM-48 silica material with pyrolytic carbon by chemical vapor infiltration using propylene as a carbon precursor [21]. Then, carbothermal reduction of the as-prepared SiO_2/C material in a temperature range $1250\text{--}1450^\circ\text{C}$ and an inert atmosphere led to almost complete conversion into high surface area SiC material ($120\text{ m}^2\text{ g}^{-1}$). Schüth and coworkers also obtained SiC with specific surface area of $159\text{ m}^2\text{ g}^{-1}$ by incipient wetness impregnation, which infiltrated furfuryl alcohol and oxalic acid into mesoporous silica SBA-15, and carbothermal reduction reaction [22]. Highly ordered mesoporous SiC ceramics with high specific surface areas (up to $720\text{ m}^2\text{ g}^{-1}$), large pore volumes (up to $0.8\text{ cm}^3\text{ g}^{-1}$), and narrow pore-size distributions (mean value of $\sim 3.5\text{ nm}$) also were successfully synthesized by Zhao and coworkers via a one-step nanocasting process using commercial polycarbosilanes as a precursor and mesoporous silica as hard templates [23]. Although the prepared SiC, using mesoporous silica as a template, has a regular pore structure and high specific surface area, the experimental conditions are usually relatively severe, and the cost of large-scale preparation is high.

2.1.2 Sol-gel Method

The sol-gel method is one of the well-established synthetic approaches to preparation of inorganic nanomaterials or porous materials under mild conditions. This method has potential control over the textural and surface properties of the materials. The sol-gel method mainly consists of a few steps to deliver the final material protocols, and those are hydrolysis, condensation, and a drying process. The formation of final materials involves different consecutive steps; initially the corresponding precursor undergoes rapid hydrolysis to produce the hydroxide solution, followed by immediate condensation that leads to the formation of three-dimensional gels. Afterwards, the obtained gel is subjected to a drying process, and the resulting product is readily converted to xerogel or aerogel based on the mode of drying. One of the key points of the sol-gel method is that it can mix many different substances at the molecular level. Guo's group is one of the most successful groups in the world in producing high specific surface area SiC using the sol-gel method [24, 25]. They evenly mixed silica and carbon precursors at the molecular level by the sol-gel process. With an appropriate catalyst, it is possible to obtain porous SiC with high specific surface area by performing a carbothermal reduction reaction at a relatively low temperature.

In Guo's work, tetraethoxysilane (TEOS) and phenolic resin are respectively used for silicon and carbon precursors. During the hydrolysis of the precursor, metal salt was added as a catalyst for the carbothermal reduction reaction, and then a gel containing carbon, silicon and metal salt could be obtained. Crude SiC containing impurities of unreacted silicon and carbon is produced in the carbothermal reduction of the xerogel at 1250°C in an argon flow (40 cm³ min⁻¹). It is purified by combustion in air and washing with a mixed solution of hydrochloric acid and hydrofluoric acid to remove excess silica, carbon, and other impurities [24, 25]. It has been found that SiC with different morphologies and structures can be obtained by adding different metal salts during the sol formation and the latter have a very important influence on the former. In general, a metal salt with a low melting point, such as aluminum, sodium, and lanthanum nitrates, will lead to formation of SiC whiskers or nanowires, while iron, cobalt, and nickel salts will lead to formation of porous SiC nanoparticles. For example, Jin and Guo proposed a method to control the specific surface area and pore size of mesoporous SiC by employing different amounts of nickel nitrate in the sol-gel process. When the Ni/Si ratio was 0.0154, the obtained SiC sample had a surface area of 112 m² g⁻¹ and an average pore diameter of about 10 nm [24]. Figure 2.4 shows the transmission electron microscope (TEM) images and pore distribution of the SiC. By adjusting the nickel content in the gel, the specific surface area of SiC can reach a maximum of 200 m² g⁻¹ or more. However, excessive amounts of nickel will make the originally formed SiC sintered, thereby significantly reducing its specific surface area [25].

Obviously, the utilization of nickel nitrate has a great influence on the structure and morphology of SiC. Charged nickel ions in the sol-gel process not only accelerate the hydrolysis and polycondensation of TEOS, but also promote self-organization of primary colloidal particles. The self-organization usually generates large secondary grains consisting of phenolic resin and embedded silica particles. The granularity analysis shows that the primary colloidal particles have sizes smaller than 10 nm, while the secondary grains have sizes larger than 1000 nm [25]. The reason for this change may be that nickel ions change the charge balance in the sol system. This change

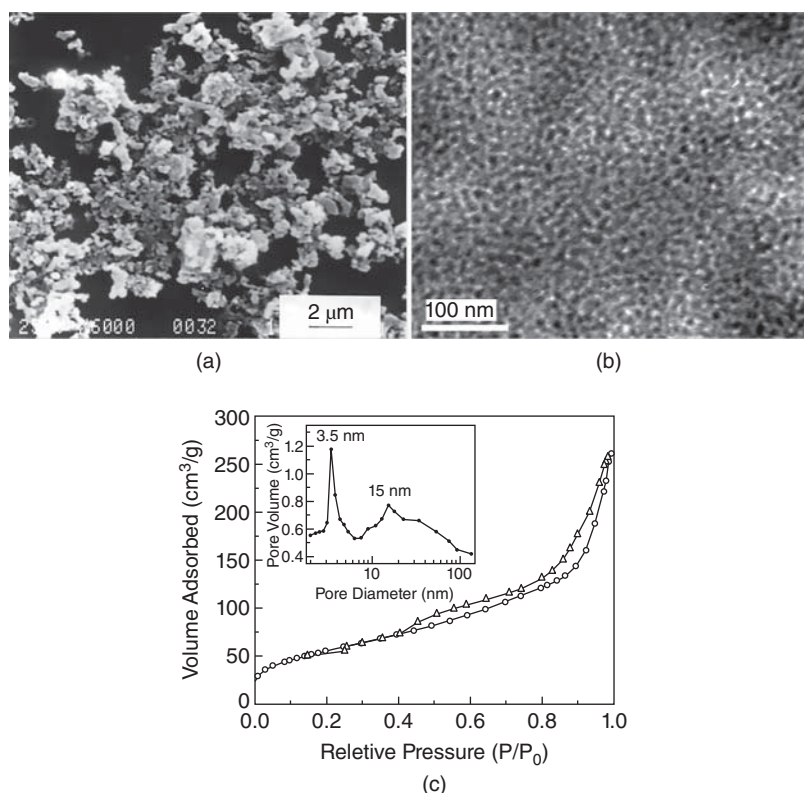


Figure 2.4 TEM image of porous SiC from sol-gel (a and b) and its pore distribution (c) [24].
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combines with the coulomb force to cause the colloidal particles to agglomerate and form larger secondary particles. The secondary grains can produce a great deal of SiO₂/C interfaces after carbonization. The SiC produced at the interfaces through carbothermal reduction forms a mesoporous framework. On the other hand, nickel may still act as a catalyst in the SiC formation [14, 26]. Melted nickel particles react with silica and produce various nickel silicide active phases including Ni₂Si:



Subsequently the melted alloy drops roll on interfaces and react with carbon:



The nickel generated from reaction (2.3) again participates in reaction (2.2). However, superfluous nickel can cause sintering of the mesoporous SiC, which usually results in collapse of the porous framework. Simultaneously, enlarged alloy drops can dissolve more SiC. The dissolved SiC can be recrystallized out and form spherical particles when the system temperature decreases [27, 28], which leading to a very low surface area. Figure 2.5 shows a cartoon of the formation of porous silicon carbide using the sol-gel method.

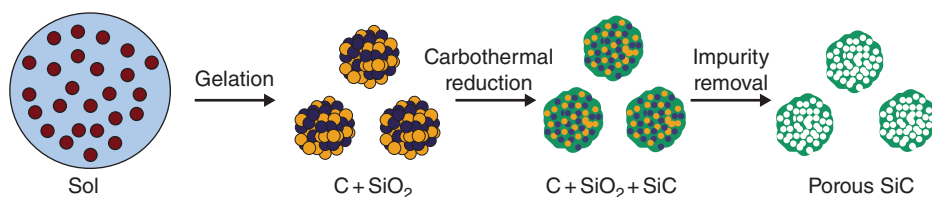


Figure 2.5 Cartoon of the formation of porous silicon carbide using the sol-gel method [10].

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In addition to phenolic resins, other carbon-rich organics can also be used as precursors for the preparation of gels. Wei and coworkers employed saccharose and TEOS as precursors to form gel [29, 30]. A thorn-ball-like SiC, with a surface area of $141 \text{ m}^2 \text{ g}^{-1}$ and a pore diameter in the range of 2–30 nm, can be obtained by the carbothermal reduction reaction of carbonaceous silicon xerogel at 1350°C . They also studied in detail the effect of different preparation conditions on the specific surface area and pore distribution of SiC. Other substances, such as biphenyl and furfural, can also be used as carbon precursors [31]. Adding a suitable amount of surfactant (such as cetyltrimethylammonium bromide, CTAB) or hydrogen-containing silicone oil during the sol formation process can also obtain high specific surface area SiC [32, 33].

2.1.3 Polycarbosilane Pyrolysis Method

Polycarbosilane (PCS) is a type of polymer compound formed by the polymerization of carbosilane, while carbosilane is an organosilicon compound containing carbon–silicon bonds in the molecule. The main chain of polycarbosilane consists of silicon and carbon atoms in turn. Usually, hydrogen or organic functional groups are attached to silicon and carbon atoms, and the molecular chains are linear or branched. Although polycarbosilane was synthesized very early, it did not catch people's attention until it was found that it could be used to prepare SiC fibers.

SiC with high specific surface area can be obtained by pyrolysis of polycarbosilane in an inert atmosphere. Makkee and coworkers prepared SiC with a surface area of $172 \text{ m}^2 \text{ g}^{-1}$ by pyrolysis of organosilicon polymer and found that this SiC had an excellent hydrothermal stability [26]. Gedanken and coworkers reported a very simple, efficient, and economical synthetic technique to produce SiC of a high surface area [34]. The cracking/dissociation of a triethylsilane precursor is carried out separately in a closed vessel cell (Swagelok) that was heated at 800°C for three hours, yielding silicon carbide–carbon nanocomposite, and at 1000°C for three hours, yielding SiC with a surface area of $149 \text{ m}^2 \text{ g}^{-1}$. Nghiem and Kim reported the synthesis of a novel polycarbosilane-*block*-polystyrene diblock copolymer by ring-opening living anionic polymerization in a tetrahydrofuran (THF) and *n*-hexane solvent system at -48°C [35]. The resulting block copolymer revealed phase-separation behavior in the nanoscale to form a self-assembled nanostructure that was converted to a mesoporous ceramic phase after heating at 800°C . The pyrolyzed ceramic product exhibited well-ordered mesoporous SiC-based ceramic structures with a high BET surface area of $1325 \text{ m}^2 \text{ g}^{-1}$ based on a N_2 adsorption–desorption isotherm measurement, and an average mesopore size of 7.8 nm containing a large amount of micropores.

2.2 Photocatalytic Water-Splitting

Hydrogen is regarded as the desired clean energy source for the twenty-first century, due to its high energy capacity and environmental friendliness, being one of the main development directions of energy strategy. Most traditional hydrogen production technologies need great energy consumption with low efficiency. Solar energy is widely accepted as a free, abundant and endlessly renewable source of clean energy, which could meet current and future human energy demand. Thus, the harvest and conversion of solar energy into a usable energy form is highly desirable. Recently, photocatalytic water-splitting into hydrogen and oxygen using semiconductor photocatalysts has become a promising strategy for converting solar energy into clean and carbon-neutral H_2 fuel via a low-cost and environmentally benign route [36–41].

A fundamental principle of semiconductor-based photocatalytic water-splitting for hydrogen generation is depicted in Figure 2.6 [42]. In general, the overall photocatalytic water splitting reaction involves three major steps: (i) absorption of light by a semiconductor to generate electron-hole pairs; (ii) charge separation and migration to the surface of the semiconductor; and (iii) surface reactions for H_2 or O_2 evolution [38]. The overall efficiency of photocatalytic water-splitting is determined by the balance of thermodynamics and kinetics of the above three steps together.

The bandgap of a semiconductor determines the wavelength range of the light absorbed by it. A semiconductor can absorb photons with energy larger than or equal to its bandgap energy. A photocatalyst absorbs UV and/or visible light irradiation from sunlight or an illuminated light source. The electrons in the valence band of the photocatalyst are excited to the conduction band, while the holes are left in the valence band [41]. Therefore, the separated negative electrons (e^-) and positive holes (h^+) migrate to the solid surface, and these charges can reduce or oxidize species absorbed

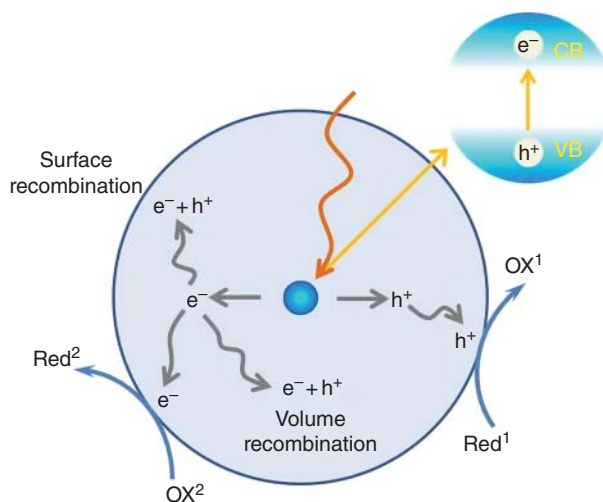
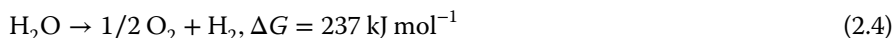


Figure 2.6 Schematic illustration of photocatalytic water-splitting over a semiconductor photocatalyst [42]. Source: Reprinted with permission from JIM publishers, Copyright 2015.

on the surface, respectively [41]. The semiconductors with either too wide or too narrow bandgaps are unsuitable for practical use.

Water-splitting into H_2 and O_2 is an uphill reaction, which needs the standard Gibbs free energy change ΔG_0 of 237 kJ mol^{-1} , as shown in Eq. (2.4) [41].



Water molecules are usually reduced by the electrons to form H_2 and are oxidized by the holes to form O_2 for overall water-splitting. Therefore, the match of the bandgap and the potentials of the conduction and valence bands are important. The bottom level of the conduction band has to be more negative than the reduction potential of H^+/H_2 (0 V vs normal hydrogen electrode [NHE]). The higher conduction band position has more negative potential, which has greater reduction ability. The top level of the valence band has to be more positive than the oxidation potential of O_2/H_2O (1.23 V). Similarly, the lower valence band position has more positive potential, which gives stronger oxidation ability. Therefore, the bandgap of a semiconductor photocatalyst should be $>1.23 \text{ eV}$ ($<1000 \text{ nm}$) to achieve water-splitting. Practically, the effects of overpotentials and band bending of semiconductors should be considered, so the minimum bandgap of semiconductors required for photocatalytic water-splitting is 1.8 eV . Moreover, to use visible light, it should be $<3.0 \text{ eV}$ ($>400 \text{ nm}$). Other factors, such as charge separation, mobility, and lifetime of photogenerated electrons and holes, also affect the photocatalytic generation of hydrogen from water-splitting. Band levels of various semiconductor materials are shown in Figure 2.7 [36, 43].

The bandgaps of SiC with different crystal structures are different; β -SiC (also known as 3C-SiC) has a bandgap of 2.4 eV , and α -type has a value of about 3.0 eV , so SiC is regarded as a high potential photocatalytic material for utilizing visible light [44]. In 1990, Inoue and coworkers reported that SiC powder prepared by the arc plasma method exhibited excellent activity for photocatalytic water-splitting reaction under light irradiation with a wavelength of $260\text{--}410 \text{ nm}$ [45]. However, they also found that the SiC surface is deactivated due to oxidation after a long period of irradiation.

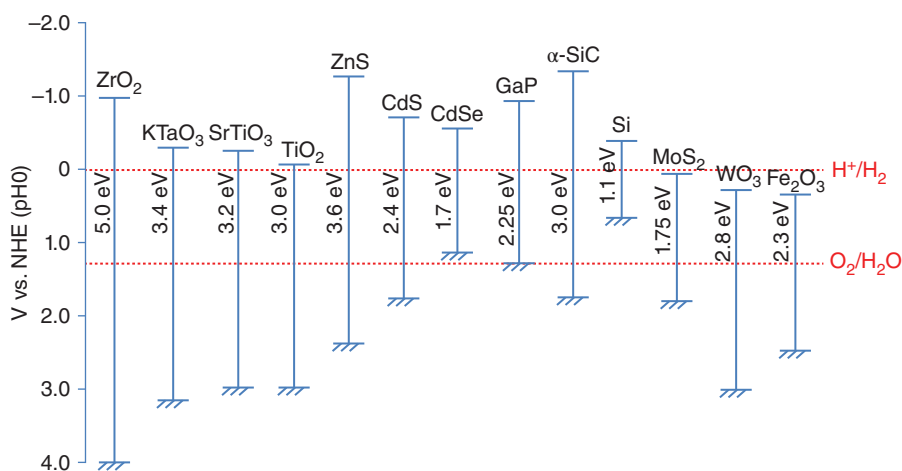


Figure 2.7 Relationship between band structure of semiconductors and redox potentials of water-splitting [36, 43].

Yuan and coworkers investigated the mechanism of water-splitting to H_2 by SiC nanoparticles through a grain surface evolution study [46]. It elucidated that two different processes are actually involved in producing H_2 , one being the photocatalytic reaction driven by SiC, and the other one being a new pathway, that is, the direct chemical reaction between SiC and water [46]. They also detected H_2 even in the dark by the latter process. Thin layers, consisting of silicon oxide or silicon oxycarbide, can form on the grain surface during the reaction process between water and SiC, which hinders the water-splitting by photocatalysis [46].

Hao et al. prepared different whiskery, wormlike and particulate SiC materials by the sol-gel and carbothermal reduction methods using different carbon and silica precursors (Figure 2.8) [47]. The specific surface areas are 45, 51 and $81 \text{ m}^2 \text{ g}^{-1}$, respectively. The photocatalytic hydrogen evolution was evaluated from pure water without any sacrificial agent. The results show that SiC with different morphologies presents different photocatalytic hydrogen evolution performance. From Figure 2.8d, the average hydrogen evolution rates for the particulate and worm-like SiC are 83.9 and $82.8 \text{ l g}^{-1} \text{ h}^{-1}$, respectively, which are much higher than for the SiC whiskers ($45.7 \text{ l g}^{-1} \text{ h}^{-1}$). The results can be ascribed to the specific surface area, crystallinity, and morphology of the samples. It is known that the specific surface area and crystallinity of photocatalysts are two key factors influencing the photocatalytic activity. The photocatalyst with a high specific surface area can offer more active sites [47]. Similarly, the photocatalyst with high crystallinity has lower concentrations of defects, which usually act as recombination centers

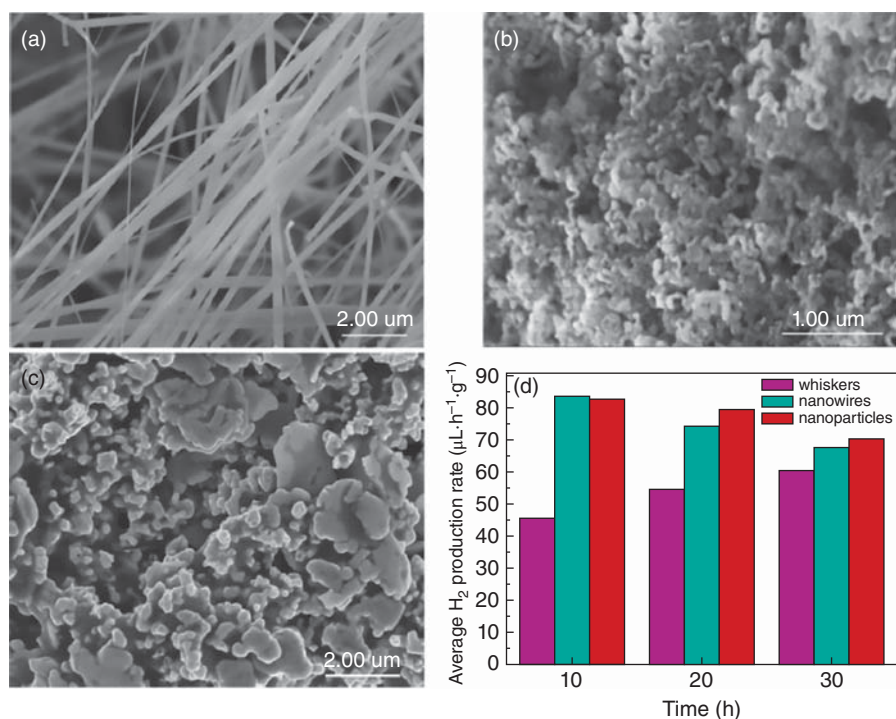


Figure 2.8 SEM images of the (a) whiskery, (b) worm-like and (c) particulate SiC materials and (d) their average H_2 production rates [47]. Source: Reprinted with permission from Elsevier, Copyright 2013.

for photo-excited carriers [47]. Moreover, the crooked and wormlike morphologies make the surface roughness of SiC nanowires higher, with more steps and sharp edges in the surface [47]. There are more dangling bonds in these locations, and these dangling bonds result in higher photocatalytic activity.

Non-equivalent facets of a catalyst are known to possess different charge distribution properties. Therefore, utilizing different crystal facets of a semiconductor is probably an efficient means to enhance surface separation of electrons and holes for increasing solar energy conversion efficiency. Chen and coworkers reported that hexagonal 6H-SiC exhibited different charge distribution and photocatalytic properties on naturally occurring Si-{0001} and {10_10} facets [48]. Selectivity of metals for in situ photodeposition occurs in these two facets, demonstrating that the photo-excited electrons are assembled only on polar Si-{0001} facets, while the holes are assembled on non-polar {10_10} facets [48]. Consequently, reduction reactions occur only on the Si-{0001} facets with noble metals, and oxidation occurs only in {10_10} with metal oxide. The activity of photocatalytic water-splitting is significantly enhanced by this kind of selective deposition resulting from charge spatial separation.

Hai et al. also modified the surface of SiC nanowires by acid oxidation using concentrated sulfuric acid and potassium permanganate [49]. The bandgap of the modified SiC nanowires decreased to 2.27 eV, which is lower than that of the unmodified SiC nanowires (2.35 eV). Accordingly, the rate of hydrogen production over the SiC nanowires before and after modification in the first run is calculated to be 46 and 81 ml g⁻¹ h⁻¹, respectively. The average H₂ evolution rate over the modified SiC in the first run is 76.1% higher than that of the unmodified SiC, which mainly results from the increase in oxygen-contained groups at the surface of SiC and lower bandgap of the modified SiC. On the one hand, these oxygen-contained groups can trap more photogenerated holes, reducing the photogenerated electron-hole recombination [49]. On the other hand, the surface modification makes SiC nanowires more hydrophilic, which can strengthen the integration between water molecules and the SiC surface [49]. This also helps to enhance the photocatalytic activity. The stable hydrogen evolution rate of the β -SiC nanowires under visible light irradiation makes it a potential candidate for a practical photocatalyst for overall water-splitting. Boron-doped β -SiC (B_xSiC) photocatalysts were prepared by in-situ carbothermal reduction of xerogel containing boric acid in the same group [50]. B atoms doped into the SiC lattice and substituted Si sites, leading to the formation of a shallow acceptor level above the valence band of SiC, which resulted in a narrowed bandgap energy (Figure 2.9a–c) [50]. Moreover, the shallow acceptor level acts as a hole-trap, preventing the recombination of photoexcited electrons and holes. Therefore, the photocatalytic H₂ evolution activity of B-doped SiC was greatly improved compared with that of SiC. From Figure 2.9d, the maximum hydrogen evolution rate is obtained when the molar ratio of B/Si is 0.05 (166 μ l g⁻¹ h⁻¹), which is more than twice that of pure SiC (75 μ l g⁻¹ h⁻¹).

Normally, the photo-generated electrons and holes are very easy to recombine in bulk or on the surface of a semiconductor (Figure 2.6), resulting in lower photocatalytic activity. Therefore, the efficient separation of a photogenerated carrier is the key problem for the photocatalytic hydrogen evolution efficiency. A semiconductor merger with another which has matching conduction band and valence band positions can not only solve the electron-hole recombination problem, but can also utilize their synergistic effect for

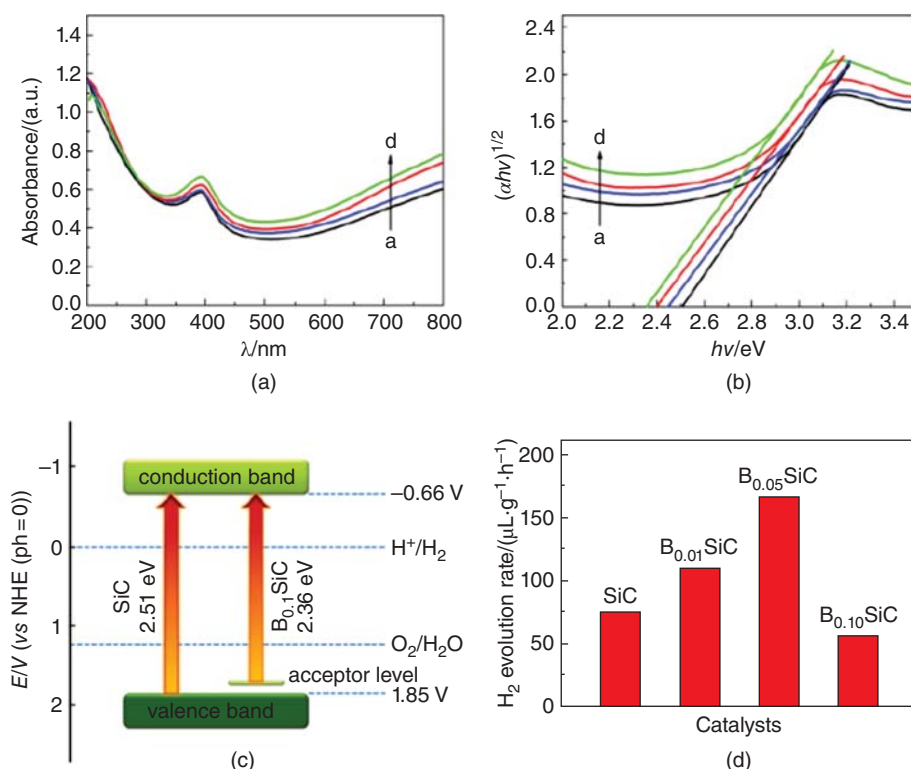


Figure 2.9 (a) UV-vis absorption spectra and (b) Tauc plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $B_x\text{SiC}$ (a, $x = 0$; b, $x = 0.01$; c, $x = 0.05$; d, $x = 0.10$). (c) Schematic illustration for bandgap narrowing mechanism of B-doped SiC. (d) Rates of hydrogen evolution over $B_x\text{SiC}$ [50]. Source: Reprinted with permission from Elsevier, Copyright 2014.

photogenerated carrier transport and separation between semiconductors with different energy levels, to promote photocatalytic activity (Figure 2.10) [51–55]. Moreover, this merger can extend the absorption spectrum of the photocatalyst and then increase sunlight utilization.

Li et al. found that a SiC (1 wt%)-TiO₂ composite material shows an activity as high as twice that of TiO₂ in the photo-stimulated water-splitting reaction [56]. Fang and coworkers synthesized novel SnO₂/SiC hollow sphere nanochains (HSNCs) by topological morphology conversion of SnO₂@C core-shell nanochains through a vapor–solid reaction (Figure 2.11a and b) [57]. Evaluation of the SnO₂/SiC HSNCs for the generation of hydrogen revealed that the total amount (4125 mmol g⁻¹) or the average rate (825 mmol g⁻¹ h⁻¹) of hydrogen production for the SnO₂/SiC HSNCs are much higher than those for the pure SiC HSNCs and bulk SiC crystals (Figure 2.11c and d). Moreover, no notable degradation of H₂ evolution is observed in the repeated runs for a photocatalytic reaction of 20 hours (Figure 2.11e). Yuan and coworkers found that the rate of visible-light-driven photocatalytic hydrogen production from water-splitting is greatly enhanced from 0 to 555 mmol h⁻¹ g⁻¹ by hybridizing a suitable amount of CdS particles onto the micro-SiC surface [58]. It suggests that the hybridization is responsible for lowering the surface activation energy of SiC, and well-connected SiC/CdS interfaces

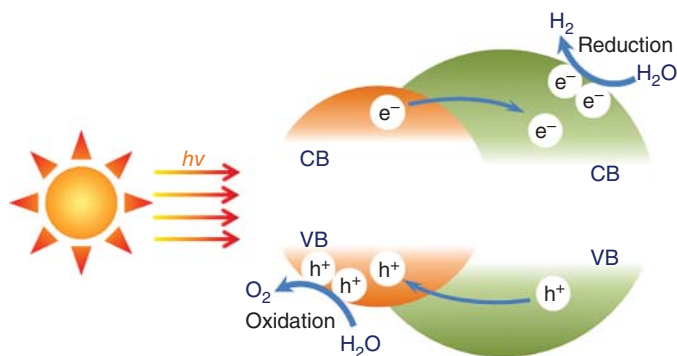


Figure 2.10 Photo-generated carrier separation in a semiconductor combination system under visible-light irradiation.

serve as active sites for photocatalytic reactions, leading to this significant enhancement. Moreover, the self-corrosion of CdS is simultaneously avoided and the composites show high stability.

Platinum, as a co-catalyst for water-splitting, could act as an acceptor of photoelectrons to separate photogenerated charge carriers efficiently, and consequently enhance corresponding photocatalytic activity [59, 60]. Chen and coworkers investigated the photocatalytic water-splitting reaction of platinum nanoparticle-decorated SiC nanowire photocatalyst under simulated sunlight irradiation [61]. The Pt/SiC catalyst shows an enhanced photocatalytic activity for water-splitting, with a high average H_2 evolution rate of $4572 \text{ ml g}^{-1} \text{ h}^{-1}$, which is 88% higher than that of SiC nanowires without Pt nanoparticle decoration. The XPS spectra show that the surrounding electrons of C atoms can be rapidly transferred to Si and Pt active sites for water-splitting. The photoluminescence spectra show that the Pt acts as an acceptor of photoelectrons to effectively restrain the electron–hole pair recombination of SiC nanowires.

It is reported that graphene could act as electronic conductive channels to separate photogenerated carriers, and consequently enhance corresponding photocatalytic activity [62–66]. Guo and coworkers prepared chemically bonded SiC-graphene composites by a chemical grafting method [67]. The Si–C bonds between SiC and graphene can form a heterojunction interface. The chemical bonding and the heterojunction interface are beneficial to the rapid transfer of photogenerated electrons from SiC to graphene, thus avoiding the recombination with holes. As a result, the composites show an enhanced activity (more than 90%) for photocatalytic splitting of water under visible light irradiation. Yuan and coworkers realized the H_2 production and graphene oxide (GO) reduction simultaneously over GO/SiC composite under visible light irradiation, with KI as the sacrifice reagent [68]. The weight content of GO was regulated in the reaction system. The rate of H_2 production reached $95 \mu\text{l h}^{-1}$ with 1% GO content in a GO/SiC composite system, which was 1.3 times larger compared with the pure SiC nanoparticles under visible light. The reduced-GO sheet can serve as an electron collector and transporter to separate the photo-generated electron–hole pairs, effectively lengthening the lifetime of the charge carriers.

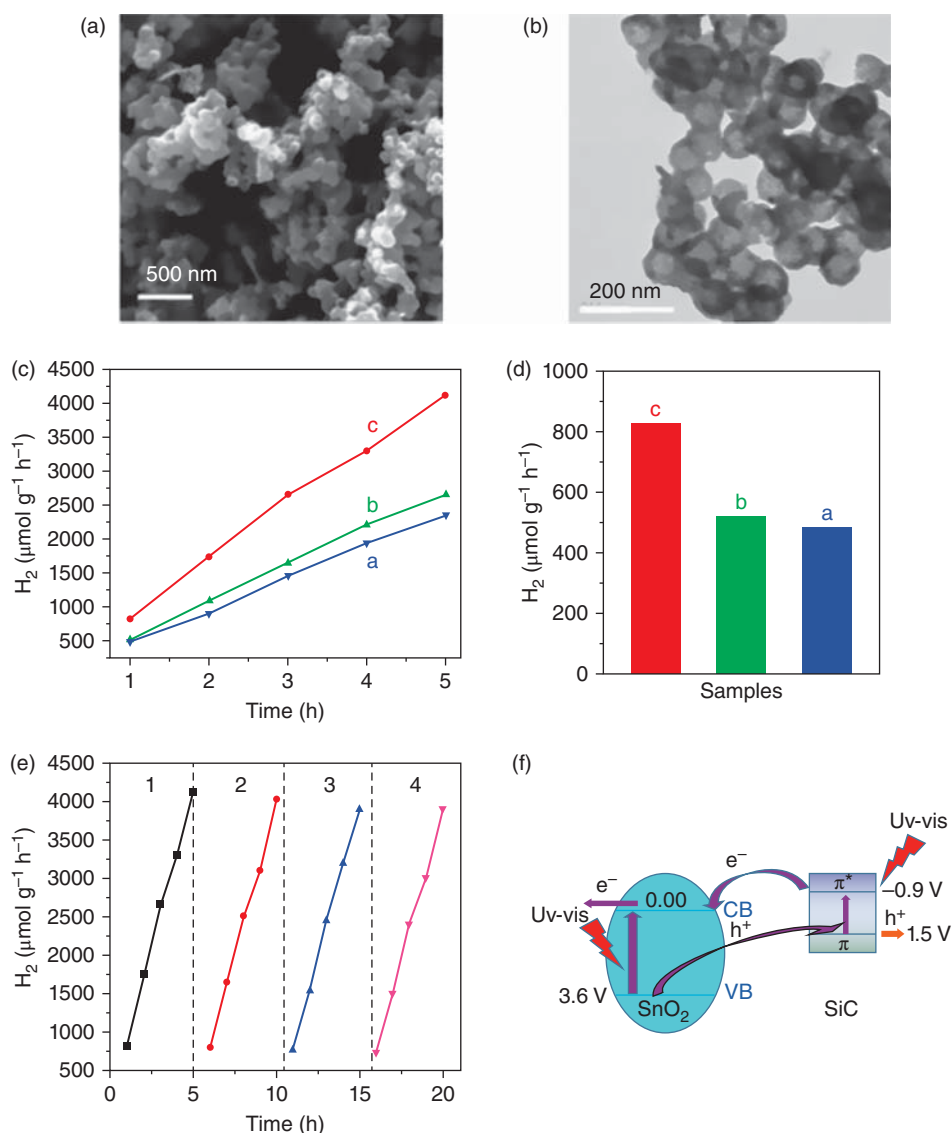


Figure 2.11 (a) SEM and (b) TEM images of the SnO_2/SiC CSNCs. (c) The total amount of H_2 produced over the three samples: [a] pure SiC HSNCs, [b] bulk SiC crystals, [c] SnO_2/SiC HSNCs. (d) Average hydrogen production rates over the three samples. (e) H_2 evolution of the SnO_2/SiC HSNCs through four noncontinuous experiments. (f) Schematic illustration of the charge separation in the SnO_2/SiC HSNC system [57]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

The photoelectrocatalytic water-splitting by semiconductors is one of the ideal ways to use solar energy to produce hydrogen. There are two main points in choosing a semiconductor material for photoelectrocatalytic hydrogen evolution reaction (HER): one is the bandgap, which determines its response to visible light in the solar spectrum; the other is the position of the energy level, which determines whether hydrogen evolution can be achieved by applying only a small bias voltage.

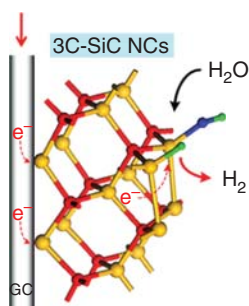


Figure 2.12 Schematic illustration of the mechanism governing the electrocatalytic HER on an ultrathin 3C-SiC/GC electrode. The 3C-SiC nanocrystal is indicated by the optimized structures of a Si-terminated (001) surface where H_2O molecules dissociate, forming a complex consisting of -H and -OH fragments. The big and small balls represent Si and C atoms, whereas the bonds protruding to the right link with O and H atoms [69]. Source: Reprinted with permission from ACS publishers, Copyright 2012.

Wu and coworkers employed a wet chemical etching method to prepare ultrathin 3C-SiC nanocrystals with an average size of 3 nm [69]. Contrary to general belief, they claimed that water molecules do not adsorb onto the surfaces of 3C-SiC nanocrystals, but rather spontaneously dissociate via a surface autocatalytic process forming a complex consisting of -H and -OH fragments bonded to two adjacent Si atoms (Figure 2.12) [69, 70]. This surface autocatalytic effect on the ultrathin 3C-SiC nanocrystals reduces significantly the activation barrier for dissociation. Obviously, the smaller the nanocrystal size, the larger the specific surface area, and consequently the higher the autocatalytic activity. Therefore, the 3C-SiC nanocrystals possessed superior electrocatalytic activity in the HER. Furthermore, the 3C-SiC nanocrystals show enhanced HER activity in photoelectrochemical cells and are very promising for water-splitting based on the synergistic electrocatalytic and photoelectrochemical actions. Pantelides and coworkers reported quantum mechanical calculations of electrochemical hydrogen evolution at ultrathin 3C-SiC nanocrystal electrodes in acid solutions, and showed that the reaction happens at pre-existing hydrogenated surface Si-H sites through a mechanism that is related to the Volmer-Heyrovsky mechanism, which occurs in metals [71]. The Heyrovsky reaction occurs as the first step, where an electron from the substrate reacts with a hydronium adsorbed at a Si-H site, creating a H_2 molecule and a Si dangling bond. The Volmer reaction follows and regenerates the Si-H. This ordering of reactions is supported by the fact that the hydrogen coverage on SiC electrodes does not depend on the applied voltage, in contrast to the cases of metal electrodes. Moreover, the Volmer reaction, which is a one-step process on a metal surface, is a two-step process here. The rise of the conduction band of ultrasmall SiC nanocrystals due to quantum confinement can enhance the reducibility of SiC and then improve the hydrogen evolution activity.

Zhang and coworkers prepared a robust p-type 3C-SiC thin film on a large silicon substrate using a low-temperature alternating supply epitaxy method [72]. The film was heavily doped with Al in order to achieve high conductivity and to allow photoelectrocatalytic splitting of water for hydrogen production under visible light. The as-grown thin film was further treated with a mild dry etching process in order to improve the surface area and induce a light trap structure. In comparison with the as-grown sample, the etched thin film possesses substantially improved photoelectrocatalytic performance

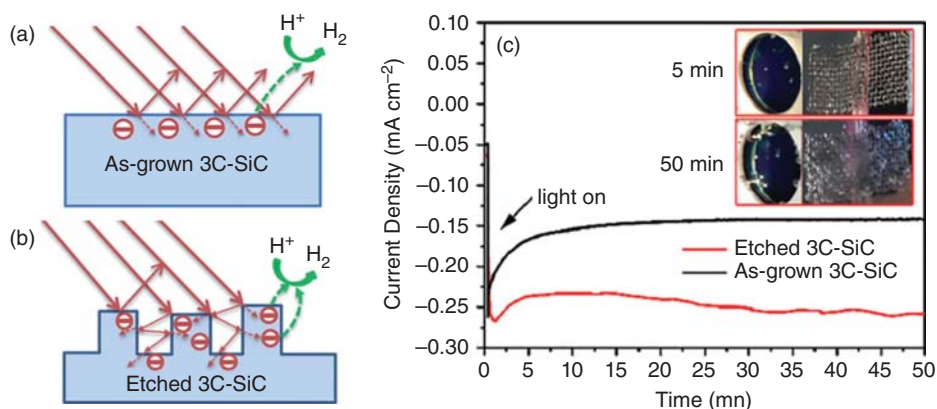


Figure 2.13 Schematic illustration of light absorption and photoelectrocatalytic production of H₂ on the as-grown (a) and etched 3C-SiC films (b), and the current-time plot of the samples at -0.8 V (c). The inset shows that H₂ appears at the SiC cathode and O₂ at the Pt anode during the photoelectrocatalytic reaction [72]. Source: Reprinted with permission from Elsevier, Copyright 2014.

due to increased light absorption, larger surface area and reduced recombination rate of photoelectrons and holes (Figure 2.13) [72].

Pessoa et al. summarized the photoelectrocatalytic properties of TiO₂ and SiC composite nanofilms from the aspects of synthesis, characterization, and applications, believing that the heterojunctions formed between TiO₂ and SiC not only have an important application in the field of photocatalytic water-splitting, but also potentially play important roles in dye-sensitized solar cells [73]. Ma et al. investigated the electrochemical properties of single-crystalline p-type 3C-SiC films on p-Si and n-Si substrate electrodes in H₂SO₄ aqueous solutions, both in the dark and under light illumination [74]. The photoelectrochemical measurements with different wavelengths of light sources indicate that the p-SiC film on p-Si substrate can generate a cathodic photocurrent as a photocathode, which corresponds to hydrogen production, and generate an anodic photocurrent as a photoanode, which corresponds to oxygen evolution. For p-SiC film on n-Si substrate, it can only generate an apparent photocurrent as a photoanode for oxygen evolution. Shi and coworkers developed a simple and effective method to fabricate highly oriented porous SiC nanowire arrays on silicon substrates by carbonization of the Si nanowire arrays [75]. The SiC nanowires have a similar diameter and length as the original Si nanowires. The porous structure provides the SiC nanowire arrays with a large specific surface area. Benefiting from this factor, the as-synthesized SiC nanowire arrays show good performance in photoelectrochemical water-splitting. The photocurrent is about 1.2 mA cm^{-2} at a bias potential of -0.2 V (vs. saturated calomel electrode, SCE), and increases to 22 mA cm^{-2} at a bias potential of 1.0 V (vs. SCE). The photocurrent of the as-synthesized SiC nanowires is about 1000 times higher than the dark current ($10^{-3} \text{ mA cm}^{-2}$).

Wu and coworkers designed a composite photoelectrochemical anode consisting of ultrathin 3C-SiC nanocrystals and ZnO nanowires deposited on both sides of a brass substrate (Figure 2.14) [76]. The ZnO nanowires serve as the hole providers. The photogenerated holes are derived under applied external bias to the 3C-SiC nanocrystals. Combined with the surface autocatalytic effect of SiC, the oxygen evolution activity was

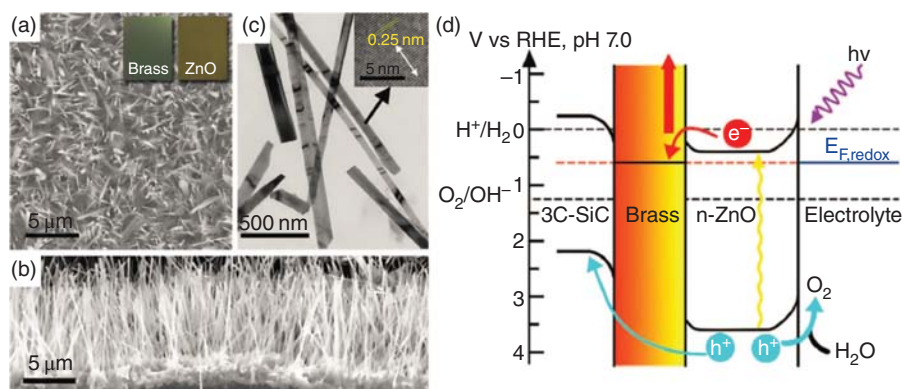


Figure 2.14 (a) SEM image of ZnO nanowire arrays on a brass substrate. The insets show the digital pictures of the brass substrates before and after growing the ZnO nanowires. (b) Cross-sectional SEM image of the nanowire sample. (c) TEM image of ZnO nanowires. The inset shows the high-resolution TEM image of a local position in a ZnO nanowire. The observed lattice fringes correspond to the (001) plane of ZnO. (d) Schematic representation of the band energies and charge transfer of SiC-polyamidoamine-ZnO photoanode. $E_{F,redox}$ stands for the potential of Fermi level (the central dashed line). The outer horizontal lines represent the water reduction potential (H^+/H_2) and oxidation potential (O_2/OH^-), respectively [76]. Source: Reprinted with permission from the Electrochemical Society, Copyright 2013.

greatly enhanced on the 3C-SiC nanocrystals. Guo et al. employed SiC nanosheets as substrates to prepare a MoS_2 -SiC composite [77]. During the solvothermal reaction of $(NH_4)_2MoS_4$ and hydrazine in an N,N-dimethylformamide suspension containing the SiC nanosheets, MoS_2 nucleated and grew along with the sheet-like SiC substrate to form a MoS_2 -SiC hybrid structure. The hybrid is composed of uniform flower-like spheres with a diameter of c. 150 nm (Figure 2.15a), which are assembled by folded flakes with a thickness of several nanometers (Figure 2.15b). While in the absence of SiC nanosheets, free MoS_2 presents as spherical particles with a diameter of c. 580 nm and their surfaces are almost smooth (Figure 2.15d). The significant difference in their morphologies indicates that the SiC nanosheets play an important role in mediating the growth of MoS_2 . During the formation of the MoS_2 -SiC hybrid, the SiC nanosheets possibly provide a facile substrate for the nucleation and subsequent growth of MoS_2 . The MoS_2 nanosheets tend to grow selectively along the edges of SiC and then form a heterojunction with the SiC substrate (Figure 2.15c). The MoS_2 -SiC hybrid catalyst shows a small overpotential of about 0.04 V. The current density of MoS_2 -SiC is 27.5 mA cm^{-2} at $\eta = 0.5 \text{ V}$ (Figure 2.15e), which is very close to that of the commercial Pt/C catalyst, suggesting that the MoS_2 -SiC possesses superior photoelectrocatalytic activity for HER. In contrast, free MoS_2 and SiC only show very low HER activity. The MoS_2 -SiC also exhibited high catalytic activity under light irradiation, whereas its overpotential and current density are only 0.38 V and 6 mA cm^{-2} ($\eta = 0.5 \text{ V}$) in the dark, respectively (Figure 2.15f). These results suggest that the total current is mainly due to the contribution of photo-generated current. Meanwhile, a mass of bubbles can be clearly observed on the working electrode after 100 scans (Figure 2.15f, inset), indicating that the MoS_2 -SiC hybrid has excellent HER activity. The SiC nanosheets in the solvothermal reaction act as nucleation substrates for the formation of ultrathin MoS_2 sheets, and thus the active edges

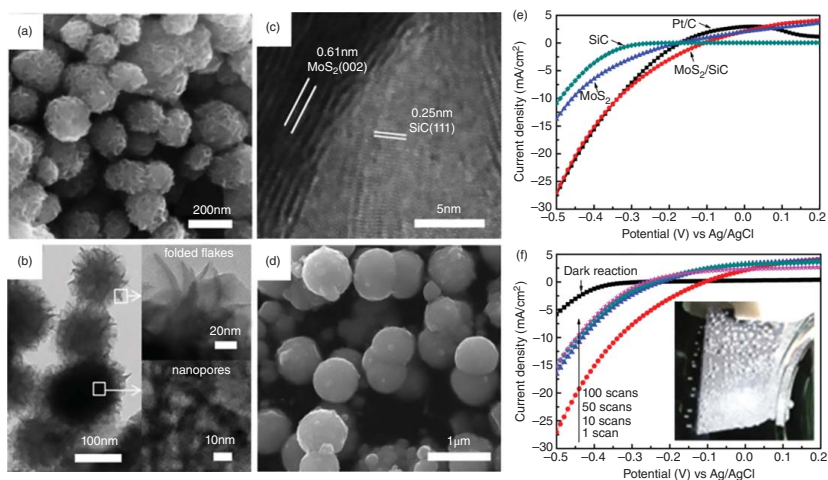


Figure 2.15 (a) SEM, (b) TEM and (c) HRTEM images of the MoS₂-SiC hybrid. (d) SEM images of pure MoS₂. (e) Photoelectrocatalytic HER activities of the MoS₂-SiC hybrid, Pt/C, free MoS₂ and SiC. (f) Contrast tests of dark and light reactions for the MoS₂-SiC hybrid; the inset in (f) is the photograph of the electrode after 100 scans [77]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

for HER massively increase in this process. Additionally, the selective growth of MoS_2 nanosheets along the edges of SiC also favors the formation of a heterojunction between MoS_2 and SiC. The electrons can be rapidly transferred from C to Si and S active edges through the heterojunction under an external electric field. As a result, the MoS_2 -SiC hybrid structure can quickly and effectively reduce dissociated -H and release H_2 on the large number of active sites.

Compared with the most commonly used photocatalyst TiO_2 , research on hydrogen evolution over SiC-based photocatalysts is in its initial stages, so there is much research worth doing in this field, such as preparation technology for SiC nanocatalyst, non-metallic element doping of SiC, transition-metal oxide/SiC composites, and so on. Although there is still a long way to go for realizing solar photocatalytic water-splitting to produce hydrogen, the superiorities of SiC, being inexpensive, non-toxic, non-polluting, and capable of responding to visible light, make its application in photocatalytic hydrogen evolution a very attractive prospect.

2.3 Photocatalytic Degradation of Pollutants

In recent years, a great deal of effort has been devoted to solving the widespread pollution of effluents from urban sources, and methods of treatment for agricultural industries with biorecalcitrant and organic pollutants. Various catalytic techniques have been applied in environmental protection. Photocatalysis has attracted increasing attention because of its widespread environmental applications such as air cleanup, water disinfection, hazardous waste remediation, and water purification. Photocatalytic degradation is a process whereby highly active free radicals produced by light absorption of photocatalyst react with organic pollutants via addition, substitution, and electron transfer, to degrade these pollutants into inorganic substances. This process does not produce secondary pollution and has unparalleled advantages over other treatment methods.

Chen and coworkers found that 3C-SiC nanowires with a hierarchical structure (Figure 2.16a) exhibited an enhanced photocatalytic activity by accelerating the photocatalytic degradation of methylene blue solution under visible light irradiation [78]. Methylene blue was degraded efficiently after five hours irradiation over the photocatalyst. The decolorization rate was up to 96% when the SiC concentration was 6 mg l^{-1} in the reaction system. The hierarchical structure of SiC nanowires can effectively enhance

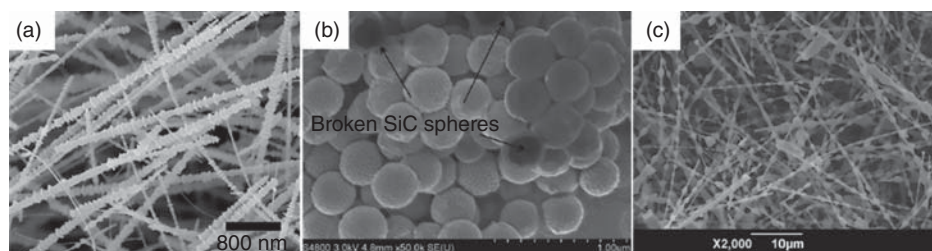


Figure 2.16 Low-magnification SEM images of the 3C-SiC nanowires with hierarchical structure (a), SiC hollow spheres (b), and SiC/SiO₂ nanochains (c) [78–80].

the specific surface area and light absorption efficiency, give it more active sites and better photogenerated carrier separation rate, and thereby improve the reactivity. Ouyang et al. prepared SiC hollow spheres (Figure 2.16b), with a diameter of 200–300 nm and a thickness of 50 nm, by a vapor–solid reaction using carbon spheres as templates [79]. The SiC hollow spheres have a high surface area of $83.5 \text{ m}^2 \text{ g}^{-1}$ and exhibit a mesoporous structure. The photo-response of the SiC hollow spheres expands to the visible-light region with a bandgap energy of 2.15 eV. The SiC hollow spheres showed photocatalytic activity for decomposition of the methylene blue in aqueous solution, with an approximately 98% photodegradation rate after 300 minutes of visible-light irradiation, due to their high surface area as well as excellent light-harvesting efficiencies.

Both above groups found that a SiO_2 layer can be observed on the surface of nanowires after the reaction, suggesting that the SiC surface is oxidized by the holes under illumination due to its thermodynamic instability in aqueous solution. Moreover, the SiO_2 layer can stop further oxidation of SiC nanowires when it reaches a certain thickness, and the photocatalyst will be kinetically stable. Ouyang and coworkers employed a simple chemical vapor reaction method to obtain a SiC/ SiO_2 nanochain (Figure 2.16c) that has equirotal beads of 650 nm and a uniform string with a diameter of 240 nm [80]. The photo-response behavior of the SiC/ SiO_2 nanochain can be expanded to the visible-light region with a high absorbance. The photocatalytic activity for decomposition of Rhodamine B over SiC/ SiO_2 nanochains was found to be better compared with that over the SiO_2 -free SiC nanowires. Zhang and coworkers also found that single-crystal β -SiC nanowires coated with amorphous SiO_2 exhibited excellent photocatalytic activity for degradation of acetaldehyde by irradiation with UV light [81]. Due to an appropriate band energy structure of SiC/ SiO_2 composite, the photogenerated electrons can easily remove to the SiO_2 layer, while holes are trapped in the valence band of SiC by the oxide layer. The process results in more efficient and longer charge separation by preventing the electron–hole recombination. So the protective oxide layer can serve as a hole-blocker. On the other hand, the generated holes react with the bridging site oxygen, resulting in oxygen vacancy. Water molecules can heal these oxygen vacancies, producing absorbed OH groups that will generate more $\text{OH}^\bullet$ radicals and simultaneously make the surface hydrophilic. Oxygen vacancies in a solid probably also make the spectral limit of a surface photochemical process red-shift to the visible region, thus improving optical conversion efficiency. In addition, nanosized SiO_2 has massive superficial OH radicals, forming activated $\text{OH}^\bullet$ radicals by easily capturing the excited electrons and holes. The hydrophilicity of nanowires is increased by the SiO_2 layer due to the enhancement of the interactions between water molecules and the SiC surface, which also enhances the photocatalytic activity.

Parida and coworkers employed a sol-gel process to fabricate a series of β -SiC- TiO_2 nanocomposites with the purpose of efficient charge (e^- , h^+) separation and the enhancement of the photocatalytic performance under solar light irradiation [82]. The narrow bandgap β -SiC extends the spectral response of the TiO_2 from the UV to the visible region. The 20 wt% β -SiC- TiO_2 exhibits a significant activity of 87% dye degradation in the presence of solar light, which is ascribed to their high surface area, low crystallite size, high generation of OH radicals, and chemical oxygen demand efficiency. Torres-Martínez and coworkers found that SiC supported TiO_2 nanoparticles exhibited better activity under UV light irradiation for the degradation of methylene blue and Rhodamine B than commercial TiO_2 powder [83]. Yamashita et al. prepared TiO_2

photocatalyst deposited on SiC ($\text{TiO}_2\text{-SiC}$) by a calcination of TiC-SiC nanoparticles obtained by a carbothermal reduction of $\text{SiO}_2\text{-TiO}_2$ [84]. From measurement of the water adsorption ability of photocatalysts, the $\text{TiO}_2\text{-SiC}$ photocatalyst exhibited a hydrophobic surface property in comparison with $\text{TiO}_2\text{-SiO}_2$ and commercial TiO_2 powder (P-25) photocatalysts. Under UV-light irradiation, the $\text{TiO}_2\text{-SiC}$ photocatalyst decomposed 2-propanol diluted in water into acetone, CO_2 , and H_2O , and finally acetone was also decomposed into CO_2 and H_2O . A well-crystallized TiO_2 phase deposited on SiC and the hydrophobic surface of the SiC support are important factors for the enhancement of photocatalytic reactivity for degradation of organic compounds in the liquid phase reaction.

Xie and coworkers synthesized porous TiO_2/SiC nanocomposite films by ball-milling and screen-printing techniques, and found that the mineralization ratio of toluene by TiO_2/SiC nanocomposite increased 1.61 times compared with pure TiO_2 in dry conditions [85]. Moreover, when TiO_2/SiC nanocomposite was applied in humid conditions the mineralization ratio increased to nearly fivefold that of pure TiO_2 in dry conditions, with up to 100% mineralization. These results were smoothly explained by the synergistic effect of $\text{TiO}_2\text{-SiC}$ heterojunction and the interaction between water and TiO_2 (SiC). Due to the special staggered-type energy band structure heterojunction, the photogenerated electrons gathered on TiO_2 , and holes enriched on SiC. Both of these participated in the degradation of toluene in more efficient ways, and owing to the hydrophilicity of TiO_2 and hydrophobicity of SiC, the mineralization capacity of photogenerated electrons and holes was largely promoted. The study indicated that the hydrophilicity (hydrophobicity) of the photocatalyst must be taken into account in gas-phase photocatalytic degradation.

Guo and coworkers employed a pyrolytic method to prepare graphene-covered SiC powder composites with different sizes and graphene layer numbers (Figure 2.17) [86]. The excellent electrical conductivity of graphene allows photogenerated electrons to migrate rapidly to the catalyst surface to participate in the reaction. At the same time, the high specific surface area of graphene makes absorption of organic pollutants on the

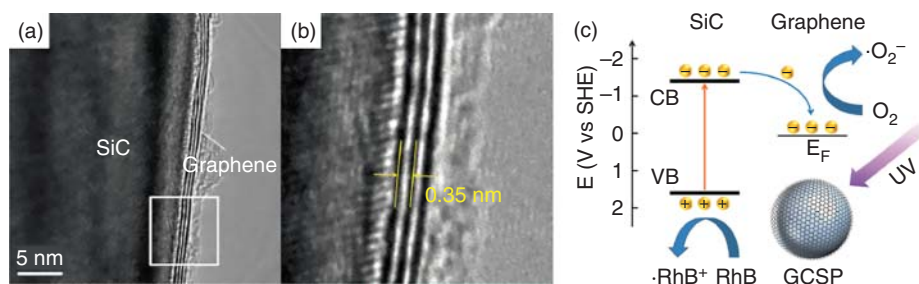


Figure 2.17 (a) HRTEM image of a graphene-covered SiC powder derived from 0.5 mm SiC particles. (b) A magnified image of the selected square in (a). (c) Suggested mechanism for the photocatalytic degradation of Rhodamine B by graphene-covered SiC powder under UV irradiation. The photo-induced electrons in the SiC particle are transferred to the graphene shell rapidly, and then captured by oxygen in solution to produce active oxygen species. The Rhodamine B can be decomposed either by the free holes in the SiC through the defect sites of graphene, or by the active oxygen species [86]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

surface easier, which further accelerates the reaction. It was observed that the thicker the graphene covering the SiC, the stronger the absorbance of the sample in the whole wavelength range. However, the conductivity of carriers was relatively poor between graphene interlayers. Hence, the thicker the graphene, the less the photogenerated carriers in the SiC transfer out to the graphene layer, which directly determines the number of carriers able to take part in the redox reaction. The composites with 4–9 layers of graphene show outstanding photocatalytic activity enhancement for the degradation of Rhodamine B among the other graphene layer numbers. Moreover, it is found that smaller particles have higher activity than the larger ones, and more than 730% improvement is achieved by the graphene-covered SiC powder derived from 0.5 mm SiC powder relative to the pristine SiC powder, which is more than six times of that of photoreduced graphene oxide/SiC composite. Since the specific surface area is inversely proportional to its size, the smaller the particle size, the larger the specific surface area, and the more reactive sites and effective absorption area. Lei and coworkers also anchored β -SiC onto the surface of reduced graphene oxide by a mild solvothermal method and found that the composite exhibited excellent activity for photocatalytic degradation of methylene blue [87].

At present, many researchers around the world have carried out a great deal of exploration and practice in semiconductor heterogeneous photocatalytic degradation of organic pollutants. Great progress has been made in the study of mechanism and dynamics. Because SiC has high chemical stability and mechanical strength, and responds well to visible light, it has broad application prospects in organic pollutant degradation, especially in organic wastewater treatment. The trend for future development will be how to use a variety of excellent performance-modified, selective adsorption materials (graphene, conductive polymers, activated carbon, zeolite, diatomaceous earth, carbon nanotubes, montmorillonite, etc.) to combine with SiC to prepare novel photocatalytic materials with high selectivity and high adsorption performance. In addition, designing a highly efficient and powerful photocatalytic reactor and utilizing sunlight as a light source for photocatalytic degradation of wastewater, to make it truly applicable in our environment, will be a very promising direction of development.

Recently, some advances were made in the design of novel photocatalytic air or water purification reactors. Keller [88], Robert [89], Zhang [90] and coworkers have conducted much research in this field. They employed medium surface area, open cell-SiC alveolar foam as a substrate to support and anchor TiO_2 , and then filled them into different reactors (Figure 2.18), and found that the photocatalytic reactors exhibit excellent activity to degrade organic pollutants, such as diuron, butanone, and sulfanilic acid, with good stability and recyclability.

2.4 Photocatalytic Selective Organic Transformations

The future development of chemistry entails environmentally friendly and energy sustainable alternatives for organic transformations. Recently, employing visible light to drive organic reactions, such as polymerization, hydroxylation of aromatic compounds, oxidation of amines, epoxidation of olefins, and carbonylation, under mild conditions, has become particularly attractive. Photocatalytic organic synthesis has become an

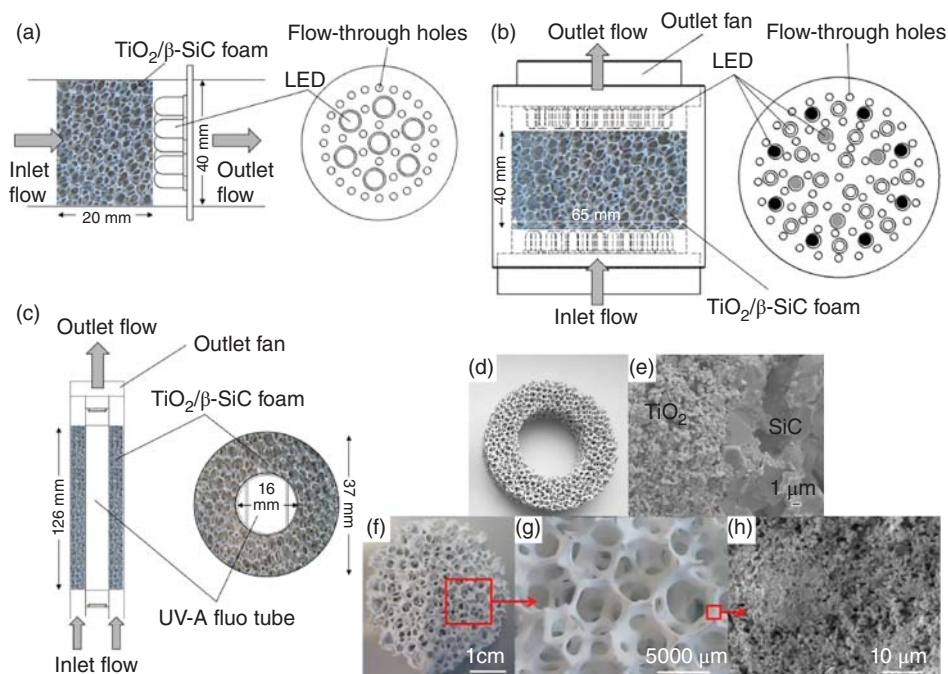


Figure 2.18 (a) Scheme for the $\text{TiO}_2/\beta\text{-SiC}$ foam and LED-based single pass flow-through photocatalytic reactor used for screening in reactivity. (b) Scheme for the flow-through structured photocatalytic reactor incorporating LEDs and the $\text{TiO}_2/\beta\text{-SiC}$ foam. (c) Scheme for the flow-through photocatalytic reactor structured by the $\text{TiO}_2/\beta\text{-SiC}$ foam material and built around a conventional UV-A fluorescent tube. (d–h) Photograph and SEM images of $\text{TiO}_2/\beta\text{-SiC}$ foam [88–90].

important frontier in the field of photocatalysis. Its unique advantage [1–3] lies in the following:

- (i) It can use solar energy as an energy source, which greatly reduces energy demand and has broad application prospects.
- (ii) Its mild reaction conditions avoid the use of toxic and corrosive chemical reagents. It is easy to operate and generally does not produce byproducts, and the catalyst can be reused.
- (iii) It generally provides a different and rapid reaction process with high selectivity for the synthesis of the target product compared with the traditional thermal reaction.

The low charge migration rates and uncertain charge diffusion directions make the charge carriers randomly walk in the semiconductor, so only a small portion of photogenerated carriers can arrive at the catalytic sites [91–93]. Thus far, use of a Schottky junction has been recognized as the best-established strategy for steering the flow of the carriers that are photogenerated in the semiconductor [94, 95]. It is well known that metal (especially for nonplasmonic metals, Pt and Pd) can serve as a sink for photogenerated electrons or holes when forming a Schottky junction with an n-type or p-type semiconductor, respectively [94, 95]. The formed Schottky barrier can inhibit the backflow of electrons or holes from metal to semiconductor. As a result, the charge

“pump” role of the Schottky junction ensures the efficient unidirectional transfer of charge carriers across the metal–semiconductor interface.

When the n-type SiC forms a Schottky contact with Pd whose work function is larger than that of SiC, the electrons of the SiC will transfer to the metal Pd. The electron transfer results in a positively charged region in SiC and a negatively charged Pd nanoparticle. The light irradiation can effectively amplify the directed electron transfer. Therefore, the photogenerated electrons can quickly transfer from SiC to Pd and thus avoid recombination with the holes, further enhancing photocatalytic activity. Jiao et al. prepared Pd/SiC catalyst with a Pd loading of 3 wt% and found that Pd/SiC catalyst displays stronger absorption than pure SiC in the UV and visible range, indicating that the light energy can be better exploited by the catalyst (Figure 2.19a–c) [96]. XPS results show that the Pd particles in the Pd/SiC catalyst are metallic and the lower binding energy (BE) of Pd_{3d} suggests electron enrichment on the Pd particles (Figure 2.19d). The catalyst in the coupling of iodobenzene and phenylboronic acid showed a high turnover frequency of 1053 h^{−1} and a selectivity of nearly 100% under visible-light irradiation at 30°C. Without irradiation (dark reaction), the conversion of iodobenzene was only 7% (turnover frequency (TOF) 74 h^{−1}), indicating the significant contribution of irradiation to the

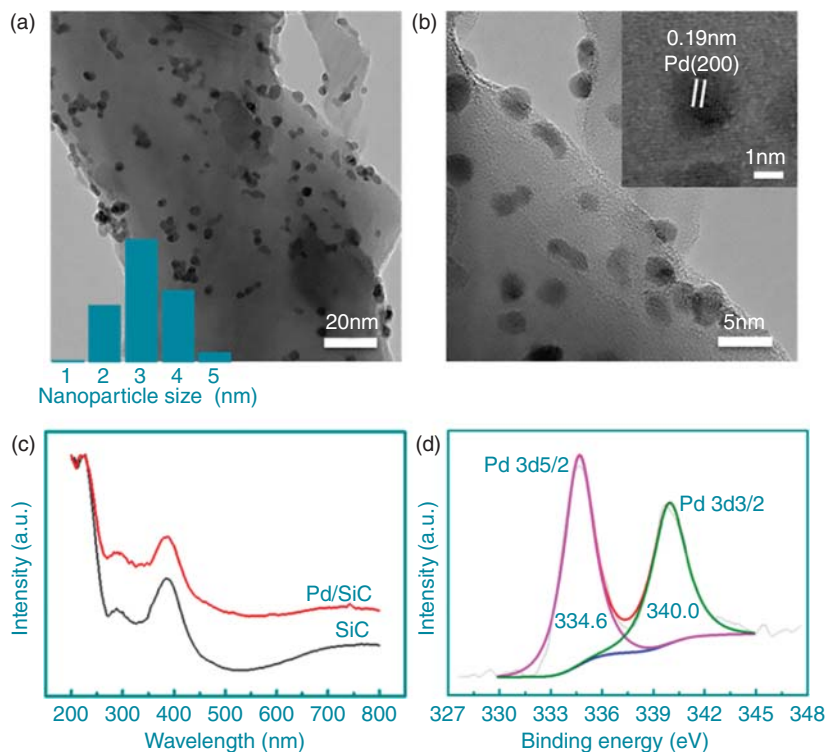


Figure 2.19 TEM images (a and b), UV-vis absorption spectra (c), and X-ray photoelectron spectroscopy results (d) of the 3 wt % Pd/SiC catalyst; the inset pictures in (a) and (b) are the size distribution of Pd nanoparticles and the HRTEM image of Pd/SiC, respectively [96]. Source: Reprinted with permission from ACS publishers, Copyright 2015.

catalytic activity, further confirmed by the dependences of catalytic activity on the irradiation intensity and wavelength (Figure 2.20a and b).

The Pd/SiC catalyst can efficiently exploit natural sunlight. Figure 2.20c shows the evolution of sunlight intensity and ground temperature in six hours of one day. The intensity of sunlight changes from 49 mW cm^{-2} at 10:00 to the maximum (67 mW cm^{-2}) at 13:00 and then to 28 mW cm^{-2} at 16:00. The temperature variation ranges from 30 to 35°C . Under this condition, the coupling reaction of iodobenzene with phenylboronic acid can proceed completely; that is, the yield of biphenyl can exceed more than 99%. This result suggests that the Pd/SiC catalyst has very good sunlight applicability. In addition, the catalyst Pd/SiC has good general applicability to different aryl iodides with electron-withdrawing or electron-donating substitutions, and even aryl bromides (Table 2.1). The electrons in Pd particles and holes in SiC play different roles in the photocatalytic Suzuki-Miyaura coupling reaction, respectively. The electron-rich Pd nanoparticles can activate iodobenzene and produce Pd adsorbed aryl. Meanwhile, the photogenerated holes on the SiC surface can assist in cleaving the carbon–boron bond in phenylboronic acid molecules (Figure 2.20d). Then the redox-activated species couple to form the final products. SiC plays an important role since it acts not only as a support in response to visible light, but also as an active phase participating directly in the reaction.

Guo and coworkers also investigated visible-light-driven photocatalytic hydrogenation of furan derivatives on Pd/SiC catalyst [97]. The Pd/SiC can greatly promote the hydrogenation of furan derivatives at a lower temperature (25°C) and pressure (1 MPa of H_2) by visible light irradiation. The yield of tetrahydrofuran from furan hydrogenation is 99% and the turnover frequency is 70 h^{-1} . The control experiment reveals that the Pd/SiC catalyst in the dark can only achieve a furan conversion of 37%. The photocatalytic hydrogenation mechanism of furan over the Pd/SiC catalyst can be interpreted by a simple model (Figure 2.21). Furan molecules usually adsorb with the molecular plane lying parallel to the surface of the Pd particles, and the C—C and C=C bonds are located respectively on the top of a Pd atom. So, the negatively charged Pd nanoparticles with more energetic electrons activate the C=C bonds in the furan rings by donating electrons back to the C=C antibonds. The holes left on the SiC support are filled by oxidizing H_2 , which generates active hydrogen. The active hydrogen then migrates to the Pd nanoparticles by reverse spillover and reacts with the C=C bonds in furan to produce THF. When the furan rings have substituent groups, the steric effect of the substituent groups can decrease the hydrogenation activity of the C=C bonds in the furan rings but promote the hydrogenolysis of the furan rings.

A Sonogashira reaction of aryl halides with terminal alkynes can also be realized by a visible-light-driven heterogeneous catalytic route using Pd/SiC as the catalyst under copper- and ligand-free conditions [98]. The Sonogashira coupling reaction does not occur using only pure SiC as catalyst under irradiation. The Pd/SiC catalyst, however, exhibited excellent photocatalytic activity under irradiation. The conversion of iodobenzene was 99% and the selectivity of diphenylacetylene was 97%. The control experiment showed that the conversion of iodobenzene was 52% in the dark under identical conditions, indicating that light irradiation greatly enhanced the intrinsic catalytic activity of Pd particles. The photocatalytic Sonogashira reaction over the Pd/SiC catalyst can be interpreted by a simple model (Figure 2.22). The concentrated photogenerated electrons with high energy on Pd nanoparticle surfaces can transfer to the iodine (or

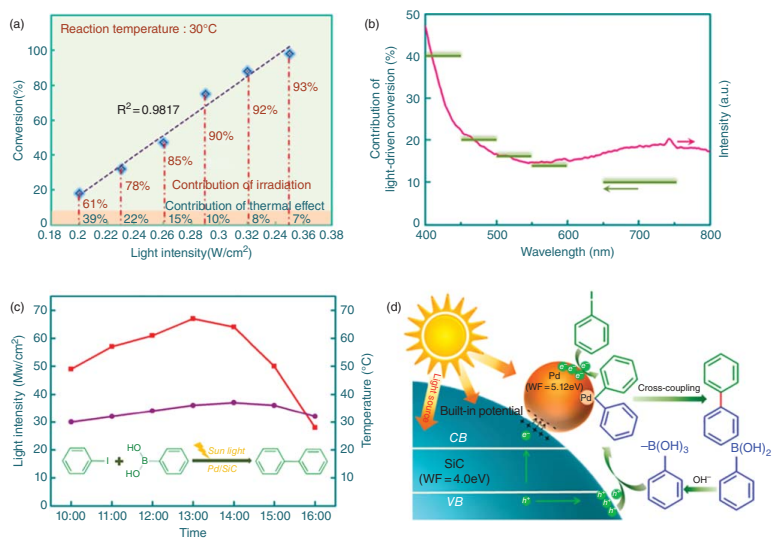
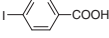
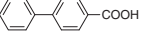
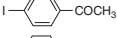
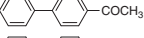
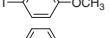
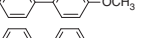
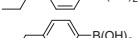
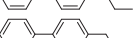
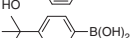
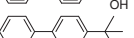
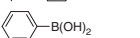
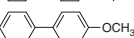
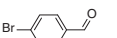
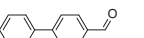
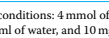


Figure 2.20 Dependences of catalytic activity of 3 wt % Pd/SiC for the coupling reaction on the intensity (a) and wavelength (b) of the irradiation. (b) shows the absorption spectrum of the catalyst in the wavelength range of 400–800 nm. (c) Evolution of sunlight intensity and ground temperature during the sunlight experiment. Reaction conditions: 0.11 ml of iodobenzene (1 mmol), 0.24 g of benzenboronic acid (2 mmol), 0.98 g of CS_2CO_2 (3 mmol), 9 ml of N,N-dimethylformamide (DMF), 3 ml of water, and 35 mg of 3% Pd/SiC catalyst. (d) The proposed mechanism for the Suzuki-Miyaura coupling reaction on Pd/SiC catalyst [96]. Source: Reprinted with permission from ACS publishers, Copyright 2015.

Table 2.1 Photocatalytic performances of Pd/SiC for the Suzuki-Miyaura coupling reaction of aryl halides with phenylboronic acids [96].^{a)}

Entry	Reactant 1	Reactant 2	Main product	Conv.(%)	Select. (%)	Turnover frequency (h ⁻¹)
1				99	99	1043
2				99	99	1043
3				99	99	1043
4				73	100	777
5				53	100	564
6				97	99	1022
7				99	100	1053
8				99	100	1053
9				96	99	1011
10 ^{b)}				93	53 ^{c)}	140
11 ^{b)}				100	63 ^{c)}	179

a) Reaction conditions: 4 mmol of iodobenzene or one of its derivatives, 8 mmol of phenylboronic acid, 3.91 g of Cs₂CO₃ (12 mmol), 9 ml of N,N-dimethylformamide (DMF), 3 ml of water, and 10 mg of 3% Pd/SiC catalyst. Reaction time is 80 minutes, temperature is 30°C, and the irradiation intensity is 0.35 W cm⁻².

b) The reaction time is prolonged to five hours and the other conditions are the same as in footnote a.

c) The other products are the debromination products of bromobenzene derivatives.

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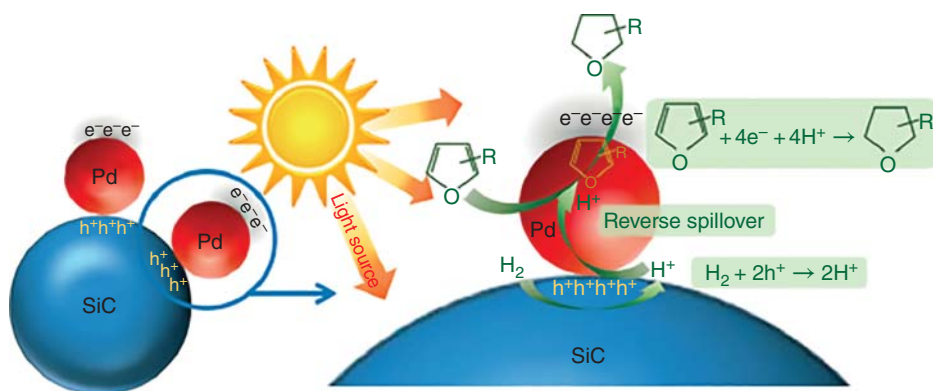


Figure 2.21 A proposed mechanism for the photocatalytic hydrogenation of furan derivatives on Pd/SiC catalyst [97]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

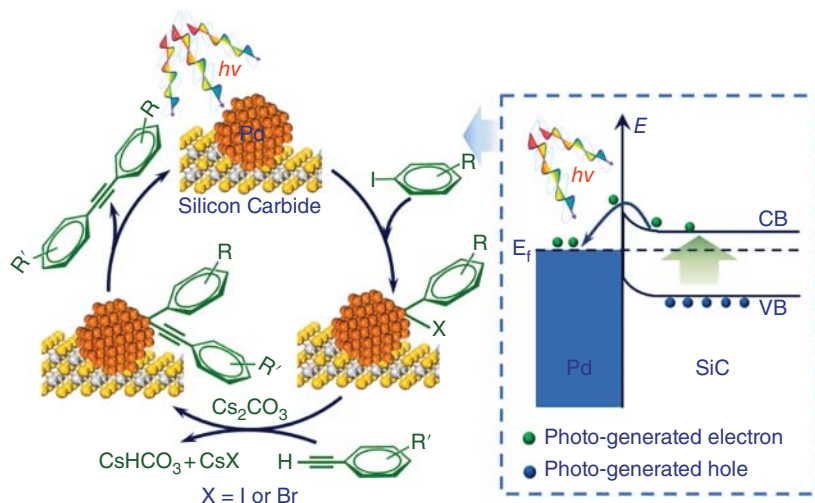


Figure 2.22 Proposed mechanism for the photocatalytic Sonogashira coupling reaction of aryl halides and phenylacetylene over Pd/SiC [98]. Source: Reprinted with permission from Elsevier, Copyright 2017.

bromine) atoms to facilitate the cleavage of the C–I (or C–Br) bond in iodobenzene (or bromobenzene) molecules to form a Ar–Pd–I (or Ar–Pd–Br) complex [18, 26]. This step is followed by a rapid substitution reaction between terminal alkynes and Ar–Pd–I (or Ar–Pd–Br) complex. Then, the final products can be achieved by reductive elimination. Among them, the first step is the rate-determining step, and the highly negatively charged Pd particles are the most active sites for the facile oxidative addition of aryl halides. Therefore, the rapid transfer of photogenerated electrons under irradiation can greatly enhance the catalytic activity. Evidently, the irradiation plays an essential role in the catalytic mechanism of the Sonogashira reaction through the activation of the reactants.

Noble metal nanoparticles have recently been recognized as a new class of efficient media suitable for harvesting light energy for chemical processes, due to their high optical absorption over a wide range of the sunlight spectrum, including both visible light and UV light [2, 5, 99–102]. Nanoparticles of some noble metals, such as Au and Ag, exhibit brilliant colors, which have been found to depend on both the particle size and shape. The light absorption property of fine Au nanoparticles has been applied to adorn some of the most majestic stained glass windows of medieval churches for centuries [2, 103]. These magnificent colors are a result of the size and shape of the nanoparticles, which determine light absorption, and are caused by the localized surface plasmon resonance (LSPR) effect of the noble metal nanoparticles. LSPR is the resonant photon-induced coherent oscillation of charge at the metal–dielectric interface, established when the photon frequency matches the natural frequency of metal surface electrons oscillating against the restoring force of their positive nuclei (Figure 2.23). Through this process the conduction electrons of nanoparticles gain irradiation energy, resulting in high-energy electrons at the surface, which is desirable for activating molecules on the nanoparticles for chemical reactions [2, 104]. Photocatalysts consisting of Au, Ag and Cu nanoparticles that function via this mechanism have been developed. The obvious advantage of such a process is that the energy of incident light is very efficiently coupled into the reactant molecules, and not dispersed into the other components of the reaction system, such as the container, solvent, and the material that supports the nanoparticles [2]. New catalyst structures could be designed to exploit the vast potential of this process, where we use light, instead of heat, as the energy source to drive reactions with unprecedented efficiency.

Most recently, integration of surface plasmon into photocatalysis has been widely explored by composing hybrid structures between noble metals and semiconductors [2, 5, 99–108]. As demonstrated by many research groups, the plasmonic Au and Ag that directly contacts a semiconductor can be excited under visible light illumination to generate and inject hot carriers into the semiconductor [93, 109–115]. Specifically, hot electrons may flow into the conduction band of an n-type semiconductor, and in the case of a p-type semiconductor, hot holes are instead injected into the valence band [93, 110, 113]. In turn, the injected electrons on the conduction band of semiconductor initiate a reduction reaction, or alternatively, the holes on the valence band participate in an oxidation reaction. As long as a semiconductor with an appropriate bandgap (i.e. wide bandgap) is selected, the redox abilities of electrons or holes can be maintained as high as those in wide bandgap semiconductors, despite the use of incident visible light with relatively low energy.

Selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols has attracted much attention recently because it is an essential step in the preparation of various fine chemicals [116, 117]. An example is the reduction of cinnamaldehyde

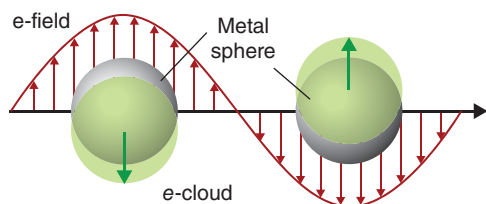


Figure 2.23 Schematic diagram of plasma oscillations of spherical metal nanoparticles. The figure shows the relative displacements between electron cloud of conduction band electrons and metal particles.

(CAL) to cinnamyl alcohol (COL), which is important for the synthesis of pharmaceuticals and perfumes [118, 119]. Selective hydrogenation of CAL is often difficult, especially under heterogeneous catalysis conditions, because hydrogenation of the C=C double bond is much more favorable than that of the C=O double bond, both thermodynamically and kinetically [120, 121]. Furthermore, when CAL adsorbs onto metals, competitive adsorption between C=C and C=O usually occurs. Significant efforts have been made in order to develop catalytic systems that are able to efficiently and selectively hydrogenate the C=O bond [122]. Guo and coworkers found that energetic electrons resulting from LSPR of Au nanoparticles migrate to the conduction band of SiC, leading to the formation of both slightly positively charged sites on the Au nanoparticle and electron-rich sites at the interface between Au and SiC, which can effectively drive reactions (Figure 2.24) [123]. Highly selective hydrogenation of CAL to COL with 2-propanol was achieved using Au/SiC as a photocatalyst. The hydrogenation reached a turnover frequency as high as 487 h^{-1} with 100% selectivity

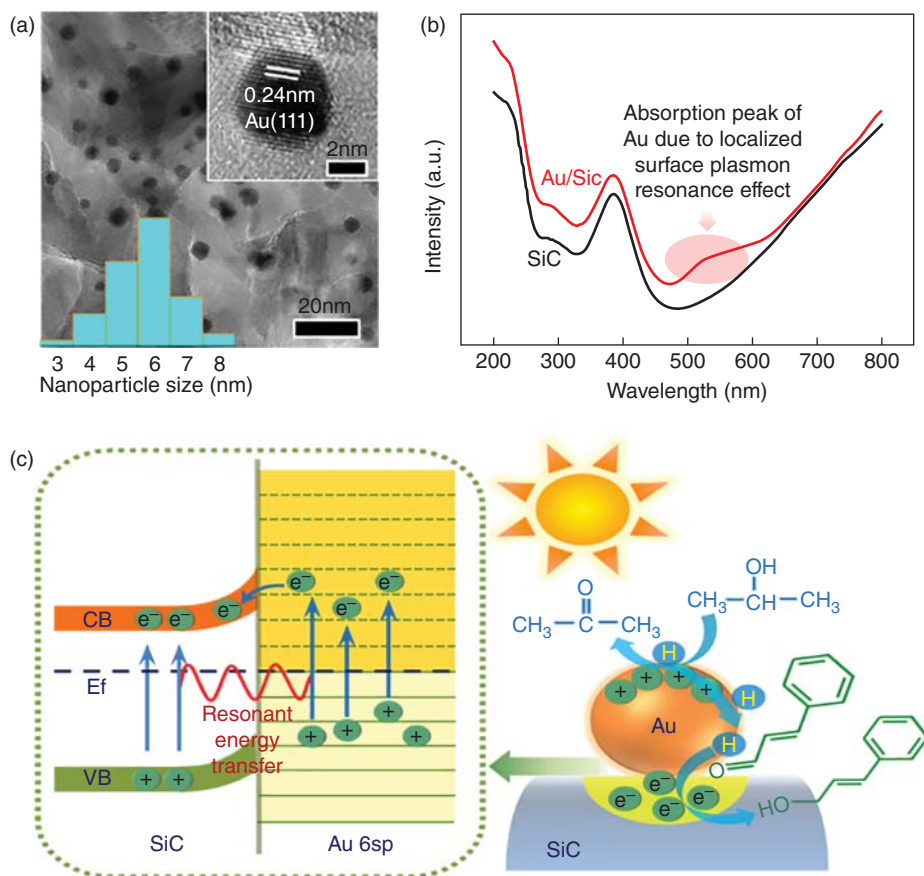


Figure 2.24 (a) TEM image and (b) UV-vis absorption spectra of the 1 wt% Au/SiC catalyst. The insets in (a) are the size distribution analysis and HRTEM image of Au nanoparticles, respectively. (c) Proposed mechanism for the light-driven selective hydrogenation of CAL to COL over Au/SiC photocatalyst [123]. Source: Reprinted with permission from ACS publishers, Copyright 2016.

for the production of alcohol under visible light irradiation at 20°C. 2-propanol can be oxidized on the relative positive sites on Au to generate acetone and active hydrogen. The latter reacts with the C=O bond of CAL to produce COL (Figure 2.24c). Both electron and steric hindrance effects at the interface should be important, as those molecules with bulky ring structures show relatively high conversion and selectivity (see Table 2.2), most likely because they favor the adsorption of CAL molecules, and the C=O bond at the end is adsorbed preferably onto the active sites at the interface. Energy transferred from the LSPR dipole at the Au/SiC interface via resonance should facilitate the charge separation, thus enhancing the visible light-driven photocatalytic activity.

In recent years, photocatalytic organic synthesis has developed rapidly and has become an important branch of photocatalysis. However, investigations on photocatalytic organic transformations by SiC-based catalysts are just getting started, and a great deal of research and exploration is still needed. Presently, the reaction can only be carried out under small-scale conditions, and the influence of many reaction conditions on the experimental results is not yet clear. Most importantly, catalytic mechanisms for some reactions are still very vague. These deficiencies will motivate people to pay more attention to their development, to further understand and study the catalytic mechanism, modify and improve the photocatalyst preparation techniques of SiC-based photocatalyst, and optimize the photocatalytic reaction system for the selective synthesis of organic compounds, thereby enhancing the photocatalytic activity. The selective synthesis of organic products by photocatalytic technology will surely become one of the most promising, effective, and green chemical processes of the twenty-first century.

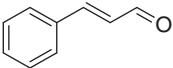
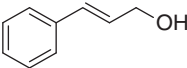
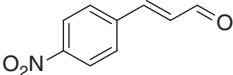
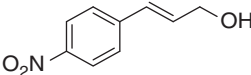
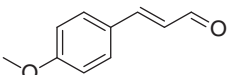
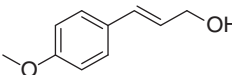
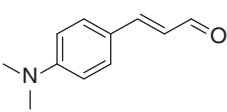
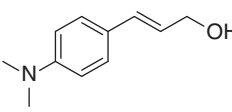
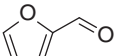
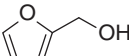
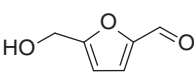
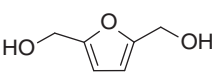
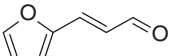
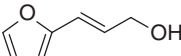
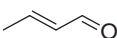
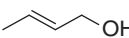
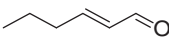
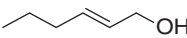
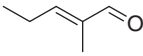
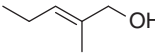
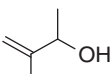
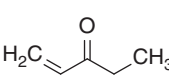
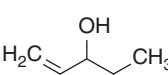
2.5 Photocatalytic CO₂ Reduction

CO₂ chemistry is an important part of C1 chemistry, and it is also the most inexpensive and abundant carbon resource in the C1 family. Research on immobilization and recycling of CO₂ is one of the most important topics of concern in the world. Utilization of solar energy to produce methane, methanol, and other fuels through photocatalytic reduction of CO₂ provides new opportunities and challenges for promoting solar energy use, reducing the greenhouse effect, and enabling the recycling of carbon resources and the development of the energy economy.

Gondal et al. employed granular α 6H-SiC as a photo-reduction catalyst for CO₂ conversion into methanol using a 355 nm laser from the third harmonic of pulsed Nd:YAG laser and a 500 W collimated xenon mercury (Xe—Hg) broad band lamp [124]. The bandgap energy of α 6H-SiC was estimated to be 3.17 eV, and XRD demonstrated that it is a highly crystalline material. The reaction cell was filled with distilled water and α 6H-SiC granules, and pressurized with CO₂ gas at 50 psi. Maximum molar concentration of methanol achieved was 1.25 and 0.375 mmol l⁻¹, and the photonic efficiencies of CO₂ conversion into methanol were 1.95% and 1.16% using the laser and the XeHg lamp respectively. The selectivity of methanol produced using the laser irradiation was 100%, compared with about 50% with the Xe—Hg lamp irradiation.

Li et al. modified SiC nanoparticles by Cu₂O and investigated their photocatalytic activities for reducing CO₂ to CH₃OH under visible light irradiation [125]. The

Table 2.2 Selective photocatalytic hydrogenation of α,β -unsaturated aldehydes over Au/SiC catalyst [123].^{a)}

Entry	Reactant	Main product	Conv. (%)	Select. (%) ^{b)}	Turnover frequency (h ⁻¹)
1			100	100	487
2			85	92	205
3			100	93	122
4			81	100	106
5			100	100	263
6			90	93	220
7			92	96	233
8			77	89	180
9			70	84	155
10			72	85	161
11			64	81	136
12			53	72	100

- a) Reaction conditions: 1.6 mmol of reactant, 30 mg of 1 wt% Au/SiC catalyst in 10 ml of isopropyl alcohol consisting of 20 mg of KOH. The reactions were conducted in an argon atmosphere at 20°C under Xe-lamp irradiation (400–800 nm) with light intensity of 1.0 W cm⁻². The reaction time was 4 hours, except for entry 1 (130 minutes) and entries 3 and 4 (8 hours).
- b) Among the other compounds generated, saturated aldehydes and saturated alcohols were the main products.

Source: Reprinted with permission from ACS.

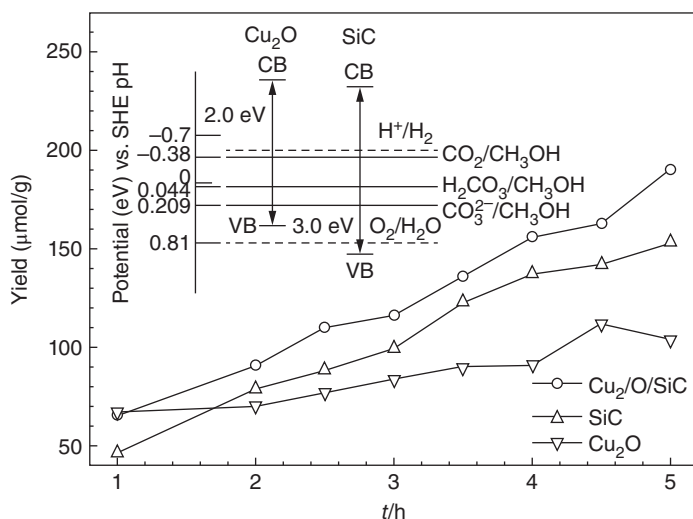


Figure 2.25 Yields of CH_3OH in the photocatalytic reduction of CO_2 with H_2O on the Cu_2O , SiC and $\text{Cu}_2\text{O}/\text{SiC}$ photocatalysts as a function of irradiation time of visible light [125]. Source: Reprinted with permission from Elsevier, Copyright 2011.

photocatalytic activities of Cu_2O , SiC and $\text{Cu}_2\text{O}/\text{SiC}$ are shown in Figure 2.25. From Figure 2.25, it can be seen that both SiC nanoparticles and Cu_2O had good photocatalytic activities and can be used as the photocatalyst for reducing CO_2 to CH_3OH . This is because the potentials of the conduction bands of SiC and Cu_2O are more negative than all those that methanol yield for CO_2 (g), H_2CO_3 , CO_3^{2-} etc. in water. The detailed band structures are shown in Figure 2.25. Although the photoabsorption performances of Cu_2O were better than those of SiC, it can be seen that the yield of methanol on SiC was larger than that on Cu_2O , which may be attributed to the fact that SiC has a much larger average pore diameter and smaller particle sizes. The existence of macrochannels and larger external surface areas can increase photoabsorption efficiency and allow efficient diffusion of gaseous molecules. In addition, all the yields of CH_3OH increased with increasing the time of visible light irradiation, and $\text{Cu}_2\text{O}/\text{SiC}$ had the best photocatalytic performance. The largest yields of methanol on SiC, Cu_2O and $\text{Cu}_2\text{O}/\text{SiC}$ photocatalysts under visible light irradiation were 153, 104 and 191 $\mu\text{mol g}^{-1}$, respectively. This was because doping Cu_2O to SiC can improve the separation of electrons and holes, and prolong the lifetime of the charge carrier, and therefore the photocatalytic activity of the photocatalyst is enhanced.

Photocatalytic CO_2 reduction is a new route not only to reduce greenhouse gas emissions, but also to enable carbon recycling by converting CO_2 to alkanes, alcohols, and other organic substances. Although major breakthroughs have been made in the photocatalytic reduction of CO_2 in recent years, most studies are based on TiO_2 , and SiC as a photocatalyst to reduce CO_2 is still a new topic. Combination of SiC with other metals or semiconductor materials to solve the problem of low efficiency of absorption and activation of CO_2 on the photocatalyst should be considered in the future.

SiC can greatly absorb visible light. It also has an excellent chemical stability and thermal conductivity, so it can be employed in many harsh reaction conditions such

as strong acids or alkalis. Prof. Adarsh Sandhu, one of the *Nature* editors, commented that SiC nanostructures are promising candidates for photocatalysts because they are wide bandgap semiconductors with large surface areas, and they absorb solar energy very efficiently (*Nature Nanotechnology*, 21 July 2006). At present, a large number of SiC-based photocatalytic works have been reported; however, the in-depth exploration of SiC and the understanding of related mechanisms are still insufficient compared with TiO₂. Therefore, based on the ability of SiC to respond to visible light, combining with various doping or modification methods will further the innovation and development of research and application of SiC-based photocatalysis.

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3

Application of Silicon Carbide in Electrocatalysis

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Electrochemical energy conversion and storage is one of important pathways to solving the energy crisis in the twenty-first century. Designing electrocatalysts and energy storage materials with high activity and long lifetime is of very great importance in this field. In the previous chapter, we mentioned that silicon carbide (SiC) can be widely used in refractory materials, abrasives, and semiconductor materials, since it has very high chemical stability, high thermal conductivity, small thermal expansion coefficient, and very good wear resistance. With the continuous development of synthesis technologies for nanomaterials, SiC nanomaterials with new nanostructures, such as high surface area, ion-doped SiC and SiC composites, have been successively developed, making them no longer confined to conventional applications. SiC mainly exists in the form of α -SiC and β -SiC crystals. Compared with α -SiC, β -SiC has good thermal conductivity, corrosion resistance, oxidation resistance, and acid and alkali resistance, making it an ideal catalyst support for different catalytic reactions. In 1988, Honji et al. prepared Pt/SiC catalyst by reduction of chloroplatinic acid with methanol, and found that Pt nanoparticles were well dispersed on the SiC surface [1]. Moreover, the Pt/SiC with Pt loading level of 23 wt% had a comparative electrocatalytic oxygen reduction activity to Pt/C catalyst [1]. Thereafter, the application of SiC in the electrochemistry field has received extensive attention and the publications of corresponding papers have been increasing. This chapter will describe in detail the application of SiC in biosensors, fuel cells, solar cells, lithium-ion batteries (LIBs) and supercapacitors, as well as the related electrocatalytic mechanisms.

3.1 Electrochemical Sensors

Electrochemical sensors usually achieve qualitative or quantitative analysis by oxidizing or reducing the target analyte at an electrode and measuring the resulting current. The electrochemical reaction of the target analyte first occurs on the surface of an electrode, and then the generated electrochemical signal is converted into an electrical signal

through a signal conversion element. Afterwards, the electrochemical detector amplifies, filters, and performs analog-to-digital conversion of the received electrical signal. Finally, the processed signal is sent to the computer for display. Electrochemical sensors have the advantages of simplicity and rapidity. The research is very well-studied and many research results have been widely used. However, there are still some deficiencies in the applications, such as the presence of electroactive substances in the sample being under-measured, complex electron transport pathways in a complex sample matrix, poor stability in long-term utilization, low sensitivity of the target analyte, poor mechanical properties of the working electrodes, and so on. Therefore, an urgent problem to be solved in the electrochemical sensor field at present is how to further improve the selectivity, sensitivity and stability of the sensor. Recently, with the development of nanomaterials science and biotechnology, many researchers have begun to turn their attention to the application of different nanomaterials for electrochemical sensors and biosensors.

Due to the excellent physical and chemical stability of SiC, it can be applied to various environments. Moreover, SiC is non-toxic and has very good biocompatibility. Additionally, SiC has good electrical conductivity, low background current, and strong anti-interference ability, indicating that it is a very promising electrochemical sensor material. Recently, SiC has been found to be useful for the electrochemical detection of inorganic molecules, ions, and organic molecules. Salimia et al. reported a chemically modified electrode as a highly sensitive and selective amperometric nitrite sensor, based on a nanocomposite containing an amine-terminated ionic liquid (IL) (1-(3-aminopropyl)-3-methylimidazolium bromide) and SiC nanoparticles ($\text{NH}_2\text{-IL/SiCnp}$) [2]. The oxidation potential of nitrite over a modified electrode of $\text{NH}_2\text{-IL/SiCnp/glassy carbon (GC)}$ appeared at +0.77 V, which is 180 and 60 mV lower than bare GC and SiCnp/GC, respectively. Moreover, the nitrite oxidation peak current at the modified electrode was 3.5 and 1.6-fold higher than that of bare GC and SiC/GC electrodes, respectively. A linear relationship between the amperometric current response and nitrite concentration was observed in the range from 50 nM to 350 μM , and the limit of detection was 20 nM ($\text{S/N (signal-to-noise ratio) = 3}$). In addition, the modified electrode has an excellent anti-interference property in the presence of other potential interfering species, as well as good operational stability and antifouling properties. Kim and Chung fabricated planar type Schottky diodes by assembly of Pd- or Pt-decorated Au dots (1 mm diameter) with porous 3C-SiC [3]. The current change was detected at a hydrogen concentration in the range of 10–40 ppm with a 3.7 V forward bias. At room temperature, the response and recovery of Pd/Au/SiC were 2.3 and 1.5 seconds respectively, which are faster than those of Pt/Au/SiC (2.5 and 2.5 seconds, respectively). Wu et al. demonstrated the electrochemical behavior of ascorbic acid (AA), dopamine (DA), and uric acid (UA) at a SiC-coated glassy carbon electrode (GCE) and the selective determination of DA in the presence of AA and UA [4]. The SiC-coated GCE exhibited low electrooxidation potentials and amplified responses of AA, DA, and UA. Moreover, the SiC-coated electrode showed high sensitivity and low detection limits for selective determination of DA in the presence of AA and UA, suggesting the proposed SiC modified electrode is a good candidate for practical applications and simultaneous determination of AA, DA, and UA.

Yang et al. employed a hydrothermal reaction of glucose to give hydroxyl functionalization of the SiC surface, and then prepared a $\text{TiO}_2\text{-SiC}$ nanohybrid through a generic in-situ growth strategy [5]. Afterwards, monodispersed ultrafine Pd nanoparticles

with a uniform size of 2.3 nm were successfully obtained on the TiO_2 -SiC surface via a chemical reduction method. The Pd-loaded TiO_2 -SiC nanohybrid (Pd@TiO_2 -SiC) modified GCE was used for the simultaneous electrochemical determination of hydroquinone (HQ) and bisphenol A (BPA). Differential pulse voltammetry was successfully used to quantify HQ and BPA simultaneously within the concentration range of 0.01–200 mM under optimal conditions. The detection limits ($S/N = 3$) of the Pd@TiO_2 -SiC nanohybrid electrode for HQ and BPA were 5.5 and 4.3 nM, respectively. The selectivity of the electrochemical sensor was improved by introducing 10% ethanol to the buffer medium. An illustration of the Pd@TiO_2 -SiC nanohybrids simultaneous sensing HQ and BPA is shown in Figure 3.1a. Moreover, Au@SiC nanocomposites were

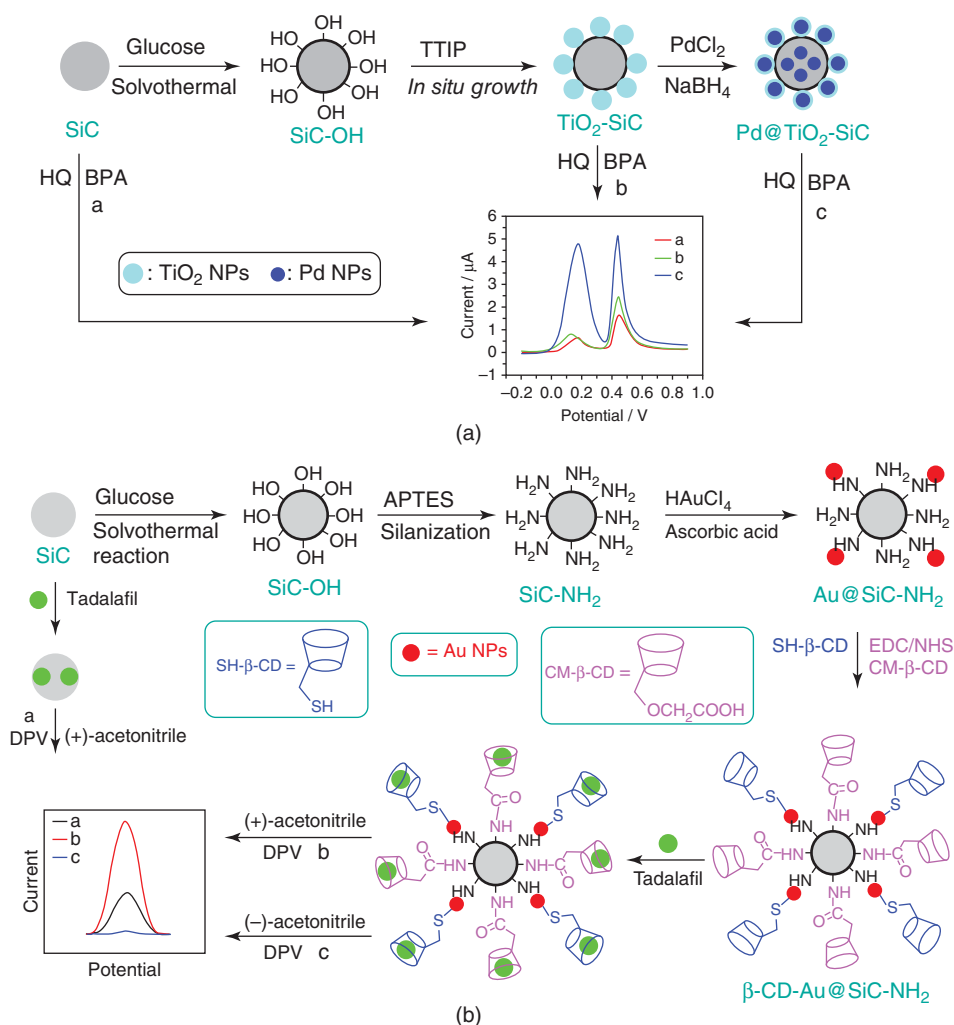


Figure 3.1 (a) Illustration of the Pd@TiO_2 -SiC nanohybrids simultaneous sensing HQ and BPA, and (b) procedure for the preparation of $\beta\text{-CD-Au@SiC-NH}_2$ nanohybrids, and sensing the guest molecule tadalafil by an electrochemical strategy in buffer medium in the presence (+) and absence (–) of 40% acetonitrile.

also prepared by the same group and used for fabrication of a label-free electrochemical immunosensor for sensitive detection of human chorionic gonadotrophin (hCG) [6]. The proposed immunosensor provided a simple and economic method with greater sensitivity and a wider concentration range for detection of hCG. Under optimal conditions, the approach provided a good linear response range from 0.1 to 5 IU^L⁻¹ and 5 to 1000 IU^L⁻¹, with a low detection limit of 0.042 IU^L⁻¹.

Some biomolecules can be grafted onto the SiC surface to improve the electrochemical activity. Yang et al. anchored uniform and monodispersed Au nanoparticles with diameter of 5.0 nm onto the amino-functionalized SiC (SiC-NH₂) via a chemical reduction process by using polyethylene glycol and sodium citrate as dispersant and stabilizing agent [7]. Carboxymethyl- β -cyclodextrin (CM- β -CD) was covalently bound on Au@SiC by combining the amine group of SiC-NH₂ with the carboxyl group of CM- β -CD, with the aid of carbodiimide hydrochloride and N-hydroxysuccinimide coupling agent. Differential pulse voltammetry was successfully used to quantify tadalafil within the concentration range of 0.01–100 μ M under optimal conditions with a detection limit (S/N = 3) of 2.5 nM. In addition, the β -CD-Au@SiC nanohybrid electrochemical sensor showed high selectivity to two other erectile dysfunction drugs, sildenafil and vardenafil. The proposed electrochemical sensing platform was used to recognize a guest molecule tadalafil as illustrated in Figure 3.1b. Ye et al. fabricated a tyrosinase/SiC/chitosan film modified GCE as an electrochemiluminescence sensor for adrenaline. SiC nanoparticles exhibit good biocompatibility with tyrosinase, and present a high sensitivity for adrenaline assay [8].

Additionally, SiC materials can also be applied to the detection of biological macromolecules. Ghavamia et al. found that GCE modified with SiC nanoparticles (SiCNP/GCE) can be effectively used for electrocatalytic oxidation of purine (guanine and adenine) and pyrimidine bases (thymine and cytosine) nucleotides [9]. That is, SiCNP/GCE can simultaneously detect the above four DNA bases without any pretreatment or separation process, and this sensor also exhibits good stability, reproducibility and long lifetime, suggesting that SiC nanoparticles are a suitable bioassay material for DNA analysis.

3.2 Direct Methanol Fuel Cells

Direct methanol fuel cells (DMFCs) are energy-converting devices with high power density, zero or low exhaust, ease of recharging, simple structure, and quick startup at low temperatures. They have attracted considerable attention in recent decades due to high energy demands, fossil-fuel depletions, and environmental pollution throughout the world [10–16]. The investigations on DMFCs have already been extensively reported in many review papers and articles [10–18]. The main active components of a DMFC are the fuel electrode (anode), oxidant electrode (cathode), and an electrolyte sandwiched between them. Figure 3.2 shows the basic operational principle of a DMFC. The DMFC converts chemical energy into electrical energy by oxidizing methanol to CO₂ and H₂O. A proton-conducting solid membrane, used both as an electrolyte and separator between anode and cathode, is sandwiched between porous structures [11]. At the anode, a methanol molecule reacts with an H₂O molecule and then produces CO₂, six protons that are free to migrate through the electrolyte toward the cathode, and six

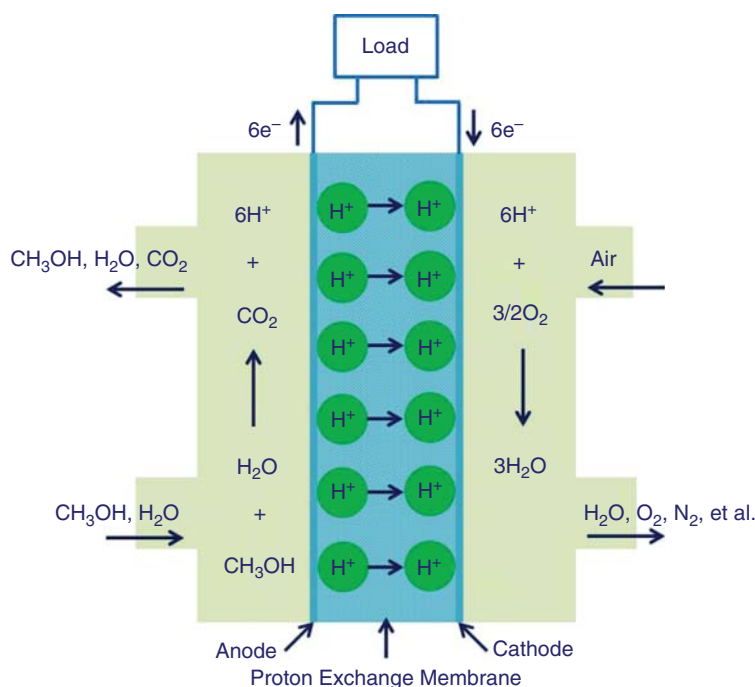
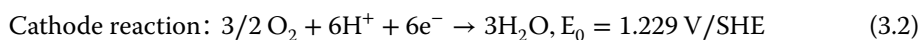
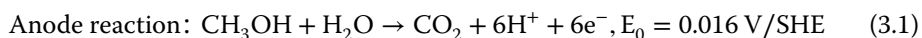


Figure 3.2 The structure and working principles of a DMFC.

electrons that can transfer through the external load [11]. The CO_2 produced in the reaction is rejected by the acid electrolyte solution. The protons migrating through the electrolyte and electrons moving via the external loaded circuit must reach a particle of catalyst on the cathode, where O_2 is electrocatalytically reduced and H_2O is produced [11]. An electric potential occurs between the electrodes because of the excess of electrons at the anode (where they are generated) compared with the cathode (where they are consumed) [11]. The relevant electrochemical reactions at the electrode surface in acidic media are as follows:



for which the standard hydrogen electrode (SHE) is used as a reference electrode.

The catalysts, including noble metals and support materials, are the most important parts in DMFCs. Usually, the dispersion of noble metals, catalytic stability, and even catalytic efficiency greatly depend on the support materials. Therefore, the study and exploration of new catalyst support materials of low cost, large surface area, abundant porous structure and high stability have attracted more and more attention. In addition to its own advantages, SiC has stronger interactions with noble metals compared with traditional carbon supports, which can improve the anti-poisoning ability of noble metal components and solve the problems of agglomeration and loss of active phases.

Tong et al. used SiC nanowires with an average diameter of 40 nm as support to prepare Pd/SiC by a cyclic voltammetric deposition method [19]. The Pd nanoparticles with a mean size of approximately 10–12 nm are uniformly distributed on SiC nanowires (Figure 3.3a,b). The high dispersion and small size of supported Pd nanoparticles enabled the catalyst to have an electrochemically active surface area of $49.5 \text{ m}^2 \text{ g}^{-1}$, which was larger than that of carbon nanotube (CNT)-supported Pd nanoparticles ($38.6 \text{ m}^2 \text{ g}^{-1}$), and that of non-supported Pd nanoparticles ($29.9 \text{ m}^2 \text{ g}^{-1}$).

Figure 3.3c presents the cyclic voltammograms (CVs) of Pd-SiC/GCE, Pd-CNT/GCE, and Pd/GCE with a potential scan rate of 50 mV s^{-1} in 0.1 M KOH + 0.5 M methanol solution. The oxidation peak potential of methanol at the Pd-SiC/GCE (about 1.03 V, vs. RHE, reversible hydrogen electrode) is lower both than that at Pd-CNT/GCE (about 1.05 V, vs. RHE) and at Pd/GCE (about 1.11 V, vs. RHE), indicating that the Pd-SiC catalyst has a higher electrocatalytic activity. The peak current density of methanol electro-oxidation in a forward scan of Pd-SiC/GCE is much larger than that of Pd/GCE, and also higher than that of Pd-CNT/GCE, due to the excellent support effect of SiC nanowires. It is far more likely that the higher current at peak potential is due to the

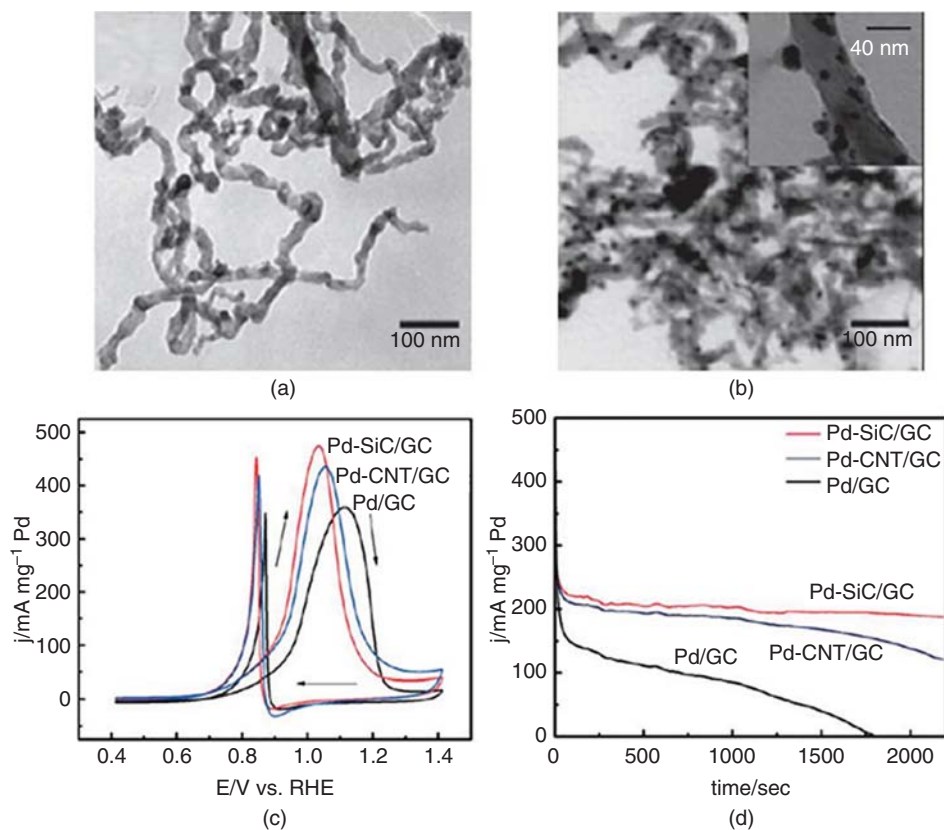


Figure 3.3 TEM images of SiC nanowires (a), SiC nanowire supported Pd nanoparticles (b), cyclic voltammograms of Pd-SiC/GCE, Pd-CNT/GCE, and Pd-GCE (c), and the chronoamperometric data for Pd-SiC/GCE, Pd-CNT/GCE, and Pd/GCE at 1 V versus RHE (d), in 0.1 M KOH + 0.5 M methanol [19]. Source: Reprinted with permission from John Wiley & Sons Ltd., Copyright 2011.

better distribution of the active catalyst particles and their less overlapped individual diffusion patterns. Besides, the unique net-like structure and the highly conductive characteristic of electrons in one-dimensional nanowires might facilitate the transport of the electrolyte onto the surface of Pd nanoparticles, and thus reduce the liquid sealing effect, which is very beneficial for the performance of fuel cells.

The long-term performance of Pd/GCE, Pd-CNT/GCE, and Pd-SiC/GCE for methanol electro-oxidation was investigated with chronoamperometry at 1 V (vs. RHE) in 0.1 M KOH + 0.5 M methanol solution. As shown in Figure 3.3d, the current density with the Pd-SiC/GCE decayed and reached an apparent steady state within 80 seconds. The current density at the Pd-SiC/GCE was c. 45% (500 seconds) higher than that at the Pd/GCE, even when the electro-oxidation reaction reached a steady state; the current density at the Pd-SiC/GCE is also higher than that at the Pd-CNT/GCE. SiC nanowires possess high chemical stability, thermal conductivity, and anti-poisoning properties, which can stabilize highly dispersed palladium. As a result, the Pd nanoparticles supported on the SiC nanowires show better steady-state electrolysis activity than the non-supported and the CNT-supported Pd nanoparticles. In addition, the Pd-SiC/GCE is stable and does not show the fouling effect in the given timeframe, indicating that the SiC nanowires can improve the poison tolerance of the electrocatalyst. Pt/SiC was also fabricated by Dong et al. via the same method [20]. This catalyst has been electrochemically characterized toward methanol oxidation, which exhibits higher catalytic activity, durability, and electrochemical active surface area, and superior CO tolerance than the electrodeposited Pt on multiwalled carbon nanotubes.

Dhiman and coworkers synthesized SiC nanocrystals using nanoporous carbon black as a template. The SiC nanocrystal-supported Pt nanoparticles as electrocatalyst have been found to have a higher electrochemical activity and stability than commercially available carbon-supported Pt catalysts [21]. Digging deeper, they found that the deconvolution of the hydrogen desorption signals in CV cycles showed a higher contribution of Pt (110) and Pt (111) peaks compared with Pt (100) for SiC-based supports than for carbon-based commercial catalysts when HClO_4 was used as an electrolyte [22]. Usually, the Pt (110) and Pt (111) facets were shown to have higher electrochemical activities than Pt (100) facets. The reaction kinetics for the oxygen reduction and for methanol oxidation with Pt/SiC were observed to be similar to the carbon-based catalysts. The SiC-based catalyst shows a higher specific surface activity than Pt/C for methanol oxidation and oxygen reduction, while the mass activity values are comparable.

Dai et al. reported that SiC-supported Pd nanoparticles with a size of 5–7 nm exhibited excellent electrocatalytic activity for electro-oxidation of alcohols in alkaline electrolytes [23]. Niu and Wang successfully synthesized macroscopic SiC nanowires at the gram level ($2\text{--}4\text{ g h}^{-1}$) by using a simple solid–vapor reaction of silicon powders and carbon oxides, assisted by ZnS [24]. The obtained products possessed a good single-crystal structure with a small size of 10–30 nm and a specific surface area of $1.6\text{ m}^2\text{ g}^{-1}$. A high electrochemical activity to H_2 adsorption/desorption and methanol oxidation was observed from CVs in H_2SO_4 and $\text{H}_2\text{SO}_4/\text{CH}_3\text{OH}$ solutions after loading with 50 wt% Pt. Moreover, the Pt/SiC catalyst displayed a high catalytic performance for oxygen reduction at -0.57 V and good chemical stability. Fang et al. prepared a Pt/SiC (5 wt% Pt loading) catalyst by an ultrasound promoted impregnation followed by calcination in hydrogen flow [25]. A strong interaction between Pt and SiC possibly affects the surface electronic structure of Pt, hence improving the electrocatalytic activity of the Pt/SiC

for ethanol electro-oxidation. Furthermore, the Pt/SiC reduced at 723 K showed much higher activity and CO tolerance for ethanol oxidation than that of Pt/C and Pt/SiC reduced at other temperatures.

Some groups used SiC-based composites as supports to further improve the conductivity and interaction with noble metals [26–28]. Zhang et al. prepared Ti-coated nano-SiC (Ti/SiC) powder by a one-pot deposition method under a vacuum, and fabricated a Ti/SiC-supported Pt electrocatalyst (Pt-Ti/SiC) by a microwave-assisted reduction method [26]. The Ti coating was strongly bonded with nano-SiC with the help of TiC and Ti_5Si_3 . The electrocatalytic performances of the Pt-Ti/SiC for the methanol oxidation and oxygen reduction reactions (ORRs) were much higher than the Pt supported on the pristine nano-SiC. Figure 3.4a,b show the CV curves of the Pt-Ti/SiC, Pt/C, and Pt/SiC electrocatalysts in 1.0 M CH_3OH + 0.5 M H_2SO_4 at 50 mV s^{-1} . The currents were normalized by the electroactive surface in Figure 3.4a. It was seen that two peaks in methanol oxidation were observed at about 0.7 and 0.5 V (vs. Ag/AgCl). In the forward scan, the peak current density for the methanol oxidation reaction appeared around 0.7 V and was in the order of Pt-Ti/SiC (1.13 mA cm^{-2}) > Pt/C (0.94 mA cm^{-2}) > Pt/SiC (0.21 mA cm^{-2}). The current density at 0.4 V for the Pt-Ti/SiC (0.12 mA cm^{-2}) was also higher than the Pt/C (0.05 mA cm^{-2}) and the Pt/SiC (0.03 mA cm^{-2}), indicating a high electrocatalytic activity of the Pt-Ti/SiC for the methanol oxidation reaction. The currents were also normalized by the Pt mass in Figure 3.4b. The Pt-Ti/SiC showed the highest mass-normalized current density ($327.84 \text{ mA cm}^{-2}$) at 0.7 V, which was much higher than Pt/C ($282.35 \text{ mA cm}^{-2}$) and Pt/SiC (42.25 mA cm^{-2}). It is noteworthy that the Pt-Ti/SiC possessed higher catalytic activity for the methanol oxidation reaction in comparison with the Pt/C, even though Pt nanoparticles dispersed similarly on both supports. Moreover, the electrochemical stability of the Pt-Ti/SiC was outstanding compared with the Pt supported on Vulcan XC-72 carbon black. The superior electrocatalytic performance of the Pt-Ti/SiC can be ascribed to the anchoring effect of the Ti coating on Pt nanoparticles and the high stability of the nano-SiC support.

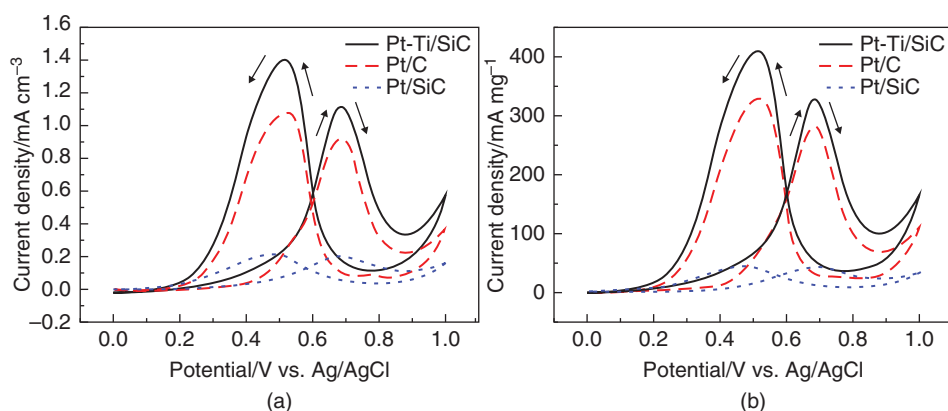


Figure 3.4 CV curves of Pt-Ti/SiC, Pt/C and Pt/SiC electrocatalysts in 1.0 M CH_3OH + 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} ; the currents were normalized by electrochemical active surface area (a) and the amount of loading of Pt (b) [26]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

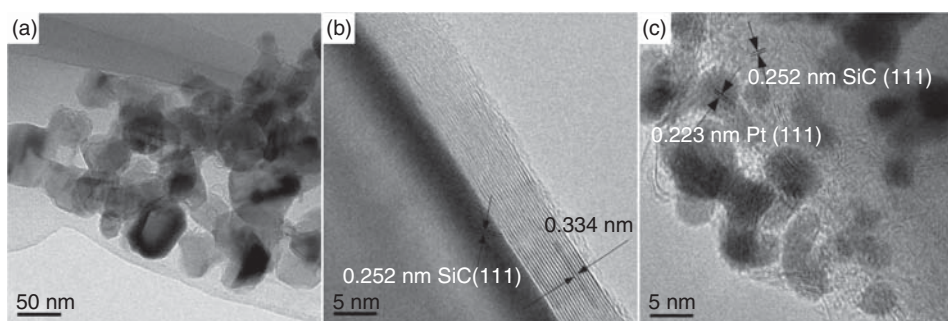


Figure 3.5 (a) TEM and (b) HRTEM images of the SiC@C powder, and (c) HRTEM image of Pt/SiC@C.

Zang et al. also used a core-shell structured SiC@C with a nanoscale SiC core covered by a graphitic carbon shell as support for Pt electrocatalyst in DMFCs, to achieve high durability and catalytic performance [27]. The SiC@C was prepared by graphitization of nano-SiC under a vacuum of 10^{-3} Pa at 1500°C (Figure 3.5a,b). The epitaxial growth carbon layer had high conductivity and an affinity for Pt catalyst metal, while the SiC core retained its high stability. The electrochemical results showed that the Pt/SiC@C (Figure 3.5c) electrocatalyst had much higher catalytic activities for methanol electro-oxidation and ORRs than the Pt/SiC. Moreover, the Pt/SiC@C electrocatalyst showed a greater stability in comparison with the traditional Pt/C. The superior electrocatalytic performances of Pt/SiC@C were ascribed to a high dispersion of Pt nanoparticles on the SiC@C support and a high stability of the SiC@C support in acid solution.

Xie et al. prepared a NiO/SiC composite by growing $\text{Ni}(\text{OH})_2$ hydrothermally on SiC. After calcination, $\text{Ni}(\text{OH})_2$ was converted to porous NiO flakes [28]. Then, CNT-Ni/SiC composites with three-dimensional hierarchical nanostructures were fabricated via in-situ pyrolysis of methane to grow CNTs on a novel flake-like NiO/SiC material (Figure 3.6) [28]. During the methane pyrolysis, NiO was converted in-situ to Ni

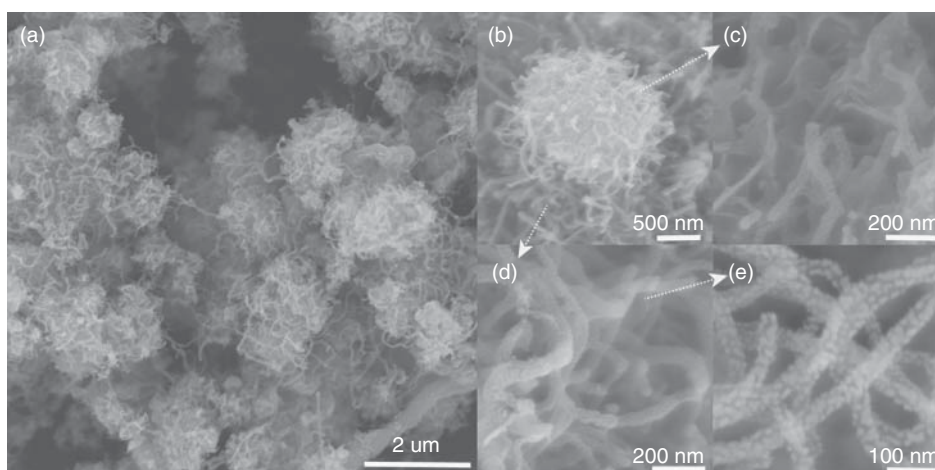


Figure 3.6 (a) Scanning electron microscopy (SEM) image of CNT-Ni/SiC prepared at pyrolysis temperature of 700°C ; (b) enlarged image of (a); (c–e) corresponding enlarged images of the area marked with an arrow [28]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

nanoparticles, which acted as the catalyst for growing CNTs. Due to the combination of Ni nanoparticles, in-situ grown CNTs and the SiC support, the CNT-Ni/SiC composites exhibit excellent catalytic activity and stability in electro-oxidation of methanol. The excellent electrochemical performance of the composite can be attributed to the uniform distribution and anchoring of Ni nanoparticles, and the good electrical conductivity of the network-like structure formed by CNTs and SiC. The catalytic activity shows a dependence on the pyrolysis temperature of methane, and a pyrolysis temperature of 700°C can lead to a mass activity of 10 A mg⁻¹ Ni, which is about 15 times higher than that of the catalyst obtained from methane pyrolysis at 500°C and about 4000 times higher than that of the original NiO/SiC catalyst.

The current bottleneck of fuel cells lies in the sluggish ORR on the cathode side due to the reaction rate being very slow, and the electrode polarization is quite serious (the potential of oxygen electrode is 200 mV lower than the thermodynamic value, even under open circuit conditions) [29, 30]. At low temperatures (<100°C), fuel cells usually require highly active electrocatalysts to achieve the desired power density [31]. Pt or its alloys are the best known ORR catalysts. However, the high cost of Pt and declining activity greatly hinder its large-scale commercialization [31]. In addition, another severe problem associated with DMFCs is that methanol gradually diffuses through the electrolyte membrane to reach the oxygen electrode [32]. This penetration not only loses part of the methanol fuel but also reduces the working potential of the oxygen electrode by formation of oxygen-methanol mixing potential, thus reducing the working efficiency of DMFCs [32]. Therefore, developing cathode catalysts with high catalytic activity, high stability, low cost, and resistance to methanol penetration remains a great challenge.

Based on density functional theory (DFT), Zhang et al. exploited the potentials of layered SiC sheets as a novel catalyst for ORR [33]. From the DFT results, it can be predicted that layered SiC sheets exhibit excellent ORR catalytic activity without CO poisoning, while the CO poisoning is the major drawback in conventional Pt-based catalysts [33]. Furthermore, the layered SiC sheets in alkaline media have better catalytic activity than a Pt (111) surface and have potential as a metal-free catalyst for ORR in fuel cells. Pan et al. prepared a shell/core structural N-doped carbon/silicon carbide (N-doped C/SiC) successively by a recarbonization and N doping process [34]. The first step was carried out on nano-SiC using an acid etching method. Nanoporous amorphous carbons were formed on the surface of SiC after acid etching, making it easy to adsorb N source and reduce the energy needed in the next step. The prepared N-doped C/SiC exhibited a high durability and good catalytic activity for ORR. Because of the excellent resistance to electrochemical oxidation of nano-SiC, Lv et al. applied it as catalyst support in proton exchange membrane (PEM) fuel cells to improve catalyst stability [35]. Homogeneously dispersed Pt nanoparticles were deposited on β -SiC (Pt/SiC) using an ethylene glycol reduction method. Furthermore, carbon was introduced into this Pt/SiC catalyst (Pt/SiC/C) to improve its electrocatalytic performance by increasing the electrical conductivity. The electrochemical stability of SiC was investigated and showed almost no changes in the redox region after oxidation for 48 hours at 1.20 V. Based on accelerated durability tests and high-resolution transmission electron microscopy (HRTEM), the electrochemical stability of Pt/SiC/C was remarkably enhanced compared with the Pt/C catalysts, which could be attributed to the excellent stability of the SiC support and the addition of high electrical conductivity carbon.

3.3 Dye-sensitized Solar Cells

Over the last few decades, photovoltaic (PV) production has had an annual growth rate of more than 20%, making it the world's fastest growing energy technology. However, present photovoltaic cells contribute only 0.04% to the world energy supply, leaving great room for improvement of existing technologies and the development of new systems [36–38]. A solar or photovoltaic (PV) cell is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. In 1954, Chapin et al. at Bell Lab demonstrated the first crystalline silicon solar cell with 6% efficiency [39]. However, the high production and environmental costs have prevented their widespread applications and prompted the search for environmentally friendly and low-cost solar cell alternatives. Dye-sensitized solar cells (DSSCs) have attracted broad interest as a promising low-cost solar cell technology since they were first reported by O'Regan and Grätzel, who applied nanocrystalline TiO_2 in DSSCs and achieved a high photoelectric conversion efficiency (PCE) of 7.9%, in 1991 [40].

The constituent components and fundamental processes of DSSCs are schematically illustrated in Figure 3.7. A typical DSSC consists of the following [36–45]: (i) a transparent glass sheet covered with a conductive or fluorine-doped tin oxide (FTO) layer is used as an anode substrate, which allows light to pass through as well as electron transport; (ii) a mesoporous oxide layer, such as TiO_2 , deposited on the substrate to transfer electrons; (iii) a monomolecular layer of dye adsorbed on the surface of the mesoporous oxide layer to harvest incident sunlight; (iv) an electrolyte for the recovery of dye and the regeneration of electrolyte itself during operation; (v) a counter electrode made of an indium tin oxide (ITO) or FTO conductive glass sheet coated with a catalyst to catalyze the redox couple regeneration reaction and collect electrons from the external circuit [36–45].

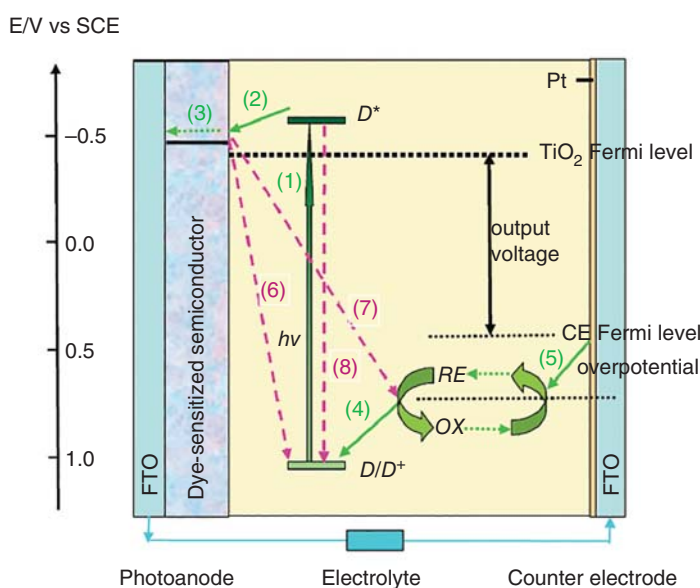


Figure 3.7 Fundamental processes and constituent components of dye-sensitized solar cells.

The fundamental processes of DSSCs include:

- (1) sensitizer photoexcitation to produce excited dye;
- (2) electron injection into the conduction band of metal oxide resulting in the production of oxidized dye;
- (3) electron transportation to the anode and flow to the counter electrode via an external circuit;
- (4) oxidized dye regeneration by accepting electrons from the reduced redox couple;
- (5) oxidized redox couple regeneration at the cathode by accepting electrons from the anode;
- (6) electron recombination by donating electrons to oxidized dye;
- (7) electron recombination by donating electrons to the oxidized redox couple;
- (8) relaxation of the excited dye to its ground state by a nonradiative decay process.

The counter electrode is an important component of DSSCs, since it undertakes three functions [45–49]:

- (i) It acts as a catalyst to promote the completion of the above processes (4) and (5). For the former, the oxidized dye is reduced by collecting electrons via ionic transport materials in solid state DSSCs; while for the latter, the oxidized redox couple is reduced by accepting electrons at the surface of the counter electrode.
- (ii) As a positive electrode of primary cells, it collects electrons from the external circuit and transmits them into the cell.
- (iii) As a mirror, it reflects the unabsorbed light from the cell back to the cell to enhance utilization of sunlight [50].

According to these basic functions, an optimal counter electrode should possess the following qualities as required: high catalytic activity, high conductivity, high reflectivity, low cost, high surface area, porous nature, optimum thickness, chemical, electrochemical and mechanical stability, chemical corrosion resistance, and an energy level that matches the potential of the redox couple electrolyte.

Tsai et al. deposited a composite film consisting of SiC nanoparticles and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (SiC-NPs/PEDOT:PSS) on a ITO substrate and used it as the counter electrode material for a DSSC [51]. SiC as the main electrochemically active material can sensitively and effectively respond to the I^-/I_3^- oxidation/reduction pair in DSSC. PEDOT:PSS can provide a rapid electron transfer channel. The content of SiC is optimized to be 5 wt% with respect to PEDOT:PSS to obtain the best power conversion efficiency (η) of 7.25% for the pertinent DSSC, which is slightly lower than that of the cell with a sputtered-Pt CE ($\eta = 7.98\%$). The SiC-NPs/PEDOT:PSS composite counter electrode can provide (i) good overall electrocatalytic ability (0.93 times that of Pt), (ii) a reasonable intrinsic heterogeneous rate constant (0.6 times that of Pt), (iii) large effective electrocatalytic surface area (1.6 times that of Pt), and (iv) high cell efficiency for its DSSC (0.91 times that of the cell with Pt), which thus offers great potential to replace the traditional expensive Pt CE for DSSCs.

Yun et al. synthesized a Pt/SiC nanocomposite with about 10 wt% Pt loading using a microwave-assisted method and used it as a counter electrode in DSSCs [52]. To measure the catalytic activities of the counter electrodes, they performed CV tests of SiC, Pt/SiC and a Pt electrode (Figure 3.8a) [52]. Two typical pairs of redox peaks are clearly

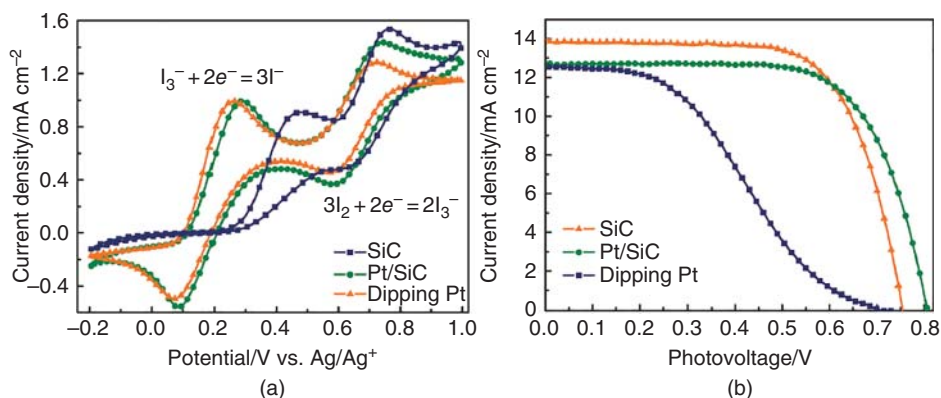


Figure 3.8 (a) CVs of SiC, Pt/SiC and Pt electrodes in a triiodide/iodide redox couple. The electrolyte solution is composed of 0.1 M LiClO₄, 10 mM LiI and 1 mM I₂ in acetonitrile. The scan rate is 0.01 V s⁻¹. Pt is used as a counter electrode and Ag/Ag⁺ works as a reference electrode. (b) J-V curves for DSSCs using different counter electrodes [52]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

observed for Pt/SiC and Pt but not for SiC. The relatively negative pair is attributed to the oxidation and redox of I^-/I_3^- , while the positive pair is attributed to the redox of I_2/I_3^- . The former directly affects the performance of DSSC, while the latter has only a slight effect. In contrast, it is clear that the profile and the location of the pairs of redox peaks of Pt and Pt/SiC are very similar, indicating that they should have similar counter electrode electrocatalytic activity. From the CV results we can conclude that a small amount of Pt (~10 wt%) loaded onto the SiC surface greatly improves its electrocatalytic activity.

To investigate the excellent catalytic activity of Pt/SiC, the photovoltaic performance of the DSSCs using Pt/SiC as a counter electrode was also evaluated. Figure 3.8b shows the photocurrent density-photovoltage (J-V) curves of DSSCs using the various counter electrodes [52]. The DSSC using Pt/SiC as a counter electrode shows an extraordinarily high power conversion efficiency of 7.07, because of its superior catalytic behavior, up to about 98.5% of the efficiency of the Pt counter electrode. The high fill factor (FF = 0.69) and high open-circuit voltage (Voc = 0.81 V) of DSSCs using Pt/SiC as a counter electrode are the main reasons for the notable power conversion efficiency values. Compared with Pt/SiC, DSSCs using SiC as a counter electrode have a remarkably low FF (0.37) and Voc (0.71 V), but only a slightly lower short-circuit current density (J_{sc} = 12.56 mA cm⁻²). This suggests that ~10 wt% Pt loaded onto the SiC surface can improve its electrocatalytic activity for I_3^- reduction, resulting in an increase in the high power conversion efficiency, matching well the photovoltaic performance of DSSCs based on Pt counter electrodes (7.18%). These results are in good agreement with the CV results. This work provides substantial support for developing low-cost Pt-loaded composite counter electrodes for DSSCs. Pt/SiC is expected to reduce the dependence on the Pt in DSSCs, while it can also be expected to be used in many chemical and electrochemical processes required to control the amount of Pt and prevent Pt nanoparticle aggregation.

3.4 Lithium-ion Batteries

Rechargeable LIBs are considered as the most promising energy storage system for a wide variety of applications owing to their long cycle life, low self-discharge, high energy density, high operating voltage, wide temperature window, no “memory effect”, and environmental friendliness [53–59]. LIBs utilize reversible electrochemical reactions to convert and store electrochemical energy. To achieve high-rate LIB performance, it is important to understand the Li-ion and electron transport pathways in the whole battery systems. Taking the discharging process as an example, Li-ion and electron transportation can be identified in the following steps (Figure 3.9) [53–59]:

- (1) The Li-ion and the electron disassociate from the anode material simultaneously and move in opposite directions via solid-state diffusion.
- (2) The Li-ion approaches the electrode/electrolyte interface, and diffuses through the electrolyte.
- (3) The electron, driven by the higher potential of the cathode side, passes through anode particles and their interfaces toward the current collector instead of riding into the electrolyte, and migrates via the external circuit to power a device.
- (4) The electron and the Li-ion enter the cathode materials concurrently via solid-state diffusion.

To meet the requirements for large-scale applications, from electric vehicles to smart electric grids, potential breakthroughs are needed to improve further the energy density and power performance of LIBs. Usually, electrode materials need to meet the following requirements [53–62]: (i) fast electrochemical reaction kinetics with Li-ions and electrons; (ii) high ionic diffusivity and electronic conductivity; (iii) short diffusion length for the electron and the ion; and (iv) robust structure for rapid insertion/removal of the Li-ion. The current choice of anode material for LIBs is graphite due to its long cycle life, abundant material supply, and relatively low cost. However, the graphite anode has the disadvantages of low energy density (375 mAh g^{-1}) and safety issues related to Li deposition. Therefore, the development of alternative suitable high-rate anode candidates with high capacity, ease of diffusion of Li-ions, along with good cycling life and free from safety concerns, is highly desirable. Diverse alternatives have sprung up, and

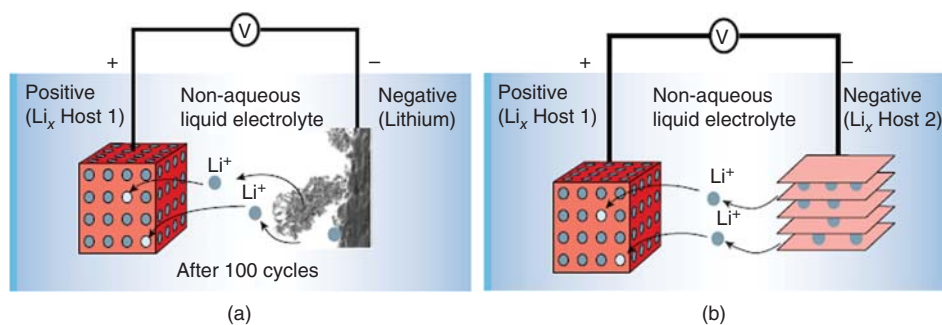


Figure 3.9 Schematic representation and operating principles of Li batteries [53]. (a) Rechargeable Li-metal battery (the picture of the dendrite growth at the Li surface was obtained directly from in-situ scanning electron microscopy measurements from *J. Power Sources* 1999, 81–82, 918–921). (b) Rechargeable Li-ion battery. Source: Reprinted with permission from Elsevier.

the reaction mechanisms between Li-ions and electrode materials can be distinguished as intercalation-, conversion-, and alloy-reactions. However, the expansion–shrinkage phenomenon always occurs during the charging/discharging process when metal, metal oxide or carbon materials are used as LIB anodes, resulting in structure collapse of the materials and then decrease in activity. SiC has good chemical stability and electrical conductivity, and could potentially be used as a structural-stable material for LIBs.

Zhang and Xu fabricated nanocrystalline SiC thin film electrodes by using modified plasma-enhanced chemical vapor deposition growth on stainless steel current collectors and employed them as anode materials for rechargeable LIBs [63]. The nanocrystalline SiC films consist of nanocrystalline 4H-SiC surrounded by amorphous SiC networks. A specific discharge capacity of 309 mA h g^{-1} of 150 nm thick nanocrystalline SiC anodes was found to be stable over 60 cycles at the C/10 (charge) rate and C/5 (discharge) rate. The effects of forming Li_4C layers in lithiation in enhancing the electrochemical behavior of nanocrystalline SiC film anodes are discussed here. Devi Kumari et al. prepared fine carbon layer covered SiC nanoparticles by a chemical vapor deposition method [64]. The material undergoes little structural change upon lithiation and delithiation, which should allow for extended cyclability. The composite delivered a reversible lithium insertion capacity of about 1200 mA h g^{-1} over 200 cycles and an excellent rate capability, holding much promise for nano-SiC as a next-generation anode material in LIBs.

In order to improve the cycle stability of silicon as an anode material, three aspects must be considered from a physicochemical standpoint. The first is controlling the reaction by the addition of an inactive material to the anode for the reaction with lithium ions. The second is to control the direct contact between the electrodes and electrolyte through structural modification of the silicon and formation of a solid electrolyte interphase layer on the silicon surface. The third is to relieve the rapid volume expansion by structural change and dispersing to add an inactive composite into the active silicon matrix [65–67]. Jeon and Lee synthesized a nano-scale silicon composite (nc-Si/SiC) with SiC crystal as a buffer matrix to the lithium ions using a plasma jet with direct current-arc discharge, to satisfy the requirements of the three aspects mentioned above [68]. The nc-Si/SiC composite particles comprised a nano-scale construction with crystalline phases of active silicon, highly disordered amorphous graphite and crystalline phases of β -SiC. Moreover, the nc-Si/SiC composite particles showed good coulombic efficiency in comparison with particles of high Si-Si bonding content due to the interplay of particles with a small proportion of carbon and the buffering effect against volume expansion by structural stabilization, and played a role as retarding media for the rapid electrochemical reactions of the SiC crystal against lithium [68]. Yang et al. showed that an anode consisting of an active silicon nanowire (Si NW), which is surrounded by a uniform graphene shell and comprises SiC nanocrystals, is capable of serving over 500 cycles in half-cells at a high lithium storage capacity of 1650 mA h g^{-1} [69]. In the anodes, the graphene shell provides a highly conductive path and prevents direct exposure of Si NWs to electrolytes, while the SiC nanocrystals may act as a rigid backbone to retain the integrity of the Si NW in the deformation process caused by repeated charging–discharging reactions, resulting in a stable cyclability.

Chen and coworkers synthesized a series of sandwich-like core-shell structure nanocomposites, such as SiC@Sn@C [70], SiC@Sb@C [71], SiC@Pb@C [72], and $\text{SiC@SnO}_2\text{@graphene}$ [73] (Figure 3.10). Such novel nanostructures can effectively buffer the mechanical stress and prevent the aggregation of the metal or metal oxide

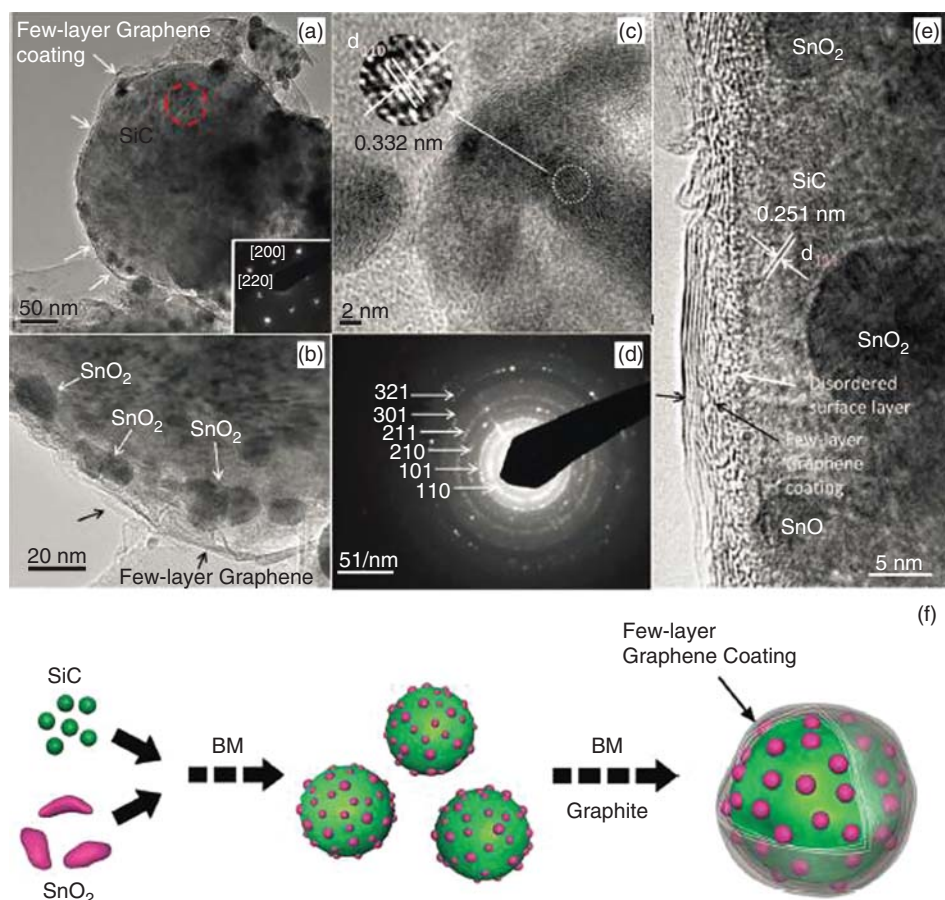


Figure 3.10 (a) TEM image of a SnO_2 -SiC/G particle and selected-area electron diffraction (SAED) pattern of SiC in the inset. (b) Magnified TEM image of the SnO_2 -SiC/G particle. (c) High-resolution TEM image of individual SnO_2 nanoparticles supported on the SiC surface. (d) The corresponding SAED pattern of SnO_2 nanoparticles. (e) High-resolution TEM image of the edge of the SnO_2 -SiC/G particle. (f) Schematic illustration of the preparation process of the SnO_2 -SiC/G nanocomposite [73]. Source: Reprinted with permission from World Scientific publishers, Copyright 2012.

nanolayer, and therefore improve the electrochemical utilization and cycling stability of the electroactive phase during a Li-storage reaction.

3.5 Supercapacitors

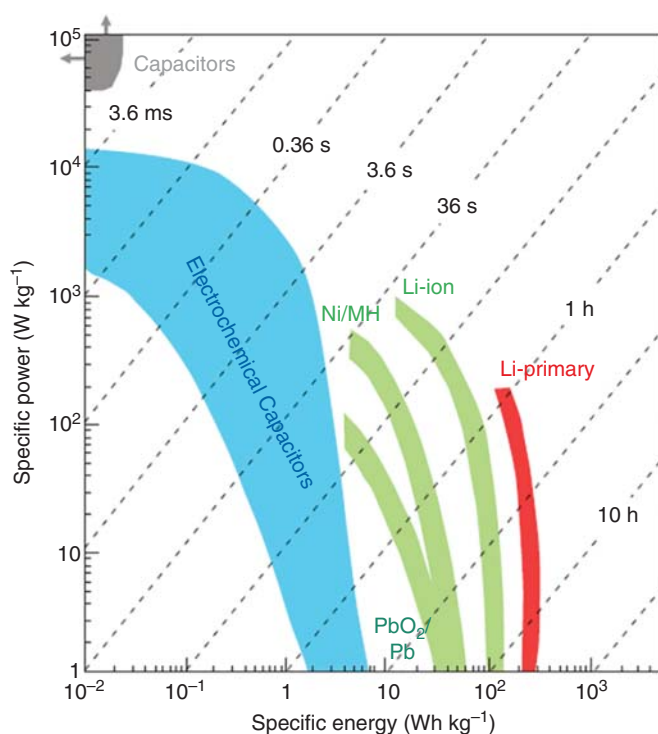
With a fast-growing market for portable electronic devices and the development of hybrid electric vehicles, there has been an ever-increasing and urgent demand for environmentally friendly high-power energy resources. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted much attention because of their pulse power supply, long cycle life (>100 000 cycles), simple principles, and high

dynamic of charge propagation [74–83]. Figure 3.11a shows the Ragone plot of power against energy density for different electrical energy storage systems, which are widely used in our daily lives [77]. Supercapacitors are expected to fill the gap between batteries and traditional capacitors due to their relatively high specific energy and power densities. Thus, supercapacitors play an important role in energy storage, showing the potential to complement batteries.

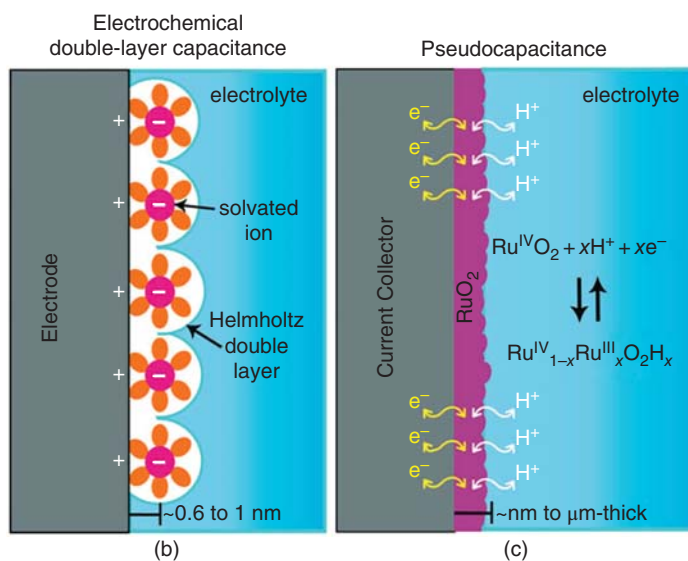
Generally, on the basis of the energy storage mechanism, supercapacitors can be classified into two categories [78]. One is the electrical double layer capacitor (EDLC), where the capacitance comes from the pure electrostatic charge accumulated at the electrode/electrolyte interface, therefore it is strongly dependent on the surface area of the electrode material accessible to the electrolyte ions (Figure 3.11b). Carbon-based materials, such as activated carbon, carbon aerogel, and carbon nanomaterials, are the most widely used electrodes because of their high specific surface area and outstanding electrical conductivity. Recently, EDLCs based on semiconductor nanomaterials (such as Si, SiC, TiN, TiO₂, etc.) have also received much attention. The other category is the pseudo-capacitor, in which fast and reversible faradic processes take place due to electroactive species (Figure 3.11c). Compared with EDLC, a pseudocapacitor normally has greater capacitance, exhibiting a much higher energy density. The materials used for pseudocapacitors mainly include metal oxides/nitrides/sulfides and conducting polymers. These two mechanisms can function simultaneously, depending on the nature of the electrode materials.

Alper et al. investigated the effectiveness of SiC nanowires as electrode material for micro-supercapacitors. SiC nanowires are grown on a SiC thin film coated with a thin Ni catalyst layer via a chemical vapor deposition route at 950°C [84]. A specific capacitance in the range of $\sim 240 \mu\text{F cm}^{-2}$ is demonstrated, which is comparable to the values recently reported for planar micro-supercapacitor electrodes. Charge discharge studies demonstrate that the SiC nanowires exhibit exceptional stability, with 95% capacitance retention after 2×10^5 charge/discharge cycles in an environmentally benign, aqueous electrolyte. They also reported Si nanowire-based micro-supercapacitor electrodes for an on-chip application using an environmentally benign aqueous electrolyte [85]. The Si nanowire, produced by low-temperature (50°C) electrochemical etching, is corroded during charge/discharge cycling in the aqueous environment, but upon coating with a SiC passivation layer, the corrosion is mitigated (Figure 3.12) [85]. The as-formed materials are in electrical contact with the substrate, requiring no additional current collector. The passivated nanowires achieve capacitance values up to $\sim 1.7 \text{ mF cm}^{-2}$ projected area (comparable to state-of-the-art, carbon-based micro-supercapacitor electrodes), exhibit robust cycling stability, and maintain capacitive behavior over a wide range of charge/discharge rates.

Gu et al. reported supercapacitor electrodes with excellent cycle stability, made of SiC nanowires grown on flexible carbon fabric [86]. A high areal capacitance of 23 mF cm^{-2} is achieved at a scan rate of 50 mV s^{-1} at room temperature, and capacitances increase with a rise in the working temperature. Owing to the excellent thermal stability of SiC nanowires and carbon fabric, no observable decrease of capacitance occurs at room temperature (20°C) after 105 cycles, which satisfies the demands of commercial applications. Further increasing the measurement temperature to 60°C, 90% of the initial capacitance is still retained after 105 cycles. The decreased Warburg diffusion element with the elevated temperature means that ions in the electrolyte can diffuse with less



(a)



(b)

(c)

Figure 3.11 (a) Ragone plot for various electrical energy storage devices [77]. Source: Reprinted with permission from World Scientific publishers, Copyright 2008. (b and c) Schematic of charge storage via the process of either (b) electrochemical double-layer capacitance or (c) pseudocapacitance [78]. Source: Reprinted with permission from Cambridge University Press, Copyright 2011.

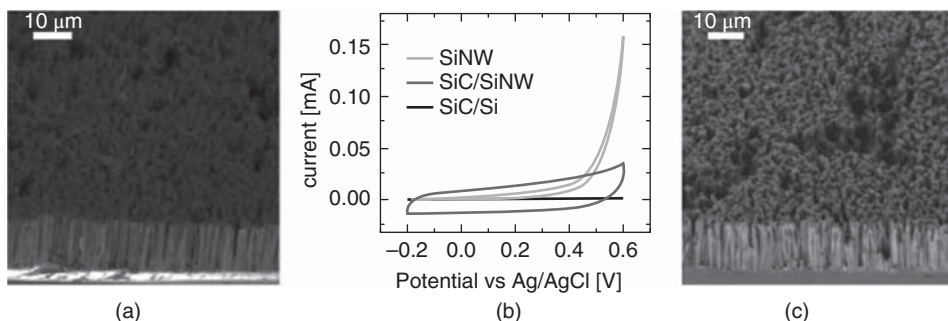


Figure 3.12 (a) Cross-sectional SEM micrograph of wet-etched Si nanowires. (b) Results of CV testing (1 M KCl at a 50 mV s^{-1} scan rate) for Si nanowire array, SiC-coated Si nanowire array and SiC-coated planar Si for comparison. (c) Cross-sectional SEM micrograph of SiC-coated Si nanowires from (a). Scale bar is 10 μm in both (a) and (c) [85]. Source: Reprinted with permission from AIP publishers, Copyright 2012.

resistance and reach the Helmholtz plane more easily, which results in a higher capacitance [87]. With an increase in temperature, the rate of parasitic reactions may be higher, leading to a decrease in leakage resistance [88–90].

Chen et al. synthesized 3C-SiC nanowire film on graphite paper by the carbothermal reduction method [91]. The high aspect ratio nanowires are flexible and intertwined with each other to form a porous network structure (Figure 3.13a–d). Electrochemical properties of SiC nanowire film on a graphite paper substrate are investigated by CV and galvanostatic charge–discharge tests in 0.1 M H_2SO_4 solution, revealing ideal capacitive behavior and low contact resistance (Figure 3.13e,f) [91]. The specific capacitances are 25.6, 37, 28, and 28 mF cm^{-2} at 0.2, 0.3, 0.5, and 2.0 A cm^{-2} , respectively. 3C-SiC nanowire film exhibits 100% discharge capacity retention after 2000 cycles, showing excellent capacity retention. The three-dimensional porous network structure of graphite paper-supported SiC nanowire film contributes to the high electrochemical performance.

Korenblit et al. obtained ordered mesoporous SiC-derived carbon by selective etching of SiC in a chlorine-containing environment, which offers a narrow distribution of micropores and one of the highest specific capacitances reported when used in EDLC with organic electrolytes [92]. The ordered mesoporous channels in the produced SiC-derived carbon serve as ion-highways and allow for very rapid ionic transport into the bulk of the SiC-derived carbon particles. The enhanced transport led to 85% capacitance retention at current densities up to 20 A g^{-1} . The ordered mesopores in the SiC precursor also allow the produced carbide-derived carbon (CDC) to exhibit a specific surface area up to 2430 $\text{m}^2 \text{g}^{-1}$ and a specific capacitance up to 170 F g^{-1} when tested in 1 M tetraethylammonium tetrafluoroborate solution in acetonitrile. Fiset et al. also synthesized high surface area SiC-derived carbon by chlorination of β -SiC with two different particle sizes (6 μm and 50 nm) showing different porosities with graphitic structure [93]. The particle size of the precursor affects the surface area and porosity of carbon. Furthermore, an additional heat treatment of the SiC-derived carbon with 50 nm particle size for 24 hours at 1000°C results in a collapse of the pore structure and reduces the surface area. The capacitive behaviors are investigated in H_2SO_4 and in tetraethylammonium tetrafluoroborate/acetonitrile. The electrochemical

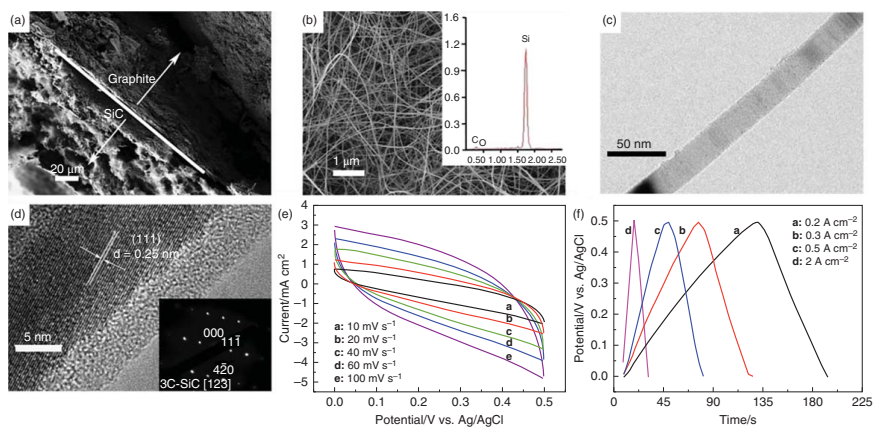


Figure 3.13 (a) SEM image of a lateral section of SiC nanowire film on graphite paper substrate; (b) SEM image of 3C-SiC nanostructures and (inset) representative EDS spectrum from the nanostructures; (c) representative TEM image of a SiC nanowire; (d) HRTEM image of SiC nanowire and (inset) the selected area electric diffraction pattern; (e) CVs of the graphite paper-supported SiC nanowire film at scanning rates of 10, 20, 40, 60, and 100 mV s^{-1} ; (f) charge-discharge curves of SiC nanowire film at different current densities.

performance of the SiC-derived carbon is influenced by the particle size, surface area, pore volume, and pore size distribution. The SiC-derived carbon exhibits capacitances in 1 M H_2SO_4 of up to 179 F g^{-1} and very stable charge–discharge performance over 5000 cycles. This study shows the crucial importance of ultra-micropores of less than 1 nm combined with nanosized particles for achieving high capacitance in aqueous electrolyte. Moreover, the graphitic degree at the surface of the Si-CDCs enhances considerably the rate capability and stability in both electrolytes.

Gu et al. prepared SiC nanowires on flexible carbon fabric by chemical vapor deposition, and then deposited $\text{Ni}(\text{OH})_2$ on the surface of SiC nanowires by electrochemical cathodic deposition [94]. The capacitive performance of the as-prepared electrode was calculated based on pure $\text{Ni}(\text{OH})_2$, and a very high rate capability is achieved. A high specific capacitance of 1724 F g^{-1} is found at 2 A g^{-1} , and the electrode still has a specific capacitance of 1412 F g^{-1} at an ultrahigh charging/discharging current density of 100 A g^{-1} . The excellent rate capability means great power characteristics for the supercapacitor electrode. With a charge/discharge rate of 100 A g^{-1} , a high power density of 27.5 kW kg^{-1} is achieved and the energy density still holds 59.4 Wh kg^{-1} . A solid-state supercapacitor based on SiC nanowires@ $\text{Ni}(\text{OH})_2$ on carbon fabric also shows good flexible and cycling properties.

Xie et al. prepared a novel C-Ni-SiC composite using sawtooth-like SiC as support and carbon as modified material by hydrothermal synthesis and thermochemical pyrolysis (Figure 3.14a) [95]. The electrochemical measurements were performed using a three-electrode beaker cell, consisting of a C-Ni-SiC working electrode, a platinum sheet counter electrode, and a saturated calomel reference electrode. CV and galvanostatic charge–discharge cycling were carried out in 1 M KOH solution at room temperature. Figure 3.14b shows the CV of C-Ni-SiC at a scan rate of 5 mV s^{-1} . In the figure, a pair of redox peaks with symmetrical shape can be observed, which result from the reversible process of insertion and extraction of OH^- anions. Figure 3.14c shows the galvanostatic charge–discharge curves of C-Ni-SiC at various current densities from 0 to 0.5 V. The corresponding specific capacitances are presented in Figure 3.14d. The C-Ni-SiC electrode exhibits a high value of 1780 F g^{-1} at a charge–discharge current density of 8.7 A g^{-1} . This value has achieved 85% of the theoretical specific capacitance of $\text{Ni}(\text{OH})_2$. Upon increase of current density, the specific capacitance displays a decrease possibly due to the insufficient Faradic redox reaction time under high discharge rates. It is demonstrated that the redox of $\text{Ni}(\text{II}) \leftrightarrow \text{Ni}(\text{III})$ is a diffusion-controlled process. Therefore, the reaction under a high discharge rate is restricted by the ion and electron transmission rates. It is noteworthy that a charge–discharge current density of 69.6 A g^{-1} is larger than most of the reported values. Moreover, at such a high discharge current, the specific capacitance of C-Ni-SiC still maintains 46% (812 F g^{-1}) of its original value.

Figure 3.14e shows the cyclic galvanostatic charge–discharge voltage profiles of the C-Ni-SiC electrode performed at 52.2 A g^{-1} (60 mA cm^{-2}). As shown in the inset, the curves for the first six and last six cycles almost keep the same shape and symmetry, indicating good reversibility. In the figure, the capacitance presents a decrease for the initial 300 cycles (retaining c. 89% of its initial value). Because the nickel is coated by carbon or filled in the bottom (top) of carbon nanotubes, the decrease of capacitance is possibly due to wettability issues, which will lead to a loss of electrical contact between these nanoparticles and the current. The subsequent increase in specific capacitance can be related to the improvement of wetting for the active particles.

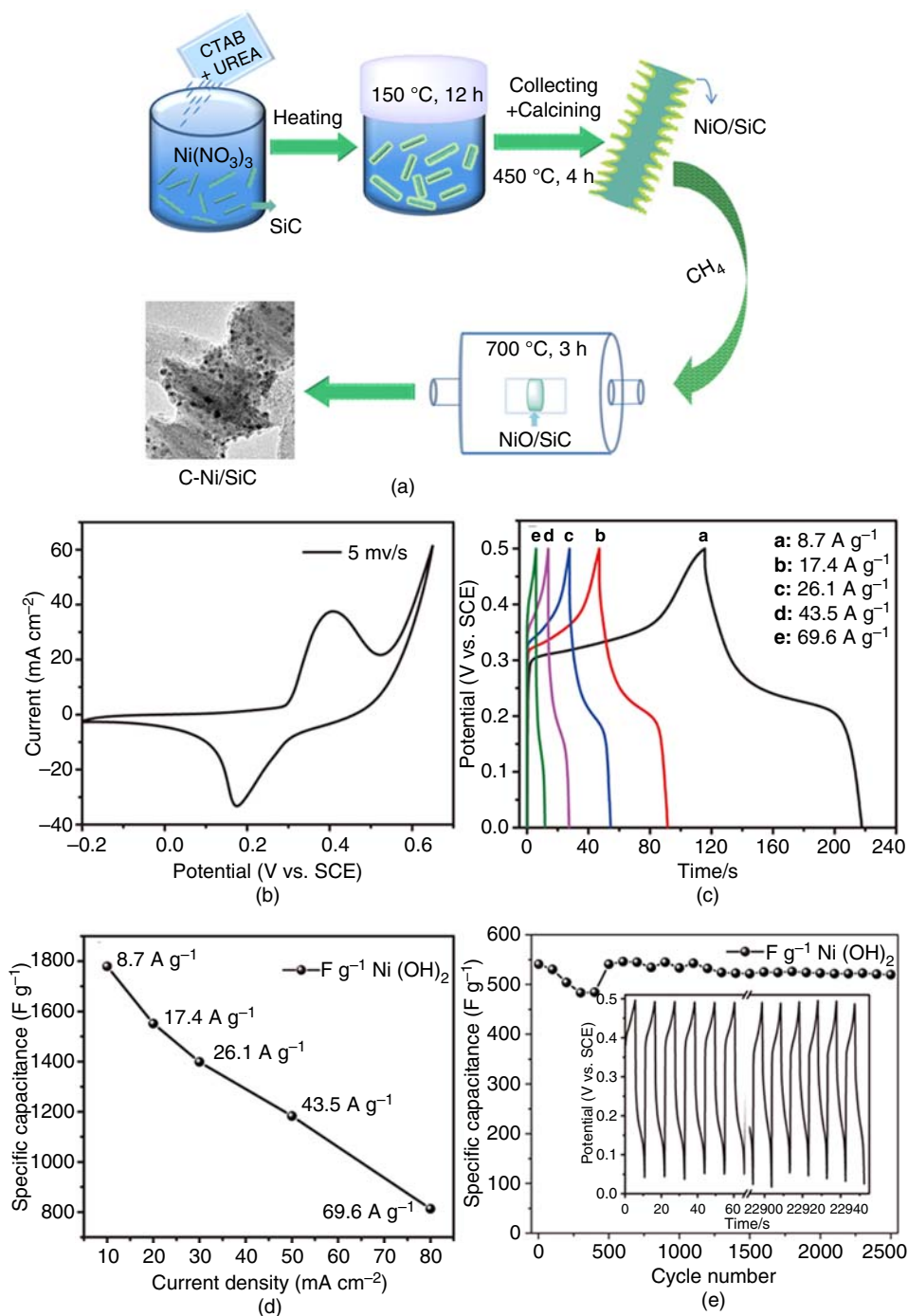


Figure 3.14 (a) Schematic diagram of the preparation of the C-Ni-SiC composite; (b) CV of C-Ni-SiC at a scan rate of 5 mV s^{-1} ; (c) charge–discharge voltage profiles of C-Ni-SiC at various current densities; (d) calculated capacitance as a function of current density according to the data in (c); (e) the capacitance as a function of cycle number at a constant current density of 52.2 A g^{-1} ; inset shows the galvanostatic charge–discharge cyclic curves of the first and last six cycles [95]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

Kim and Kim prepared SiC microsphere/birnessite-type MnO_x (SiC/B-MnO_x) composites by removal of a SiO_2 layer with redox deposition of birnessite-type MnO_x for supercapacitor electrode materials [96]. The capacitive properties of the as-prepared SiC/B-MnO_x electrodes were measured in a three-electrode system using 1 M $\text{Na}_2\text{SO}_4(\text{aq})$ as the electrolyte. The SiC/B-MnO_x [6] electrode, fabricated using a MnO_x/SiC feeding ratio of 6:1, displayed a specific capacitance of 251.3 F g^{-1} at 10 mV s^{-1} . Such excellent electrochemical performance is attributed to an increase in the electrical conductivity in the presence of SiC, an increase in the effective interfacial area between MnO_x and the electrolyte, and the contact area between MnO_x and SiC. The same group also prepared SiC-N-MnO_2 by packing growing MnO_2 nanoneedle crystal species in only one direction on the SiC surface [97]. Active carbon was oxidized by thermal treatment in order to introduce oxygen-containing functional groups. Owing to the high capacitance and excellent rate performance of SiC-N-MnO_2 (negative electrode) and active carbon (positive electrode), as well as the synergistic effects of the two electrodes, a constructed asymmetric supercapacitor exhibited superior electrochemical performance. The optimized asymmetric supercapacitor could be cycled reversibly in the voltage range from 0 to 1.9 V, and it exhibited a specific capacitance of 59.9 F g^{-1} at a scan rate of 2 mV s^{-1} and excellent energy density and power density (30.06 Wh kg^{-1} and 113.92 W kg^{-1} , respectively) with a specific capacitance loss of less than 3.1% after 1000 charge–discharge cycles, indicating excellent electrochemical stability. These encouraging results show great potential in terms of developing energy storage devices with high energy and power densities for practical applications.

SiC materials exhibit superior performance in many electrochemical fields because of their excellent electrical conductivity, stable physicochemical properties, and good biocompatibility. However, compared with carbon materials and other semiconductors, the application of SiC is still very limited. To improve the electrochemical performance and application of SiC materials, much research work is still needed, such as increasing the specific surface area of SiC materials, the controllability of surface modification by functional group, and the control synthesis of SiC nanostructures. et al.

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4

Carbon Nitride Fabrication and Its Water-Splitting Applications

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4.1 Introduction

With the rapid growth in global energy demand, extensive use of fossil fuels has brought severe issues, including the depletion of resources and environmental pollution, which make development of clean energy an increasingly urgent task. Hydrogen has been considered as potentially one of the most clean energy sources, with water as the only product, and has attracted a large amount of research input. Photocatalytic and photoelectrochemical water-splitting to hydrogen has an unparalleled advantage in terms of clean energy consumption compared with conventional hydrogen production methods (such as pyrolysis of fossil fuels and water electrolysis), due to the direct use of inexhaustible solar energy to drive the reaction. Since the first report of water-splitting on single crystal TiO_2 in 1972 [1], semiconductor compounds have been widely studied for photocatalytic hydrogen production over the past 40 years [2, 3]. However, most of the reported high-activity photocatalysts, such as TiO_2 , can only utilize the ultraviolet part that accounts for 4% of the total solar energy, resulting in low hydrogen production efficiency. Developing visible-light-active photocatalysts has become one of the most important tasks in working towards the effective use of the 43% of solar energy in the visible region.

The ideal visible light photocatalyst for water-splitting usually requires a bandgap of 2.0–3.0 eV (absorption edge of $\sim 400\text{--}600\text{ nm}$), where the conduction band (CB) energy level is more negative than $\phi_{\text{H}^+/\text{H}_2}$ and the valence band (VB) energy is more positive than $\phi_{\text{H}_2\text{O}/\text{O}_2}$ to ensure the thermodynamic driving force for hydrogen evolution and oxygen evolution reactions. The reported visible-active photocatalysts can be mainly divided into metal oxides, nitrides, and sulfides. In 2001, Zou et al. reported the $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ ($x = 0\text{--}0.2$) photocatalyst that pioneered the study of visible-light hydrogen production [4]. However, the efficiency of the oxide photocatalyst is still low in the visible region, and the bandgap manipulation range is limited. On the other hand, the VBs of sulfide and nitride are composed of S_{3p} and N_{2p} orbitals, which is more negative than O_{2p} and provides significantly smaller bandgap than that of oxide, and thus has a great advantage for visible-light hydrogen production. The nitride solid solution $\text{Ga}_{1-x}\text{Zn}_x\text{N}_{1-x}\text{O}_x$ ($x = 0.13$) reported by the Domen group shows a bandgap of only 2.58 eV, which greatly improves the hydrogen production efficiency

of visible light water-splitting [5]. However, these developed photocatalysts often require expensive elements and are usually prepared in harsh conditions. The most widely studied sulfide photocatalyst, CdS, has the highest quantum efficiency (QE) in the visible region after the loading of the appropriate cocatalysts [6]. However, CdS has high toxicity and low stability, thus limiting its range of applications.

Among the developed visible-light responsive photocatalysts, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is one of the most promising candidates owing to its suitable bandgap energy E_g of 2.7 eV, visible light absorption (absorption edge of ~ 470 nm), high abundance and low cost. It is commercially available or can easily be fabricated by polymerization of cheap molecules, such as urea [7]. On the other hand, carbon nitride is one of the oldest polymer materials prepared by chemists (Berzelius in ~ 1830), being first named “melon”. It was also demonstrated in 2006 that the visible light activity of TiO_2 after urea treatment was due to the formation of “melon” [8]. In 2009, Wang et al. first reported the photocatalytic H_2 production activity of $g\text{-C}_3\text{N}_4$ made from thermal condensation of urea, with detailed optical properties and electronic structure [9].

$g\text{-C}_3\text{N}_4$ -based photocatalysis has grown very rapidly in the years since Wang’s pioneering work in 2009 on visible-light photocatalytic water-splitting (with over 1300 publications and over 38 000 citations with “carbon nitride” and “hydrogen evolution” as the subjects: data from ISI Web of Science, May 20th, 2017). Since then, $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ -based composites have been widely used in photocatalytic water-splitting, CO_2 reduction, pollutant degradation, organic syntheses, and bacterial disinfection, which have been summarized in several reviews [7, 10–14]. However, grand challenges still exist for photocatalytic water-splitting applications, including the poor visible light absorption (< 470 nm), difficult charge separation, the requirement of sacrificial reagents, and poisoning by the produced H_2O_2 [15, 16]. The key issue of the $g\text{-C}_3\text{N}_4$ -based photocatalysts for H_2 production relies on optimizing the composition and structure to promote the efficiency to a practical application level.

This chapter will mainly focus on the recent progress in photocatalytic water-splitting for H_2 production using $g\text{-C}_3\text{N}_4$, specifically the effect of bandgap tuning, nanostructuring, and compositing. Besides traditional compositing strategies with metals and semiconductors, emphasis is also put on photocatalysis promoted by carbon materials, earth-abundant cocatalysts, and Z-scheme heterojunctions. Finally, the main themes are summarized and some perspectives are given regarding the main constraints of $g\text{-C}_3\text{N}_4$ -based photocatalysts in the process of water-splitting for H_2 production.

4.2 Preparation of Pristine $g\text{-C}_3\text{N}_4$

The structures of all known carbon nitride materials are based on one of two building blocks: the triazine (1,3,5-triazine, C_3N_3) and the heptazine (1,3,4,6,7,9,9b-heptaazaphenalene, C_6N_7) core, which are both aromatic molecules with an alternating arrangement of carbon and nitrogen atoms in the ring [7]. There are a series of triazine- and heptazine-based molecules that are important precursors and byproducts in the synthesis of higher molecular weight polymers and solids. Currently developed $g\text{-C}_3\text{N}_4$ photocatalysts are mainly based on tri-s-triazine units (Figure 4.1a), which is energetically favored and is the most stable phase among all phases of carbon nitride. The X-ray diffraction (XRD) patterns of $g\text{-C}_3\text{N}_4$ show two diffraction peaks at c. 27.4°

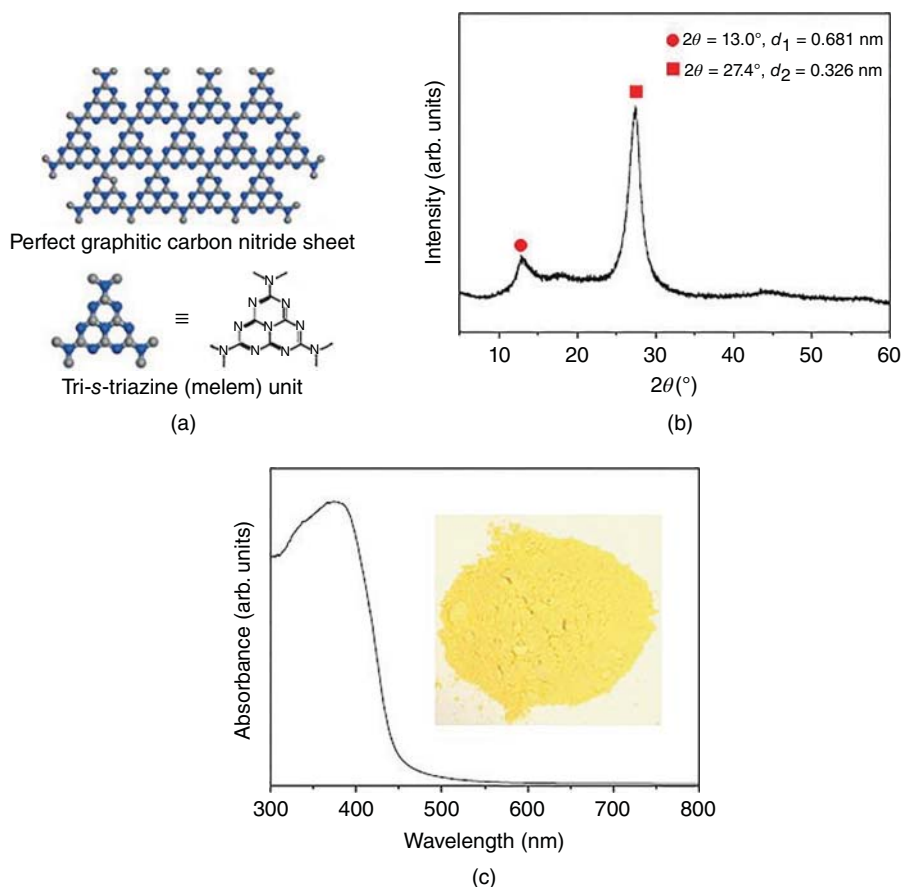


Figure 4.1 (a) Schematic structure diagram, (b) XRD pattern, and (c) UV-vis diffuse reflectance spectrum of the polymeric $g\text{-C}_3\text{N}_4$. Inset: Photograph of the photocatalyst. The XRD peak at 27.4° corresponds to an interplanar distance of 0.326 nm in a graphitic structure [9]. Source: Reprinted with permission from Springer Nature, Copyright 2009.

and c. 13.0° (Figure 4.1b) [9], among which the former can be indexed as the 002 peak characteristic for interlayer stacking of aromatic systems in graphitic materials, which is also the origin of the naming of “graphitic carbon nitride.”

As a polymeric semiconductor, $g\text{-C}_3\text{N}_4$ possesses a series of advantages for photocatalytic applications. For example, it has a bandgap of ~ 2.7 eV, with prominent visible absorption and a light yellow color (Figure 4.1c). More importantly, the CB and VB positions are located respectively at c. -1.1 eV and c. $+1.6$ eV vs a normal hydrogen electrode (NHE), which enables hydrogen and oxygen evolution for water-splitting. It was also demonstrated that $g\text{-C}_3\text{N}_4$ is thermally stable even in air up to 600°C , due to its aromatic C–N heterocyclic structure. $g\text{-C}_3\text{N}_4$ is also chemically stable in most solvents due to the strong van der Waal’s interactions between the layers. Other advantages include the high specific surface area, the composition from earth-abundant elements, and low fabrication costs.

4.2.1 Effect of Precursors

As a polymeric semiconductor, $g\text{-C}_3\text{N}_4$ can be easily fabricated by thermal polymerization of abundant nitrogen-rich molecular precursors, such as urea, thiourea, cyanamide, dicyandiamide, melamine, and other carbon- and nitrogen-containing molecular compounds or mixtures thereof (Figure 4.2), at certain temperatures [15]. It has been demonstrated that the polycondensation of these precursors formed a melon polymer from the melem units. The basic procedure is still similar to the originally reported method in 2009, with variations [9]. For instance, a certain amount of urea powder (or other precursor) was put into a crucible with a cover and then heated to temperatures around 500–550°C at relatively slow rates (such as 0.5–3°C min⁻¹) in a muffle furnace, and maintained at this temperature for 3 h. $g\text{-C}_3\text{N}_4$ was obtained after cooling down to room temperature. It worth mentioning that the precursor molecules go through stepwise conversion and polymerization, such as conversion of either cyanamide or ammonium dicyanamide to dicyandiamide, subsequent cyclization of cyanamide or dicyandiamide (or urea) to melamine, melamine dimerizes to form melam, melam rearranging to melem, and finally melem oligomers to melon (Figure 4.2) [15].

The structural manipulation of pristine $g\text{-C}_3\text{N}_4$ can be realized through variation of the precursors, and the annealing temperature and time. Tremendous efforts have contributed to the manipulation of the C/N ratio, bandgap, porosity, and defects, through exploring the synthetic conditions. Of the tested nitrogen-rich precursors, urea was found to be a superior precursor for high surface area $g\text{-C}_3\text{N}_4$, as it can produce very thin, sheet-like $g\text{-C}_3\text{N}_4$ [17, 18], while a small surface area was reported for melamine-derived $g\text{-C}_3\text{N}_4$ [19]. Besides precursors, the surface area of $g\text{-C}_3\text{N}_4$ also depends on the preparation conditions. The thickness of the $g\text{-C}_3\text{N}_4$ samples was reduced from 36 to 16 nm, along with a surface area increase from 31 to 288 m² g⁻¹, as the pyrolysis time of urea at 550°C (excluding heating-up time) increased from 0 to 240 min [18]. High surface area $g\text{-C}_3\text{N}_4$ can also be obtained by modifying the nitrogen-rich precursors using inorganic acids before thermal condensation. For example, the $g\text{-C}_3\text{N}_4$ prepared from sulfuric-acid-treated melamine shows higher surface area than that from untreated melamine, which may be due to the modification of melamine by sulfuric acid resulting in a different condensation process with suppressed sublimation of melamine [20]. Another strategy is post-synthesis heat treatment in a N₂ flow at elevated temperatures. For example, heating a mixture of melamine and sulfur (S₈) at 650°C for 2 h resulted in $g\text{-C}_3\text{N}_4$ materials with higher surface areas and narrower bandgaps [21]. Also it was observed that this sulfur-mediated synthesis did not bring sulfur doping, but just affected the polymerization process, acting as the solvent and chemical mediator.

4.2.2 Effect of Reaction Parameters

Since $g\text{-C}_3\text{N}_4$ is mainly prepared by thermal polymerization, the annealing parameters play a key role in the C/N stoichiometry, bandgap, surface groups and defects. Yan et al. found a C/N ratio increase from 0.721 to 0.742 and a bandgap decrease from 2.8 to 2.75 eV, as the heating temperature increased from 500 to 580°C with melamine in a semiclosed system [19]. The smaller C/N molar ratio, deviating from an ideal $g\text{-C}_3\text{N}_4$

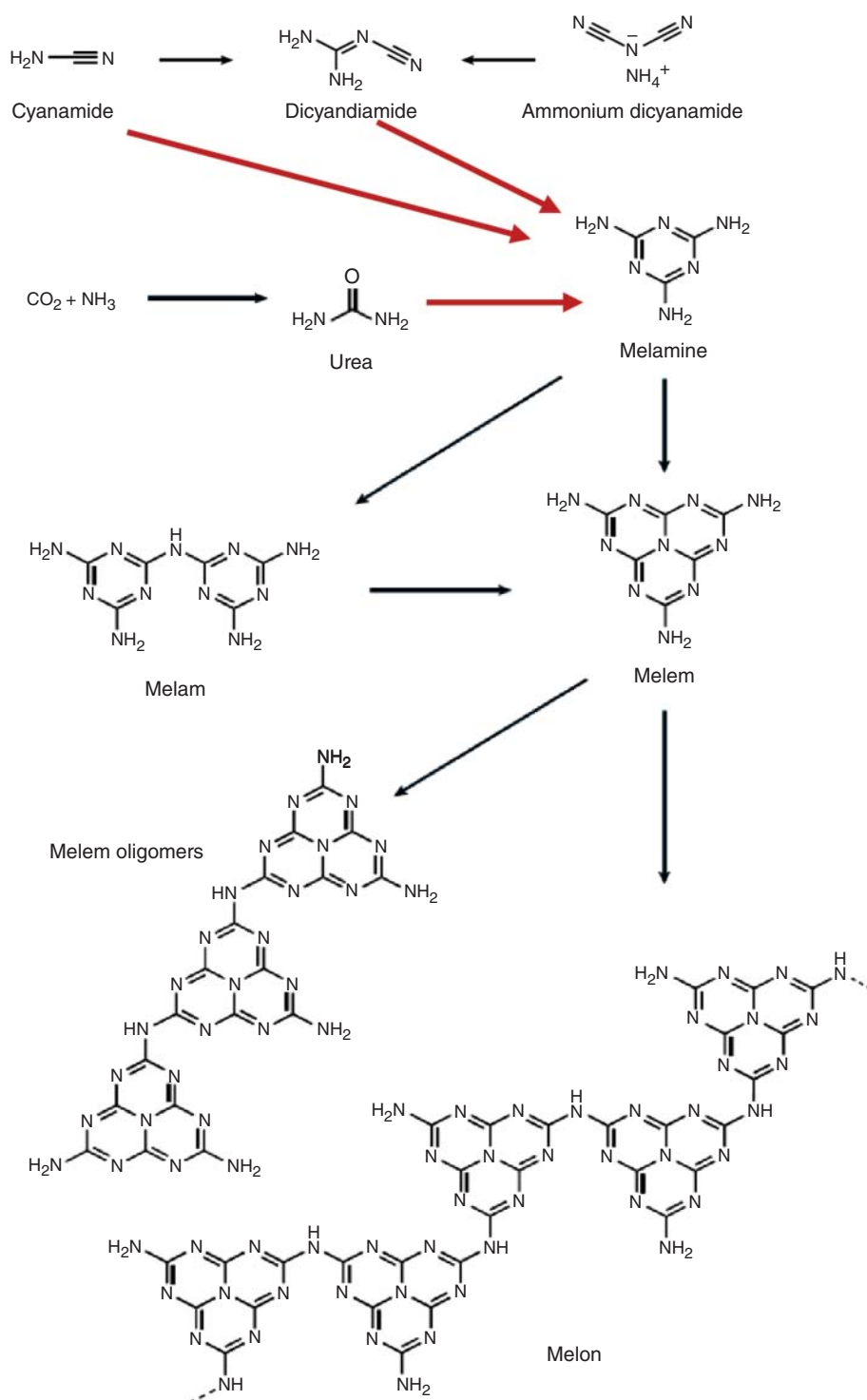


Figure 4.2 Precursor structure and synthetic pathways to carbon- and nitrogen-containing molecules and extended carbon nitride materials. The arrows indicate the heating transformation of the small precursor molecules before final thermal polymerization to $\text{g-C}_3\text{N}_4$ [15]. Source: Reprinted with permission from Springer Nature, Copyright 2017.

(0.75), may be due to the presence of amine groups with incomplete condensation. It worth mentioning that an ideal $g\text{-C}_3\text{N}_4$ with a stoichiometric C/N ratio of 0.75 is difficult to fabricate with commonly employed procedures. However, a suitable off-stoichiometry and trace amount of defects in $g\text{-C}_3\text{N}_4$ could be useful for bandgap manipulation as well as charge separation enhancement. Besides, the existing amine groups could partially increase the surface reactivity of $g\text{-C}_3\text{N}_4$, its interaction with target reactants, and also the coordination with incorporated or doped metal ions. Of course, it is widely reported that continuous decrease of the C/N ratio could be disadvantageous and should be avoided, even if narrow bandgaps are obtained, because the incomplete condensation often brings excessive defects that are harmful for charge migration and separation in photocatalysis. In the case of thiourea, Zhang et al. reported that an increase in heating temperature from 450 to 600°C is beneficial for polycondensation of $g\text{-C}_3\text{N}_4$ with improved structural interconnectivity and electron delocalization [22]; bandgaps of 2.71, 2.58 and 2.76 eV were obtained for the $g\text{-C}_3\text{N}_4$ prepared at 450, 550, and 650°C. The bandgap enlargement with further increase of annealing temperature to 650°C may result from the decomposition and size reduction of $g\text{-C}_3\text{N}_4$. However, this decomposition effect upon thermal annealing at elevated temperatures could be used for the controllable oxygen doping and also exfoliation of $g\text{-C}_3\text{N}_4$ into ultrathin nanosheets [23]; this will be discussed in Section 4.4.2.

4.3 Bandgap Engineering by Doping and Copolymerization

Pristine $g\text{-C}_3\text{N}_4$ has a bandgap around 2.7 eV, and thus limited visible-light absorption range, which is problematic for photocatalysis. Bandgap engineering of $g\text{-C}_3\text{N}_4$ plays a critical role in the control of light-absorption ability and redox potential to enhance photocatalytic performance. The main strategies to adjust the band structure of $g\text{-C}_3\text{N}_4$ are elemental doping and copolymerization [7, 24]. The bandgap can be determined by UV-vis absorption spectra. The VB energy position is usually measured with X-ray photoelectron spectroscopy (XPS) valence-band spectra or UV photoelectron spectroscopy (UPS). The CB energy can be obtained by combining VB and bandgap energies.

4.3.1 Doping of $g\text{-C}_3\text{N}_4$

Doping with nonmetallic or metallic elements is a commonly employed strategy for bandgap narrowing, as well as trap states introduction in semiconductor materials [25–28]. Doping of $g\text{-C}_3\text{N}_4$ is achieved by introducing additional elements and impurities into the $g\text{-C}_3\text{N}_4$ framework for tuning the optical, electronic, luminescent and other physical properties. Various atomic-level doping strategies have been developed to overcome the existing problems of $g\text{-C}_3\text{N}_4$, including nonmetal doping (such as C, B, O, S, P, Br, and I) [29–35], metal doping (K, V and Fe) [36–38] and metal/nonmetal co-doping [39, 40].

4.3.1.1 C-doping and N-vacancy

N-vacancy defects play an important role in the electronic structure, the charge separation and recombination properties, and subsequently the photocatalytic activity of $g\text{-C}_3\text{N}_4$ photocatalysts. Several methods have been developed for the introduction of

N-vacancies into $g\text{-C}_3\text{N}_4$, such as controlling the polycondensation temperature [32], hydrogen reduction [33], hydrothermal treatment using ammonium thiosulfate as an oxidant [41], and alkali-assisted polycondensation [42]. The Liu group reported a series of $g\text{-C}_3\text{N}_4$ photocatalysts with introduced nitrogen vacancies [32, 33]. The overall photocatalytic activity of the $g\text{-C}_3\text{N}_4$ was remarkably improved, including the ability to generate OH radicals, photodecomposition of Rhodamine B, and photocatalytic hydrogen evolution under both UV-visible and visible light. Steady-state and time-resolved photoluminescence (PL) spectra indicate that the radiative recombination of electrons and holes in $g\text{-C}_3\text{N}_4$ is greatly suppressed as a result of the decreased short-lived charge carriers and increased long-lived charge carriers, due to the existence of N-vacancies [32]. Recently, Yu et al. reported a simple alkali-assisted strategy to prepare nitrogen-defective $g\text{-C}_3\text{N}_x$ for bandgap engineering (Figure 4.3) [42]. Two kinds of nitrogen defects (bulk and surface) were selectively in-situ introduced during the thermal polymerization of urea, melamine, or thiourea, which redshifted the $g\text{-C}_3\text{N}_x$ absorption edge and could be easily tuned by the KOH:urea ratio. The obtained $g\text{-C}_3\text{N}_x$ products possess tunable band structures controlled by cyano groups in the bulk and surface N vacancies, and are

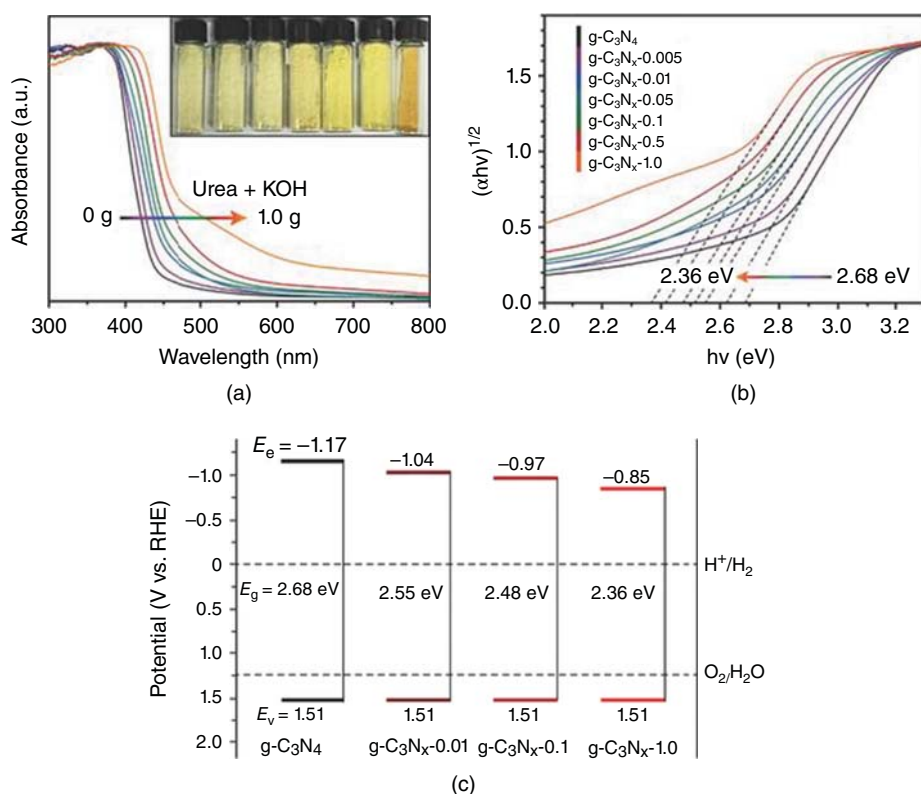


Figure 4.3 (a) UV-vis absorption spectra and (b) plots of transformed Kubelka–Munk function versus photon energy, for $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_x$ prepared using urea as precursor with different amounts of KOH (ranging from 0 to 1.0 g in 10 g of urea). Inset in (a) shows the corresponding digital photograph of samples. (c) Band energy alignments for pristine $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_x$ [42]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2017.

able to harvest visible light and separate photoexcited charge carriers more efficiently than pristine $g\text{-C}_3\text{N}_4$. KOH addition during the synthesis of $g\text{-C}_3\text{N}_x$ lowers the concentration of $\text{N}=\text{H}$ groups and introduces $\text{-C}\equiv\text{N}$ groups. The organic elemental analysis (OEA) indicated that the bulk N/C ratio for all $g\text{-C}_3\text{N}_x$ samples was similar to that of pristine $g\text{-C}_3\text{N}_4$, so the formation of cyano groups does not result in N loss in the bulk. However, XPS measurement, with a small surface penetration length, showed a progressive decrease of N/C ratio (from 1.35 to 0.85) on the surface of $g\text{-C}_3\text{N}_x$ with increasing KOH usage, suggesting the introduction of surface N defects. The $g\text{-C}_3\text{N}_x\text{-0.01}$ sample was the most active, affording a H_2 evolution rate of $0.440 \text{ mmol g}^{-1} \text{ h}^{-1}$ without Pt, and $6.9 \text{ mmol g}^{-1} \text{ h}^{-1}$ with Pt, in 25 vol% aqueous lactic acid solution under visible-light irradiation ($\lambda > 420 \text{ nm}$), both of which were approximately twice that of pristine $g\text{-C}_3\text{N}_4$. However, the amount of N defects has to be controlled at a relatively low level for photocatalytic H_2 production. The enhanced photocatalytic activities of $g\text{-C}_3\text{N}_x\text{-0.005}$ and $g\text{-C}_3\text{N}_x\text{-0.01}$ can be attributed to the increased visible-light absorption and improved charge separation brought by N defects [42].

4.3.1.2 S-doping

Liu et al. reported sulfur-doped $g\text{-C}_3\text{N}_4$ ($\text{C}_3\text{N}_{4-x}\text{S}_x$) with a unique electronic structure that displays an increased VB width in combination with an elevated CB minimum and a slightly reduced absorbance [29]. The $\text{C}_3\text{N}_{4-x}\text{S}_x$ shows a photoreactivity of H_2 evolution 7.2 and 8.0 times higher than for $g\text{-C}_3\text{N}_4$ under $\lambda > 300$ and 420 nm , respectively. The complete oxidation process of phenol under visible illumination ($\lambda > 400 \text{ nm}$) was also observed for $\text{C}_3\text{N}_{4-x}\text{S}_x$, which is not possible for $g\text{-C}_3\text{N}_4$. The unique electronic structure and subsequently excellent photoreactivity of $\text{C}_3\text{N}_{4-x}\text{S}_x$ is attributed to the homogeneous substitution of sulfur for lattice nitrogen and a concomitant quantum confinement effect. Hong et al. also reported the in-situ sulfur-doped mesoporous $g\text{-C}_3\text{N}_4$ from thiourea, using SiO_2 nanoparticles as the hard template [31]. The doped sulfur was proposed to substitute carbon from XPS analysis. The resultant product has a high surface area, mesopores of $10\text{--}20 \text{ nm}$, a downshift of 0.25 eV in its CB, and a much lower density of defects. Consequently, the sulfur-doped mesoporous $g\text{-C}_3\text{N}_4$ shows 30 times higher activity than the native $g\text{-C}_3\text{N}_4$ for photocatalytic H_2 evolution, with a high quantum efficiency of 5.8% at 440 nm .

4.3.1.3 P-doping

Zhu et al. reported the phosphorus-doped $g\text{-C}_3\text{N}_4$ nanostructured flowers by a co-condensation method without any templates [43]. The porous structure, together with the P-doping, promotes light trapping, mass transfer, and charge separation, which result in largely improved photocatalytic hydrogen evolution activity under visible light irradiation. Sometimes the doping, nanostructuring and/or compositing can be achieved simultaneously. Guo et al. further reported the simultaneous P-doping and nanostructuring by a supramolecular precursor method, where P-doped hexagonal tubular $g\text{-C}_3\text{N}_4$ with a layered stacking structure was obtained from a hexagonal rod-like precursor (Figure 4.4) [44]. The tubular structure was formed through phosphoric acid-assisted partial hydrolysis of melamine into cyanuric acid, and subsequently the formation of melamine–cyanuric acid single crystal supramolecular rods. The tubular structure contributes to the enhancement of photocatalytic H_2 production by increasing light scattering and providing more active sites. On the other hand,

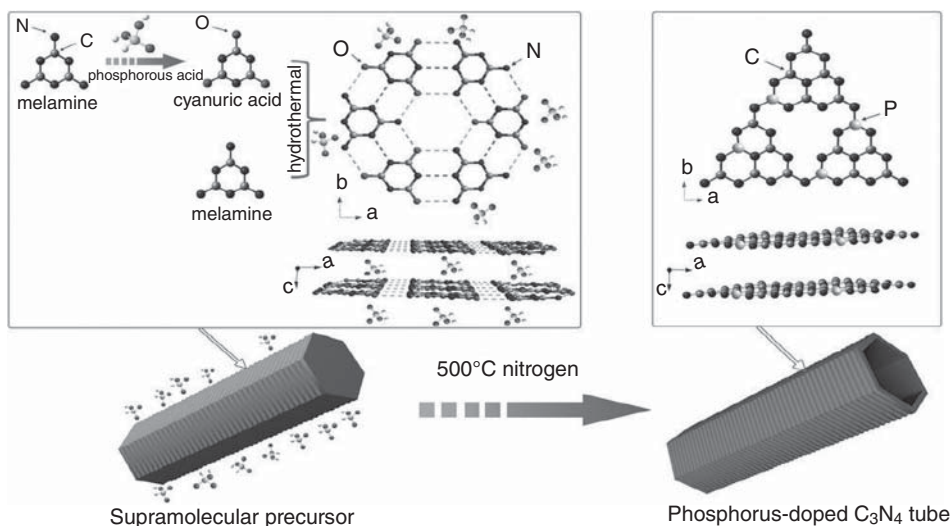


Figure 4.4 The formation process of phosphorus-doped tubular g-C₃N₄ with simultaneous P-doping and nanostructuring [44]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

P-doping reduces the bandgap to 2.55 eV and increases electric conductivity compared with pristine g-C₃N₄. As a result, a high hydrogen evolution rate of 67 mmol h⁻¹ (0.1 g catalyst, $\lambda > 420$ nm) using sacrificial agents was obtained, with a high apparent quantum efficiency (AQE) of 5.68% at 420 nm.

4.3.1.4 Metal doping

Wang et al. first reported that the electronic and optical functions of g-C₃N₄ can be easily modified by the inclusion of Fe, where the metal species reduces the bandgap and expands the light absorption of the material, while keeping a sufficient overpotential for oxidation reactions [36]. Yue et al. developed a simple soft-chemical method for Zn doping of g-C₃N₄, resulting in a significant red shift in the absorption edge of Zn/g-C₃N₄ and a 10 times higher hydrogen evolution rate for 10%-Zn/g-C₃N₄ sample compared with pure g-C₃N₄, with an AQE of 3.2% at 420 nm [45]. Polymetal or non-metal/metal co-doping of g-C₃N₄ was also explored for bandgap engineering, such as Fe and Pd co-doped g-C₃N₄ [46], as well as Fe and P co-doped g-C₃N₄ [40], with increased defect sites and superior charge carrier properties.

4.3.2 Copolymerization of g-C₃N₄

As mentioned above, pristine g-C₃N₄ suffers from limited visible-light absorption with a bandgap around 2.7 eV and also fast charge recombination. In addition to the atomic-level doping strategies introduced above, molecular-level copolymerization represents another important class of strategy for the structural modification of g-C₃N₄. Conjugated polymers with fully π -conjugated systems emerged as a promising class of heterogeneous photocatalysts for hydrogen production, owing to their robustness, nontoxicity, and visible-light activity [24]. The π -conjugation of g-C₃N₄

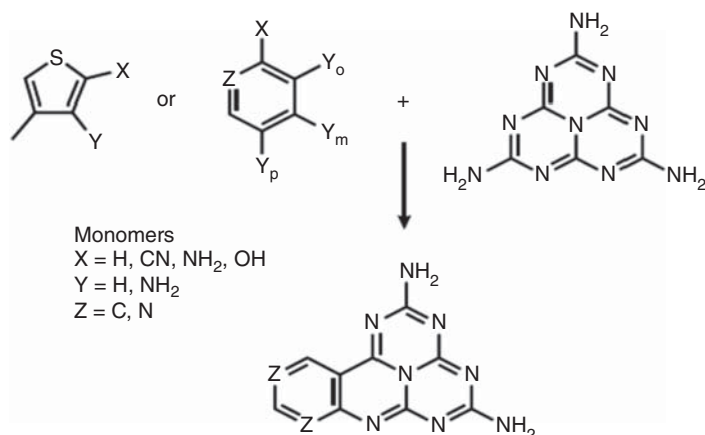


Figure 4.5 Representative molecular structure of the organic co-monomers suitable for copolymerization with the N-rich precursors for preparation of modified $\text{g-C}_3\text{N}_4$ materials [15]. Source: Reprinted with permission from Springer Nature, Copyright 2017.

can be enhanced by introducing structure-matching co-monomers into the molecular structure of melon that can be further co-polymerized or crosslinked, which has a dramatic effect on their electronic structure and subsequent optical and photocatalytic properties. The organic co-monomers can be classified into π -conjugated aromatic molecules (such as benzene and derivatives), π -rich aromatic molecules (such as thiophene and derivatives), and π -deficient aromatic molecules (such as pyridine-based motifs) (Figure 4.5). Wang's group first reported that the optical absorption of $\text{g-C}_3\text{N}_4$ semiconductor materials is extendable to about 750 nm by copolymerization with organic monomers like barbituric acid. The samples were synthesized by mixing dicyandiamide with different amounts of barbituric acid in water, and the resultant solids after removing water were calcined at 550°C for 4 h in air to obtain the final products [47]. The same group further synthesized organic molecules bearing amino and/or cyano functionalities to integrate them directly into $\text{g-C}_3\text{N}_4$, which allows ample choice of organic co-monomers and provides a promising strategy for manipulating electronic structure and optical properties of the $\text{g-C}_3\text{N}_4$ -based photocatalysts [48]. Among these works, $\text{g-C}_3\text{N}_4$ with introduced phenylene groups by co-polymerization of 2-aminobenzonitrile with dicyandiamide shows a prominent red shift of absorption up to 700 nm for $\text{g-C}_3\text{N}_4$ with 0.5 g of 2-aminobenzonitrile (into 3 g of dicyandiamide), which shows a largely improved photocatalytic hydrogen evolution rate ($147 \mu\text{mol h}^{-1}$ at $\lambda > 420 \text{ nm}$) compared with pristine $\text{g-C}_3\text{N}_4$ ($18 \mu\text{mol h}^{-1}$). Recently, lots of organic conjugated polymers with promising properties have been fabricated for photocatalytic H_2 evolution, where the AQE has been increased from 0.015 to 38.8% at $\lambda = 420 \text{ nm}$ after rational structure design [24]. It clearly indicates that copolymerization represents one of the most promising strategies for $\text{g-C}_3\text{N}_4$ modification due to the unique advantage of molecular-level covalent structure and property modification to advance the photocatalytic reactions.

In summary, atomic-level doping by nonmetal or metal ions of $\text{g-C}_3\text{N}_4$ can effectively reduce the bandgap to increase visible light absorption, and also introduce defect states that can enhance charge separation under proper control (Figure 4.6). Molecular doping by copolymerization provides the precise structure manipulation for both the tuning of

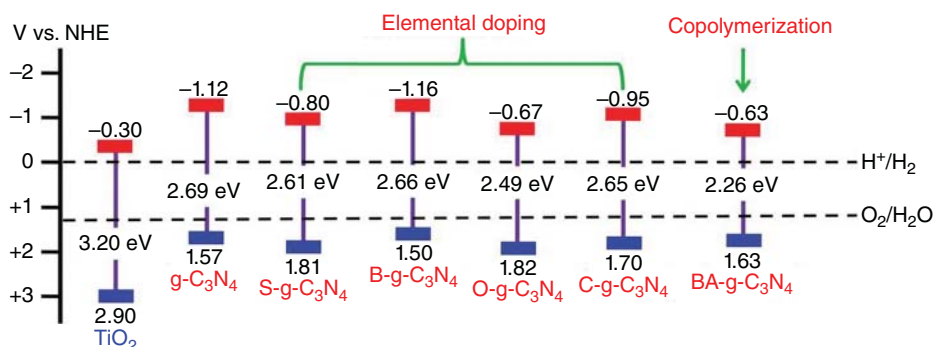


Figure 4.6 Summarized schematic band structures of typical g-C₃N₄ materials by doping and copolymerization in comparison with TiO₂ [11]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2015.

bandgap and band energy levels. Additionally, doping and copolymerization can also bring morphology and porosity change that provides extra enhancement for photocatalytic H₂ production activity. There is a great potential for doping and copolymerization strategies for the design of more effective visible-light photocatalysts, by synergistically tuning the microstructure, electronic structure and density of defect states.

4.4 Nanostructure Engineering of g-C₃N₄

Nanostructure engineering plays a critical role in the control of morphology, crystallinity, surface area and electron–hole separation efficiency of g-C₃N₄. Tremendous efforts have been made to explore nanostructuring strategies, with an increasing number of publications in recent years, including hard templating methods, soft templating methods, template-free methods, supramolecular preorganization of monomers, exfoliation strategies, and top-down etching methods [7, 49]. The developed g-C₃N₄ nanostructures are roughly divided into three classes: ordered mesoporous nanostructures, 2D nanosheets, and 0D quantum dots (QDs).

4.4.1 Ordered Mesoporous Nanostructures of g-C₃N₄

The porous structure of pristine g-C₃N₄ prepared with certain precursors (such as urea) plays a critical role for photocatalysis in terms of the high surface area and abundant active sites. More importantly, further nanostructure engineering toward 3D ordered hollow spaces or channels can provide extra advantages for light trapping effects and spatial separation of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) reaction sites [49]. Templating is a well-developed, promising strategy for modifying the morphology and porosity of semiconductor materials, giving them greater surface areas, more active sites, and more efficient charge separation [50].

4.4.1.1 Hard Templating Methods

Hard templating methods for preparation of g-C₃N₄ usually involve three steps: filling or coating a rigid template with a precursor, converting that precursor to g-C₃N₄, and removing the template to get a replica with an ordered porous structure. Silica materials

are the most frequently used templates [51]. The Wang group reported the synthesis of g-C₃N₄ hollow nanospheres sized in the optical range using silica nanoparticles as templates [52]. These hollow spheres with tunable shell thickness can function as both light-harvesting antennae and nanostructured scaffolds that improve photocatalytic activity, with a high hydrogen evolution AQE of 7.5%. This can be attributed to the advantages of the inner optical reflection and improved structure condensation that together provide a remarkably enhanced photocatalytic activity. Furthermore, it provides more opportunities to use hybrid nanoarchitectures for constructing highly organized photosynthetic systems, such as space-separated deposition of the cocatalysts or other semiconductors onto the exterior/interior surfaces [53]. This will improve the charge separation and surface redox reactions toward the efficient utilization of solar energy. Based on this design, the same group further developed a simple approach for specifically depositing Pt and Co₃O₄ nanoparticles onto the interior and exterior surfaces, forming Janus structured hollow g-C₃N₄ spheres by using mesoporous silica as the template (Figure 4.7) [53]. This design allows spatially separated oxidation and reduction centers for the evolution of H₂ and O₂, and also favors the controlled migration of the electrons and holes on the Janus surfaces, which prevents the charge recombination and the reverse reaction of water-splitting. The Janus structured Co₃O₄/HCNS/Pt composites not only significantly improved the photocatalytic H₂ and O₂ evolution with sacrificial reagents, but also the activity of overall water-splitting into H₂ (3.1 μmol h⁻¹) and O₂ (1.5 μmol h⁻¹) without sacrificial reagents.

Numerous silica templates have been used, such as monodispersed silica nanospheres [54, 55], 3D opal structure from self-assembly of monodispersed spheres [56], and mesoporous silica molecular sieves with interconnected channels (such as SBA 15) [57], from which hollow spheres, inverted opals, and 1D mesoporous structures of g-C₃N₄ have been prepared, respectively. Moreover, a simple variation of hard templating is the sol-gel approach, in which a silica precursor (tetra-ethylorthosilicate, TEOS) and a molecular precursor (such as cyanamide) are mixed and thermally condensed [58]. Selective removal of the in-situ formed silica template gives various mesoporous g-C₃N₄ with outstanding hydrogen evolution activity up to 616 μmol h⁻¹, 20 times higher than bulk g-C₃N₄.

Although huge progress has been achieved on the nanostructuring of g-C₃N₄ by various hard templating methods, an inherent drawback still limits their potential for wide application: the time-consuming process of template removal that often requires the involvement of toxic hydrofluoric acid (HF) or NH₄HF₂. In comparison, various soft templating and template-free methods offer potentially greener alternatives for the nanostructure engineering of g-C₃N₄.

4.4.1.2 Soft Templating Methods

The soft templates, including surfactants, amphiphilic block copolymers and ionic liquids, have been used as structure-directing agents to introduce porosity into the g-C₃N₄ framework [59–61]. For example, Wang et al. reported mesoporous g-C₃N₄ by polymerization reaction of dicyandiamide with various soft templates, such as nonionic surfactants, amphiphilic block polymers (such as Triton X-100, P123, F127, Brij30, Brij58, and Brij76), and also ionic liquids (such as 1-butyl-3-methylimidazolium dicyanamide (BmimDCN), 1-butyl-3-methylimidazolium chloride (BmimCl), and 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆)) [60]. Some of the

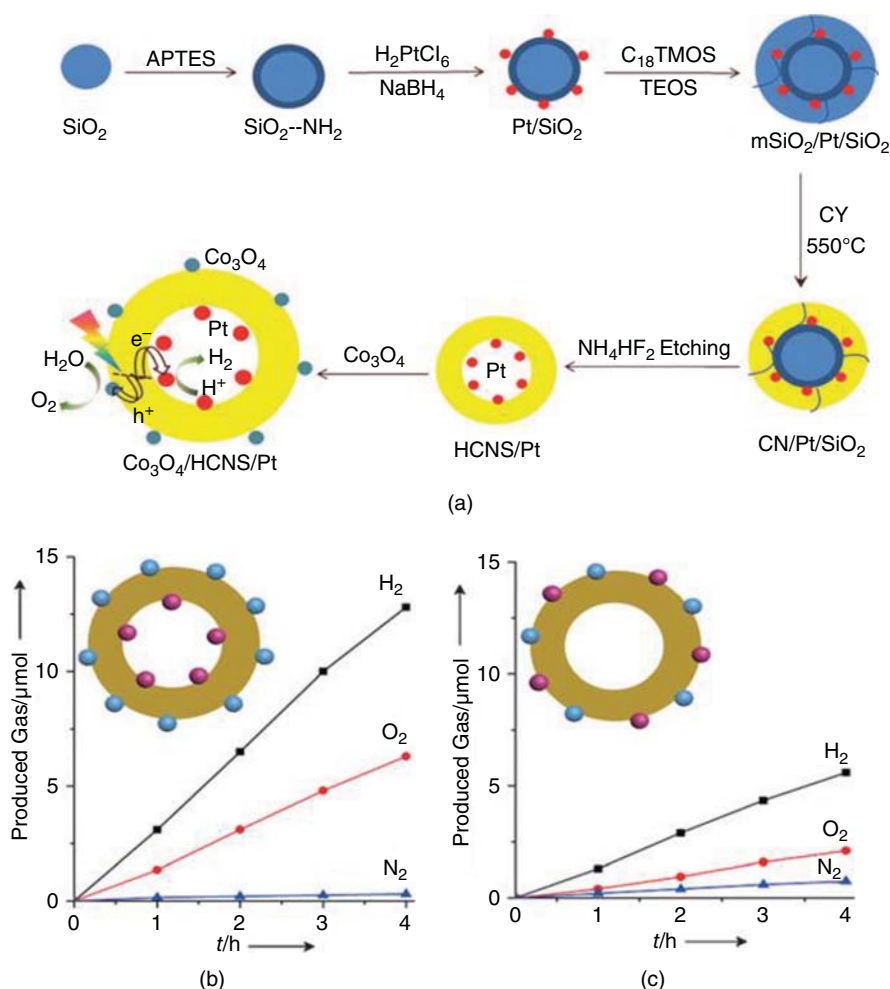


Figure 4.7 (a) Schematic illustration of the preparation of $\text{Co}_3\text{O}_4/\text{HCNS}/\text{Pt}$ composites with spatially separated Pt and Co_3O_4 cocatalysts deposited on the interior and outer surfaces of hollow $\text{g-C}_3\text{N}_4$ spheres (HCNS). Time courses of photocatalytic H_2 and O_2 evolution using (b) $\text{Co}_3\text{O}_4/\text{HCNS}/\text{Pt}$, and (c) $(\text{Co}_3\text{O}_4 + \text{Pt})/\text{HCNS}$ under UV irradiation ($\lambda > 300 \text{ nm}$) [53]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

as-prepared $\text{g-C}_3\text{N}_4$ samples possessed an enlarged specific surface area, a large pore volume, and high conductivity, which all contribute to improved photocatalytic activity. However, decomposition of the template materials may also result in the pores in $\text{g-C}_3\text{N}_4$ sealing again and high leftover carbon contents, hence lowering the photocatalytic activity. This issue can be partly resolved by replacing dicyandiamide with a less reactive melamine precursor and using Pluronic P123 surfactant with a low carbon content as the soft template [61]. The resultant mesoporous $\text{g-C}_3\text{N}_4$ with worm-like pores and a narrow pore size distribution shows a moderately higher surface area of $90 \text{ m}^2 \text{ g}^{-1}$ compared with bulk $\text{g-C}_3\text{N}_4$ ($27 \text{ m}^2 \text{ g}^{-1}$), and also an absorbance edge redshift up to 800 nm , showing photocatalytic H_2 evolution activity even at $\lambda > 700 \text{ nm}$.

Besides nanostructure tuning, ionic liquids (such as 1-butyl-3-methylimidazolium tetra-fluoroborate ([Bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆])) also contribute to the preparation of boron and fluorine co-doped g-C₃N₄, or phosphorus-doped g-C₃N₄, where the ionic liquids act as the reaction medium, structure-directing agent and dopant source simultaneously [60].

4.4.1.3 Template-free Methods

Molecular self-assembly, also known as supramolecular preorganization, has been widely explored for the template-free preparation of g-C₃N₄ nanostructures, such as hollow spheres, nanoflowers, nanorods and nanofibers [62–64]. The supramolecular preorganization is often produced by linking the melamine precursor with triazine derivatives to form hydrogen-bonded molecular assemblies, such as melamine-cyanuric acid, melamine-trithiocyanuric acid mixtures, or related derivatives. g-C₃N₄ of different morphologies has also been obtained by changing types of solvent. Jun et al. reported the synthesis of mesoporous g-C₃N₄ using flower-like, layered spherical aggregates of melamine cyanuric acid complex formed by precipitation from dimethyl sulfoxide (DMSO) [63]. The preformed flower-like, layered spherical structure is successfully maintained in the formed g-C₃N₄ materials after thermal polycondensation at 550°C. The layered structure enables simultaneous optimization of the textural and photoelectric properties, including stronger optical absorption, increased lifetime of the photoexcited charge carriers, and subsequently improved photocatalytic activity for RhB degradation. Gu et al. reported solvothermal preparation of g-C₃N₄ microspheres by using melamine and cyanuric chloride as precursors, thus giving a significantly enhanced H₂ generation rate, 2.3 times higher than that of bulk g-C₃N₄ [64].

Besides the above traditional template-free methods, great progress has been made recently by sintering freeze-drying-assembled dicyandiamide fiber networks [65, 66] and by creating pores via selective breaking of the hydrogen bonds [67]. Han et al. reported a g-C₃N₄ “seaweed” architecture by direct calcination of the freeze-drying-assembled, hydrothermally treated dicyandiamide (HTD) fiber network [66]. The mesoporous seaweed network of g-C₃N₄ nanofibers exhibits a high H₂ evolution rate of 9900 μmol h⁻¹ g⁻¹ (30 times higher than bulk g-C₃N₄), and an AQE of 7.8% at 420 nm, due to the enhanced light harvesting, charge separation and utilization of the active sites. They further prepared an interconnected framework of mesoporous g-C₃N₄ nanofibers merged with in-situ incorporated nitrogen-rich carbon, where iodine-loaded HTD is used for the oxidation reaction of the pyrrole monomer for the in-situ polypyrrole coating on the HTD nanofibers (Figure 4.8) [65]. The mesoporous g-C₃N₄ nanofibers exhibit an extremely high hydrogen evolution rate of 16885 μmol h⁻¹ g⁻¹, and a remarkable AQE of 14.3% at 420 nm without any cocatalysts. This is a much higher efficiency than most reported g-C₃N₄-based photocatalysts (even with Pt), and it is attributed to the unique composition and structure of the nanofibers and the strong coupling between the components that enable improved charge separation and a multidimensional electron transport path. Recently, the Liu group reported the introduction of increased band tails and abundant pores by selective breaking of the hydrogen bonds of g-C₃N₄ via a simple controlled post-sintering process at temperatures ranging from 540 to 610°C for 2 h in argon [67]. As a result of volume shrinkage with the breaking of hydrogen bonds, abundant pores formed throughout the g-C₃N₄ particles and promoted the charge transfer to the lateral

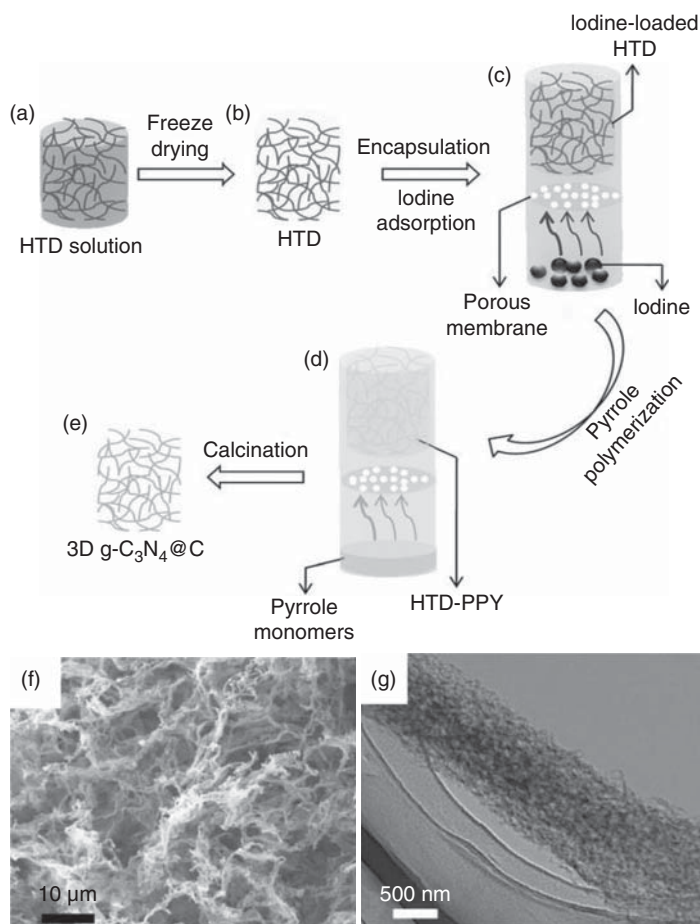


Figure 4.8 Fabrication procedure (a–e) and scanning electron microscopy (SEM) (f) and TEM (g) images of the 3D g-C₃N₄@C (mesoporous g-C₃N₄ nanofibers with in-situ incorporated nitrogen-rich carbon). (a) HTD (hydrothermally treated dicyandiamide) solution; (b) freeze-dried HTD; (c) iodine-loaded HTD; (d) HTD-PPY; (e) g-C₃N₄@C [65]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

surface of the pores by providing additional reductive reaction sites (Figure 4.9). The photocatalytic H₂ evolution activity of g-C₃N₄ under visible light is greatly improved by tens of times.

4.4.2 Exfoliation to 2D Nanosheets of g-C₃N₄

Inspired by the delamination of graphene from bulk graphite, delaminating g-C₃N₄ into ultrathin nanosheets of a few layers by post-treatments plays an important role in nanostructuring of g-C₃N₄ because of its intrinsic 2D nature that can advance the surface, optical, and electronic properties [68, 69]. Great efforts have focused on the exfoliation of the bulk g-C₃N₄ materials by ultrasound-assisted exfoliation, ball milling, acid intercalation, thermal etching, as well as combinations of these strategies.

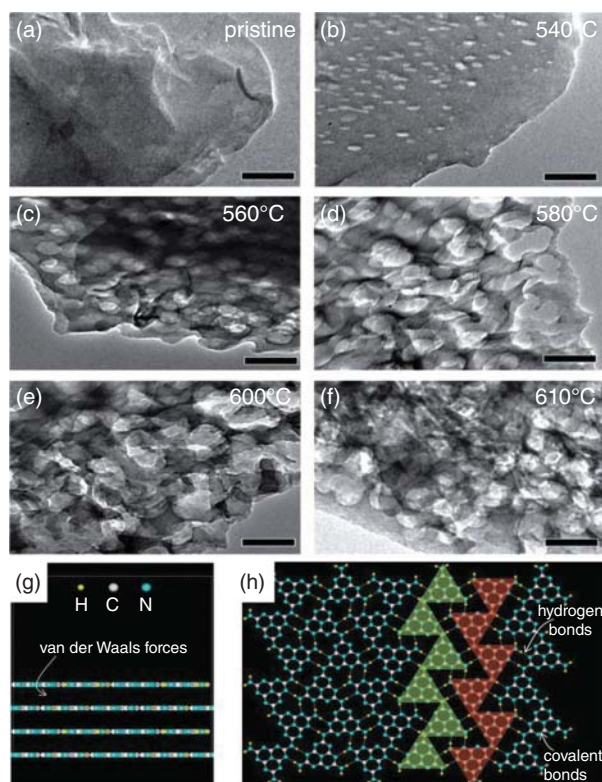


Figure 4.9 TEM images for morphology evolution of layered $g\text{-C}_3\text{N}_4$ on thermal treatment temperature. (a) The pristine layered carbon nitride; (b–f) the layered $g\text{-C}_3\text{N}_4$ products obtained by heating pristine $g\text{-C}_3\text{N}_4$ made from dicyandiamide in argon at different temperatures of 540, 560, 580, 600, and 610°C; (g) side and (h) top views of the atomic structure of layered $g\text{-C}_3\text{N}_4$ indicating the selective breaking of the hydrogen bonds. Scale bars: 100 nm [67]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

Ultrathin $g\text{-C}_3\text{N}_4$ nanosheets can be effectively obtained by ultrasound-assisted exfoliation in suitable solvents when the acoustic energy of the ultrasonic wave overcomes the van der Waal's forces between the layers [69]. The liquid exfoliation strategy has been widely explored by a large number of researchers for exfoliation of $g\text{-C}_3\text{N}_4$ in various organic solvents, such as isopropanol (IPA), N-methyl-pyrrolidone (NMP), acetone, and ethanol. Among these solvents, NMP is the most effective, similar to the exfoliation of other 2D materials [69], while other more common solvents (such as IPA) have advantages of low cost and low boiling points for easy removal. Yang et al. reported the exfoliation of commercially available $g\text{-C}_3\text{N}_4$ powder (Carbodeon Ltd) in various solvents including IPA [70]. The resulting nanosheets are about 2 nm thick, with a N/C atomic ratio of 1.31 and bandgap of 2.65 eV, exhibiting excellent photocatalytic activity with a hydrogen evolution rate of $93 \mu\text{mol h}^{-1}$ under visible light and AQE of 3.75% at 420 nm, much higher than bulk $g\text{-C}_3\text{N}_4$ ($10 \mu\text{mol h}^{-1}$) and even higher than the reported highly ordered mesoporous $g\text{-C}_3\text{N}_4$. Recently, water was also found to be an effective exfoliation medium as the surface energy of water (102 mJ m^{-2}) matches well with that of $g\text{-C}_3\text{N}_4$ (115 mJ m^{-2}), implying a good dispersal capability for water

[71]. Lin et al. further explored several mixed solvents, such as ethanol/H₂O, IPA/H₂O, and dimethylformamide (DMF)/H₂O, for the liquid exfoliation of bulk g-C₃N₄ to monolayer g-C₃N₄ nanosheets, focusing on the tunable concentrations (0.1–3 mg ml⁻¹) [72]. For ethanol/H₂O, decreasing the organic solvent (ethanol) led to a gradual increase in the suspension concentration, and a milky dispersion was obtained with the maximum concentration of g-C₃N₄ (3 mg ml⁻¹) with 75% of H₂O, while only a very low concentration of g-C₃N₄ in the suspension was achieved in pure water (c. 0.5 mg ml⁻¹) and pure organic solvent (c. 0.2 mg ml⁻¹). More importantly, ultrasound-assisted in-situ exfoliation and deposition has also been demonstrated to be an effective strategy for the simple preparation of g-C₃N₄ based composite photocatalysts with CdS, Zn_{1-x}Cd_xS (0 < x < 1), and MoS₂ nanoparticles [73–76].

In addition to the liquid exfoliation methods, thermal oxidation etching methods for bulk g-C₃N₄ in air and other atmospheres have been reported, with the advantages of low cost, easy scaling, and environmental friendliness. As the hydrogen-bond structure within the g-C₃N₄ layers is unstable against oxidation processes in air, a gradual decrease in the thickness of bulk g-C₃N₄ can be achieved by a layer-by-layer thermal etching process. g-C₃N₄ nanosheets with thickness down to c. 2 nm can be obtained, resulting in a high surface area of 306 m² g⁻¹, improved lifetime, and enhanced charge carrier transport ability for enhanced photoactivity [77]. Further improvement was achieved by thermal annealing of thiourea-derived g-C₃N₄ in H₂ atmosphere, showing a strikingly higher photocurrent than that of g-C₃N₄ exfoliated under air or N₂ due to the improved exfoliation of g-C₃N₄ nanosheets and also the enhanced π -conjugated electronic structure [78]. Recently She et al. reported an oxygen-modified monolayer g-C₃N₄ with high crystallinity and high yield via controlled thermal oxidation (Figure 4.10) [79]. The simultaneously achieved partial oxygenation of g-C₃N₄ provides both the structural and electronic advantages for photocatalytic hydrogen evolution. The oxygen-modified monolayer g-C₃N₄ exhibited a H₂ production rate of 44.37 μ mol h⁻¹ (equivalent to 8874.7 μ mol g⁻¹ h⁻¹) under visible light irradiation and an AQE of 13.7% at 420 nm using the oxygen-modified monolayer g-C₃N₄ nanosheets with triethanolamine as hole scavenger.

4.4.3 0D Quantum Dots of g-C₃N₄

In addition to 2D nanosheets, further downsizing g-C₃N₄ to 0D QDs represents another important area of g-C₃N₄ nanostructuring. Several strategies have been developed, such as thermal-chemical etching, hydrothermal treatment, consequential sulfuric acid-nitric acid and ammonia treatment (Figure 4.11), ethanediamine refluxing, as well as enzyme-catalyzed degradation of g-C₃N₄ [80–83]. A microwave-assisted process was also reported for g-C₃N₄ QDs from guanidine hydrochloride and ethylenediaminetetraacetic acid (EDTA), which was used for chemiluminescence [84]. The Kang group reported a series of g-C₃N₄ QDs derived from g-C₃N₄, which were also referred to as N-doped carbon dots [85–92]. These g-C₃N₄ QDs show strong blue emission with high quantum yield as well as upconversion PL behavior, and have been applied in bioimaging, sensing, solar cells, and photocatalysis. It worth mentioning that the g-C₃N₄ QDs show PL behavior that is distinct from standard carbon dots due to the existence of the g-C₃N₄ core, which gives them excellent temperature-dependence of PL and enables temperature sensing applications [91].

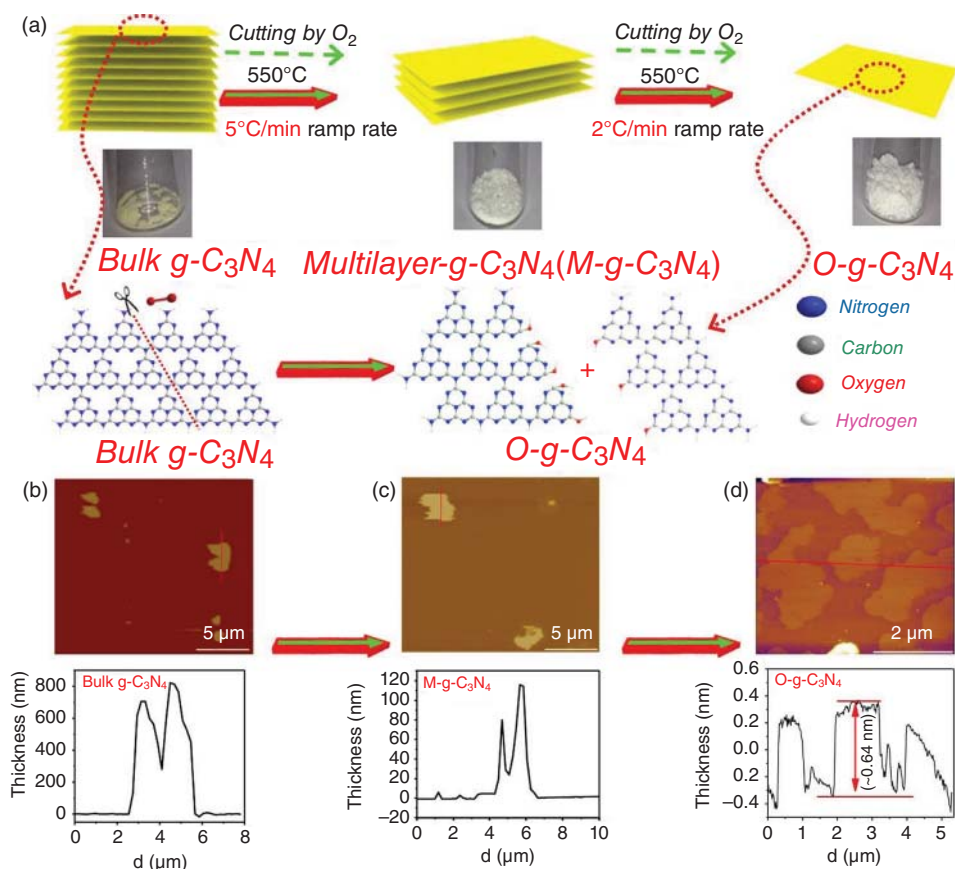


Figure 4.10 Schematic illustration of the thermal exfoliation method to form an O-g-C₃N₄ nanosheet: simultaneous exfoliation and O-doping [79]. Source: Reprinted with permission from Elsevier, Copyright 2016.

Although great progress has been made on the preparation and optical properties of g-C₃N₄ QDs, its application has been mainly limited to bioimaging [80], solar cells [82] and photocatalytic degradation. For photocatalytic application, g-C₃N₄ QDs have been combined with InVO₄/BiVO₄, AgVO₃, and rutile TiO₂, to make composite photocatalysts, which show increased photocatalytic activity due to increased visible light absorption and efficient charge separation by g-C₃N₄ QDs, mainly for dye degradation application [93–95]. Extensive density functional theory based calculations suggest that proper modification of the electronic nature of the g-C₃N₄ QDs could lead to efficient visible or near-infrared (NIR) light response, and the passivated QDs are better catalysts for H₂ evolution, making them better functional materials for photocatalytic applications [96]. There have only been very few reports for photocatalytic H₂ production so far. Wang et al. prepared g-C₃N₄ QDs from bulk g-C₃N₄ by a direct thermal–chemical etching process [81]. The g-C₃N₄ QDs show strong blue emission as well as upconversion behavior, which can be used for universal energy-transfer components in visible-light-driven metal-free photocatalytic systems (Figure 4.12).

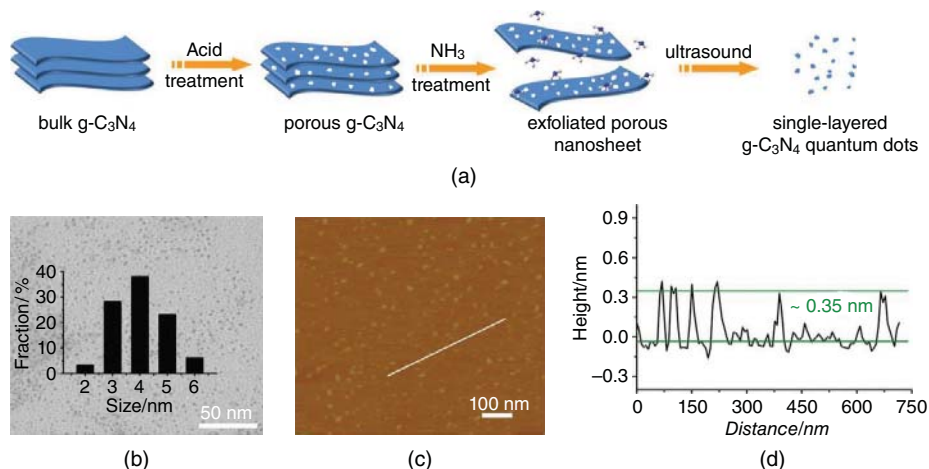


Figure 4.11 (a) Schematic illustration of the preparation strategy, (b) TEM image and the corresponding size distribution, (c) atomic force microscopy (AFM) image and (d) corresponding height profile of the $\text{g-C}_3\text{N}_4$ QDs [80]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2014.

Interestingly, the $\text{g-C}_3\text{N}_4$ QDs themselves show no photocatalytic activity for H_2 evolution. By combining with bulk $\text{g-C}_3\text{N}_4$, the $\text{g-C}_3\text{N}_4$ quantum dot (CNQD)– $\text{g-C}_3\text{N}_4$ suspension shows dramatic increase in the H_2 evolution rate up to $137.84 \mu\text{mol h}^{-1}$, 2.87 times higher than that of bulk $\text{g-C}_3\text{N}_4$ in the presence of 1 wt% Pt as a cocatalyst and 10% triethanolamine as a sacrificial agent (Figure 4.12c). This result demonstrates that the $\text{g-C}_3\text{N}_4$ QDs act as an energy transfer component and can effectively enhance the visible-light-driven photocatalytic activity of H_2 production. Deeper study is needed to better exploit the advantages of the $\text{g-C}_3\text{N}_4$ QDs in photocatalyst design for water-splitting.

4.5 $\text{g-C}_3\text{N}_4$ Composite Photocatalysts

4.5.1 Metal/ $\text{g-C}_3\text{N}_4$ Heterojunctions

Formation of metal/ $\text{g-C}_3\text{N}_4$ heterojunctions is another effective strategy for enhanced charge separation, surface reaction rates and/or visible light absorption by the localized surface plasmon resonance (SPR) [7, 11]. Metals play two important roles as cocatalysts: as charge separation sites, and as active reaction sites in most cases, while the additional SPR effect is mainly observed in Au and Ag. The charge separation effect is achieved by the formation of a Schottky barrier and a space charge region (or depletion layer) at the interface, due to the different work functions and Fermi level of the metal and $\text{g-C}_3\text{N}_4$ upon close contact (Figure 4.13a). This redistribution of charges between metal and $\text{g-C}_3\text{N}_4$ generates an internal electric field that accelerates the transfer of photoexcited electrons from $\text{g-C}_3\text{N}_4$ and prohibits the electron–hole recombination. Series of metals have also been extensively explored on $\text{g-C}_3\text{N}_4$ for photocatalytic applications, such as Pt, Pd, Au, Ag, Cu, Ni, Co, and their alloys [46, 97–102].

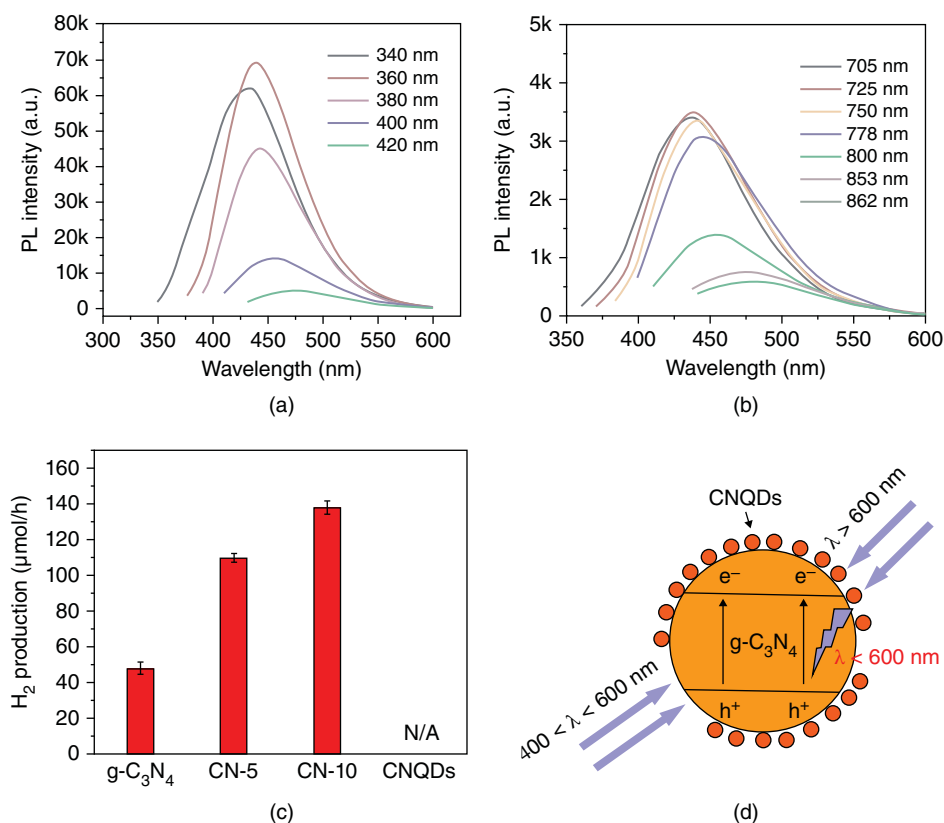


Figure 4.12 (a) PL and (b) upconversion PL spectra of g-C₃N₄ QDs at various excitation wavelengths. (c) Photocatalytic H₂ evolution over g-C₃N₄, g-C₃N₄ quantum dot (CNQD)–g-C₃N₄ composites, and pure g-C₃N₄ QDs with 1 wt% Pt under visible-light irradiation ($\lambda > 420$ nm). CN-5 and CN-10 refers to g-C₃N₄ with the addition of 5 and 10 ml of g-C₃N₄ QD solution, respectively. (d) Mechanism for photocatalytic H₂ production with the participation of upconversion PL using CNQD–g-C₃N₄ under visible light [81]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

Pt is the most widely used cocatalyst in g-C₃N₄-based photocatalysts. In the pioneering work by Wang et al., Pt was deposited as the cocatalyst and resulted in an increase in H₂ production rate with increasing Pt content up to a plateau at ~2–4%, beyond which it decreases again due to shielding of the light absorption [9]. The deposited Pt nanoparticles facilitate charge separation and also simplify H₂ production by the more favorable hydrogen elimination from Pt-H surface bonds, compared with that from the hydrogenated g-C₃N₄ surface. The Pt/g-C₃N₄ composites can be prepared by various strategies including physical mixing, solvothermal reduction, photodeposition, and annealing of the Pt precursors. Lots of effort has been spent looking at the loading amount, deposition condition and size control of the Pt nanoparticles and the engineering of the Pt/g-C₃N₄ interfaces. Recently, Li et al. further reported the isolated single-atom Pt embedded in the sub-nanopores of 2D g-C₃N₄ as a highly efficient cocatalyst (Figure 4.14) [103]. The Pt-g-C₃N₄ was prepared by low-temperature annealing (125°C) in Ar atmosphere of the H₂PtCl₆ precursor adsorbed into the sub-nanoporosity

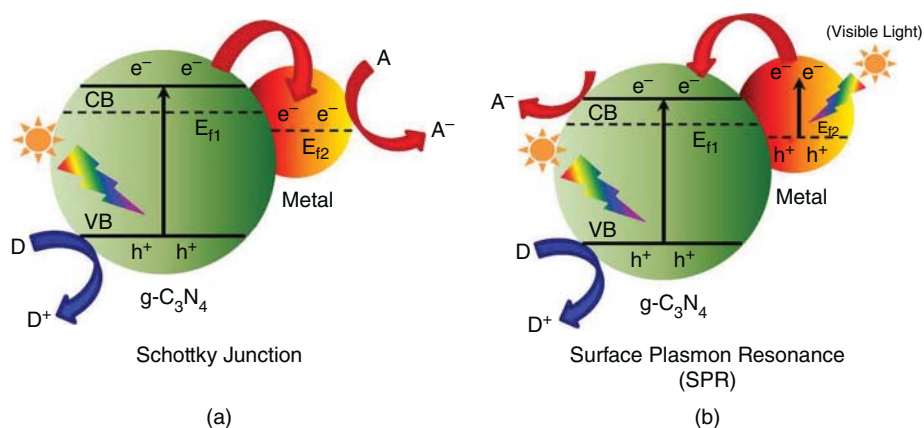


Figure 4.13 Schematic illustration of the energy band structure and charge transfer processes of the metal/g-C₃N₄ heterojunction: (a) Schottky junction of metal/g-C₃N₄ nanohybrids, and (b) surface plasmon resonance (SPR) effect in noble metal/g-C₃N₄ nanohybrids. A, D, and E_F denote electron acceptor, electron donor, and Fermi level, respectively [7]. Source: Reprinted with permission from ACS publishers, Copyright 2016.

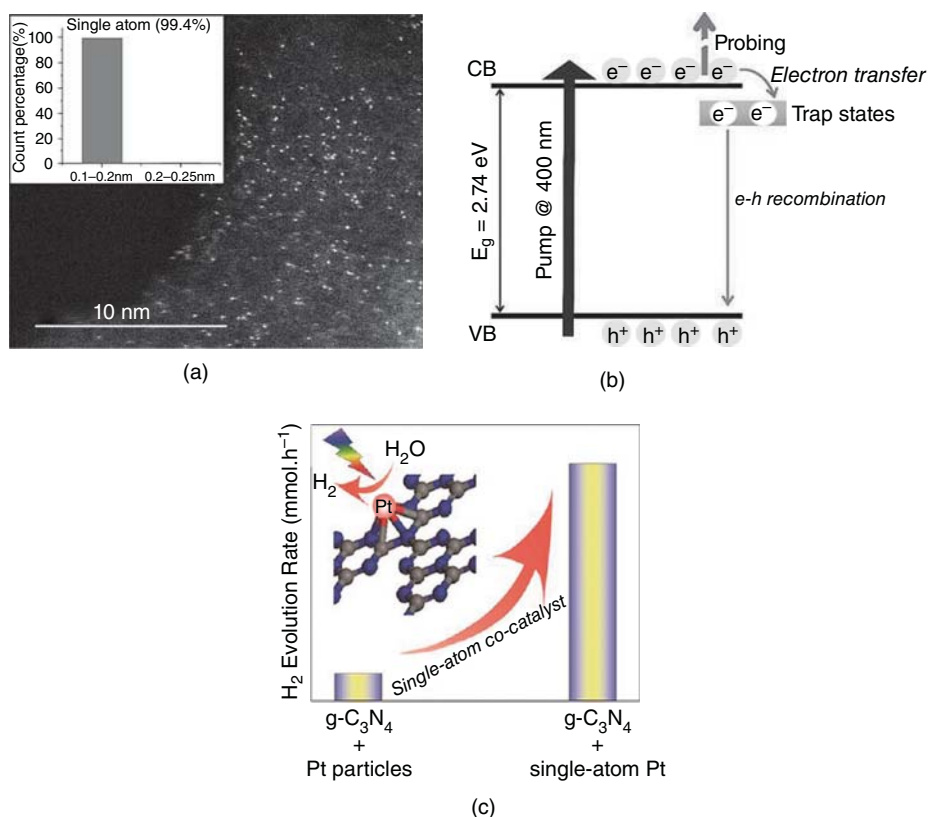


Figure 4.14 (a) HAADF-STEM image of Pt-CN. Inset is the size distribution of the bright spots. (b) Schematic illustration of the mechanisms for the effective charge separation processes. (c) Schematic models of Pt-g-C₃N₄ for the single-atom cocatalytic effect [103]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

of $g\text{-C}_3\text{N}_4$. The single-atom Pt cocatalyst gives the maximum atom efficiency and also alters the surface trap states of $g\text{-C}_3\text{N}_4$, which greatly enhances photocatalytic H_2 evolution activity: 8.6 times higher than Pt nanoparticles and 50 times higher than bare $g\text{-C}_3\text{N}_4$.

In addition to acting as efficient cocatalyst for charge transfer and surface reaction, Ag and Au are also widely known for their SPR effect which can greatly improve the visible light absorption [101, 104]. As shown in Figure 4.13b, the SPR effect occurs when the frequency of incident photons matches the frequency of the free electrons of the noble metal nanoparticles, from which the excited electrons can be injected into the CB of $g\text{-C}_3\text{N}_4$, leaving a positively charged metal nanoparticle. More importantly, the resonant photon frequency can be tuned with various noble metals and particle size, which provides a widely tunable visible light absorption and subsequently better opportunity for the manipulation of the energy and/or charge transfer processes between the metals and $g\text{-C}_3\text{N}_4$. Di et al. investigated the deposition of gold nanoparticles on the surface of $g\text{-C}_3\text{N}_4$ by deposition-precipitation, photodeposition, and impregnation methods to make metal–semiconductor junctions for photocatalytic hydrogen evolution [105]. The best photocatalytic activity was obtained by using the deposition-precipitation method due to the formation of tight $\text{Au}/g\text{-C}_3\text{N}_4$ heterojunctions, effectively promoting the charge transfer. The $\text{Ag}/g\text{-C}_3\text{N}_4$ composite photocatalysts have also been prepared by reflux treatment of Ag nanoparticles with $g\text{-C}_3\text{N}_4$ nanosheets [106], and in-situ reduction during thermal polymerization of the nitrogen-rich precursors [101, 107], which all give enhanced photocatalytic activity from a combined interaction of the enhanced light absorption intensity by the SPR effect and high separation efficiency of photogenerated electrons and holes.

Most research attention has focused on noble metal cocatalysts due to their superior performance. However, if photocatalytic water-splitting is going to be widely adopted, it must be cheap to produce and operate, which is also one of the most prominent advantages of $g\text{-C}_3\text{N}_4$. Therefore, the development of cocatalysts that comprise only inexpensive, earth-abundant elements is inevitable [108, 109]. Recently there has been tremendous work on the development of noble-metal-free cocatalysts to accelerate the electron transfer from $g\text{-C}_3\text{N}_4$ to metals such as the transition metals (Ni, Fe, and Cu), transition metal compounds and graphitic carbon nanomaterials for the reduction reactions. Several earth-abundant metals, including Fe, Co, Ni, Cu and Bi, have been explored to combine with $g\text{-C}_3\text{N}_4$ for photocatalytic H_2 production [46, 97, 100, 102, 110]. An interesting strategy might rely on the development of bimetallic or alloyed metals, such as Fe and Pd co-doped $g\text{-C}_3\text{N}_4$ [46]. The graphitic carbon nanomaterials and transition metal compounds are discussed in Sections 4.5.2 and 4.5.4, respectively.

4.5.2 Graphitic Carbon/ $g\text{-C}_3\text{N}_4$ Heterojunctions

As mentioned above, the high binding energy of the photogenerated excitons (electron/hole pairs) is a main challenge of $g\text{-C}_3\text{N}_4$ as a conjugated polymer for photoelectric applications, which requires structure design for effective charge separation and transfer. Besides metals, π -conjugated carbon nanomaterials such as graphene, carbon nanotubes (CNTs), carbon nanodots and even carbon black have been demonstrated as effective supports and/or reduction cocatalysts to enhance the charge transfer and relieve the charge recombination (Figure 4.15) [111, 112].

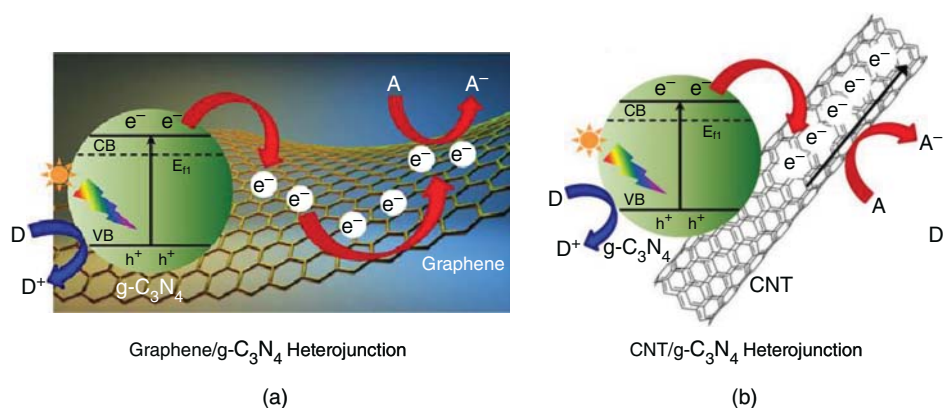


Figure 4.15 Schematic illustration of (a) the graphene/g-C₃N₄ and (b) CNT/g-C₃N₄ heterojunctions for photocatalysis [7]. Source: Reprinted with permission from ACS publishers, Copyright 2016.

Graphene is a perfect example to promote the charge transfer and separation of photocatalysts owing to its high conductivity, electron mobility, and high surface area. More importantly, formation of the intimate 2D/2D face-to-face interaction by the hybridization of g-C₃N₄ and graphene can largely improve the photocatalytic activity due to the large contact surface area and the facilitated charge transfer [111]. Again, the simplest approach for graphene/g-C₃N₄ nanohybrids is the in-situ thermal annealing of a mixture of graphene oxide (GO) and the nitrogen-rich precursors, similar to the semiconductor/g-C₃N₄ and metal/g-C₃N₄ composites. Xiang et al. prepared graphene and g-C₃N₄ composite photocatalysts by a polymerization of melamine in the presence of GO (precursors) and hydrazine hydrate (reducing agent) [113]. The 2D graphene sheets act as electronic conductive channels to efficiently separate the photogenerated charge carriers and, consequently, to enhance the visible-light photocatalytic H₂ production activity of g-C₃N₄. The optimal H₂ production rate is 451 $\mu\text{mol g}^{-1} \text{h}^{-1}$ with 1.0 wt% of graphene, 3.07 times higher than pure g-C₃N₄. Besides the above in-situ polymerization method, graphene/g-C₃N₄ composites can also be prepared by immobilizing the as-prepared g-C₃N₄ into GO suspension upon sonication-assisted delamination of bulk g-C₃N₄ by utilizing GO as a conducting substrate. Graphene has also played an important role in the construction of g-C₃N₄-based multicomponent photocatalysts, either as a structural template or as an electron transfer mediator, such as in the case of g-C₃N₄ nanosheets/nitrogen-doped graphene/layered MoS₂ and C₃N₄-WO₃-rGO composite photocatalysts [114, 115].

CNTs represent another attracting carbon allotrope with superior electronic properties, high tensile strength, excellent conductivity along the 1D direction, and a large surface area. Ge and Han reported the multiwalled carbon nanotubes (MWCNTs)/g-C₃N₄ composite photocatalysts via a simple heating method [116]. The optimal H₂ evolution rate is 7.58 $\mu\text{mol h}^{-1}$ with 2.0 wt% of MWCNTs, about 3.7-fold that of pure g-C₃N₄ in methanol aqueous solution. Suryawanshi et al. reported the preparation of g-C₃N₄/MWCNTs by a similar method, where 100% improvement of photocatalytic water-splitting activity was achieved with an optimized MWCNT loading amount of 0.5 wt% [117]. MWCNTs may lead to efficient separation of the photogenerated charge carriers and, consequently, enhance the visible light photocatalytic

H₂ production activity due to the excellent electron storage capability and the reduced recombination rate of charge carriers.

In addition to these fine-controlled carbon nanostructures, other low-cost graphitic carbon nanomaterials have also been explored for compositing with g-C₃N₄, including carbon black, carbon fiber, and ordered mesoporous carbon, showing improved physicochemical properties and photocatalytic activities [7, 112, 118]. However, these carbon allotropes often suffer from a severe light-shielding effect due to the high light absorption by these black micro-sized materials themselves.

Carbon nanodots (CDots) or graphene QDs have attracted huge attention owing to their excellent optical and electronic features, such as the broad visible light absorption, and excellent capability as electron reservoirs [119]. The unique quantum-size 0D structure distinguishes CDots from other carbon allotropes, in terms of high surface area, abundant surface functional groups and subsequently surface-dependent optical, electronic and catalytic properties. Many researchers have extensively explored the metal-free CDots/g-C₃N₄ composites for photocatalytic water-splitting [120–124]. In addition to the increased charge separation effect, similar to other carbon materials, it has been reported that the combination of CDots with g-C₃N₄ contributed to an improved surface water reduction or oxidation reaction rate, enhanced visible light absorption, as well as NIR light utilization through an upconversion PL process [119].

Recently, the Kang group further reported a robust CDots-C₃N₄ composite photocatalyst that can split water into H₂ and O₂ with an AQE up to 16% at 420 nm and a solar-to-hydrogen (STH) efficiency of 2.0% (Figure 4.16) [16]. The used CDots were synthesized by a typical electrochemical method followed by hydrothermal treatment with ammonia, and the CDots-C₃N₄ composites were then prepared by heating a mixture of ammonia-treated CDots (capped with -NH₂) and urea powder at 550°C for 3 hours. More importantly, instead of the traditional one-step four-electron reaction, the CDots-C₃N₄ composite catalyzes water-splitting to hydrogen and oxygen via a stepwise two-electron/two-electron two-step pathway (Figure 4.16), where g-C₃N₄ is responsible for the first step (photocatalytic production of H₂ and H₂O₂), and CDots are responsible for the second step (chemical catalysis of H₂O₂ decomposition). The concentration of CDots in the composite plays a key role in the QE of water-splitting that relies on sufficient proximity between the H₂O₂ generation sites on C₃N₄ and the CDots. The results demonstrate the great potential of the CDots-C₃N₄ photocatalyst for visible-light-driven hydrogen production by overall water-splitting.

4.5.3 Semiconductors/g-C₃N₄ Heterojunctions

Construction of semiconductor–semiconductor heterojunctions is an effective and widely adopted strategy to enhance the activity of semiconductor photocatalysts by promoting charge separation. The polymeric nature of g-C₃N₄ gives high flexibility to the 2D sheets, as well as a tunable surface structure that favors the construction of heterojunctions with various semiconductors with a close interface contact [7]. A large number of semiconductors, including metal oxides, metal sulfides, and metal nitrides, have been coupled with g-C₃N₄ via approaches of physical mixing, in-situ deposition or growth on pre-synthesized nanosheets, and in-situ formation during thermal polymerization [7, 14, 125]. In terms of efficient charge separation and utilization, mainly two

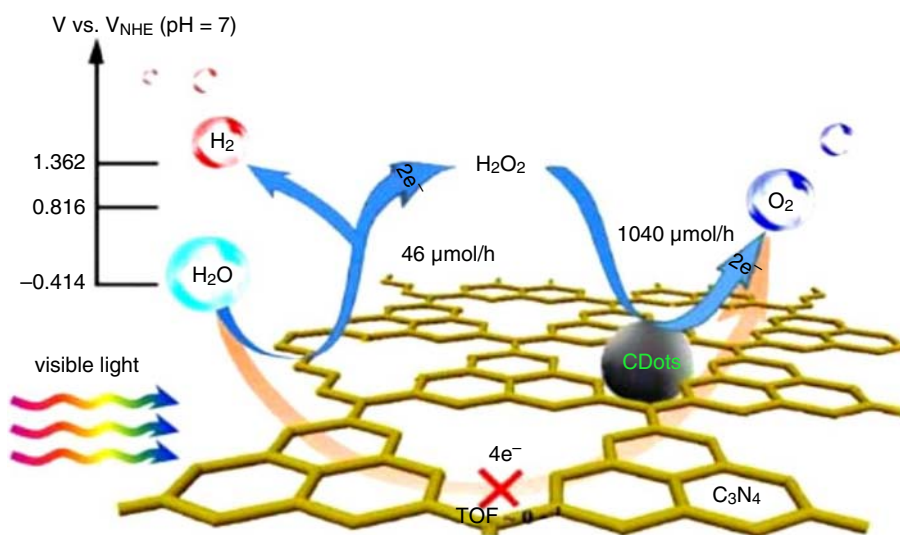


Figure 4.16 The proposed reaction mechanism for visible-light-driven water-splitting by CDots-C₃N₄ via the stepwise two-electron/two-electron two-step pathway. Source: Adapted from Liu et al. (2015) with permission from AAAS publishers, Copyright 2015.

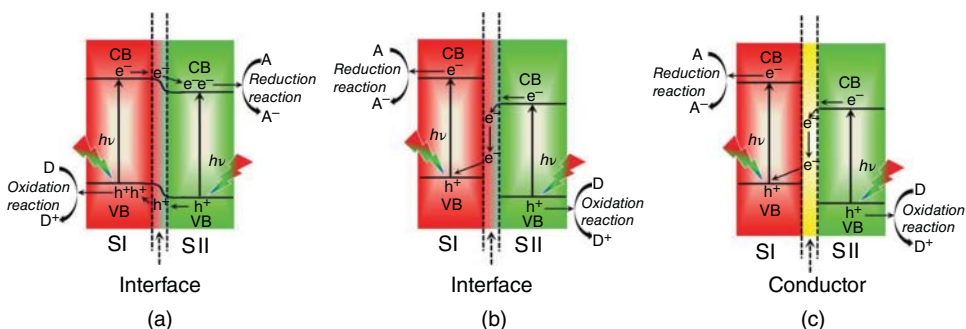


Figure 4.17 Schematic illustration of the semiconductor heterojunctions for photocatalytic reactions: (a) traditional type-II heterojunction; (b) all-solid-state S-S Z-scheme heterojunction without any electron mediator; (c) all-solid-state S-C-S Z-scheme heterojunction with a conductor as the electron mediator. SI, SII, A, and D represent semiconductor I, semiconductor II, electron acceptor, and electron donor, respectively [126]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2014.

types of heterojunctions are preferred and have been intensively studied: traditional type-II heterojunctions, and all-solid-state Z-scheme heterojunctions (Figure 4.17).

4.5.3.1 Type-II Heterojunction

In a g-C₃N₄-based traditional type-II heterojunction, both the CB and VB positions of g-C₃N₄ are higher or lower than those of another semiconductor. This band energy difference between the two semiconductors results in band bending at the heterojunction interface and induces a built-in electric field, which can effectively drive the migration of photogenerated electrons and holes in opposite directions (Figure 4.17a).

In particular, when both semiconductor units of the heterojunction are simultaneously excited, directed distribution of electrons on the semiconductor with lower CB and holes on the semiconductor with higher VB can be achieved, which represents one of the important goals in the development of semiconductor photocatalysts. For example, Hu et al. reported on g-C₃N₄/nano-InVO₄ type-II heterojunction photocatalysts by in-situ growth of 20 nm InVO₄ nanoparticles onto the surface of g-C₃N₄ nanosheets via a hydrothermal process [127]. The nanoparticles dispersed uniformly on the surfaces of the g-C₃N₄ sheets. The morphology and structure of the g-C₃N₄/nano-InVO₄ nanocomposites was observed to rely on the g-C₃N₄ content. The intimate contact of g-C₃N₄ and nano-InVO₄ resulted in effective charge separation and greatly enhanced H₂ evolution compared with bare g-C₃N₄ and g-C₃N₄/micro-InVO₄ composites. Jiang et al. reported Ag₂S-modified g-C₃N₄ (Ag₂S/g-C₃N₄) composite photocatalysts via a simple precipitation method, where the enhanced photocatalytic activity was mainly attributed to the effective charge transfer between g-C₃N₄ and the simultaneously photodeposited Ag/Ag₂S as an efficient cocatalyst for the g-C₃N₄ [128].

4.5.3.2 Z-scheme

Although efficient charge separation can be achieved with the traditional type-II heterojunction, the spontaneous charge flow results in the weaker reducing ability of electrons and oxidizing ability of the holes due to the less negative CB of semiconductor II and the less positive VB of semiconductor I (Figure 4.17a). This shortcoming severely restricts its application potential for overall water-splitting. To overcome this disadvantage, two new types of all-solid-state Z-scheme heterojunctions have been developed, where the photogenerated electrons in semiconductor II with lower CB combine with holes in semiconductor I with a higher VB (Figure 4.17b) [126]. This leaves the electrons in semiconductor I (higher CB) and holes in semiconductor II (lower VB) with superior redox abilities, with the price of intended deactivation of the remaining photogenerated electrons (in semiconductor II) and holes (in semiconductor I). The Z-scheme heterojunctions can be divided into two types: the semiconductor–semiconductor (S–S) (Figure 4.17b) and semiconductor–conductor–semiconductor (S–C–S) (Figure 4.17c). The conductors used in the S–C–S heterojunctions include noble metals and graphene. Lots of studies have contributed to the development of Z-scheme heterojunction photocatalysts [55, 94, 114, 129–135]. For example, Lu et al. reported a Z-scheme g-C₃N₄/Ag/MoS₂ ternary plasmonic photocatalyst in a flower-like architecture, which exhibits enhanced visible-light-induced photocatalytic activity in both degrading Rhodamine B (RhB) and production of H₂ from water, respectively [129]. The excellent photocatalytic activities were attributed to an Ag-mediated Z-scheme mechanism with rapid separation and slow recombination of the photogenerated electrons and holes (Figure 4.18).

4.5.3.3 0D/2D Heterostructures

Among the extensively studied g-C₃N₄/semiconductor composites, 0D/2D QDs/nanosheets heterojunctions have attracted increasingly more attention due to the combined advantages of the high surface area of 0D QDs [136] and the high charge mobility of the 2D nanosheets. Various semiconductor QDs have been combined with g-C₃N₄, including CdS, Bi₂WO₆, silver silicate, CdS–TiO₂, Ta⁴⁺ doped Ta₂O₅, and vanadate (AgVO₃, BiVO₄, InVO₄ and CuV₂O₆) QDs, among which Bi₂WO₆/g-C₃N₄ forms a Z-scheme heterojunction and the rest are mainly type-II. Ge et al. reported

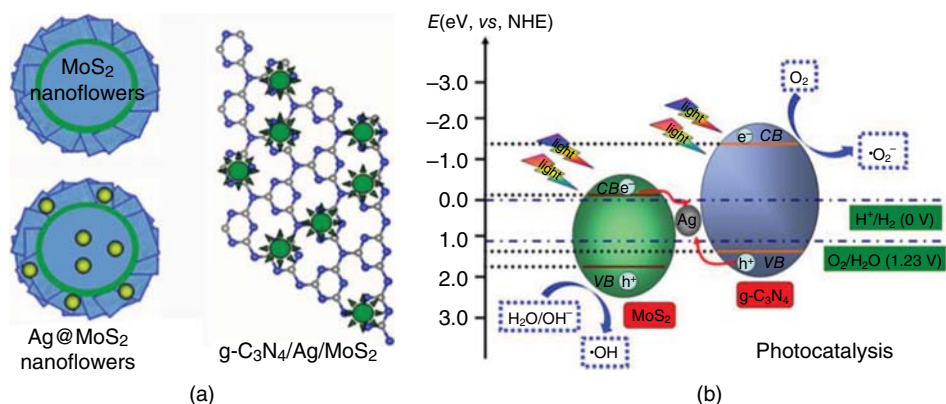


Figure 4.18 (a) Schematic structure illustration and (b) photocatalysis mechanism of g-C₃N₄ and Ag co-modified MoS₂ microspheres [129]. Source: Reprinted with permission from ACS publishers, Copyright 2017.

CdS QDs/g-C₃N₄ composite photocatalysts by simply mixing the CdS QDs with thioglycolic acid and the as-prepared g-C₃N₄ powder, followed by stirring for 24 h [137]. The Wang group reported CdS QDs deposited onto the exterior surface of hollow g-C₃N₄ spheres (HCNS) to fabricate inorganic-polymeric heterojunctions with facilitated charge separation and enhanced H₂ evolution with visible light [138]. The enhanced photocatalytic activity can be attributed to combined effects of the unique three-dimensional (3D) hollow architectural framework, the intimate interfacial contact, and subsequently the facilitated surface charge separation and mass transfer. Such inorganic-polymer hybrid nanoarchitectures also provide a valuable platform for biostructural mimicking of hollow soft semiconductors, with controlled deposition of stiff QDs for developing photofunctional architectures.

Besides the traditional metal sulfide QDs, recently several metal oxide QDs, especially multimetal oxides with promising visible light absorption and high stability, have been explored to form 0D/2D heterojunctions with g-C₃N₄. Ye et al. reported 0D/2D heterojunctions of vanadate (AgVO₃, BiVO₄, InVO₄ and CuV₂O₆) QDs with g-C₃N₄ nanosheets prepared by dicyandiamide condensation followed by oxidation etching, in which the metal ions can be easily adsorbed onto the negatively charged surface (Zeta potential of about 17.0 mV) through electrostatic interaction, or captured into the tri-s-triazine units by the nitrogen-coordinating sites [139]. The vanadate QDs were formed in-situ on g-C₃N₄ nanosheets by adding NH₄VO₃ under sonication (Figure 4.19) [139]. The 0D/2D heterojunctions show superior visible-light-driven photoelectrochemical (PEC) and photocatalytic performance due to the strong coupling and band alignment resulting from the nitrogen-coordinating sites of g-C₃N₄ nanosheets and the highly dispersed vanadate nanocrystals.

4.5.3.4 g-C₃N₄ Homo Junctions

Among various g-C₃N₄-based photocatalysts, the homo junctions or isotype junctions formed by differently structured g-C₃N₄ occupy a unique role due to their simple preparation, the intimate interfacial contact, and the enhanced charge transfer properties. Several strategies have been reported for the construction of g-C₃N₄

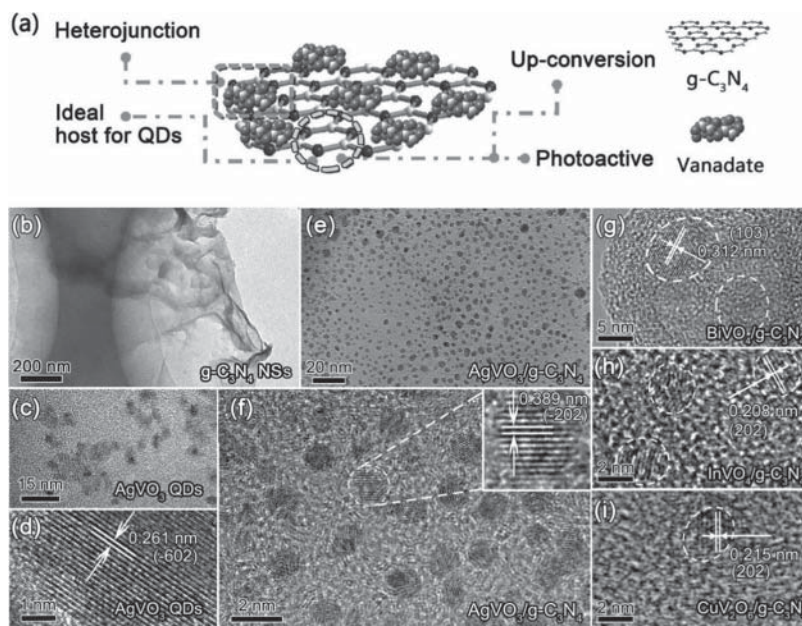


Figure 4.19 (a) Schematic structure of the 0D/2D heterojunction of vanadate QDs/g-C₃N₄ nanosheets. TEM images of g-C₃N₄ nanosheets (b), AgVO₃ QDs (c and d), AgVO₃/g-C₃N₄ (e and f), BiVO₄/g-C₃N₄ (g), InVO₄/g-C₃N₄ (h), and CuV₂O₆/g-C₃N₄ (i) [139]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2017.

homojunctions, such as molten-salt synthesis of isotype triazine-/heptazine based g-C₃N₄ heterojunctions [99], in-situ formed isotype heterojunctions by thermal reaction with lithium chloride [140], in-situ bond modulation with cyano terminal C≡N groups of defected-g-C₃N₄ to form p-n homojunctions [141], and (C-ring)-C₃N₄ plane heterostructural nanosheets with rapid photoelectron transfer [142]. For example, the Ye group reported the preparation of defect-modified g-C₃N₄ (DCN) photocatalysts under mild conditions by introducing NaBH₄ followed by heating at different temperatures, showing bandgaps decreasing from 2.75 to 2.00 eV (Figure 4.20) [141]. More importantly, cyano terminal groups are introduced into the DCN sheet edge, which act as the electron acceptors and endow the DCN with both n- and p-type conductivities. Consequently, this gives rise to the generation of p-n homojunctions with efficient charge transfer and separation, resulting in five times higher H₂ evolution activity. Room-temperature electron paramagnetic resonance (EPR) spectra indicated that the EPR signal in the DCN samples is much enhanced due to the redistribution of π -electrons. The introduction of the cyano terminal groups also extends the π -conjugated system which can efficiently improve the photoinduced production of radical pairs.

4.5.3.5 Dyes Sensitization

g-C₃N₄ can be further sensitized with dyes, such as eosin Y, metal phthalocyanines, erythrosine B, fluorescein and dibromofluorescein, to extend the active range of

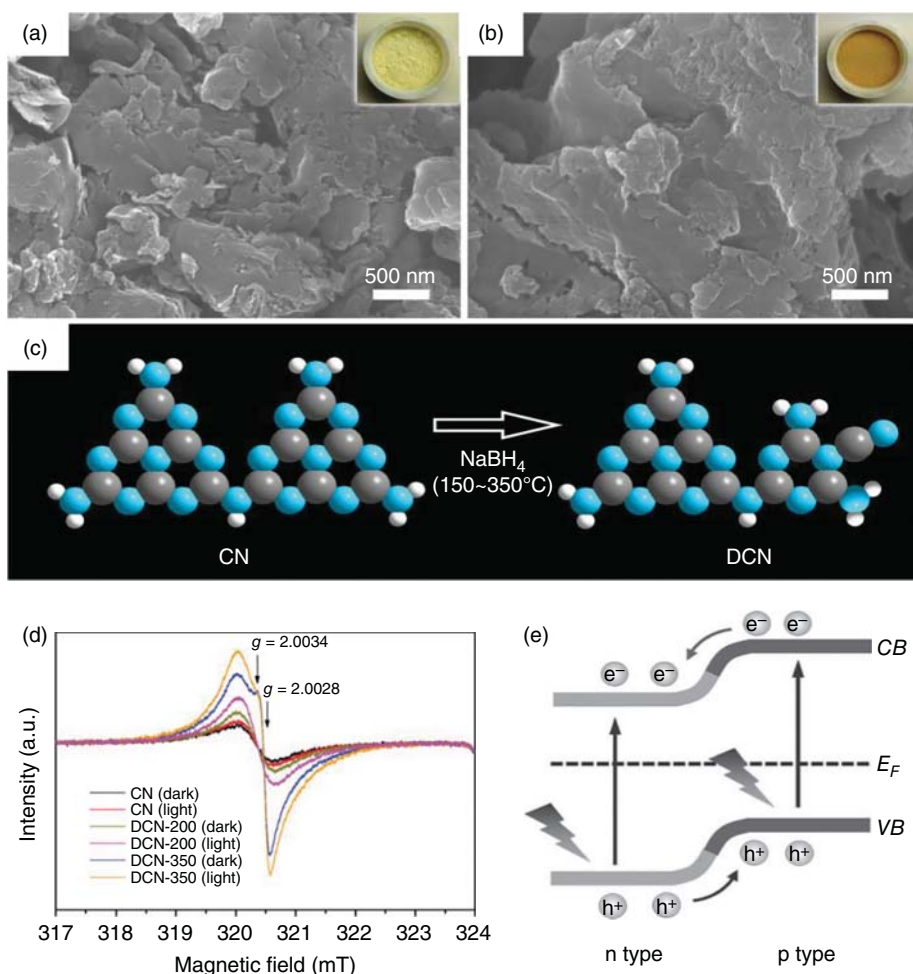


Figure 4.20 SEM images of (a) g-C₃N₄ and (b) DCN-350 and the corresponding photographs of the samples. (c) Illustration of the preparation process of DCN. (d) Room-temperature EPR spectra for g-C₃N₄ (CN), DCN-200, and DCN-350 measured with and without the light irradiation. (e) Schematic charge transfer process in the p–n homojunction of DCN [141]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

photocatalytic H₂ production [7, 109, 143, 144]. Although there is no heterojunction formed, the electron transfer is proposed to proceed from excited dye molecules to g-C₃N₄ that acts as a transducer and finally reach the cocatalyst [144]. Recently, Li et al. reported a novel g-C₃N₄-Pt²⁺ system with broadened light absorption in the visible-near-infrared (vis-NIR) range resulting from metal-to-ligand charge transfer (MLCT) by incorporating a trace amount of Pt²⁺ (less than 1.8 mg Pt per gram of catalyst, 0.18 wt%) (Figure 4.21) [145]. Photocatalytic H₂ production of the g-C₃N₄-Pt²⁺ complex was dramatically enhanced under vis-NIR irradiation. The MLCT works locally in the N-conjugated aromatic units, separately from the conventional HOMO-LUMO transition of g-C₃N₄, which avoids long-distance charge transport. This can also be

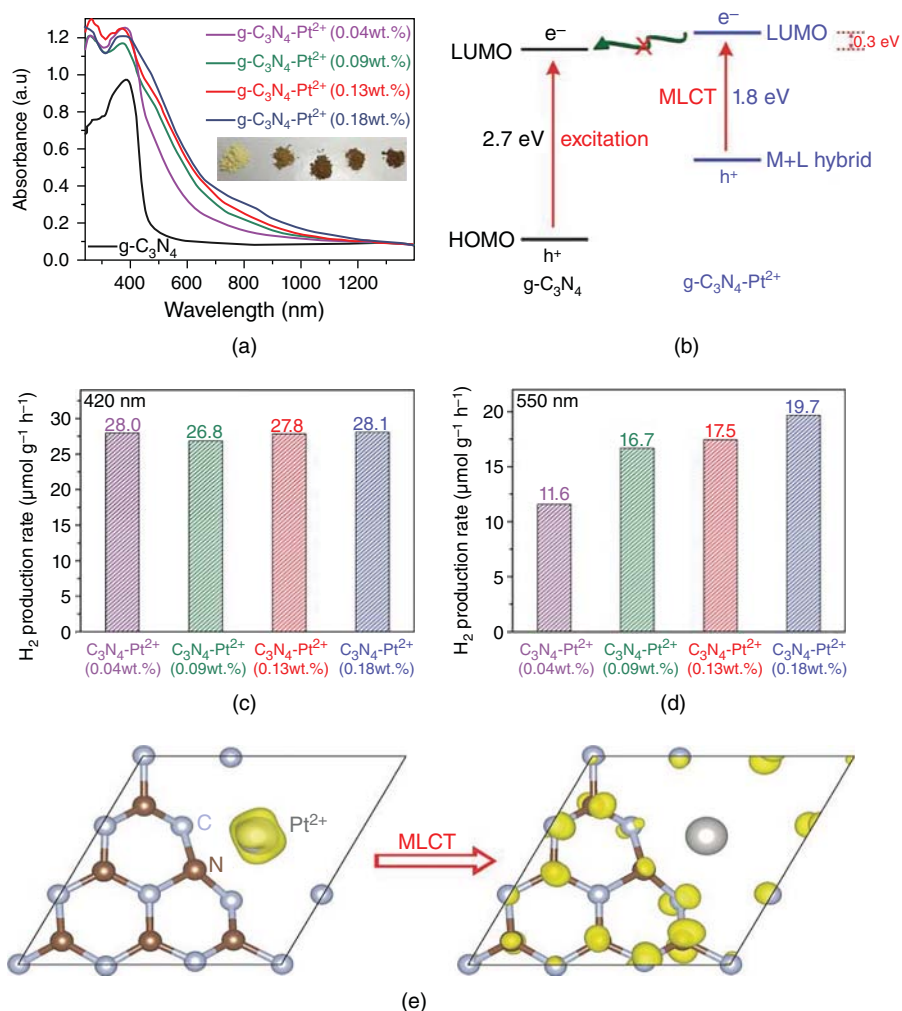


Figure 4.21 (a) UV-vis absorption spectra of g-C₃N₄ and g-C₃N₄-Pt²⁺ with various Pt concentrations. (b) Schematic illustration of the mechanism under irradiation of $\lambda > 400$ nm. Photocatalytic H₂ production rates using g-C₃N₄-Pt²⁺ with various amounts of Pt under irradiation of (c) 420 nm, and (d) 550 nm. (e) Photoexcited charge density transition from the Pt²⁺-induced hybrid HOMO states (in the range of 0–1 eV below the Fermi level) to the LUMO of g-C₃N₄-Pt²⁺ (in the range of 2–3 eV above the Fermi level), indicating the MLCT process, where the shaded bubble represents the electron population [145]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

applied to the coordination of g-C₃N₄ with Cu⁺, paving the way to further reducing material cost using non-noble metals.

4.5.4 Deposition of Earth-Abundant Cocatalysts

The photocatalytic water-splitting reaction includes three crucial steps: solar light absorption, charge separation and transportation, and the surface catalytic reactions of

H_2 and O_2 evolution. For $\text{g-C}_3\text{N}_4$ photocatalysts, significant achievements have been made in optimizing the light absorption and charge separation and transportation steps by bandgap engineering and heterostructure design, while much less effort has focused on the surface catalytic reactions, which mainly rely on the loading of cocatalysts. As discussed above, cocatalysts for $\text{g-C}_3\text{N}_4$ are still mainly based on rare and expensive noble metals, which makes seeking cheap and earth-abundant cocatalysts an inevitable task to achieve cost-effective photocatalytic water-splitting suitable for large-scale application. Meanwhile, with the explosive growth of research on electrocatalysts for H_2 and O_2 evolution, there is a great opportunity for the development of $\text{g-C}_3\text{N}_4$ photocatalysis with the incorporation of these low-cost earth-abundant materials as photocatalytic cocatalysts [108, 109, 146]. A number of non-noble-metal cocatalysts have been combined with $\text{g-C}_3\text{N}_4$ -based photocatalysts for H_2 evolution, such as Co_3O_4 [147], NiS [148, 149], nickel complexes (such as nickel dimethylglyoxime ($\text{Ni}(\text{dmgH})_2$)) [150], MoS_2 [147], WS_2 [151], and WC [152]. It has also been reported that combining $\text{g-C}_3\text{N}_4$ with graphene or other carbon materials gives extremely high photocatalytic H_2 evolution activity [153].

Hou et al. reported the growth of a thin layer of MoS_2 on $\text{g-C}_3\text{N}_4$ via impregnating $\text{g-C}_3\text{N}_4$ with $(\text{NH}_4)_2\text{MoS}_4$ in aqueous solution, and subsequent sulfidation with H_2S gas at 350°C (Figure 4.22) [154]. With MoS_2 as the cocatalyst, the 0.5 wt% $\text{MoS}_2/\text{g-C}_3\text{N}_4$ performs even better than 0.5 wt% $\text{Pt/g-C}_3\text{N}_4$ under the same conditions, which is

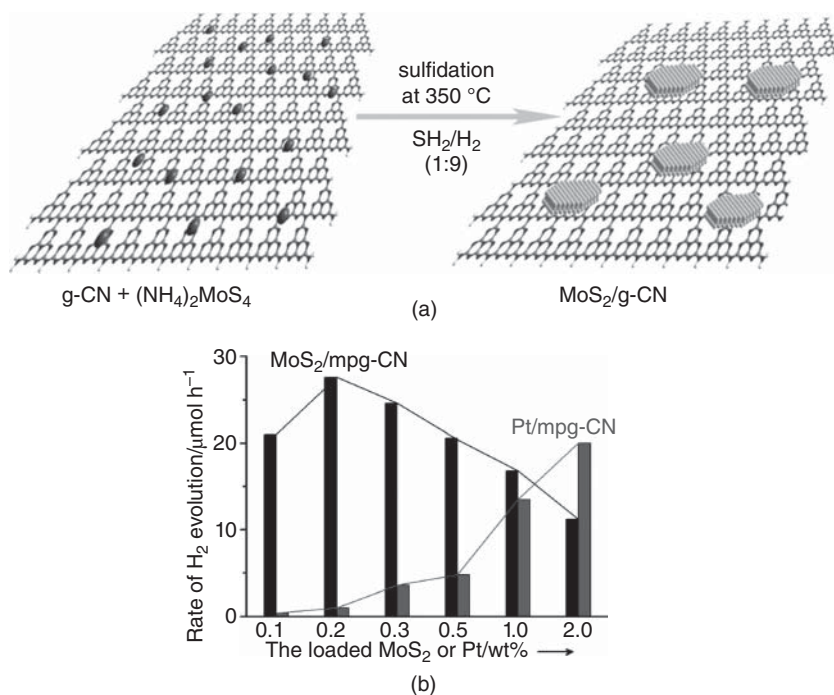


Figure 4.22 (a) The schematic procedure for $(\text{NH}_4)_2\text{MoS}_4$ impregnation and gas-phase sulfidation, and the idealized structural model of the resultant $\text{MoS}_2/\text{g-C}_3\text{N}_4$ layered junctions. (b) The H_2 production rates over $\text{g-C}_3\text{N}_4$ photocatalysts with different amounts of MoS_2 or Pt as the cocatalyst [154]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2013.

attributed to the geometric similarity in the layered structures of MoS_2 and $\text{g-C}_3\text{N}_4$ and the formation of the thin, planar $\text{MoS}_2/\text{g-C}_3\text{N}_4$ interface, promoting photoactivity. New strategies, such as photodeposition [155] and covalent cross-linking [156], have also been explored regarding more intimate interfacial contact as well as higher catalytic activity for H_2 evolution. Recently, Driess et al reported the synthesis of Ni_2P combined with a sol-gel prepared mesoporous $\text{g-C}_3\text{N}_4$ (sg-CN) by mixing the Ni salt, sodium hypophosphite and sg-CN, and sintering in Ar (Figure 4.23) [157]. The best photocatalytic H_2 generation rate of $330 \mu\text{mol H}_2 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ was obtained with 2 wt% Ni_2P (in first 1 h, 60 times higher than bare sg-CN), equal to $8400 \mu\text{mol}_{\text{H}_2} \text{ m}^{-2} \text{ h}^{-1}$ with triethanolamine (TEOA) as the sacrificial agent under visible light irradiation ($>420 \text{ nm}$). The cocatalyst Ni_2P mainly has two roles in a photocatalytic reaction: (i) to decrease the charge recombination, and (ii) to accelerate the surface chemical reaction. The enhanced carrier transfer at the Ni_2P -sg-CN heterojunction is the prime source for improved activity, as demonstrated by time-resolved PL (Figure 4.23b,c) and EPR spectroscopies (Figure 4.23d,e).

4.6 Conclusions and Outlook

In summary, significant progress has been made in the preparation, structure and property manipulation as well as photocatalyst design of $\text{g-C}_3\text{N}_4$ -based materials. Numerous strategies have been successfully developed for tuning the composition, nanostructure, bandgap and surface groups by varying the precursors, synthetic parameters and post-treatment conditions. Nanostructuring of $\text{g-C}_3\text{N}_4$ (such as ordered mesoporous structures, ultrathin 2D nanosheets and 0D QDs) plays a crucial role in the development of $\text{g-C}_3\text{N}_4$ -based photocatalysts, providing not only high surface area and more active sites, but also more prompt charge separation as proved by recent ultrafast spectroscopy studies. A large number of metals, graphitic carbons, semiconductors and earth-abundant cocatalysts have been explored to form heterostructure photocatalysts with $\text{g-C}_3\text{N}_4$ to increase the visible-light absorption, to promote charge separation and migration, and to enhance surface catalytic reaction.

However, visible-light photocatalytic activity is still far from the requirements of practical applications toward a sustainable, clean energy system relying on H_2 and the sun only. Some of the limitations come from difficulties related to effective bandgap narrowing, the preparation of single-layer $\text{g-C}_3\text{N}_4$ nanosheets, precise control of the active sites, and the formation of intimate and defect-free interfaces within the $\text{g-C}_3\text{N}_4$ -based heterojunctions. One of the most critical challenges may rely on the large-scale production of $\text{g-C}_3\text{N}_4$, and, more importantly, single-layer $\text{g-C}_3\text{N}_4$ nanosheets. Although it is usually claimed that $\text{g-C}_3\text{N}_4$ is a low-cost material, since the starting precursors (urea or cyanide) are very cheap, the slow thermal condensation process is highly energy-consuming and not suitable for continuous production. Researchers outside the photocatalysis field are probably needed to address the issues of industrial production, such as the rational design of the reaction-ware, maintenance of the nanostructure, and the specific properties during scale-up from the chemical engineering viewpoint. Besides the enormous progress on nanostructuring, doping and post-treatment, the understanding of synthesis of $\text{g-C}_3\text{N}_4$ itself is still very rough, lacking precise control of the atomic structure and molecular weight that has been

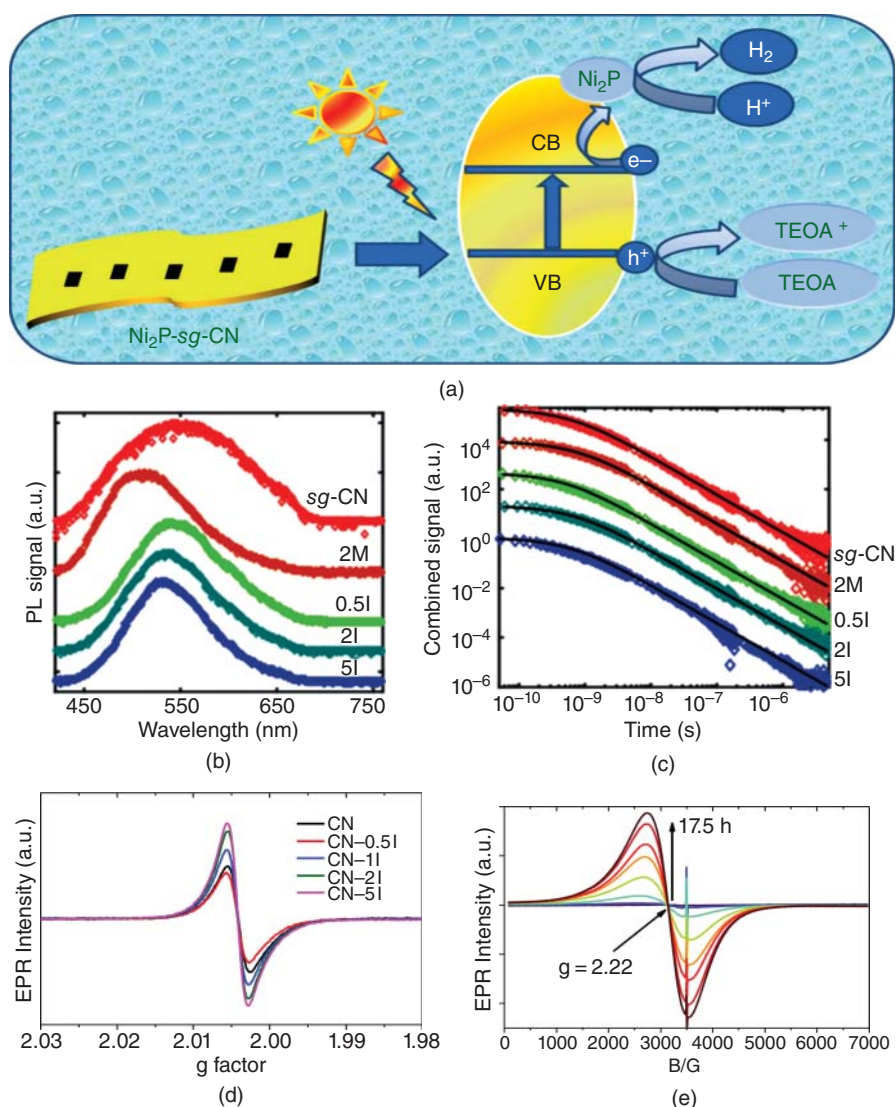


Figure 4.23 (a) Schematic processes of the charge separation and transfer in the valence band (VB) and conduction band (CB) in integrated $\text{Ni}_2\text{P-sg-CN}$ during photocatalytic H_2 evolution under visible light irradiation. (b) Comparison of the photoluminescence spectra and (c) combined wavelength integrated traces of time-resolved photoluminescence (TRPL) spectra of the integrated systems and 2 M with sg-CN . (d) Electron spin resonance (ESR) spectra showing the CB electron signal of $\text{Ni}_2\text{P-sg-CN}$ without any irradiation at 300 K. (e) ESR spectra showing the formation of Ni_0 particles during continuous irradiation (>420 nm) of 2I dispersed in $\text{TEOA:H}_2\text{O}$ (1:10) at 300 K. [157] The samples were denoted as xI or xM (where x = wt% of Ni_2P from initial concentration, I = integrated structure of $\text{Ni}_2\text{P-sg-CN}$, M = mixed structure of $\text{Ni}_2\text{P-sg-CN}$) [157]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2017.

accomplished in other polymer systems. In other words, g-C₃N₄ is more often treated as a raw material instead of a polymer molecule in most cases. More importantly, given the rapid growth of the research on g-C₃N₄ photocatalysis, it is worth noting that there are always controversial effects of these manipulation strategies on the photocatalytic activity, which brings the issue that compromise and optimization are inevitable in most cases. Typical examples include the bandgap narrowing vs. increased charge recombination upon doping, the increased surface area vs. quantum-confined-induced bandgap enlargement upon nanosheet exfoliation, and the enhanced charge separation vs. light shielding effect upon cocatalyst loading. It would be of great interest to explore novel structure design and preparation strategies to alleviate the side-effects and take full advantage of the positive effects.

Currently, most of the reported works focus on the H₂ evolution reactions only. Our understanding of the O₂ evolution and overall water-splitting is limited and requires more research. Recently, increasing efforts have been paid to the development of g-C₃N₄ photocatalysts for overall water-splitting that can produce H₂ and O₂ without any sacrificial reagents. The strategies include Z-scheme heterojunctions [114, 158, 159], spatial separation of the HER and OER components [53], successive two-electron/two-electron H₂O/H₂O₂ and H₂O₂/O₂ pathways in g-C₃N₄/CDots [16], and fast photoelectron transfer in (C-ring)-C₃N₄ plane heterostructural nanosheets [142]. However, the efficiency of overall water-splitting is still far from the requirement for practical application. For this goal, profound understanding of the photocatalytic reaction mechanism is required. Modern characterization techniques have brought huge progress and may further bring revolutionary changes for photocatalytic water-splitting using g-C₃N₄, the most promising polymeric semiconductor composed of two of the most earth-abundant elements. These techniques include (but are not limited to) XANES (X-ray absorption near edge structure) and Cs-corrected STEM (spherical aberration corrected scanning transmission electron microscopy) for characterization of the precise atomic structure, ambient pressure XPS and scanning electrochemical microscopy for the surface properties during the actual catalytic process, and ultrafast laser spectroscopy for profound understanding of the charge transfer mechanism.

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5

Carbon Materials for Supercapacitors

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5.1 Introduction

Supercapacitors, also known as electrochemical capacitors, represent an important kind of electrochemical energy storage device with high power density, long cycle life, and high rate capability. Electrical double layer capacitors (EDLCs), one kind of supercapacitors or ultracapacitors, are new electronic components with high-power electrochemical energy storage. The cost of EDLCs in the last decade has been decreasing significantly faster than that of batteries. Performance improvements in EDLCs have been noticeably more rapid as well. As a result, the range of commercial applications of electrochemical capacitor technology is expanding (Figure 5.1).

Energy storage in EDLCs is based on the adsorption of electrolyte ions on the large specific surface area (SSA) of electrically conductive porous electrodes. There have been three models to describe and explain the charge storage mechanism of the electrical double layer (EDL): the Helmholtz model (Figure 5.2a), the Gouy-Chapman model (Figure 5.2b), and the Stern model (Figure 5.2c). The Helmholtz model [3] describes the charge separation at the electrode/electrolyte interface when an electrode of surface area S (m^2) is polarized. Under this condition, ions of opposite sign diffuse through the electrolyte to form a condensed layer with a thickness of a few nanometers in a plane parallel to the electrode surface to ensure charge neutrality. Since the Helmholtz model did not take into account several factors such as the diffusion of ions in the solution and the interaction between the dipole moment of the solvent and the electrode, Gouy and Chapman proposed a diffuse model of the EDL, in which the potential decreased exponentially from the electrode surface to the bulk fluid (Figure 5.2b). However, the Gouy-Chapman model is insufficient for highly charged double layers. In 1924, Stern [4] suggested a model that combined the Helmholtz and Gouy-Chapman models by counting the hydrodynamic motion of the ionic species in the diffuse layer and the accumulation of ions close to the electrode surface (Figure 5.2c).

Carbon-based materials have attracted considerable interest in the electrochemical field due to their abundance, chemical and thermal stability, processability, and the possibility of tuning their textural and structural characteristics to fulfill the requirements

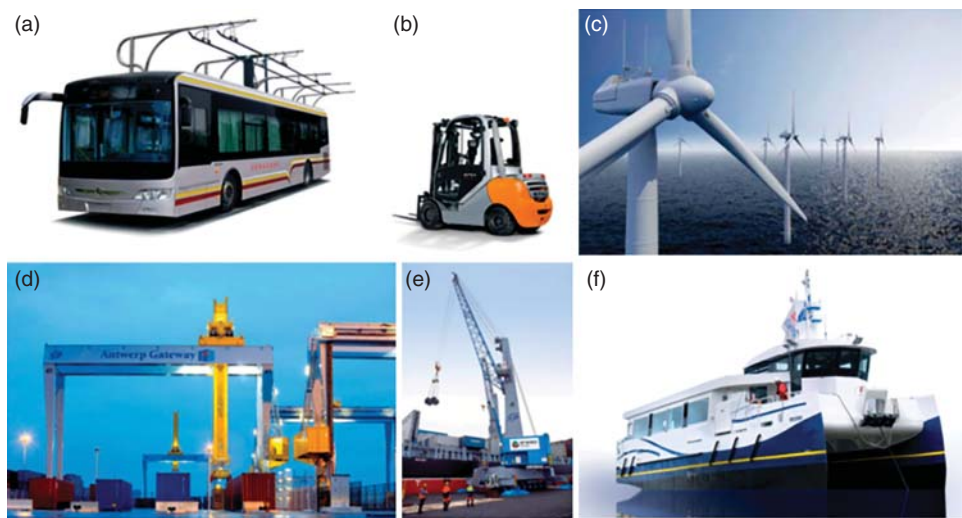


Figure 5.1 Examples of the large-volume applications of electrochemical capacitors [1]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2014.

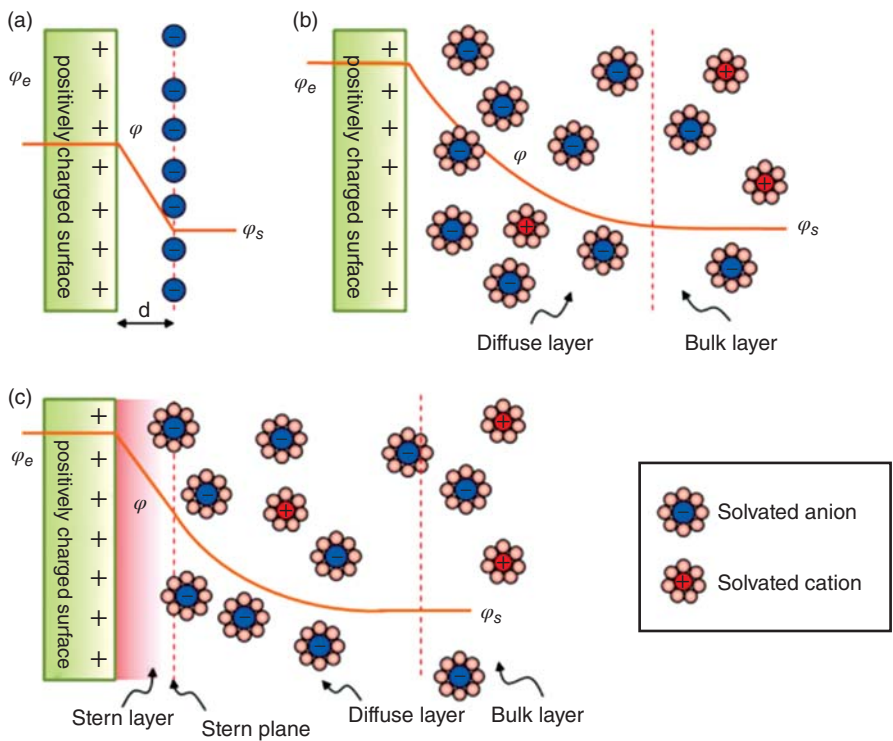


Figure 5.2 (a) The Helmholtz, (b) Gouy-Chapman, and (c) Stern models of the electrical double layer formed at a positively charged electrode in an aqueous electrolyte. The electrical potential, ϕ , decreases when transitioning from the electrode, ϕ_e , to the bulk electrolyte at infinity away from the electrode surface, ϕ_s . The Stern plane marks the distance of closest approach of the ions to the charged surface. Note the absence of charges/ions in the Stern layer. The diffuse layer starts in the range of 10–100 nm from the electrode surface [2]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2014.

of specific applications. In particular, various types of novel carbon materials with a high surface area, high electrical conductivity, and with a range of shapes, sizes and pore-size distributions, are being constantly developed and tested as potential supercapacitor electrodes.

5.2 Affecting Factors

Carbon materials have high SSA, excellent conductivity, unique chemical stability, and at the same time are relatively cheap, with abundant raw material sources, and so the production technology is more mature. It is still the most widely used electrode material in supercapacitors. The EDL of capacitor electrode material is characterized to identify SSA, pore size, length of pore, surface functional groups, electrolyte, and so on.

5.2.1 Specific Surface Area

The specific capacitance of carbon materials increases as the SSA increases. The theoretical value for an EDLC of clean graphite is $20 \mu\text{F cm}^{-3}$. For example, activated carbon (AC) has an SSA of $500\text{--}3000 \text{ m}^2 \text{ g}^{-1}$, so by this reckoning, a single electrode can reach as high as over 500 F g^{-1} . However, the actual specific capacitances of AC materials are only $75\text{--}250 \text{ F g}^{-1}$ in the water system and $40\text{--}100 \text{ F g}^{-1}$ in the organic system. So a large number of experiments prove that the specific capacitance of carbon materials does not always increase linearly with the increase in SSA. That measured in experiments is far less than the theoretical specific capacitance, and as a result, advantage has not yet fully been taken of a larger SSA.

5.2.2 Pore Size

EDL formation requires electrolyte infiltration of the carbon material surface. The International Union of Pure and Applied Chemistry (IUPAC) divides the porous materials into macroporous ($>50 \text{ nm}$), mesoporous ($2\text{--}50 \text{ nm}$) and microporous ($<2 \text{ nm}$). The traditional understanding of a carbon material micropore is that it makes a notable contribution to the surface area, but as a result of electrolyte ions not entering into it, these pores do not contribute to the capacitance. Chmiola et al. [5] demonstrated that charge storage in pores smaller than the size of solvated electrolyte ions will lead to enhanced understanding of ionic transport in porous media and microporous carbons with pores smaller than 1 nm , allows a volumetric capacitance increase from 55 to 80 F cm^{-2} . In 2015, Galhena et al. [6] skillfully chose graphene oxide (GO) as the model of study, replacing the pore size with the spacing of layers. Because the surface contains rich oxygen-containing functional groups, the interlayer spacing of GO is 0.82 nm . When GO is immersed in a TEA-BF₄/PC solution, variations in the interlayer spacing of GO electrodes combined with in-situ X-ray diffractometry (XRD) and electrochemical capacitor testing are used to directly assess how the specific capacitance of the model electrodes scales with interlayer constriction size (Figure 5.3a). The authors concluded that when the pore size is 0.7 nm , the capacitor value is the largest because this size is just enough for tetraethylammonium (TEA⁺) (0.68 nm) ions to enter. The microporous energy storage mechanism was not explained until 2008 [7]: to measure the

capacitance in the series of carbon materials studied herein (with pores smaller than the size of the solvated ion), there must be at least partial removal of the solvent shell. The results show that a decrease in the pore size causes an increase in the number of solvent molecules removed, along with a similar increase in the capacitance. This result points to a mechanism by which removing the solvent shell leads to some form of charge/energy storage (for example, see Figure 5.3b.)

Furthermore, Salitra and coworkers [8–10] studied EDLC performance of ACs with different pore diameter distributions in aqueous solutions of LiCl, NaCl and KCl, as well as propylene carbonate solution of LiBF_4 and $(\text{C}_2\text{H}_5)_4\text{NBF}_4$, which show a remarkable difference due to the different molecular sizes. Hence pore size distribution is a very important parameter, and according to different electrolytes, the required minimum pore size is also different. Qu and Shi [11] systematically discussed the role of pore sizes

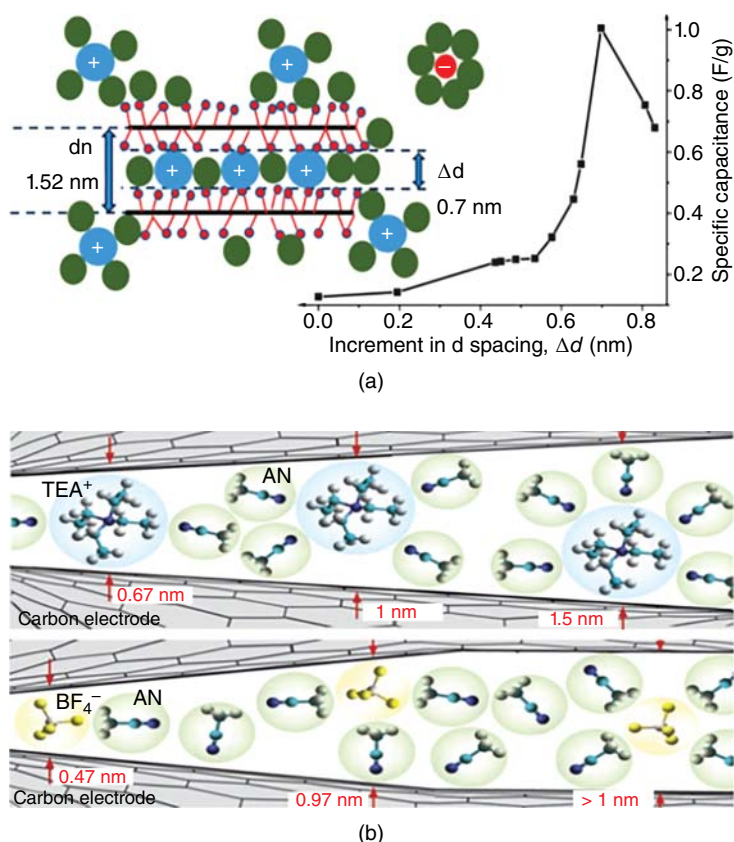


Figure 5.3 (a) A model system based on graphene oxide, which employs interlayer constrictions as a model for pore sizes that can be both controllably tuned and studied in-situ during supercapacitor device use [6]. Source: Reprinted with permission from ACS publishers, Copyright 2015. (b) Geometric confinement of ions in extremely small pores. Both anions and cations enter the pores with no solvent-molecule screening charge at pore sizes below 1.5 and 1 nm, respectively. Therefore, it can be asserted that in these experiments, the ions enter the pores either bare or with partial solvent shells (TEA^+ = tetraethylammonium, AN = acetonitrile) [7]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2008.

and their distribution in porous carbon materials for electrochemical capacitors. They compared the EDLC and BET (N_2) to determine the surface areas of different carbon materials. Under different conditions for preparation of microporous and mesoporous AC fibers, research shows that ions move slowly in the narrow pores with low EDLC, while mesoporous AC fibers improve the formation of EDL and the transportation ability of ions in the pores, furthermore improving the EDLC, for specific AC fiber in the organic system. When pores greater than 2 nm account for more than 50% of the volume, specific capacity increases linearly with the increase of SSA.

The larger the pore size in the carbon material, the higher the rate capability. But for areal capacitance, different electrolytes need to match different apertures. The highest utilization of the material surface can be achieved only if the pore size matches the solution ionic radius. In the end, pore size distribution also affects the low-temperature performance, because at low temperatures the greater the pore size in the carbon electrode, the smaller the loss in capacity.

5.2.3 Surface Functional Groups

Carbon material surface has a lot of functional groups, and therefore has dangling bonds, which can easily form organic functional groups by adsorption or physical chemical treatment, for example, quinone, carboxyl, hydrogen, phenol, hydroxide radical, and so on. Organic functional groups can be introduced onto the surface of carbon materials through electrochemical oxidation, low-temperature plasma oxidation, chemical oxidation, and adding surfactants.

These functional groups undergo a redox reaction during charging and discharging to cause a pseudocapacitance, thereby increasing the specific capacity of the carbon material. Electrochemical oxidation or cryogenic plasma oxidation treatment can also cause partial oxidation on the surface of carbon materials, increasing oxygen-containing functional groups, so that the charge and discharge capacity of the electrode increases significantly. Rychagov et al. [12] proved that the contribution of surface functional groups of the pseudocapacitance effect contrast can sometimes reach more than 50%. However, when too much carbon material content of surface functional groups has a negative impact on the performance of the capacitor, the greater the contact resistance of the material, so capacitor equivalent resistance will be increased. Meanwhile, a carbon material surface with a high oxygen content will enhance the natural potential of the electrode, which leads to the capacitor at operating voltage undergoing a hydrogen or oxygen evolution reaction, and affecting the cycle life of the capacitor. Through using inert gas in heat treatment methods of modification, there can be an increase in the surface area and porosity of AC, reducing the concentration of functional groups to improve wettability.

5.2.4 Electrical Conductivity

The electrical conductivity of carbon materials is the most important factor for equivalent series resistance and charging and discharging performance. In general, high electrical conductivity of carbon materials as electrodes can improve the specific power of the capacitor. The electrical conductivity of carbon materials is also influenced by SSA, density, graphitization degree, pore size, and other factors. Taking AC as an example,

electrical conductivity of the carbon material decreased with an increase in SSA, which was attributed to the following reasons: as the surface area of carbon increases, the distributed carbon content of micropore walls reduced, at the same time as pore size and pore depth, wettability between the electrolyte and active carbon on the surface of materials, contact area between the AC particles, and so on, all of which will produce a huge effect on the electrical conductivity of the capacitor [13, 14].

5.3 Electrolyte

The electrolyte is an important part of the supercapacitor, since with the charging process of the supercapacitor, internal electrolytes form a double electron layer on the surface of the active material on the positive and negative electrodes, so as to achieve energy storage. In the process of discharge, due to there being a potential difference between the positive and negative electrodes, EDL storage charge current is formed by the external circuit.

5.3.1 Aqueous Electrolyte

Aqueous electrolyte was first applied to supercapacitors, and it has many advantages, such as high electrical conductivity, low internal impedance, smaller-diameter electrolyte molecules, fully impregnated micropores, fully used surface area, and low cost [15, 16]. Mainly the study of electrolytes focuses on the acids, neutral and alkali aqueous solutions; among them the most commonly used are H_2SO_4 and KOH aqueous solutions.

Aqueous electrolyte conductivity ($\sim 1 \text{ S cm}^{-1}$) is higher than organic electrolyte, which brings higher power to the system performance. The most commonly used acidic solution is H_2SO_4 aqueous solution, due to its electrical conductivity and high degree of ionic concentration, low internal resistance, and effective series resistance. But H_2SO_4 aqueous solution as the electrolyte is corrosive, so the current collector cannot use metals; should the capacitor suffer destruction, this could lead to a leakage of sulfuric acid. Other experiments have used HBF_4 , HCl , HNO_3 and H_3PO_4 as electrolyte.

For alkali electrolytes, the most commonly used is KOH aqueous solution, and the concentration is commonly 1 or 6 mol l^{-1} . Using carbon materials for the electrode, a KOH concentration of 6 mol l^{-1} gives the best performance, but for a metallic oxide electrode it is best at 1 mol l^{-1} . In addition to using KOH aqueous solution, the use of LiOH and NaOH aqueous solutions have been suggested as electrolytes.

In order to reduce acid corrosion characteristics of the media, neutral electrolytes were studied. Neutral electrolytes are mainly potassium, sodium, and lithium salts, and the most studied is KCl aqueous solution since it has the best performance.

Although aqueous electrolytes are used widely, the decomposition voltage is low (the theoretical decomposition voltage for water is 1.23 V, while the operating voltage is relatively low at $\sim 1 \text{ V}$). The narrow liquid water range from freezing point to boiling point gives poor low-temperature performance for the capacitor, and either the alkali or the acid electrolyte has strong corrosivity, so more and more people are keen to study organic electrolytes.

5.3.2 Organic Electrolyte

Commonly used cations for organic electrolytes are mainly of quaternary ammonium salts, such as Me_4N^+ , Et_4N^+ , Bu_4N^+ , Me_3EtN^+ and so on; besides, Li^+ and R_4P^+ also have been reported, with anions of ClO_4^- , BF_4^- , PF_6^- and AsF_6^- . Frequently-used solvents include γ -butyrolactone (BL), propylene carbonate (PC), and N,N -dimethylformamide (DMF). All the organic electrolytes mentioned above have a high decomposition voltage (2–4 V) [1] to give a higher energy density, with a wide working temperature range, are relatively safe for metal material, have a higher electrochemical stability and high pressure resistance.

5.3.3 Ionic Liquid Electrolytes

An ionic liquid (ILs) refers to a substance that is liquid at room temperature and consists completely of ions. The radii of the anions and cations in ILs are generally quite big and asymmetric, and in the IL anions and cations cannot be effectively stacked on the microscopic scale due to the space steric hindrance role. Hence, the anion and cation vibrate at room temperature, the orderly crystal structure is destroyed, and the acting force between ions is also reduced to reduce the melting point of this kind of ionic compound, hence becoming a liquid at room temperature [17–19].

Usually ILs can be classified according to the different cations into, such as imidazole, pyridine, pyrrole and quaternary salt; in contrast, they can be divided according to the anion: organic fluorine, inorganic fluoride, nitrile, acid, ester and halogen. ILs have superior physical and chemical properties for use in a supercapacitor, compared with traditional liquid electrolytes. For instance, they have better electrochemical stability (wide electrochemical window). This means that the electrode material in IL electrolytes has a wider range of working voltage, so using ILs as electrolyte can provide a high energy density supercapacitor. In addition, ILs have good thermal stability, with little tendency to be flammable or explosive, which improves the security of the supercapacitor [19]. Moreover, ILs have almost no saturated vapor pressure, since they are non-volatile, and will not pollute the environment. The most important point is that IL electrolytes can be devised by selecting particular anions and cations from the range available, thus giving a different electrolyte performance.

5.4 Electrode Materials

5.4.1 Activated Carbons

At present, activated carbon materials are outstanding for use in a supercapacitor, due to their high surface area ($>1000 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($>0.5 \text{ cm}^3 \text{ g}^{-1}$), and relatively low cost. Activated carbon (AC) is the oldest and the most common type of porous carbon. The use of AC in Egypt was described as early as 1550 BCE, and the first industrial production of AC was in the United States at the beginning of 1913. The first industrial production of ACs began nearly a century ago, but despite extensive research and improved activation processes, achieving accurate control of the pore structure is still very challenging. The pores of AC lie within the range of 0.4–4 nm, but the pore size distribution is relatively wide, which may limit their application to some of the

double layer capacitors. The activation of carbon materials can be divided into two ways: (i) physical and (ii) chemical.

- (i) *Physical activation.* The physical activation process utilizes different oxidizing gases, such as air, O_2 , CO_2 , steam, or their mixtures [20, 21]. A carbon precursor is first exposed to pyrolysis in an inert atmosphere at 400–900°C to eliminate the bulk of volatile matter, followed by partial gasification using an oxidizing gas at 350–1000°C. Initially, the active oxygen in the activating agent burns away the tarry pyrolysis off-products trapped within the pores, leading to the opening of some closed pores. Then the microporous structure is developed as the oxidizing agent burns away the more reactive areas of the carbon skeleton, resulting in CO and CO_2 ; the extent of burn-off depending upon the nature of the gas employed and the temperature of activation. CO_2 , air and steam are used as activating agents. The chemical and physical nature of ACs is very much dependent on the precursor, the oxidizing agent employed, the temperature of activation, and the degree of activation. Depending on these factors, ACs with moderately high porosity can be achieved, as well as with varying surface chemistry (i.e. amount and type of oxygen groups). As a general trend, the higher the activation temperature/activation time, the greater the porosity development. However, higher porosity developments are usually accompanied by a broadening of the pore size distribution.
- (ii) *Chemical activation.* The chemical activation process consists of the heat treatment of a mixture of the carbon precursor under a normal temperature range of 450–900°C. It has the following advantages over physical activation: it usually involves only one step, lower pyrolysis temperatures are used, a much higher carbon yield is obtained, materials with a very high surface area ($3600\text{ m}^2\text{ g}^{-1}$) can be produced, and the microporosity can be well developed, controlled and tailored to be narrowly distributed. These last two strengths of the chemical activation process are very important in applications such as energy storage in supercapacitors or in gas (H_2 , CH_4 or CO_2) storage, which demand materials with large surface areas and a microporosity adjusted to the size of the electrolyte ions for supercapacitors or 0.7–1 nm for gas storage. Many reagents have been proposed for chemical activation; $ZnCl_2$ [22], H_3PO_4 [23] and KOH [24] are the most commonly used. $ZnCl_2$ and H_3PO_4 act as dehydrating agents, whereas KOH acts as an oxidant. H_3PO_4 promotes dehydration at a lower temperature than the thermal treatment alone, and the evolution of CO and CO_2 commence with a lower temperature. During heat treatment, the activating agent present in the interior of the particles produces a dehydrating effect on the carbon precursor.

A comparison of the highest surface areas reported for different porous materials is shown in Figure 5.4 [25]. It can be seen that only some metal–organic frameworks (MOFs), covalent organic frameworks (COFs) and porous polymers exhibit higher surface area than KOH-ACs. However, some of the most porous possess limited physicochemical stability, whereas AC is highly stable. Furthermore, KOH-activated AC displays the highest surface area.

During electrode formation, due to the different carbon sources, there are many kinds of microstructure of AC, such as powders, particles, fabrics, fibers, and so on (Figure 5.5) AC powders have well-developed manufacturing technologies, easy

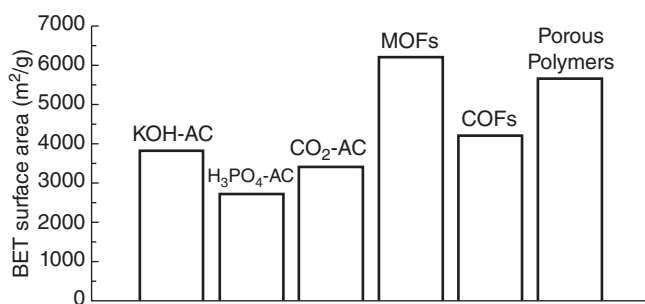


Figure 5.4 Comparison of the highest value of BET surface area reported for different types of porous materials: KOH-AC, H₃PO₄-AC, CO₂-AC, MOFs, COFs, and porous polymers [25]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

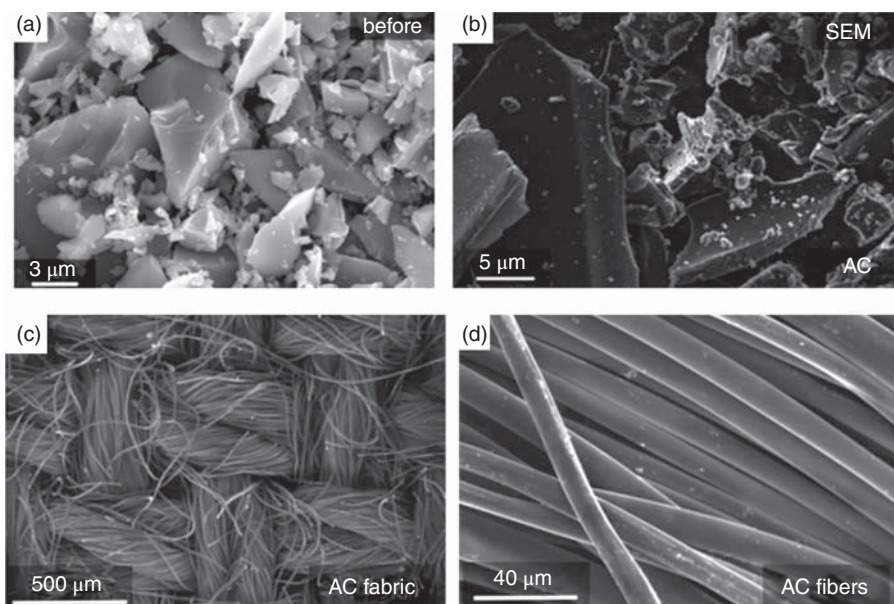


Figure 5.5 SEM micrographs of AC materials. (a) AC powders [26], (b) AC particles [1], (c) AC fabrics [27], (d) AC fibers [27]. Source: (c) and (d) reprinted with permission from John Wiley and Sons Ltd, Copyright 2013.

production in large quantities, a high surface area, relatively low cost, and great cycle stability [28]. Commercial ACs commonly offer SSA in the range of 700–2200 m² g⁻¹ and moderately high specific capacitance in the range of 70–200 F g⁻¹ in aqueous electrolytes, and 50–120 F g⁻¹ in organic electrolytes [1]. Furthermore, recent developments in the synthesis of ACs have greatly enhanced specific capacitance (up to 250–300 F g⁻¹ in aqueous, organic, and IL-based electrolytes), which demonstrates that, for a significant portion of EDLC applications, ACs may remain the material of choice. In order to achieve higher surface area, and remove the bottleneck of pores at the same time, the smallest micropores are produced in the process of carbonization of organic precursors. Wei et al. [29] used an environmentally friendly, low-temperature

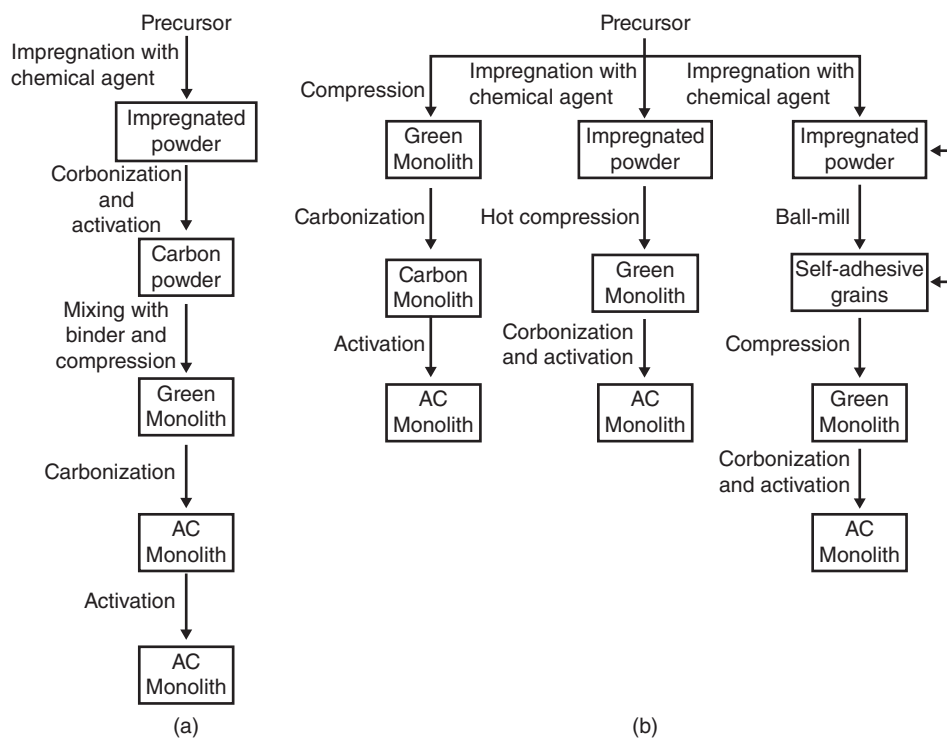


Figure 5.6 Synthesis procedures for the generation of activated carbon monoliths: (a) with a binder, and (b) binderless [25]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

hydrothermal carbonization, to introduce a network of carbon structures within the distribution of oxygen. With micropore surface areas of the AC of up to $2387 \text{ m}^2 \text{ g}^{-1}$, the specific capacitance of the electrode is close to 236 F g^{-1} , which is measured with a symmetrical configuration when in the organic electrolyte.

For the practical application of AC as adsorbent or storage medium, not only is storage capacity important, but volumetric capacity may be a key parameter [25]. In this case, high quality of AC monoliths to increase the bulk density is essential, especially for high ACs, which can reach extremely low densities. AC monoliths synthesize procedures obtained with a binder and binderless; a detailed description is shown in Figure 5.6. Monoliths can be more easily dissolved than powders, and their use is essential for the preparation of supercapacitor electrodes. For instance, AC binderless monoliths can be synthesized from a mesophase pitch, with a high SSA of up to $2650 \text{ m}^2 \text{ g}^{-1}$. They present high capacitance values of 334 F g^{-1} in H_2SO_4 electrolyte, and low electrical resistivity, and as an energy storage device, 12 W h kg^{-1} maximum energy density, with $12\,000 \text{ W kg}^{-1}$ maximum power density. Long-term cycling experiments show excellent stability, with a reduction in the initial capacitance values of 19% after performing 23 000 galvanostatic cycles at $\sim 300 \text{ mA g}^{-1}$ [30].

In contrast to the monolithic electrodes, however, AC fiber electrodes with nano-size diameters giving a high SSA can offer very high mechanical flexibility. AC fibers show high power characteristics originating from the smaller electrode thickness and the

presence of a large number of macroscopic/mesoporous single fibers. The use of supercapacitor electrode binders generally reduces the electrical and electrochemical properties of supercapacitors. The AC fiber electrodes give excellent speed capability, but suffer from low density. The high power density of an AC fiber electrode is lower than that of an AC powder electrode, which leads to the lower volumetric capacitance. Hence, some studies have worked on improving this above phenomenon with various measures and suggestions. For example, carbonization was performed at 650°C with a chemically activated (KOH) mesophase pitch to obtain AC fibers with a SSA value of 2436 m² g⁻¹, and moreover exhibited higher values of specific capacitance [31]. Physical activation parameters can be similarly used to control the density and porosity of carbon fibers [32].

From the discovery of AC to the present, researchers have been interested in AC derived from biomass. The application of biomaterials as a biological template is known for the nanostructuration of various inorganic materials and metal nanoparticles, in which cellulose and polysaccharide nanocrystals play a significant role [33]. The use of biomass resources for a wide range of AC electrode materials demonstrates that the complex functionalities of living systems is a highly attractive research theme. It is certain from a survey of published articles that biomass carbons have an outstanding capability to be applied as electrodes in energy devices [34]. Several ACs have been obtained by pyrolysis of biomass precursors. It is important that obtaining AC from biomass wastes is especially cheap, and hence biomass waste can be considered as a potential raw material source for the preparation of AC electrodes, and exhibit excellent electrochemical capacitive performance in capacitors.

The simplest approach to accessing AC from biomass, such as from plant, industrial wastes, domestic wastes, and marine wastes, is pyrolysis of native biomaterial under closed conditions or in an inert atmosphere. Liu et al. [35] took biomorphic cotton fibers, pretreated under the effect of NaOH/urea swelling on cellulose, and subsequently used them as a biomass carbon source to mold a porous microtubule structure through a certain degree of calcining. Thanks to favorable structural features, the hierarchical porous carbon fibers exhibit an enhanced EDL capacitance (221.7 F g⁻¹ at 0.3 A g⁻¹) and excellent cycling stability (only 4.6% loss was observed after 6000 cycles at 2 A g⁻¹). Zhu et al. [36] used auricularia in two steps to get AC: the first step (up to 200°C) is related to the adsorbed-water desorption, and the second step (200–650°C) is associated with dehydration and decarboxylation. To create porosity in the framework, as well as to improve the electronic conductivity, a pyrolysis step was applied to AC, which displayed an inherently superior capacitive property (196 F g⁻¹ in 6 M KOH). Moreover, to further validate the promising applications for a hybrid capacitor, the discharge capacity of 16 mA h g⁻¹ can be obtained from a hybrid capacitor at a current density of 0.167 A g⁻¹, and the specific energy density of up to 9.4 W h kg⁻¹ is achieved at low power density and 8.0 W h kg⁻¹ is retained at a power density of 500 W kg⁻¹. Waste celtuce leaves were used to prepare porous carbon by air-drying, pyrolysis at 600°C in argon, followed by KOH activation. The as-prepared porous carbon has a very high SSA of 3404 m² g⁻¹ and a large pore volume of 1.88 cm³ g⁻¹. As an electroactive material, the porous carbon exhibits good capacitive performance in KOH aqueous electrolyte, with specific capacitances of 421 and 273 F g⁻¹ in three- and two-electrode systems, respectively [37]. ACs prepared from fir-woods by means of a steam activation method at 900°C for 1–7 hours are demonstrated as promising

materials for supercapacitors. These carbons exhibit high-power, low equivalent series resistance and highly reversible characteristics between -0.1 and 0.9 V in aqueous electrolytes, and as estimated from cyclic voltammetric curves measured at 200 mV s^{-1} , have achieved the capacitance 120 F g^{-1} between -0.1 and 0.9 V in acidic electrolytes [38]. In addition to the above, Jisha et al. [39] obtained disordered carbonaceous materials by pyrolysis of coffee shells at 800 and 900°C with porogen ZnCl_2 as electrode material in symmetrical electrochemical supercapacitors. Furthermore, there are other possible biomass carbon sources for AC: hair, a high-nitrogen energetic material, can be utilized as a precursor for nitrogen-doped porous carbon. The preparation procedures for obtaining AC samples from hair (SSA, $441.34 \text{ m}^2 \text{ g}^{-1}$) shows higher capacitance (154.5 F g^{-1}) compared with nitrogen-free commercial ACs (134.5 F g^{-1}) at 5 A g^{-1} in a three-electrode system. The capacitance remains at 130.5 F g^{-1} even when the current load is increased to 15 A g^{-1} . The capacitance loss is only 5% in 6 M KOH after 10 000 charge and discharge cycles at 5 A g^{-1} [40].

High carbon content wastes can also be used for AC. For example, sugarcane bagasse, via activation and carbonization, can provide an AC electrode; sugarcane bagasse [41] prepared by ZnCl_2 activation has demonstrated a high SSA of more than $1000 \text{ m}^2 \text{ g}^{-1}$, and the surface area is found to increase with the weight ratio increase of ZnCl_2 bagasse. Specific capacitances as high as 300 F g^{-1} were observed in supercapacitor cells containing $1 \text{ M H}_2\text{SO}_4$ electrolyte and exhibit specific energy of up to 10 Wh kg^{-1} . An AC electrode was prepared from sugarcane bagasse through a simple microwave-induced ZnCl_2 activation to limit the pore size from 2.5 to 7 nm [42]. AC can also be devised from waste paper. The author obtained AC by simple KOH activation of waste newspaper – a development for use of waste paper as a valuable energy storage material. The AC surface area was $416 \text{ m}^2 \text{ g}^{-1}$, and the electrochemical capacitance value was 180 F g^{-1} at a 2 mV s^{-1} scan rate in 6.0 M KOH [43].

Different types of waste shells can also be used as carbon sources for AC. AC electrode materials have been synthesized by carbonizing a common livestock biowaste in the form of chicken eggshell membranes, which contain around 10 wt% oxygen and 8 wt% nitrogen [44]. The obtained materials, with surface area of $221 \text{ m}^2 \text{ g}^{-1}$, showed specific capacitances in a three-electrode system of 297 and 284 F g^{-1} in basic and acidic electrolytes, respectively. Furthermore, the electrodes revealed brilliant cycling stability: only 3% capacitance loss after 10 000 cycles at a current density of 4 A g^{-1} .

Despite recent improvements in AC electrodes, the key challenge with traditional AC technology is how to independently control the SSA, pore volume, pore size and shape in these materials. Thus, other synthesis techniques have been developed to address these limitations.

5.4.2 Graphene

Graphene is a two-dimensional allotrope of elemental carbon. Carbon atoms are closely arranged in a honeycomb lattice, to form a two-dimensional crystal material with a thickness of a single carbon atom. In graphene, the hybrid carbon atom is connected to the other hybrid carbon atoms by nonpolar covalent bonding (Figure 5.7). An article in the journal *Science* reported for the first time this new carbon material [46], and since its discovery, graphene has made carbon materials once again a major focus of research in the field of nanotechnology. One of the first studies of graphene structures

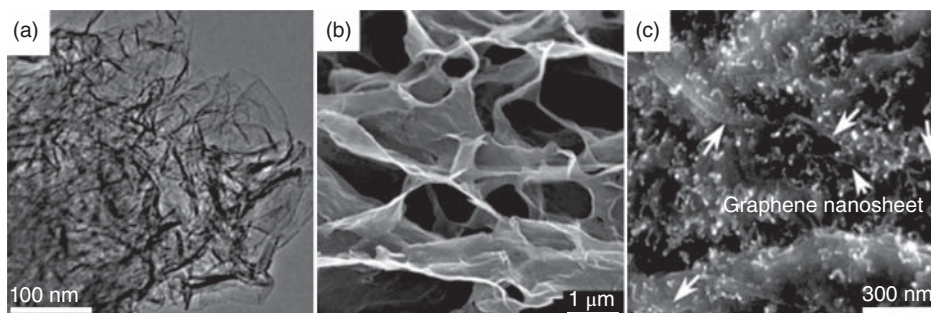


Figure 5.7 (a) TEM image of graphene-based nanosheets; (b) SEM image of a self-assembled graphene hydrogel; (c) SEM image of a CNT/graphene composite [45]. Source: Reprinted with permission from RSC publishers, Copyright 2011.

in different electrolytes was reported in 2008 [47]. Graphene materials can be prepared via various approaches, including mechanical cleavage of graphite with Scotch tape, epitaxial growth on single-crystal silicon carbide (SiC), chemical vapor deposition (CVD) on metal surfaces, chemical coupling reactions, or exfoliation of graphite powder via solution oxidation, sonication/intercalation, or ball milling.

However, graphene sheets tend to form irreversible agglomerates or even restack to form graphite due to their strong π - π stacking and van der Waal's interactions between the intersheets of graphene, resulting in a dramatic decrease in the surface area. Additionally, the best utilization of graphene sheets is to exploit the limited cross-plane ion diffusion due to their large sheet aspect ratio. In order to fully utilize and further explore the new functions of graphene for use in supercapacitors, many researchers have tried to solve the problem of π - π stacking. Graphene-based materials have a theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ [48], and thus a supercapacitor based on it could, in principle, achieve a capacitance as high as $\sim 550 \text{ F g}^{-1}$ if their entire surface area could be used [49]. Nevertheless, the specific capacitances of 135 and 99 F g^{-1} measured in aqueous and organic electrolytes, respectively [49, 50], fall far below the theoretical value.

In addition, graphene is a semi-metal with a bandgap of zero, which makes it impossible to turn electric conduction off below a certain limit. Transformation of graphene into a semiconductor has attracted wide attention [51]. The presence of the so-called small quantum capacitance (C_Q) in series for nanocarbon electrodes, arising from their low electronic density of states at the Fermi level ($\text{DOS}_{(\text{EF})}$), overwhelms the high double layer capacitance (C_{dl}), further reducing the already limited capacitance and low energy density [52]. Therefore, reduced graphene oxide (rGO) is often used as an electrode material in supercapacitors. During the reduction of GO to obtain rGO, induced defects improve the electrochemical performance. The Ramakrishna Podila group used experimental and density function theory (DFT) to calculate engineering defects in graphene, as shown in Figure 5.8, which demonstrates that controllably induced defects in specific configurations can achieve 150% enhancement ($\approx 50 \text{ } \mu\text{F cm}^{-2}$) in measurable capacitance of graphene a few layers thick [52].

The first procedures for the synthesis of GO were developed several decades ago by Brodie, Staudenmaier, and Hummers et al. and still remain in use today with only minor modifications [53]. Commonly, GO is obtained by the Hummers method at present, through the oxidation of potassium permanganate (KMnO_4) and concentrated sulfuric

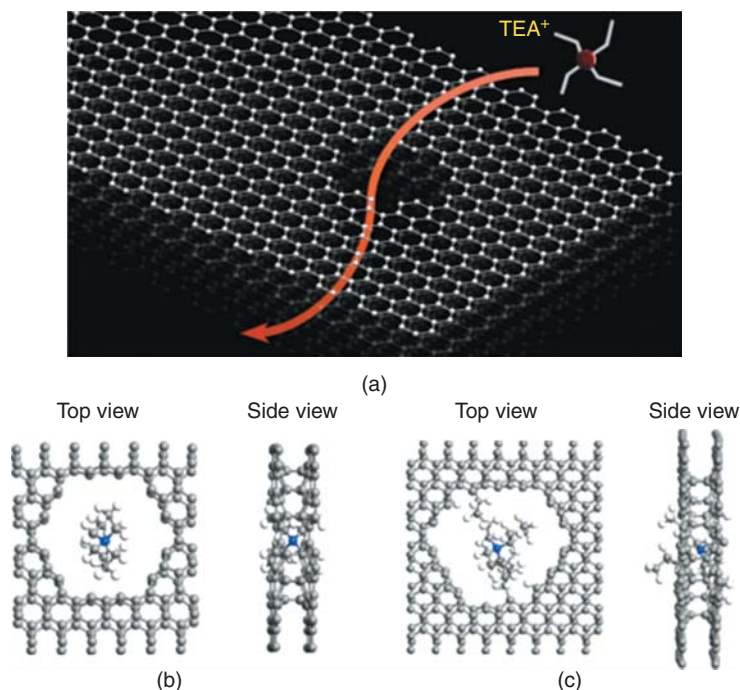


Figure 5.8 The interaction of electrolyte ions with defect-induced pores. (a) Defect-induced pores in few-layered graphene can open otherwise inaccessible surface area by transporting electrolyte ions (e.g. tetraethylammonium [TEA⁺]) to interlayer gallery space. Density functional theory calculations show that the intercalation of (b) TEA⁺ is more favorable compared to (c) tetra-*n*-butylammonium (TBA⁺) [52]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2016.

acid (H₂SO₄), and the GO generally exhibits a deep brown color, low transmittance, weak fluorescence, and low zeta potential (−25 to −30 mV). Xu and Gao [54] further modified Hummers, adopting a three-stage oxidation process to obtain highly soluble single-layered GO. Compared with the traditional Hummers method, the additional oxidization step further enhances the solubility of GO sheets and improves the optical performance of GO dispersions, showing an orange color (inset Figure 5.9a), higher transmittance, stronger fluorescence (about four-fold larger than Hummers GO), and higher zeta potential (−64 mV). The higher zeta potential of GO indicates stronger repulsive forces between GO sheets, making the aqueous GO dispersions more stable, with higher transmittance and stronger fluorescence facilitating the optical observations on the dispersions.

So far, various types of reduction methods have been reported to obtain rGO sheets [55], such as chemical reduction, photochemical reduction, thermal exfoliation, photothermal reduction, sonolysis, microwave-assisted reduction, and electrochemical reduction. Among these methods, chemical reduction is the most versatile, with many reduction agents being used, such as hydrazine, strong alkaline media, vitamin C or ascorbic acid, bovine serum albumin (BSA), bacterial respiration, and hydriodic acid.

Electrochemical reduction is green and fast, and will not result in contamination of the reduced material. In-situ electrochemical reduction of GO was proposed in 2009;

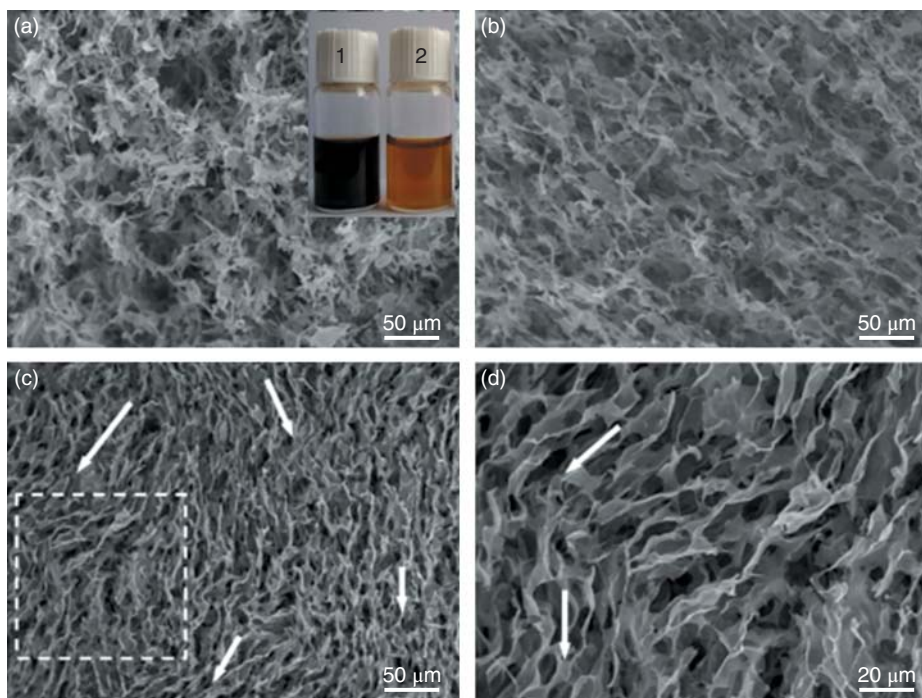


Figure 5.9 SEM images of example GO freeze-dried foams. Inset: The aqueous solutions of conventional GO obtained from Hummers method (1) and GO (2) [54]. Source: Reprinted with permission from ACS publishers, Copyright 2011.

this reduction process can be in-situ monitored and controlled [56], exhibiting higher electrochemical capacitance of 164.8 F g^{-1} at 20 mV s^{-1} , and better cycling durability (after 2000 cycles the electrode exhibited impressive specific capacitance of 165 F g^{-1} in $0.1 \text{ M Na}_2\text{SO}_4$ solution) [56]. Moreover, electrodes prepared from natural as well as synthetic graphite were used for supercapacitors in $1 \text{ M Et}_4\text{NBF}_4$ acetonitrile electrolyte. As a function of the degree of rGO, the graphite layer distance was varied between 0.46 and 0.33 nm as well as specific capacitance of up to 220 F g^{-1} for samples with a graphene layer distance of 0.44 nm [57].

An electrode of rGO formed by thermal exfoliation showed a specific capacitance as high as 117 F g^{-1} in aqueous H_2SO_4 . In the ionic liquid, a specific capacitance of $\sim 75 \text{ F g}^{-1}$ is attained with an energy density of 31.9 Wh kg^{-1} [47]. Mattevi et al., through electrical, chemical, and structural properties, investigated the evolution of GO as a function of reduction treatment, and demonstrated that annealing at 450°C or above is equivalent to chemical reduction via hydrazine monohydrate at 80°C followed by heating at 200°C [58]. Du et al. compared two methods of thermal exfoliation of graphite oxide [59]. The first method used thermal exfoliation of GO at low temperature ($250\text{--}400^\circ\text{C}$) in air, and the second used carbonization at higher temperature ($700\text{--}900^\circ\text{C}$) in N_2 . The results of electrochemical tests are as follows: the specific capacitance value of the first kind of functionalized graphene sheets in aqueous 2 mol l^{-1} KOH electrolyte is about 230 F g^{-1} , but the second material gives only about 100 F g^{-1} , although it has a higher BET surface area than the first kind [59].

The Rodney S. Ruoff group use chemically modified graphene to get suspended GO sheets in water, and then reducing them by using hydrazine hydrate, by which materials with high BET SSA of $705 \text{ m}^2 \text{ g}^{-1}$ showed a high specific capacitance of 135 and 99 F g^{-1} in 5.5 M KOH electrolyte and organic electrolyte based on 1 M TEATFB salt, respectively [50]. In an effort to reduce agglomeration of individual graphene layers, a gas-based hydrazine reduction of GO was proposed [60]. This process obtained a specific capacitance of 205 F g^{-1} (reduced to 170 F g^{-1} after 1200 cycles) with a power density of 10 kW kg^{-1} at an energy density of 28.5 Wh kg^{-1} in 30% KOH solution; the low measured BET SSA value is $320 \text{ m}^2 \text{ g}^{-1}$, presumably due to the pseudocapacitance contribution of the functional groups positioned near the defects [60].

The electrochemical performance of nitrogen doping the rGO electrode was tested [61]; GO was reduced via a hydrogen plasma process and the samples were annealed at 300°C for 3 hours to remove residual functional groups. In contrast to other studies, it displayed an excellent capacitance value of 282 F g^{-1} in 6 M KOH and stability of $>95\%$ after 10 000 cycles, besides a very impressive 220 F g^{-1} in organic TEATFB-based electrolyte according to galvanostatic charge–discharge tests in a three-electrode configuration.

Another unusual way is to reduce exfoliated GO with p-phenylene diamine (PPD), which induces a positive surface charge on the graphene sheet by adsorbing the oxidation product of PPD. The specific capacitance is up to 164 F g^{-1} in 6 M KOH [62]. Another special method is GO suspension in DMF by heating to 150°C in an oil bath to partially reduce GO, which showed a specific capacitance of $\sim 180 \text{ F g}^{-1}$ when evaluated from cyclic voltammetry (CV) tests, and up to 276 F g^{-1} when evaluated by galvanostatic charge–discharge (GCD) tests in 1 M H_2SO_4 [63]. In addition, rGO has been manufactured by hydrobromic acid [64]. rGO can be re-dispersed in water and 2–3 layers of graphene can be observed by transmission electron microscopy (TEM), showing excellent affinity with water. The electrochemical properties are also investigated in the IL electrolyte, at a current density of 0.2 A g^{-1} , when the maximum capacitance values of 348 and 158 F g^{-1} are obtained in 1 M H_2SO_4 and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆), respectively.

In addition to the graphene material of rGO as an electrode material, researchers have also devised various covalent and noncovalent chemistries for making graphene materials, otherwise termed functionalization of graphene, with the bulk and surface properties needed for efficient energy conversion and storage [65]. Figure 5.10A schematically shows the functionalization possibilities for a graphene sheet at both molecular and supramolecular levels, including edge functionalization, basal-plane functionalization, noncovalent adsorption on the basal plane, asymmetrical functionalization of the basal plane, and self-assembling of functionalized graphene sheets. After functionalization, the graphene basal plane could cause significant distortion of the π - π conjugation and the associated physicochemical properties. However, the graphene basal plane structure remains largely unchanged with noncovalent functionalization.

5.4.3 Carbon Nanotubes

Carbon nanotubes (CNTs), a new type of carbon nanomaterial (Figure 5.11), were discovered by Sumio Iijima, an electron microscope expert at NEC electronics company in Japan in 1991 [67]. The discovery of CNTs has greatly promoted the development

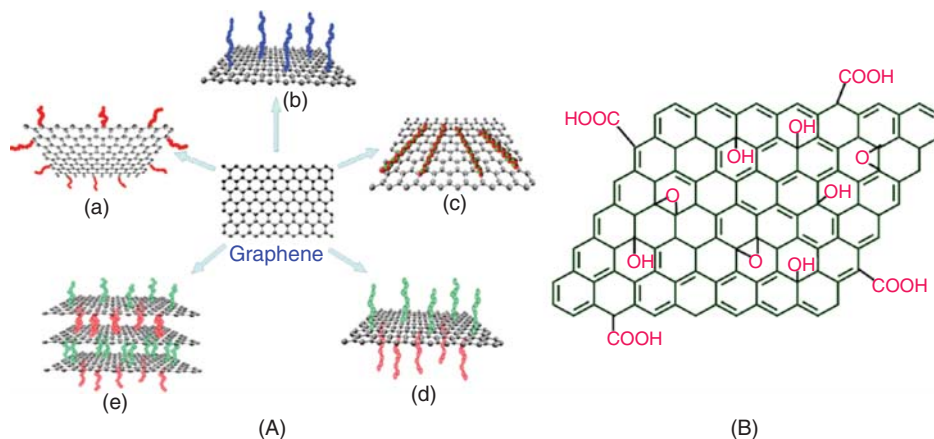


Figure 5.10 (A) Functionalization possibilities for graphene: (a) edge functionalization, (b) basal-plane functionalization, (c) noncovalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, and (e) self-assembling of functionalized graphene sheets. (B) Chemical structure of graphene oxide [65]. Source: Reprinted with permission from ACS publishers, Copyright 2013.

of carbon material families. Because of its small diameter, higher anisotropy and tubular structure, much research has focused on the design and fabrication of CNT nanocomposites for energy storage and conversion. Due to its unique hollow structure and nanometer scale, the material exhibits good electrical conductivity. Accordingly, CNTs are ideal electrode materials for supercapacitors. In addition, they are expected to have potential applications in catalysis, emission and other fields.

CNTs have chemical bonds similar to graphite, with high crystallinity and good conductivity, and exhibit a one-dimensional electronic structure. A large number of electrons can move in one direction along the shell of pipe so that they can carry high currents. Another important feature of CNTs is their unique hollow lumen structure (with apertures ranging from 2 to 50 nm), interwoven and meshed, and the size of the pores can be controlled by the synthesis process. Owing to CNTs having large SSA, suitable pore structure and high conductivity, that are considered as ideal electrode materials for electrochemical capacitors.

Most of these systems are mainly dilute acid or alkali solutions. Niu et al. [68] first reported on the content of the film electrode prepared by catalytic pyrolysis of hydrocarbons and its performance as an electrode material for electrochemical capacitors. The diameter of CNTs is around 8 nm and the SSA is $430 \text{ m}^2 \text{ g}^{-1}$, and it was treated with nitric acid, filtered, washed and dried. Finally, the capacitor was assembled using an electrolyte of 38 wt% H_2SO_4 . The specific capacitance reached $49\text{--}113 \text{ F g}^{-1}$, and the power density was greater than 8 kW kg^{-1} at frequencies varying from 0.00 to 100 Hz. An et al. [69] studied the performance of single-walled CNTs synthesized by the arc method as electrochemical capacitor electrode material. The influence of binder, carbonization temperature, collector, charge time and discharge current density on the material was investigated. In a 7.5 mol l^{-1} KOH electrolyte, the maximum specific electrical capacity was 180 F g^{-1} , and the power density was 20 kW kg^{-1} with an energy density of $6.5\text{--}7 \text{ Wh kg}^{-1}$, which shows good electrical double-layer characteristics. Chen et al. [70] grew the CNTs on graphite sheets. They were used as electrode material,

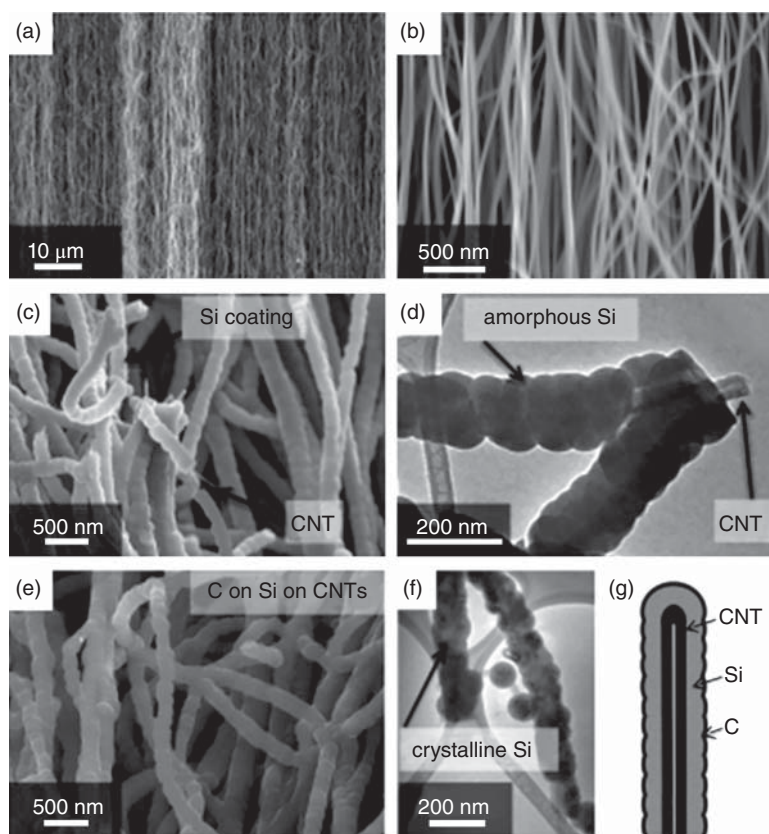


Figure 5.11 Cross-sectional SEM (a–c,e) and TEM (d,f) images of: (a,b) synthesized, vertically aligned carbon nanotubes, (c,d) Si-coated vertically aligned carbon nanotubes, and (e,f) C- and Si-coated vertically aligned carbon nanotubes. (g) Schematic image of the final individual tube morphology [66]. Source: Reprinted with permission from John Wiley and Sons Ltd, Copyright 2012.

with a platinum wire as the auxiliary electrode and saturated calomel electrode as the reference electrode, and cyclic voltammetry was performed in a three-electrode system. The catalyst residue was removed by 15 wt% HNO_3 before electrochemical testing, while the surface activity was increased. The high specific electrical capacity of 115.7 F g^{-1} was obtained in $1.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution.

Frackowiak and Beguin [71] used three different multiwalled carbon nanotubes (MWCNTs) as supercapacitors. In the process of electrode preparation, 5 wt% conductive acetylene black and 10 wt% polyvinylidene fluoride adhesive were added, $6 \text{ mol l}^{-1} \text{ KOH}$ was used as an electrolyte, and the specific electric capacity of different CNTs was measured. MWCNTs prepared by cobalt-catalyzed pyrolysis of acetylene at 700°C gave the highest specific capacitance, reaching 80 F g^{-1} , and there was a good electrochemical cyclic voltammetry curve. After the MWCNTs are treated with nitric acid at 80°C for an hour, the specific capacitance rises to 137 F g^{-1} . However, the SSA is basically constant, and remains at about $410 \text{ m}^2 \text{ g}^{-1}$, indicating that the treatment of nitric acid increases the functional groups on the surface of the material. The AC

nanotubes were observed by TEM and nitrogen adsorption experiments. It was found that there are many defects on the outer walls of activated materials, the higher the number of micropores and the increase of SSA, which are beneficial to the permeation of electrolyte and improve the properties of materials. CNTs are used as electrode materials for supercapacitors. The specific capacitance of inorganic electrolyte systems is higher than that of organic electrolytes, but the charge and discharge voltages in organic electrolytes are higher. Equipment corrosion is less, which is conducive to practical applications.

When pure CNTs are used as capacitor electrode materials, the performance is not very good. For instance, the reversible specific capacitance is not high, the charging and discharging efficiency is low, the spontaneous discharge phenomenon is serious, while simple CNTs reunite easily, and the cost is higher, so they do not meet the actual needs very well. In order to improve the performance of the capacitor, work should take place to fully use its EDL and pseudocapacitor possibility to store charge. Pure CNTs need to be modified, and thus researchers reported the preparation, microstructure, and capacitive properties of CNT-based composite materials. These novel materials can be divided into two categories: metal-oxide/CNT electrodes and conducting polymer/CNT electrodes (Figure 5.12).

Metal oxides (MnO_2 , RuO_2 , Ni(OH)_2 , etc.) are the next and more environmental friendly group of pseudocapacitance materials used for capacitor applications. They have a high theoretical capacitance but low utilization ratio and poor rate performance.

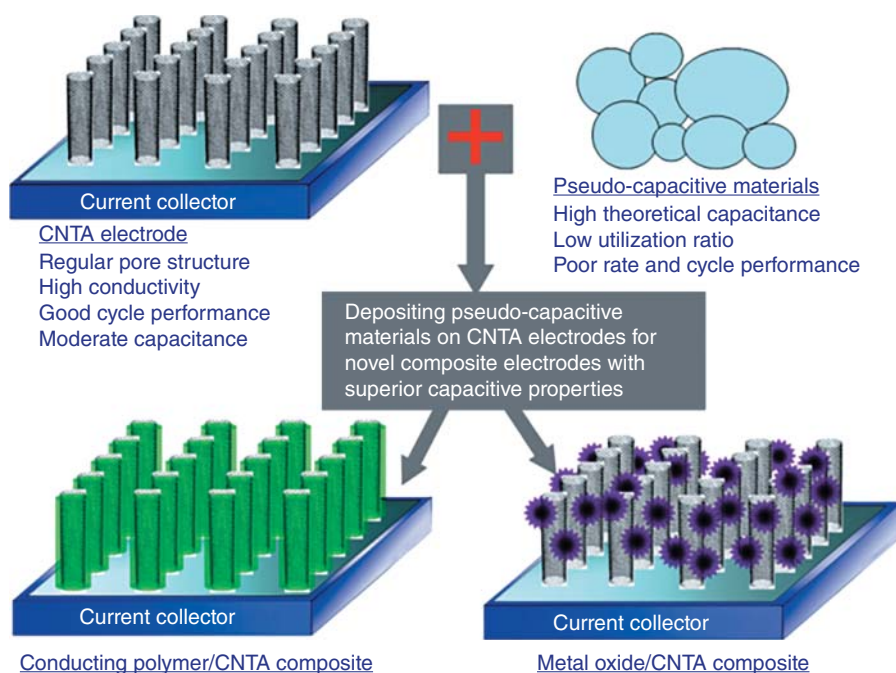


Figure 5.12 A schematic diagram illustrating how pseudo-capacitive materials may be deposited on carbon nanotube array electrodes for novel CNTA-based composite electrodes [72]. Source: Reprinted with permission from RSC publishers, Copyright 2009.

In the case of hydrous oxides, which have a significant resistivity, a well-conducting percolator must be used. Hence, CNTs play a perfect role in such composites. According to the study of Zhang et al., using manganese oxide nanoflower/CNT array composite electrodes with a hierarchical porous structure and a surface area of $234 \text{ m}^2 \text{ g}^{-1}$, these binder-free electrodes present excellent rate capability (50.8% capacity retention at 77 A g^{-1}), high capacitance (199 F g^{-1} and 305 F cm^{-3}), and long cycle life (3% capacity loss after 20 000 charge/discharge cycles), with strong promise for high-rate electrochemical capacitive energy storage applications [72].

Early polypyrrole (PPy) composites have been reported [73, 74], and electrochemical properties are slightly different by different methods. Chen et al. modified the PPy onto CNTs by electrodeposition. Thus, a homogeneous PPy film was formed, which increases conductivity [74]. In the $1.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ electrolyte, the specific capacitance of the composite reaches 172 F g^{-1} , which is greater than the sum of the pure CNTs (78 F g^{-1}) and the simple PPy (90 F g^{-1}). The compound improves the charge and discharge voltage of the capacitor, prolongs the cycle life, and is beneficial to practical application. Compared with CNTs@metal oxide composite electrode materials, CNTs@conductive polymer composites can not only increase the specific capacity of electrochemical capacitors but also reduce the cost, and the pseudocapacitor effect is more stable.

Yang et al. [75] inserted the MWCNTs into the interlayer of electrochemical rGO. Composites (rGO/MWCNTs) with different mass ratios were prepared. When the SSA of the composite increases, its specific capacitance is higher than that of rGO. When the mass ratio of rGO to MWCNTs is 5 : 1, the specific capacitance of the composite is the highest. When the current density is 1 A g^{-1} , the specific capacitance is as high as 165 F g^{-1} , and the retention rate is 93% after 4000 cycles of charging and discharging. Ramezani et al. [76] prepared graphene/CNTs composite by chemical reduction of graphite oxide. Subsequently, MnO_2 nanoparticles were grown in-situ on the composite, and MnO_2 /graphene/CNTs composites were prepared. Electrochemical tests showed that the composite material (367 F g^{-1}) at a scan rate of 20 mV s^{-1} showed higher capacitance than the pure MnO_2 (55.7 F g^{-1}), MnO_2 /CNTs (180 F g^{-1}), or MnO_2 /graphene (310 F g^{-1}), and after 3000 cycles of charge–discharge, the retention rate was 83%. The capacitors prepared by graphene/CNTs composite show a higher specific capacitance, which indicates that this kind of composite material has great potential for capacitor applications. Jung et al. [77] prepared rGO/CNTs composite by a chemical method as electrode material for a supercapacitor. The layer spacing of the composite material can be up to 0.55 nm, and the volume-specific capacitance of the supercapacitor prepared by the development is 165 F cm^{-3} .

The composite electrode material can make full use of the principle of double layer and pseudocapacitance to store charge. The properties of the composite are better than that of pure CNTs. Low-cost metal oxides, composite oxides, conductive polymers, graphene, and CNTs composites will be a future direction of development. However, different types of CNTs are used as electrode materials, with electrochemical properties related to SSA, morphology, microstructure, pore-size distribution, degree of graphitization, surface chemical composition, impurity content, and the content of doped components. They are also related to the treatment process of CNTs, electrolyte species, electrolyte infiltration, electrode material, electrode preparation processes, and so on. In short, the development of electrochemical capacitor electrode materials is not very mature, so we should draw on the rich experience with the capacitor and develop

high-performance composite materials. With the further development of CNTs, we believe that there will be new breakthroughs in the development of electrode materials for capacitors.

5.4.4 Carbide-Derived Carbon

Carbide-derived carbon (CDC) is formed when a metal element in a carbide block or powder is removed and leaves carbon containing a large amount of voids. This carbon material has a large number of micropores, and the pore size and distribution of CDC can be controlled by selecting different carbide precursors, adjusting the ratio of metal elements to carbon elements in the carbides, or changing the preparation process. CDC material was originally produced from quartz as a raw material to produce porous carbon waste. The first mass production process for CDC was developed in 1918 and was used until the 1960s as a method for producing SiCl_4 from SiC in a dry Cl_2 etching agent at more than 1000°C . Figure 5.13 shows a schematic diagram of the CDC reactor, which was used to grow the carbon films. The CDC synthesis was performed at atmospheric pressure, and Ar, Cl_2 , and H_2 were supplied as the carrier, chlorination, and treatment gases, respectively [78]. Figure 5.14 shows the process flow used for the fabrication of mesoporous CDC with aligned channels. The pore size of CDC can be very uniform, which is due to the highly uniform distribution of carbon within such precursors, and continuous extraction of large chloride molecules from CDC during their formation [79]. These features prevent pore collapse and necking. From 1959, when Mohun divided CDC into three kinds of amorphous carbon, namely hard carbon, soft carbon and carbon black, CDC began to attract widespread attention. This carbon is obtained by chlorination of inorganic carbides and is called “mineral carbon” in order to distinguish it from organic carbon sources. And because CDC contains a lot of hydrogen and other elements, it is different from organic carbon, and is termed real amorphous carbon.

Because CDC has a large amount of micropores and mesopores, the pore-size distribution and size can be controlled by changing the preparation process and carbide precursor of CDC. At the same time, it also has very high SSA and controllable pore size and structure, so it has potential applications in many fields, especially in the field of supercapacitors. Among them, it is noteworthy that, in 2003, Gogotsi and Barsoum found that when a ternary carbide ceramic Ti_3SiC_2 was used as precursor, the pore size of CDC

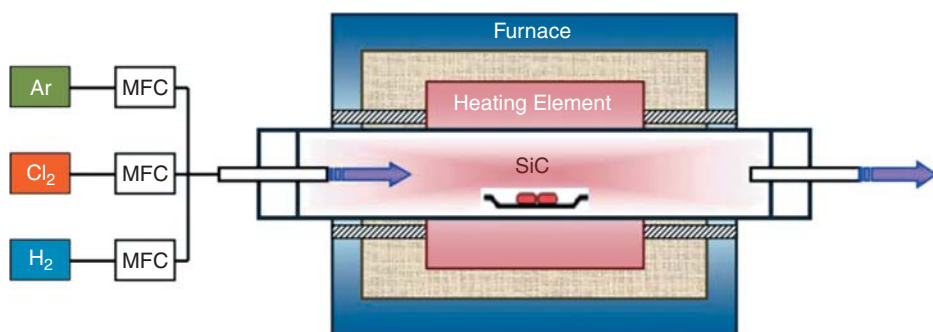


Figure 5.13 Schematic diagram of a CDC reactor used to prepare carbon films [78]. Source: Reprinted with permission from the Ceramic Society of Japan, Copyright 2014.

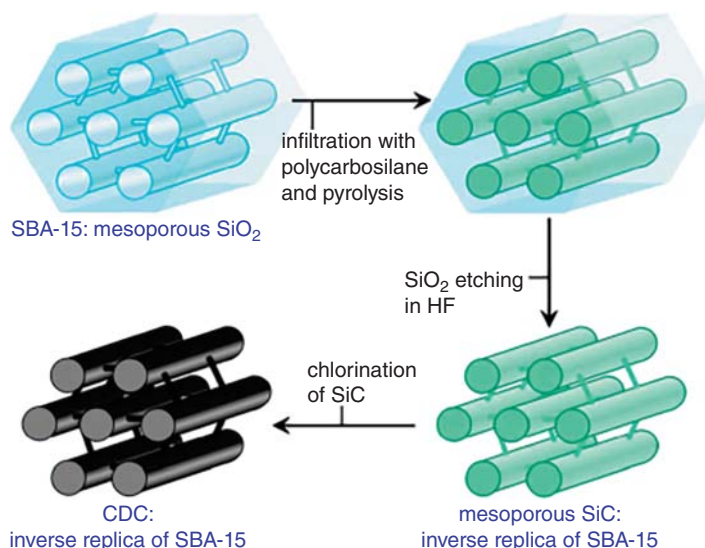


Figure 5.14 Schematic illustration of the fabrication of CDC with aligned mesopores [79]. Source: Reprinted with permission from ACS publishers, Copyright 2010.

could be controlled accurately by varying the reaction condition of high-temperature chlorination [80]. In subsequent studies, a series of CDCs with different microstructures were prepared with different carbides as precursors.

The high-temperature etching of carbide precursors includes binary and ternary carbides. The common binary carbides used for preparing CDC include SiC, TiC, and so on; similarly, the ternary carbides include Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC . In the case of binary carbides, a simplified reaction can be written as: $\text{MeC}_x + 0.5\text{Cl}_2 = \text{MeCl}_y + x\text{C}$, where Me stands for Al, B, Ca, Cr, Mo, Si, Ti, V, W, Zr, and other transition metal elements. The commonly used synthetic methods are pressureless sintering (PLS), hot pressing (HP), hot isostatic pressing (HIP) sintering, self-propagating high-temperature synthesis (SHS), spark plasma sintering (SPS), mechanization alloy (MA) chemical vapor deposition, and so on. While various carbon structures can be found in CDC, including nanodiamond, carbon onions, graphene, graphite, and very dense vertically aligned CNTs, simple disordered carbon was found to be the most attractive and abundant material for EDLC applications.

Among the many synthetic methods, the preparation of CDC by hydrothermal methods needs to be carried out under the severe conditions of high temperature and high pressure; the reaction rate is very slow and the product is impure. Selective etching by high-temperature halogen is commonly done using chlorine; this method is simple and feasible, easy to operate, with a fast reaction rate, and easily controllable degree of reaction. CDC can also be prepared with moderate temperature and atmospheric pressure; in addition, the volatile metal chlorides are gaseous in the reaction carrier gas as it is discharged; the purity of the CDC is high, but chlorine is a poisonous gas with a strong pungent odor, so exhaust gas treatment is needed.

For EDLC application, a TiC-CDC film [81] was used as a supercapacitor electrode, presenting high volumetric capacitance of up to 180 F cm^{-3} at 20 mV s^{-1} scan rate in

1.5 M TEA-BF₄/acetonitrile. Volumetric capacitance decreases as chlorination temperature decreases from 400 to 250°C, because as chlorination temperature decreases, the average pore size becomes smaller, which constrains TEA cation adsorption/desorption in pores. Presser et al. [82] prepared nanofibrous felts of CDC, in which chlorination was carried out at 600°C to synthesize the precursor, the TiC-CDC nanofibers showing an average pore size of ~1 nm, and a high SSA of 1390 m² g⁻¹. The nanofibers have graphitic carbon ribbons embedded in a highly disordered carbon matrix. As electrode material for supercapacitor application without the addition of any binder, they revealed a high gravimetric capacitance of 110 F g⁻¹ in aqueous electrolyte (1 M H₂SO₄) and 65 F g⁻¹ in organic electrolyte (1.5 M TEA-BF₄ in acetonitrile). Because of the unique microstructure of TiC-CDC nano-felts, the capacitance decline is only 50% at a high scan rate of 5 V s⁻¹. When tested in 1 M H₂SO₄ at 1 V s⁻¹, there is only 15% decline observed for nano-felt film electrodes, resulting in a high gravimetric capacitance of 94 F g⁻¹.

The specific capacity of CDC in aqueous electrolytes is moderately high, depending on the preparation conditions and the choice of the initial carbide precursor. Decreasing the particle size of CDC to submicron range was also shown to increase its surface area and specific capacitance. A systematic study on SiC-CDC with varying particle size and synthesis temperature showed up to a 200% increase in pore volume and up to a 30% increase in BET SSA by decreasing the size of CDC particles to 20 nm. The specific capacitance in tetraethylammonium tetrafluoroborate (TEATFB)-based electrolyte was found to increase with increasing synthesis temperature and decreasing particle size, and the highest value of 135 F g⁻¹ at 20 nm for SiC-CDC was achieved with a synthesized temperature of 800°C [83].

The carbide precursor layer is etched from the outside to the inside by metal atoms, with carbide lattice CDC as template, which molecular structure can be upregulated at the molecular level and the pore size and distribution can be accurately controlled in the nanometer range; thus CDC has been widely used in supercapacitors.

5.4.5 Carbon Aerogels

Carbon aerogels, also known as carbonized organic aerogels or carbonized plastic aerogels, come from poly-condensation of some organic monomers through a sol-gel transition procedure, and have attracted significant interest from both academia and industry due to their extremely low bulk density, tunable surface functionality, high SSA, dielectric strength, thermal and electrical properties, and diverse applications [84]. Aerogels are highly porous solid materials derived from gels, where liquid components are replaced by gases. In the 1930s, Kistler reported the first aerogel made from silicon dioxide; it was produced from water glass by an acid-catalyzed reaction, followed by washing, solvent exchange and supercritical fluid drying [85]. In 2004, CNT aerogel was observed as an intermediate state during the production of CNT fibers [84]. In 2009, Wang et al. [86] converted GO solution into an aerogel by a relatively complex procedure including ultrasonic-induced gelation, drying and thermal reduction. One of the first reports on using carbon aerogels for EDLC applications dated to 1993 [87]. Despite the long history of research and modest SSA, the reported values of aerogel capacitance are quite moderate. The nanostructure of aerogels is the main factor that determines their properties and applications, such as precursor materials and preparation processes for different metal-doped carbon aerogels (Figure 5.15).

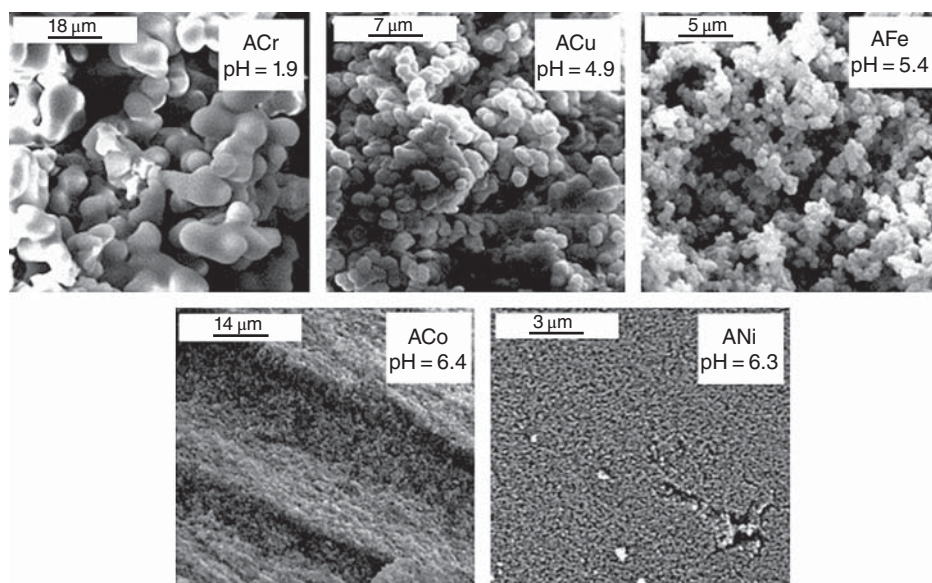


Figure 5.15 SEM microphotographs of metal-doped carbon aerogels [88]. Source: Reprinted with permission from Elsevier, Copyright 2005.

The process for preparing carbon aerogels involves adding another stage at temperatures above 1000°C to treat the organic aerogel in an atmosphere of nitrogen or argon gas; this stage is called carbonization or pyrolysis [89]. Carbon aerogels exist in the form of monoliths, beads, powders or thin films. A major advantage of carbon aerogels is that the volume percentage of mesopores and micropores can be controlled by raw materials, curing and drying methods, and carbonization conditions [90]. They have high porosity, high crystallinity, a network structure, high SSA, controllable pore structure, and good double-layer capacitance and conductivity ($25\text{--}100\text{ S cm}^{-1}$) [91].

The large surface area of carbon aerogels gives them high electrosorption properties, enabling storage of more charge than conventional capacitors. This means a thin polarization layer having high capacity would be formed when an external voltage is applied. Once the applied electric field is removed, the charged ions stored in the double layer can release back to the electrolyte quickly, which explains the good reversibility. For instance, an electrode based on cellulose nanofibrils/reduced GO-CNT electrodes had a high specific capacitance of 252 F g^{-1} (equivalent to 216 mF cm^{-2}), which retained 99.5% of its capacity after 1000 charge–discharge cycles; these supercapacitors showed a high areal energy density of 28.4 W h cm^{-2} (8.1 mW h g^{-1}) and an area power density of 9.5 mW cm^{-2} (2.7 W g^{-1}) [92]. The CO_2 AC aerogels have a high SSA up to $3431\text{ m}^2\text{ g}^{-1}$ and specific capacitance three times higher than that of the raw carbon aerogels. The AC aerogels gave a specific capacitance of 152 F g^{-1} and energy density of 27.5 W h kg^{-1} at a current density of 0.3 A g^{-1} in $1\text{ M Et}_4\text{NBF}_4\text{--AN}$ electrolyte [93]. Boron-doped carbon aerogel monoliths with BET SSA up to $800\text{ m}^2\text{ g}^{-1}$ have been produced using pyrocatechol as a carbon source and boric acid as a catalyst, showing an impressive specific capacitance of 183 F g^{-1} (185 F cm^{-3}) in $1\text{ M H}_2\text{SO}_4$ electrolyte [94].

Compared with the traditional porous materials, carbon aerogels have the advantages of electrical conductivity, mechanical elasticity and stability in harsh environments, and they have a wide range of applications. Carbon aerogels prepared by the solution method have recently attracted intense attention, likely due to low cost yet unique structure and satisfactory properties. In particular, these aerogels will positively impact two major fields of applications: energy storage electrodes, and environmental water purification and contaminant removal. Graphene aerogels have been more intensively investigated than CNT aerogels due to low cost. However, it is a great challenge to use the solution method to develop graphene aerogels with high strength and electrical conductivity at reasonable costs. To improve the mechanical strength of aerogels, many methods have been tried, such as crosslinking, impregnating epoxy after the formation of the aerogels, or incorporating nanomaterials which have larger portions of interface in composites than micro-materials. Nevertheless, the mechanical strength of the aerogels is far below rubber bands, and the electrical conductivity is well below the requirement for fast charging/discharging supercapacitors; using large lateral dimensions and high structural integrity, water-processable graphene would be essential to address these formidable challenges. Fruitful future research opportunities include the development of cost-effective aerogels with high surface area and electrical conductivity and excellent mechanical robustness and flexibility.

5.5 Conclusion and Outlook

Carbon in its various forms, such as powder, fiber, cloth, felt, aerogel, CNTs and so on, is the most widely used electrode material for the construction of supercapacitors. Although its surface area is the primary feature affecting the capacitance, other factors, such as carbon structure, pore size, particle size, conductivity, and surface function, also influence the capacitance and ultimately determine the performance of the supercapacitor. Carbon materials will play an important role in electrochemical energy storage in the future and will be a focus for research.

Compared with other carbon materials, graphene-based materials have high SSAs, good electrical conductivity and thermal conductivity, exhibiting a potential application prospect in energy storage material, particularly rGO in supercapacitors. rGO itself has structural advantages: firstly, introducing the part-oxygen-containing functional groups to the sheet not only avoids layer stacking, but also increases hydrophilicity; secondly, the processes of oxidation and reduction bring in defects that increase the value of capacitance. rGO is a kind of electrode material that cannot be ignored in the research field of supercapacitors.

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6

Diamond/ β -SiC Composite Films

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6.1 Introduction

Since the first fabrication of diamond/ β -silicon carbide (β -SiC) composite films with chemical vapor deposition (CVD) techniques in 1992, they have been developed as superior composite materials with strengthened properties [1]. The endeavor has continued to combine the outstanding properties of both diamond and β -SiC for wide applications. In the last 20 years, control over the phase distribution, crystallinity, orientation of the diamond and β -SiC phases in the diamond/ β -SiC composite films has been achieved. The diamond/ β -SiC composite films now have applications for protein adsorption, the fabrication of diamond networks with controlled porosity as well as buffer layers for adhesion improvement on multiple substrates. This chapter will start from a basic introduction of the deposition instruments, condition and control of the film properties, and characterization; then move on to discuss the growth mechanisms of the diamond/ β -SiC composite films; and finally the example applications for protein absorption and diamond networks will be presented.

6.2 Deposition Instruments

Diamond/ β -SiC composite films have been synthesized by microwave plasma chemical vapor deposition (MWCVD) and hot filament chemical vapor deposition (HFCVD) techniques. By means of both of the two techniques, highly compact diamond films or diamond/ β -SiC composite films have been fabricated. With the assistance of bias enhanced nucleation (BEN), multilayered films and more complex structures can also be fabricated.

A microwave plasma CVD is schematically shown in Figure 6.1, which consists of the main chamber, the microwave generator, and gas inlets [2]. The power of the reactor can vary from 1500 to 5000 W depending on the reactor model applied. Water cooling of the chamber is applied to stabilize the plasma and protect the steel wall of the chamber. There are three quartz windows on the chamber walls for plasma observation during the reaction. An external infrared pyrometer can be used through the quartz windows to measure the substrate surface temperature. There is a loading door on the remaining

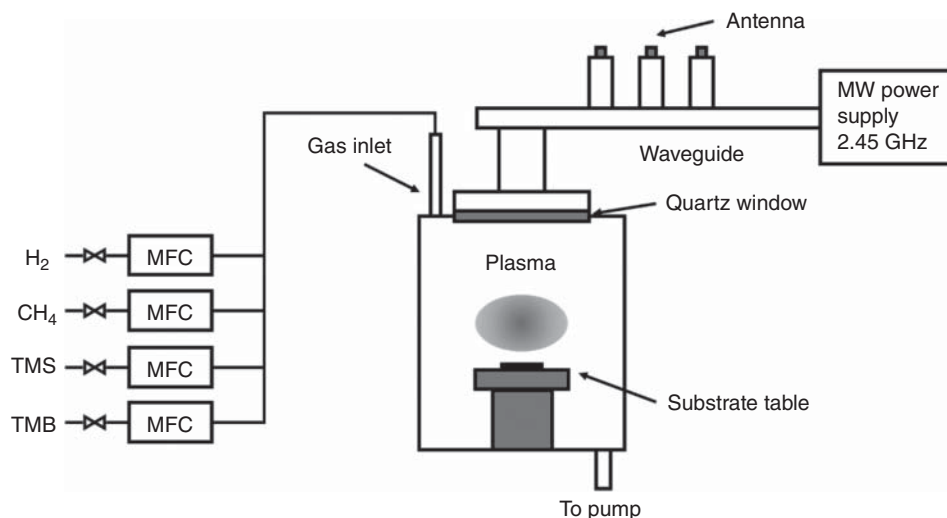


Figure 6.1 Scheme of a microwave plasma CVD [2]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2013.

side of the chamber at the same level as the quartz windows. The microwave generator can generate high frequency (2.45 GHz) microwaves and transfer their energy through the quartz window to activate the gas mixture generating plasma over the substrate; through the wave guide, the microwave can be tuned with three antennae [3].

Films can also be deposited by using a HFCVD technique. A schematic image of a HFCVD reactor is shown in Figure 6.2 [4]. The reaction gases are guided into the vacuum chamber through an inlet tube, and undergo decomposition through the hot filaments at approx. 2000°C into atomic H, hydrocarbon species, and so on. These activated species reach the surface of the sample, and form diamond films. HFCVD has been widely used for diamond deposition in industry due to its unique advantages of low cost and scalability for deposition of diamond on large substrates [5, 6]. This deposition process can be well controlled and optimized by independently adjusting process parameters, namely gas composition, gas pressure, filament power and substrate temperature. The main modules of the reactor are a water-cooled vacuum chamber, a filament frame, a water-cooled substrate holder, a gas intake system, and a vacuum control system.

6.3 Conditions of the CVD Process

The fabrication feasibility of diamond/ β -SiC composite films was revealed via a simple thermodynamic calculation [7]. The co-deposition of diamond and β -SiC phases was predicted to be possible by the addition of tetramethylsilane (TMS) into the H₂ and CH₄ gas mixture during the diamond deposition [7]. But this deposition process is only possible in a certain temperature region. A too high or too low substrate temperature will lead to the growth of only pure β -SiC films. Subsequently, diamond/ β -SiC composite films have been successfully synthesized by MWCVD and HFCVD techniques. Similar to the deposition of pure diamond thin films, a surface pretreatment process is required to enhance the diamond nucleation density on the target substrates prior to deposition.

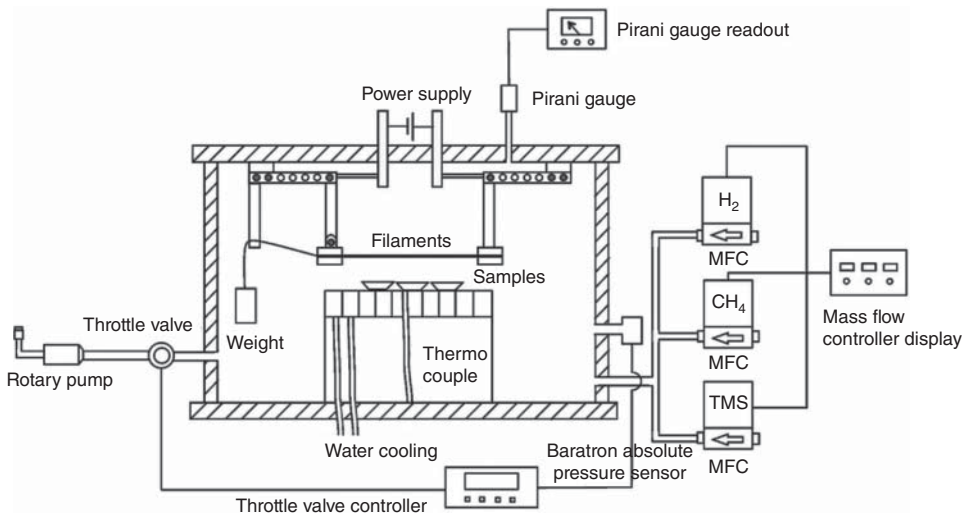


Figure 6.2 Scheme of a HFCVD reactor [4]. Source: Courtesy of T. Wang.

This can normally be done by BEN [8], abrasion of the substrate surface using diamond powder [9], or ultrasonic seeding [10]. The pretreated substrates will then be positioned on a holder inside the reactor chamber for deposition. The deposition conditions of composite films are similar to those of diamond deposition (substrate temperature of 700–1000°C, $\text{CH}_4/\text{H}_2 = 0.5\text{--}2\%$). The main differences lie in the gas phase composition: a very low concentration of TMS (125–500 ppm) is added into the gas phase for co-deposition of the β -SiC phase along with diamond. Diluted TMS (1% in H_2) is supplied to achieve such low concentrations. A simple conversion is that if the total gas flow rate is fixed at 400 standard cubic centimeters per minute (sccm), the supply of 5 sccm TMS corresponds to a TMS concentration of 125 ppm in the gas mixture.

Figure 6.3 shows some typical scanning electron microscopy (SEM) in-lens mode images of the nanocrystalline diamond/ β -SiC composite films deposited in a MWCVD reactor with a microwave power of 700 W [11]. Not surprisingly, phase contrast has been observed. The films consist of brighter and darker regions corresponding to the diamond and β -SiC phases, respectively. The H-terminated diamond surface has a very high secondary electron yield [12] compared with β -SiC; and the in-lens SEM mode detects the secondary electrons directly produced by the primary electrons, which is very sensitive to the surface conditions of the films. Therefore, the diamond phase can be seen as much brighter in the in-lens mode of SEM images. With increasing TMS flow rate, the β -SiC/diamond ratio in the composite film increases. A quantitative determination of the volume fraction of the β -SiC phase in the film with different TMS flow rates has been done through a calculation based on the electron probe microanalysis (EPMA) of the composite film. As shown in Figure 6.4 [11], it can be observed that the volume fraction of the β -SiC phase has a linear relationship with the TMS flow rate, showing that the composition of the film is determined by the TMS flow rate as other parameters (substrate temperature, microwave power, gas phase pressure, total gas flow rate, methane concentration) are kept constant. Almost 100% volume fraction of β -SiC can be achieved with a TMS flow rate of 20 sccm.

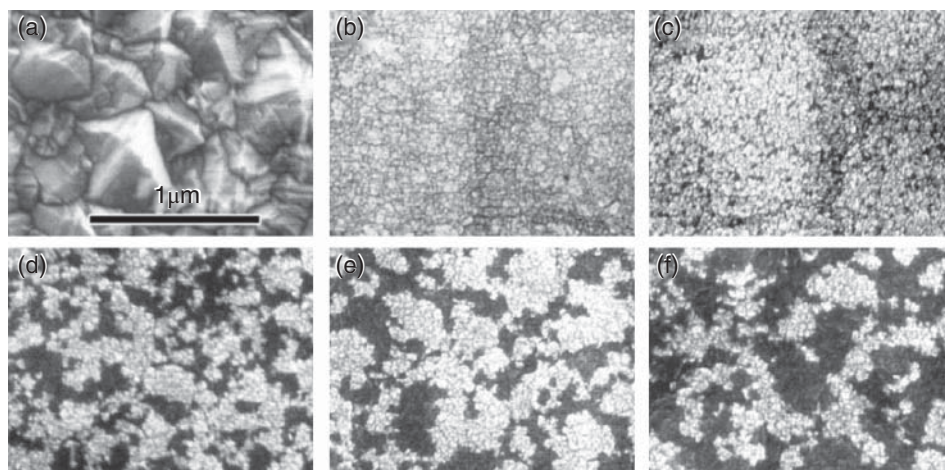


Figure 6.3 In-lens mode SEM images of the morphology of nanocrystalline diamond/ β -SiC composite films deposited with TMS gas flow rate of (a) 0, (b) 2.5, (c) 5, (d) 10, (e) 15, and (f) 20 sccm, respectively [11]. Source: Reprinted with permission from Springer Nature, Copyright 2008.

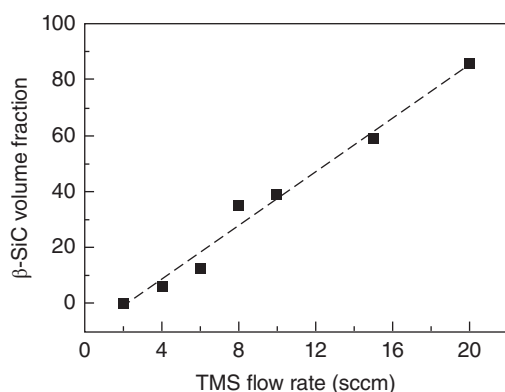


Figure 6.4 Variation of β -SiC volume fraction (%) with TMS flow rate [11]. Source: Reprinted with permission from Springer Nature, Copyright 2008.

6.4 Film Quantity (Phase Distribution, Orientation, and Crystallinity) and Characterization

In Figure 6.3, the results show that only nanocrystalline diamond and nanocrystalline β -SiC phases are observed in the composite films. The random reaction of Si- or C-containing species with diamond or β -SiC surfaces interrupts the growth of both phases, and results in only nanocrystalline composite films. This argument is supported by the energy dispersive X-ray measurements [13], which detected Si content in the diamond region. Nevertheless, owing to the different surface properties, the reactivities of CH_3 and SiH_3 species with different diamond facets are different. Using frontier orbital theory, the reaction occurrence of CH_3 and SiH_3 species with different facets of diamond can be analyzed. The analysis is carried out by judging the energy differences between the frontier molecular orbitals (FMOs) of the reactants diamond and CH_3/SiH_3 [14]. Figure 6.5 shows the energy levels of FMOs and other nearby orbitals of CH_3 , diamond nanoparticle ($\text{C}_{54}\text{H}_{56}$), and SiH_3 , determined at the HF/6-31G(d,p)

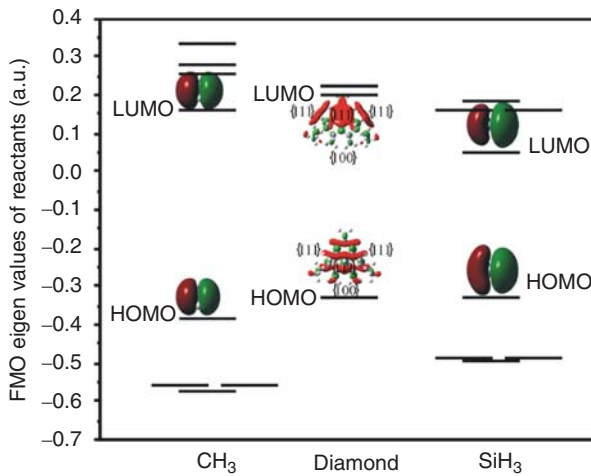


Figure 6.5 The energy levels of FMOs and other nearby orbitals of the reactants of CH_3 , diamond nanoparticle ($\text{C}_{54}\text{H}_{56}$), and SiH_3 [14]. Source: Reprinted with permission from American Institute of Physics, Copyright 2008.

level of theory. The diamond nanoparticle, expressed by the formula $\text{C}_{54}\text{H}_{56}$, has a tetragonal pyramid shape with its four {111} facets on the side and one {100} facet at the bottom. The diamond surface dangling bonds are saturated by H, because of the H-rich atmosphere during diamond growth. It can be observed from Figure 6.5 that the highest occupied molecular orbitals (HOMOs) of diamond are closer to those of SiH_3 than CH_3 , implying the higher probability of the reaction occurrence between diamond and SiH_3 . Moreover, {111} diamond facets show denser isosurfaces compared with the {100} facets. In this regard, the {111} facets will react more easily than {100} facets with the SiH_3 species in the gas phase. This leads to the conclusion that secondary nucleation occurs more easily on the {111} diamond facets. Such a result provides us a possibility of obtaining a (100)-textured growth of diamond phase on the composite film, which is then experimentally realized (Figure 6.6).

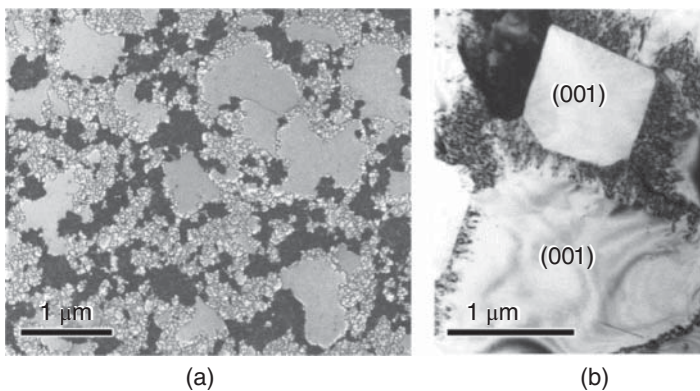


Figure 6.6 (a) SEM and (b) TEM surface images of the composite film with (100) diamond crystals [14]. Source: Reprinted with permission from American Institute of Physics, Copyright 2008.

Figure 6.6 shows the SEM and transmission electron microscopy (TEM) images of the composite film surfaces with large (100) oriented diamond crystals deposited at relatively low substrate temperatures (600–700°C). The film was deposited with the TMS addition of 0.05% to H_2 and CH_4 (corresponding to a TMS flow rate of 20 sccm). It exhibits significant [001] texture of the diamond grains. The {100} facets of the crystals are restrictively parallel to each other and to the substrate surface. The TEM image shown in Figure 6.6b depicts that, even though some of the grain boundaries of the diamond crystals are parallel to {100} planes, most of them are parallel to {110} planes. In the {111} growth zone along the grain boundaries, there exists defects such as dislocations, twins, and stacking faults. Nevertheless, the dark β -SiC phase domains composed of nanocrystals are formed between the (001) diamond facets and/or cover the (111) diamond facets. On the surface ({100} facets) of the diamond crystals, no obvious defects are observed. In this regard, the growth of (100)-orientated diamond crystals in the composite film by the selective deposition of Si-containing species on the non-{100} facet has been achieved.

From the above results, the growth of large (100)-orientated diamond crystals is possible. But it only happens locally, and the rest of the diamond phase as well as the β -SiC phase are still nanocrystalline. It is well understood that an amorphous carbon phase exists in the grain boundaries of both diamond and β -SiC crystals. This amorphous phase deteriorates the intrinsic properties of both diamond and β -SiC phases (i.e. thermal conductivity, electrical resistivity, transparency, etc.). In order to minimize such negative effects, it is essential to obtain high-quality microcrystalline diamond and β -SiC phases over the whole composite film. The main factor that hinders us in achieving this goal is the high density of defect sites induced by the random reaction of Si- or carbon-containing species on diamond and β -SiC crystals. These defect sites act as secondary nucleation sites and limit the size of the crystals. Therefore, in order to obtain high-quality composite films, it is essential to minimize the occurrence of the secondary nucleation process. For the growth of pure diamond films, the concentration of atomic hydrogen ([H]) is believed to be a crucial factor in the determination of its phase quality. Increasing [H] will increase the etching rate of graphite and other defect centers on diamond, and hence impede secondary nucleation of diamond, resulting in an increased film quality and growth rate [15, 16]. In the context of composite film deposition, a similar effect was also expected. In order to obtain a high [H], a high microwave power density (MWPD) was applied. Figure 6.7 shows the SEM images of the composite film deposited at a MWPD of 33 W cm^{-3} (2250 W, 55 Torr). This is more than three times higher than the MWPD used to deposit the composite films shown in Figures 6.3 and 6.6 (10 W cm^{-3} at microwave power of 700 W with a gas phase pressure of 25 Torr). According to the theoretical calculation of Silva et al., [H] increases by a factor of more than 10 for an increase in the MWPD of a factor of 3 [17]. Micrometer-sized diamond ($\sim 1 \mu\text{m}$) and β -SiC ($\sim 0.5 \mu\text{m}$) grains are clearly observable, indicating an improved quality of the film. As for the β -SiC phase, a pyramidal shape with (111) side-planes meeting at a common point shows highly (100)-orientated characteristics. The cross-sectional image (Figure 6.7b) of the film depicts a columnar structures of diamond and β -SiC crystals, connoting the independent growth of the diamond and β -SiC phases. Furthermore, the textured growth characteristics of the β -SiC phase can also be seen in this image (marked with small arrow indicators). The deposition conditions of this film (i.e. gas phase composition, substrate temperature, gas flow rate, etc.) are identical to

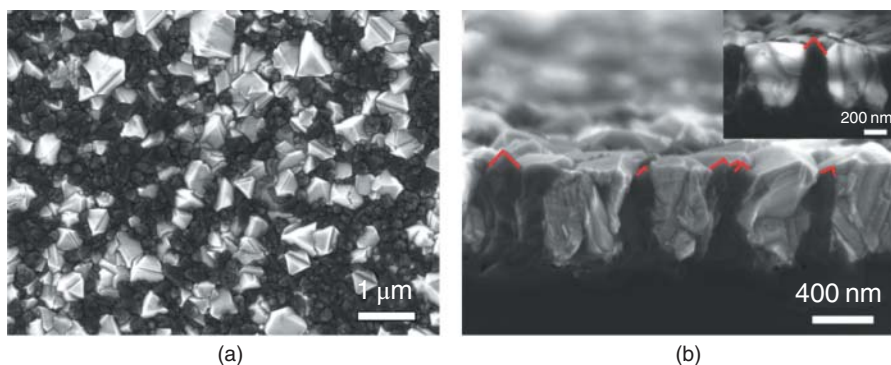


Figure 6.7 (a) Surface and (b) cross-sectional SEM images of the composite film deposited at high [H]. The film is deposited at a TMS flow rate of 5 sccm, methane flow rate of 4 sccm, and substrate temperature of 800°C [73]. Source: Reprinted with permission from Elsevier, Copyright 2011.

those of the nanocrystalline composite films shown in Figure 6.3. Therefore the high [H] generated by the high MWPD is believed to be the main reason for the improved film crystallinity. At high [H], the defect sites formed on diamond and β -SiC crystals by the random reaction of SiH_3 and CH_3 radicals can be very efficiently etched away, and the surface dangling bonds are then saturated with hydrogen for further reaction until they bond with the “correct” radicals. As a result, the secondary nucleation rate becomes slow on both diamond and β -SiC crystals, and micrometer-sized diamond and β -SiC grow. In this context, a model shown in Figure 6.8 [18] was proposed to elucidate the mechanism, described as the “hydrogen induced selective growth model.”

- 1) The excited plasma contains several reactive species, namely H_2 , H, CH_3 , and SiH_3 , which are responsible for the etching of the defects, diamond growth and β -SiC growth. The diamond and β -SiC surfaces at any stage are terminated by H. Partial H-terminated surface is re-activated by the impingement of the plasma species, thus providing free unsaturated sites for further growth (Figure 6.8a). Subsequently, the SiH_3 and CH_3 species bond with the activated surface sites by incorporation of SiH_3 and CH_3 , respectively (Figure 6.8b).
- 2) The bonded SiH_3 /excess CH_3 is not that stable on the diamond/ β -SiC surface. At high [H], the high-energy atomic H will immediately etch the defect sites away and saturate the surface again with H bonds (Figure 6.8c). At the same time, more surfaces are activated and bond with the correct species.
- 3) The above two processes continuously take place and result in a layer-by-layer growth of the diamond and β -SiC crystals (Figure 6.8d).

It can easily be inferred from this growth model that it is difficult for the SiC phase to form on pure diamond at high [H] during the composite film growth. In other words, a composite film will not even grow on a pure diamond area at relatively high TMS flow rates. This offers the opportunity to control the lateral distribution of diamond and β -SiC phases to obtain patterned diamond/ β -SiC composite films. As illustrated in Figure 6.9, this can be achieved by the deposition of composite film on patterned diamond substrates. In this context, a thin patterned diamond film is essentially required, which can be obtained by either dry etching [19, 20] or selective

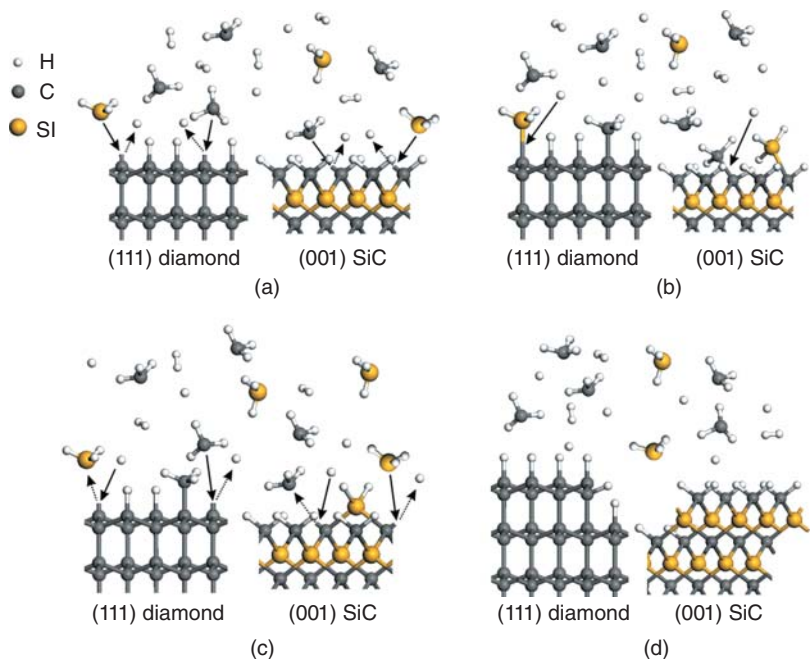


Figure 6.8 Hydrogen induced selective growth model for the deposition of high quality diamond/ β -SiC composite films at high [H]. The growth is illustrated on a (111) diamond and (111) β -SiC surfaces (see text for details) [18]. Source: Reprinted with permission from Springer Nature, Copyright 2015.

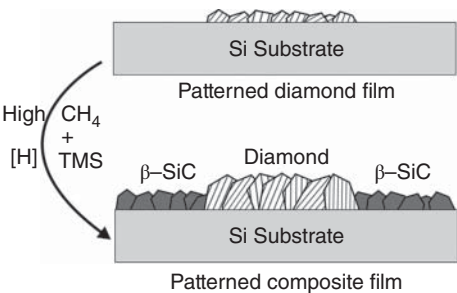


Figure 6.9 Schematic illustration of the growth of patterned diamond/ β -SiC composite film [73]. Source: Reprinted with permission from Elsevier, Copyright 2011.

area deposition techniques [21–30]. Figure 6.10 shows two patterned diamond thin films, seeded using micro-contact-printing of diamond nanoparticles and then followed by diamond growth in MWCVD [21]. On these two samples, the growth of patterned composite film has been achieved, which is depicted in Figure 6.11. The boundaries of the two phases are well defined by the previous selective area deposition, which leads to the conclusion that no β -SiC was able to grow on the already existing diamond phase. Due to the prolonged growth time, the overgrowth of the diamond phase is clearly observed. The edges of the diamond pattern are not as sharp as the original printed pattern (see Figure 6.10). Moreover, the thickness of the diamond phase is a little bit greater than that of the β -SiC phase, which might be due to the pre-growth of the diamond phase and the differences in the growth rate of each phase. Nevertheless,

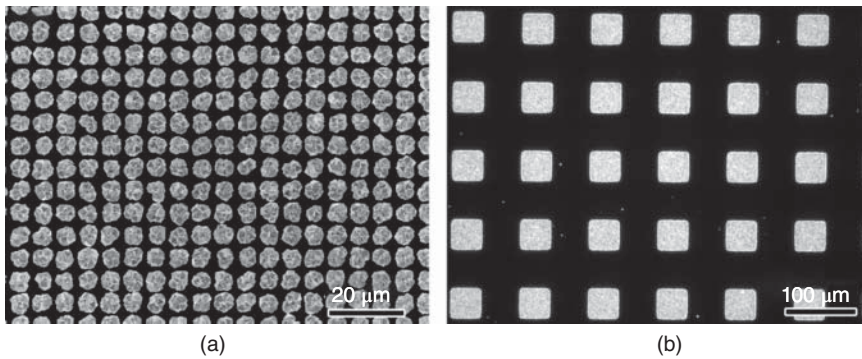


Figure 6.10 Diamond film with different pattern sizes. (a) $\sim 5 \mu\text{m}$; (b) $\sim 50 \mu\text{m}$ [21]. Source: Reprinted with permission from American Chemical Society, Copyright 2011.

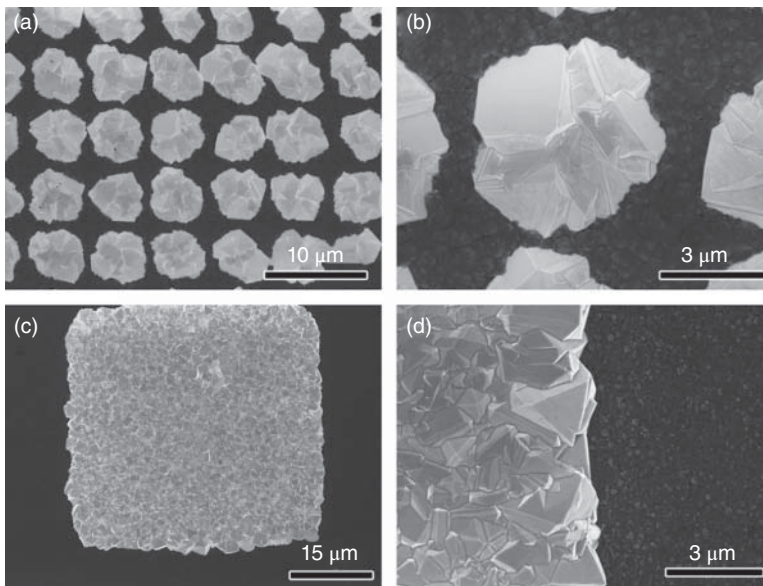


Figure 6.11 Patterned diamond/ β -SiC composite films deposited on the samples shown in Figure 6.9: (a) $\sim 5 \mu\text{m}$ pattern; (b) magnified image of (a); (c) $\sim 50 \mu\text{m}$ pattern; (d) magnified image of (c) [18]. Source: Reprinted with permission from Springer Nature, Copyright 2015.

the successful deposition of the patterned composite film not only proves the validity of the “hydrogen induced selective growth” model; owing to the excellent electrical and mechanical properties of diamond and β -SiC, it also opens the door to numerous attractive electrical- and mechanical-based applications for the composite film.

6.5 Growth Mechanism

To understand the growth mechanism of the composite films, the growth process has been carefully monitored by observing their cross-section. It reveals the space

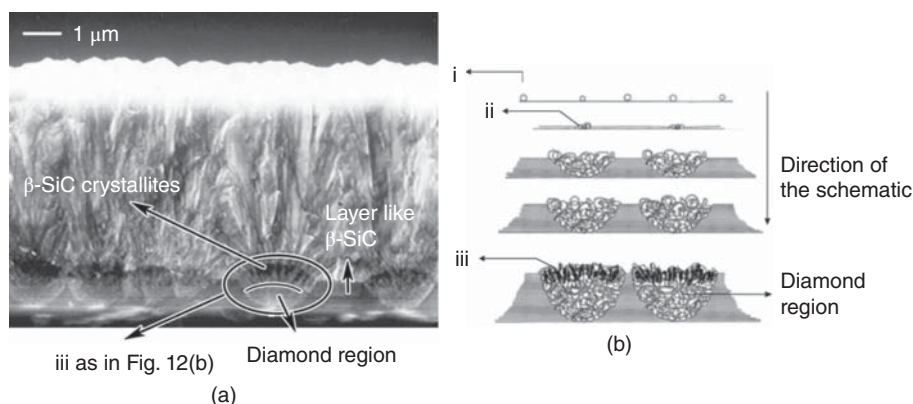


Figure 6.12 (a) SEM cross-sectional structure of a diamond/ β -SiC composite film deposited with a constant TMS content of 0.025% in the gas phase. The TMS supply was cut off after six hours, followed by the deposition of a pure diamond top layer. (b) Schematic of the initial nucleation and growth process during the deposition of diamond/ β -SiC composite film: (i) the Si substrate is uniformly seeded by diamond after a pretreatment process; (ii) beginning of the nucleation and growth of diamond on the diamond seeds via adsorption of diamond growth precursors from the activated gas phase, and simultaneous nucleation and growth of β -SiC on “blank” Si surfaces; (iii) nucleation of β -SiC crystallites on diamond surfaces in the diamond-rich regions, and equilibrium of the diamond/ β -SiC ratio in the composite film is reached [13]. Source: Reprinted with permission from American Institute of Physics, Copyright 2006.

competition between diamond and β -SiC to occupy the space available on the substrate during growth [13]. Figure 6.12a shows the cross-sectional SEM images of one composite film. Figure 6.12b shows the schematic illustration of the initial nucleation and growth process [13]. At the initial growth stage, island-like diamond and layer-like β -SiC crystals grow. This is because, at this stage, diamond can only grow on the sites where there are diamond seeds or surface defects, and form three-dimensional (3D) clusters; whereas β -SiC prefers to grow on a virgin Si surface by layered growth, even though it can also grow on diamond seeds, defects, and so on [13]. The diamond clusters expand with increasing growth time and the layered β -SiC region becomes narrower and narrower. This process continues until the diamond/ β -SiC surface ratio reaches a certain critical value at the given methane/TMS ratio. β -SiC then starts to nucleate and grow on some of the diamond clusters. At this point, an equilibrium state in the diamond/ β -SiC ratio in the composite film is reached, which continues until the TMS gas supply is changed [13]. Finally, the films exhibit structures shown in Figure 6.3. Therefore, the volume ratios of β -SiC in the composite films are determined by the different TMS/ CH_4 ratios in the gas composition.

While considering the TMS/ CH_4 ratio, it is interesting to note that the volume of CH_4 and TMS is at a great disparity in the feed gas even at a high TMS flow rate (for a TMS flow rate of 20 sccm, the TMS/ CH_4 ratio is only 0.08). A microscopic level of understanding of the gas phase reaction is required to achieve further control of the synthesis. In this context, theoretical calculations have been carried out using HF/6-31G(d,p) level of theory [31]. It reveals that, in the plasma environment, the Si-C bond in TMS is broken by atomic hydrogen (H), described by the following reactions [31]:

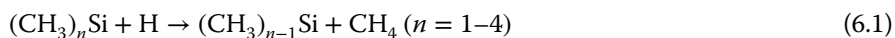
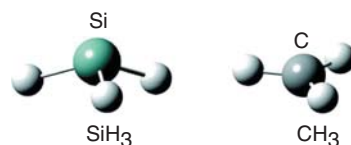


Figure 6.13 Geometric structures of SiH_3 and CH_3 [31].
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Si sources like SiH_{n-1} ($n = 1-4$) are produced by breaking the Si–H bond of TMS with the assistance of H radicals, described by the following reactions:



CH_4 can also go through a similar process to produce CH_{n-1} ($n = 1-4$), as shown in the following:



Among the various CH_n and SiH_n ($n = 1-4$) radicals, CH_3 and SiH_3 are the main parts contributing to the growth of both diamond and β -SiC crystals [31]. Nevertheless, they have slight differences in their structures which result in their different reactivities: the SiH_3 radicals remain as a good sp^3 hybridized structure, whereas the CH_3 radicals change to an sp^2 planar structure, as shown in Figure 6.13. Such differences in the ion structure lead to different attaching rates for the species, when these species contribute to the growth of diamond and β -SiC phases composed of sp^3 carbon and Si atoms. It then in turn results in the differential growth rates of diamond and β -SiC. Moreover, the activation energies (ΔE_a) of Reaction (6.2) are much lower than those of Reaction (6.3); and reaction heats (ΔH_f) of Reaction (6.2) are more negative than those of Reaction (6.3). Based on the above result, a much easier occurrence of Reaction (6.2) than of Reaction (6.3) is indicated. To obtain comparable diamond content in the final composite film, a much higher concentration of methane than that of TMS in the gas phase is required, in combination with the good sp^3 hybridized structure of SiH_3 .

6.6 Applications

6.6.1 Improvement of the Film Adhesion

Even though diamond thin films possess excellent mechanical properties, their application as a protection layer has been hampered by poor adhesion on technologically important materials. The main obstacle to improving the adhesion is the large residual stress at the film/substrate interface. This is caused by the significant differences in the thermal expansion coefficient and hardness between the coating and the substrates. If we take WC-6%Co, the widely used cutting tool material, as an example, its thermal expansion coefficient and hardness are $4.6 \times 10^{-6} \text{ K}^{-1}$ and 17 GPa, respectively, which are significantly different from those of the diamond films ($1 \times 10^{-6} \text{ K}^{-1}$ and 60–100 GPa, respectively). These differences make it difficult to obtain well-adhered diamond coatings on the WC-6%Co. In this context, a graded interlayer with properties varying smoothly from the substrate material to the diamond layer presents an excellent candidate in solving this problem. Among the options, diamond/ β -SiC composite film fulfills the above requirements. First, its properties are dependent on the composition (see Figure 6.14 for the hardness change of the composite film with increasing

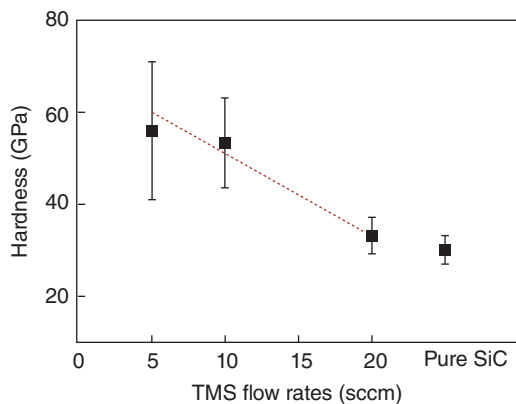


Figure 6.14 Berkovich hardness of the composite film with different TMS flow rates (different diamond/ β -SiC ratios) [81]. Source: Reprinted with permission from Cambridge University Press, Copyright 2011.

β -SiC content). Secondly, its composition can be tuned in-situ by controlling the gas phase composition, and can range from β -SiC-rich to diamond-rich. Lastly, the thermal expansion coefficient ($4 \times 10^{-6} \text{ K}^{-1}$) and the hardness (30 GPa) of the β -SiC-rich composite film are close to those of WC-6%Co. By applying such graded composite film as an interlayer, the residual stress in the composite film as well as in the top pure diamond layer is expected to be drastically reduced [32], resulting in improved adhesion of the film. Nevertheless, it requires a basic understanding of the influence of composite interlayers on the overall film properties before applying it to the cutting tools. Therefore, research has been carried out to apply the gradient composite interlayer firstly on standard substrates, such as Si, W, and Mo.

The deposition of the gradient composite interlayer is straightforward. It can be obtained by continuously reducing the TMS flow rate from a high value (i.e. 20 sccm) to 0 sccm throughout deposition. As the process continues when the TMS flow rate reaches 0, a pure diamond top layer forms. Therefore, just one process can be used to grow a pure diamond top layer and the gradient composite interlayer. Figure 6.15 shows the cross-sectional image of one gradient composite film with a pure diamond top layer on Si substrate. The top diamond layer is nearly stress-free owing to the gradual release of residual stress in the gradient layer, as characterized by Raman spectroscopy [32]. Similar results have also been observed on metallic substrates. The stress test

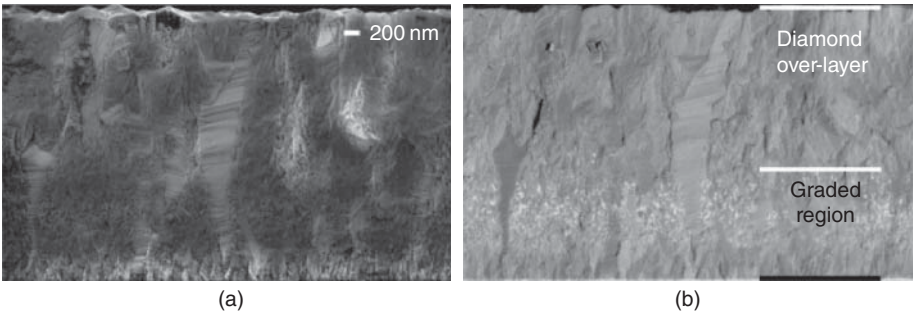


Figure 6.15 (a) SEM cross-sectional morphology of the gradient composite film deposited on Si, and (b) the corresponding backscattered electron image. The brighter spot-like regions in (b) represent the β -SiC phase [32]. Source: Reprinted with permission from Elsevier, Copyright 2009.

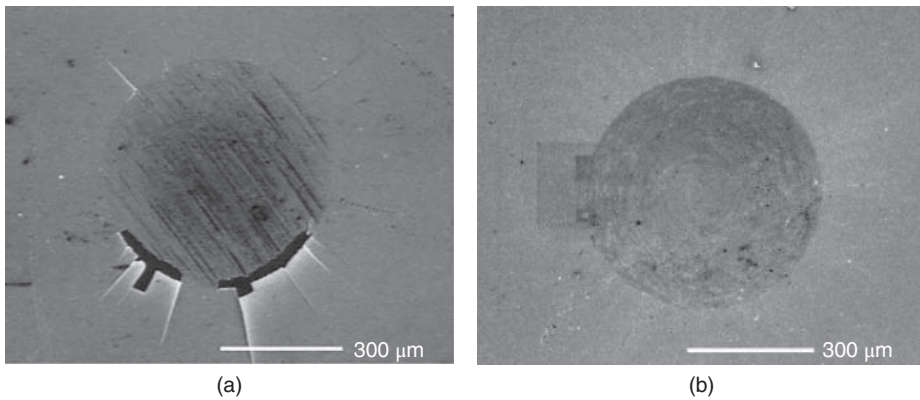


Figure 6.16 SEM images of the indentation zones that result by applying an indentation load of 125 kgf on different films. (a) Delamination of a diamond film directly coated on the substrate. (b) Crater with lateral cracks of a diamond top layer on a gradient composite film [33]. Source: Reprinted with permission from Elsevier, Copyright 2007.

shows that the diamond films grown on gradient composite layers on W and Mo substrates exhibit 25% less residual biaxial stress than those without an interlayer [33]. The reduced residual stress implies improved film adhesion. To confirm this, the Brinell indentation test has been carried out and the results are shown in Figure 6.16 [33]. An indentation load of 62.5 kgf is sufficient to induce significant film delamination in the case of pure diamond film directly coated on W and Mo. When a gradient interlayer was introduced, the film delamination did not occur up to a normal load of 100 kgf. Moreover, even though a load larger than 100 kgf initiated the formation of cracks, the film remained attached to the substrate. These results strongly indicate that the gradient composite film interlayer can be a very promising candidate in improving the adhesion of diamond film on technologically important substrates.

After the above-mentioned basic understanding, the gradient composite interlayer can then applied to improve the adhesion of diamond film on the WC-6%Co cutting inserts. A successful lifetime improvement of the cutting inserts is observed by cutting AlSi₂O material. For the uncoated tool, it can only machine an area of 75 cm² before failure. Coating of the tool with pure diamond (without interlayer) can improve its machining area to 300 cm². When a gradient composite interlayer is introduced between the cutting tool and the diamond layer, the machining area can be further improved to 400 cm² before failure. These results indicate improved adhesion of the film in the existence of the gradient interlayer [3, 34].

6.6.2 Biosensor Applications

The diamond/ β -SiC composite film also qualifies as a good candidate for biosensor applications because of the biocompatibility and diverse sensing abilities of diamond and β -SiC [35–39]. However, while fabricating thin film-based biosensors, the surfaces are often treated chemically or physically to make them clean and highly active [40–42]. This is to enhance the adhesion of the chemical or biochemical species on the solid surface while minimizing the nonspecific adsorption of those species, which disturbs

the sensing process [43, 44]. In this context, the wettability of the thin film surface is important to explain its interactions with chemicals or biological species. It has been illustrated that different surface hydrophilicities or hydrophobicities are required for different biotechnological applications [45–50]. Therefore, to fabricate the composite film-based biosensors, it is essential to firstly understand and modify the surface status of the films. To make the diamond/ β -SiC composite films produced above suitable for diverse biotechnological activities, which require varying surface wettability, a tunable surface wettability has been observed by varying its composition [51]. This is achieved by selective H-termination of the diamond phase and OH-termination of the β -SiC phase in the composite film. It is well known that diamond can be easily H-terminated through H_2 plasma treatment, while the β -SiC surface is known for its difficult H-termination. The conventional methods used for diamond (H_2 plasma) and Si (HF etching) H-termination do not work on the SiC surface, leaving an OH-terminated surface. Therefore, the simultaneous H-termination of diamond and OH-termination of β -SiC in the composite films can be easily done by oxidizing the whole composite film (i.e. treating in an oxidizing mixture of boiling H_2SO_4 and KNO_3) followed by H_2 plasma treatment.

Figure 6.17a shows the variation in the water contact angle on the composite film surfaces before and after chemical treatment. The “as deposited” composite films are all H-terminated with a water contact angle higher than 70° , because of the H_2 -rich atmosphere during deposition. Nevertheless, due to the slight oxidation of the β -SiC phase in air, a slight decrease of the contact angle is also observed. The water contact angle drastically decreases from $92.6 \pm 2.5^\circ$ to $32.7 \pm 2.8^\circ$ after chemical treatment with increasing TMS flow rate, which indicates an increase in hydrophilicities. The surface status of the composite films was elucidated by secondary ion mass spectrometry (SIMS) measurement [52], which showed the oxygen content on the surface increased drastically with increasing β -SiC content. Since the diamond phase can be easily H-terminated under

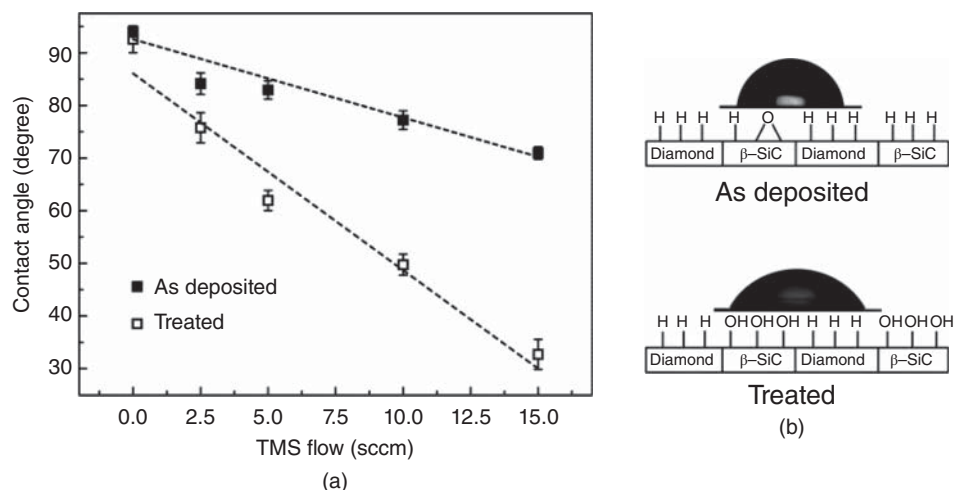


Figure 6.17 (a) Water contact angle variation on the surfaces of the composite films with the applied TMS flow rate; (b) contact angle photo illustration, along with the surface termination schematic of the as-deposited and chemically treated composite films [51]. Source: Reprinted with permission from American Chemical Society, Copyright 2010.

H_2 plasma, the increasing oxygen content on the surface is attributed to the increase of OH-terminated β -SiC phase after the chemical treatment. Figure 6.17b shows the surface termination status of the composite film before and after chemical treatment schematically along with the photo illustration of the water contact angle.

Based on the above discussions, if the diamond/ β -SiC ratio on the same surface can be controlled, a thin film surface with gradient wettability and thereby the surface energy can be fabricated. Such a surface is highly desirable in the application of bio-microfluidic devices. However, to obtain such a surface, good control in the growth process is required. It has been previously discussed that a space competition exists between the diamond phases and β -SiC phases during the composite film growth. This phenomenon leads to the formation of composite films with different diamond/ β -SiC ratios. Therefore, by controlling the lateral diamond nucleation density over the substrate surface, a gradient diamond/ β -SiC composite film can be obtained. Figure 6.18a–e shows the SEM plane view images of the composite film surface with a gradient from the left edge to the right edge over a length of 15 mm. The left edge of the film is dominated by the diamond phase (see Figure 6.18a), while the right edge of the film is dominated by the β -SiC phase (see Figure 6.18e). Figure 6.18f shows the variation of water contact angle on this surface. A decrease is clearly observed in the water contact angle from 86.7° to 25.1° . Such a surface has comparable contact angle values as the self-assembled monolayer (SAM) modified surfaces [52–54]. However, it is more promising for biological applications because of its much higher stability in electrolyte solution.

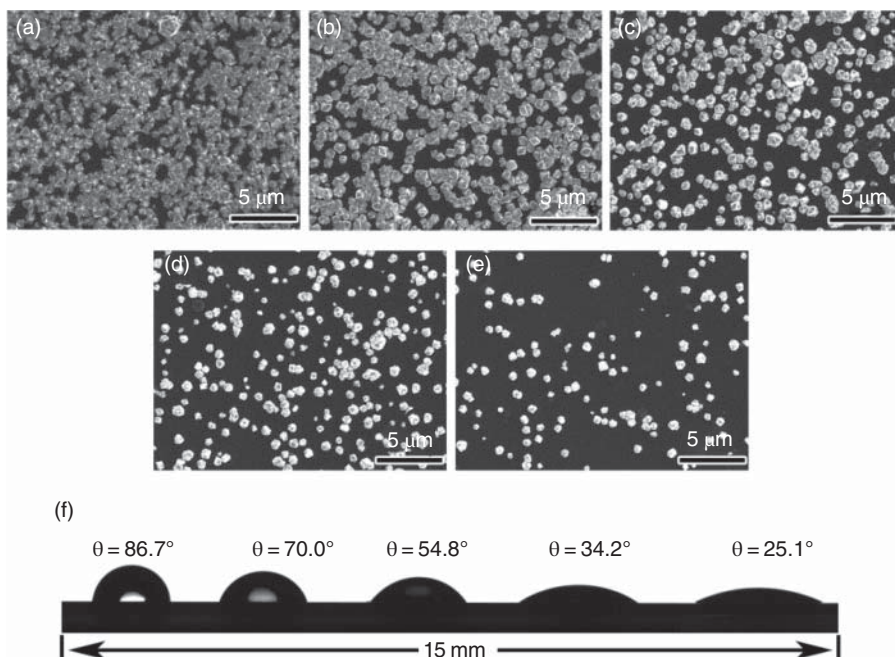
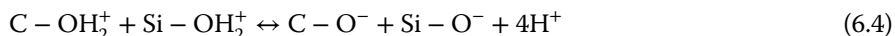


Figure 6.18 A surface with gradient hydrophilicities. (a)–(e) SEM images of the composite film, the surface morphologies of the gradient film from the left edge (high diamond nucleation density) to the right edge (low diamond nucleation density); (f) the contact angle change [51]. Source: Reprinted with permission from American Chemical Society, Copyright 2010.

The surface of the chemically treated composite film is charged in solutions with different pH values, because of the OH-terminated β -SiC phase [44, 46]. Since the biomolecules are also charged in the solutions, this implication is very important when considering a modified thin film surface for biosensoric applications. If the charge of the surface is of the opposite sign with respect to that of the biomolecules to be sensed, nonspecific adsorption of the biomolecules onto the substrate surface will take place. The specificity and sensitivity of the sensor will be drastically reduced [44]. As shown in the following equation, on the OH-terminated β -SiC phase in the composite films, the ionized bonds are present as $C-O^-$, $Si-O^-$ or $C-OH_2^+$, $Si-OH_2^+$ in solution [44, 46]:



Therefore, the surface will be negatively charged at high pH (majority of the hydroxyl groups exist as $C-O^-$ and $Si-O^-$) and positively charged at low pH (majority of the hydroxyl groups exist as $C-OH_2^+$ and $Si-OH_2^+$). In this context, through the determination of its pH at the point of zero charge (PZC), the surface charge status of the film at given pH can be determined. According to Čerović et al., the surface charge density σ can be expressed as [44, 55]:

$$\sigma/F = \frac{\gamma_L}{2.303RT} \times \frac{d(\cos \theta)}{d(pH)} \quad (6.5)$$

where F is the Faraday constant, γ_L is the surface tension of probe solution, R and T are the gas constant and absolute temperature, respectively, and θ is the contact angle. The pH of PZC can be obtained by plotting the cosine of the contact angle versus pH. Figure 6.19 shows the plot of $\cos \theta$ versus pH for the “treated” samples. It can be observed that the PZC is at pH ~ 4 for all the “treated” surfaces. This is not surprising because only the OH-terminated β -SiC phase will be influenced by the pH change, and the PZC of the composite film is determined by the PZC of β -SiC. At pH = 7.5–8.5, which is the most suitable pH for DNA hybridization activities [56], the composite surfaces will be negatively charged, thus enhancing the sensitivity of the DNA sensor [44].

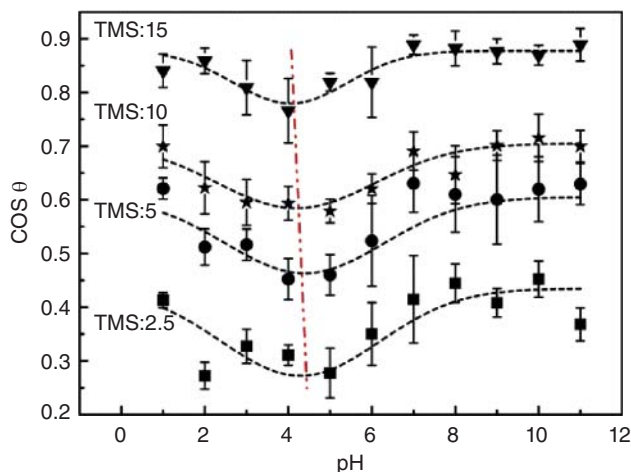


Figure 6.19 Plots of cosine of the contact angle on the “treated” composite film surfaces versus pH. The PZCs of the films were pH ~ 4 [51]. Source: Reprinted with permission from American Chemical Society, Copyright 2010.

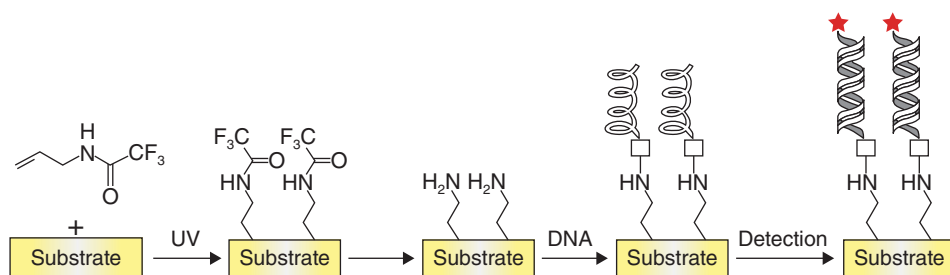


Figure 6.20 Schematic illustration of the main procedures in the photochemical functionalization of diamond/ β -SiC composite films for DNA biosensor applications [18]. Source: Reprinted with permission from Springer Nature, Copyright 2015.

The advantages mentioned above motivated the fabrication of composite films as DNA biosensors. However, both diamond and β -SiC phases in the film are chemically inert. Therefore, surface functionalization is essentially required to make the film bioactive prior to the attachment of biomolecules. In this context, a photochemical method was used to link allylamine – a three-carbon chain unsaturated amine – onto the composite film surface. The schematic illustration of the main procedures in the functionalization process is shown in Figure 6.20. Before functionalization, the amine group is protected by trifluoroacetic acid group. This is to prevent the oxidation of the amine group under UV illumination. The sample is washed after the attachment to remove any nonspecifically attached allylamine. Then in a solution that contains fluorescent dye to indicate a successful hybridization process, the amine group is deprotected and linked to a single-stranded DNA for further detection of the DNA hybridization event. Figure 6.21 shows the fluorescence microscopy images of the functionalized and unfunctionalized areas on the same sample. Clear contrast on the fluorescence signal can be observed: in the functionalized area, a high-intensity fluorescence signal is observed. This indicates that DNA has been attached onto the composite

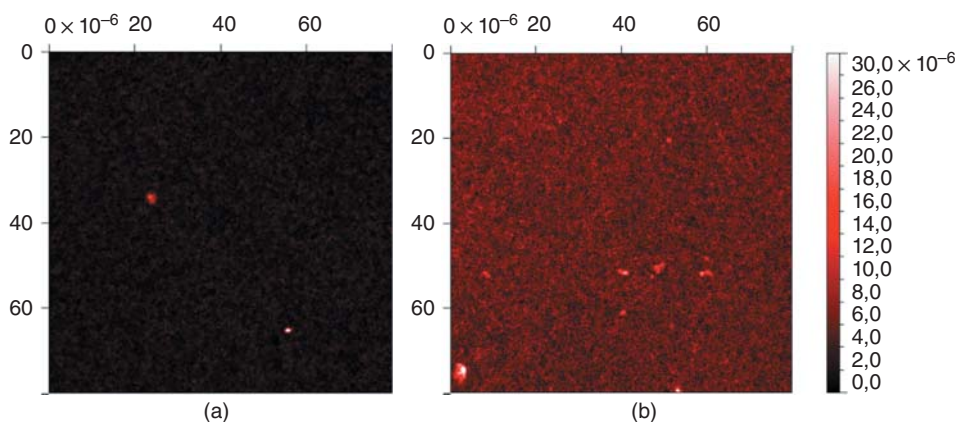


Figure 6.21 Fluorescence microscopic images of DNA functionalized composite film surface: (a) unfunctionalized area; (b) functionalized area [18]. Source: Reprinted with permission from Springer Nature, Copyright 2015.

film surface through the allylamine linkage and is still bioactive. Such an observation not only shows the suitability and possibility of the biosurface functionalization of the composite film, but also opens a door for the application of composite films as the platform to construct DNA biosensors.

6.6.3 Preferential Protein Absorption

Besides biosensor applications, diamond and SiC can also be promising candidates for other biomedical applications due to their extraordinary biocompatible, electronic, and chemical properties. It has been suggested that the first stage of implant integration is the surface adsorption of protein on the implant surface in all biological processes; it is then followed by cell attachment [57, 58]. Thus, in determining the biocompatibility and biointegration of biomaterials, protein adsorption and adhesion play prominent roles. In this context, novel diamond/ β -SiC gradient surfaces with continuously varying surface chemistry have been synthesized and characterized in detail to study the surface chemistry and biointerfacial properties of diamond/ β -SiC composite films systematically. The adsorption behavior of two important proteins, bovine serum albumin (BSA) and fibrinogen, was unraveled. It provides useful clues for the future development of diamond/ β -SiC-based biomaterials by showing an intimate relationship to the local surface chemistry and composition of the diamond/ β -SiC composite films. The gradient diamond/ β -SiC composite films were synthesized by HFCVD with a special filament/substrate configuration. The film was first heated at 250°C for 30 minutes in an oxidizing mixture of concentrated H_2SO_4 and KNO_3 in a beaker. Afterwards it was dipped into HF solution ($\text{HF}/\text{HNO}_3 = 1/15$) in order to remove the SiO_2 on the surface. After oxidation, the samples were treated in HFCVD with H_2 at a gas pressure of 10 mbar for 15 minutes.

Figure 6.22 shows the changes of the surface morphology (SEM), surface topography (AFM) and protein adsorption (fluorescence microscopy) on the gradient surface, at distances of 1 to 7 mm away from the edge of the sample. Figure 6.22a shows the surface morphologies of the local areas of composite gradient films. The surface changed from pure β -SiC to pure diamond over a distance of 7 mm. The areas with bright contrast (i.e. with higher secondary electron emission intensity) correspond to diamond, whereas the areas with dark contrast correspond to β -SiC. At 1 mm there was only β -SiC in the film because the area was the furthest away from the hot filaments. At 7 mm, which was nearest to the filaments, pure diamond crystallites were detected. The gases were less activated for diamond growth with increasing distance between filaments and the substrate, which resulted in a lower content of diamond in the film. Therefore, the diamond/ β -SiC ratio gradually decreased with increasing distance between filaments and substrate along the length of the film. The surface topographies of the gradient film in the same areas are shown in Figure 6.22b. The RMS (root mean square) roughness, determined at a scan size of $10 \times 10 \mu\text{m}^2$ of local areas at 1, 3, 4, and 7 mm were 8.8, 66.8, 77.3, and 58.1 nm, respectively. With increasing content of diamond in the diamond/ β -SiC composite film, diamond crystallites were found to be about 250 nm higher than β -SiC. Accordingly, the roughness increased. For the pure diamond film there were no β -SiC domains, hence the roughness decreased again.

After deposition of the diamond/ β -SiC composite gradient films, oxidation and H-treatment were performed. It can change the surface terminations, resulting in

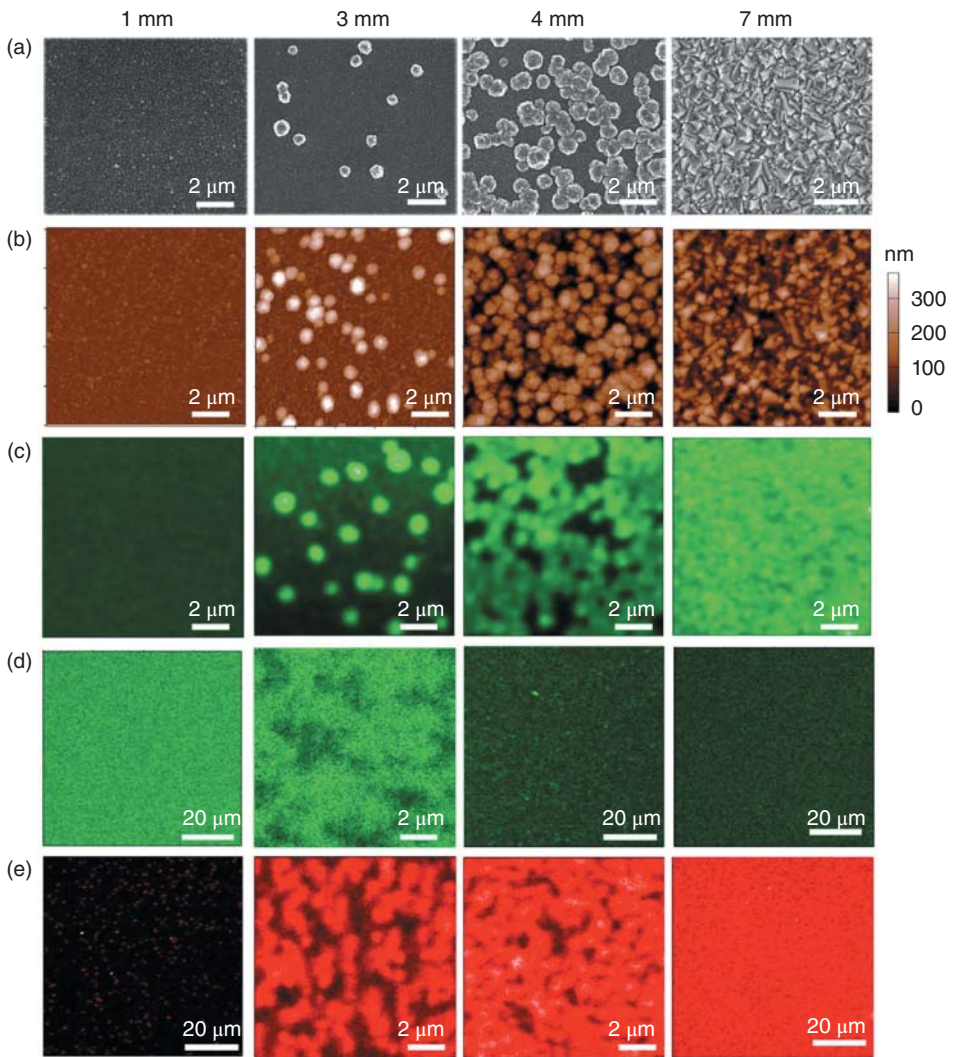


Figure 6.22 (a) FE-SEM and (b) AFM topography images at different positions (1, 3, 4, and 7 mm away from the edge of the film) on a diamond/ β -SiC composite gradient film. Confocal fluorescence images of (c) albumin^{FITC} adsorbed on an oxidized gradient film, (d) albumin^{FITC} adsorbed on a H-treated gradient film, and (e) fibrinogen^{Alexa Fluor} adsorbed on an oxidized gradient film at different positions [82]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

different wettabilities (Figure 6.24) and protein adsorption abilities (Figure 6.22c–e). To evaluate the surface chemical composition and the species present at the surface, X-ray photoelectron spectroscopy (XPS) spectra were recorded for β -SiC, diamond and diamond/ β -SiC composite surfaces after oxidation and H-treatment. On the oxidized surface, each surface Si atom is bound to only one oxygen atom (Si–O, 101.5 eV) [59, 60]. After HF etching during the oxidation process, the SiO_2 was removed. After H-treatment, there are 50% Si–O and 6% silicon in a high oxidation state, that is, SiO_2 on the surface [59], rather than silicon atoms bound to hydrogen. Bernhardt et al. have

found that after hydrogen plasma or etching in hydrogen flow, the surface of β -SiC was covered by a highly ordered monolayer of silicon dioxide [61]. The arrangement of surface oxygen could also be changed, but the oxygen could not be replaced by hydrogen after H-treatment in our experiment. Except for these Si atoms, the remaining surface is occupied by C atoms. A C–O bond (283.7 eV) on the surface carbon atoms was found on both treated surfaces [59, 60]. However, there is only $\text{Si}_3\text{C-H}$ (284.0 eV) bound on the H-treated surface, as one carbon atom is bound to three silicon atoms and one hydrogen atom [62, 63]. Accordingly, on the oxidized β -SiC surface, silicon atoms are bound to oxygen and the carbon atoms are also predominantly bound to oxygen. After H-treatment, silicon atoms are mainly bound to oxygen; nearly half of carbon atoms are bound to oxygen, and the other half are bound to hydrogen. For the surface of the pure diamond, a survey scan shows that there is 6.8% O atoms on the oxidized surface, but no detectable O signal on the H-treated surface. On the oxidized diamond surface, sp^3 bonded carbon in bulk (284.8 eV) [64, 65], sp^2 bonded carbon (283.7 eV) [64], C–O–C ether bonds (285.9 eV) and C=O ketone bonds (288.0 eV) [64] were detected. The strong peak at 284.2 eV on the H-treated diamond surface is attributed to sp^3 bonded carbon in bulk diamond. The weak peak at 285.0 eV can be ascribed to carbon atoms bonded in polyhydride configurations ($-\text{C-H}_x$, $x \geq 2$) adsorbed on the surface [65]. Due to H radicals in the gas phase, after H-treatment, the bonds of the sp^2 C–C, C–O–C, and C=O are all etched away.

The surface chemical state of the composite film is a combination of diamond and β -SiC. Accordingly, a broad range of combinations of surface terminations can be obtained after oxidation and H-treatment. Furthermore, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been employed to analyze each surface after oxidation and H-treatment of diamond and β -SiC samples (Figure 6.23). The mass fragments of C^- , CH^- , O^- , OH^- , C_2^- and C_2H^- at $m/z = 12.000, 13.008, 15.995, 17.003, 24.000$, and 25.008 were observed, respectively. The relative signal intensities were compared by computing I/I_0 , where I is the signal intensity observed for a certain mass fragment, and I_0 is the sum of all intensities calculated by adding all peak intensities of one spectrum. For diamond films, the relative fraction of OH and O at the oxidized surface is higher than that on the H-treated surface, whereas the relative fraction of C, C_2 and C–H bonds at the oxidized surface is much lower than that on the H-treated surface. The XPS results also showed that on oxidized diamond there are C–O–C and C=O bonds, but on H-treated diamond, no oxygen was detected. Recent studies also showed that diamond is H-terminated after hydrogen plasma treatment, but O-/OH-terminated after oxidation [44, 66, 67]. Both our results and the literature thus indicate that, after oxidation, the surface of diamond is OH- and O-terminated; and the surface of diamond is H-terminated after H-treatment. For oxidized and H-treated β -SiC films, the relative fraction of C, C_2 and C–H bonds is similar, whereas the relative fraction of O and OH on oxidized β -SiC film is more than that on H-treated β -SiC films. The XPS results indicate that there are Si–O and C–O bonds on both treated β -SiC, but $\text{Si}_3\text{C-H}$ only on the H-treated surface. Previous work also showed that, due to the inability of HF to remove the last oxygen layer at the oxide/SiC interface, HF etching of oxidized SiC leads to OH termination [59]. Therefore on oxidized β -SiC surface, the carbon and silicon are OH-terminated. After H-treatment, there is not only OH termination on the surface, but also a fraction of C–H bonds on the β -SiC surface. The concentration of $\text{Si}_3\text{C-H}$ bonds on SiC was calculated to be 21%, and the remaining

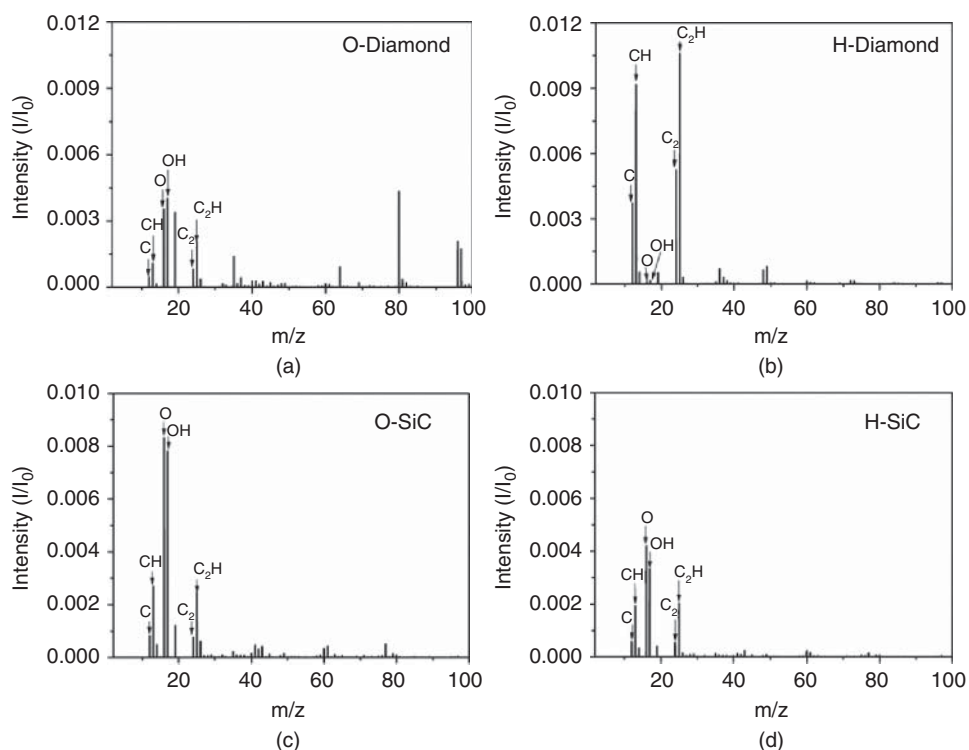


Figure 6.23 ToF-SIMS spectra of pure diamond and β -SiC films after oxidation (O-) and H-treatment (H-) [82]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

surface bonds are OH at a concentration of 79%. The ToF-SIMS data are in agreement with the XPS data.

Figure 6.24 shows the variations of contact angle of water on the surfaces after oxidation and H-treatment. The contact angles on the oxidized samples changed from below 10° to $28^\circ \pm 2^\circ$ from the β -SiC-dominated surface to the diamond-dominated surface. The surfaces were OH-terminated, resulting in a highly hydrophilic surface. On the other hand, the contact angles on the H-treated gradient surfaces decreased from $90^\circ \pm 2^\circ$ to $24^\circ \pm 1^\circ$. This result is similar to former work on films deposited by MWCVD [51]. The H-terminated diamond surface was hydrophobic. The surface gradually changed from hydrophilic to hydrophobic with increasing content of diamond in the composite film. This is because of the increasing fraction of H-terminated diamond and decreasing fraction of OH-terminated β -SiC. The wettability of diamond/ β -SiC composite films hence strongly depends on the diamond/ β -SiC content ratio.

Figure 6.25a,d shows a simplified schematic of protein adsorption on oxidized and H-treated diamond/ β -SiC composite films. Figure 6.25b,c,e,f shows the fluorescence emission intensities versus surface chemistry on the gradient film. After oxidation, the surface of SiC is covered with hydroxyl groups, which tightly bind the H_2O network to the surface. The H_2O network hinders proteins from reaching the surface of SiC. Figure 6.25b shows that there was less protein adsorbed on the oxidized gradient surface with increasing OH (on SiC) concentration. Figure 6.25b,c,e,f was plotted using the

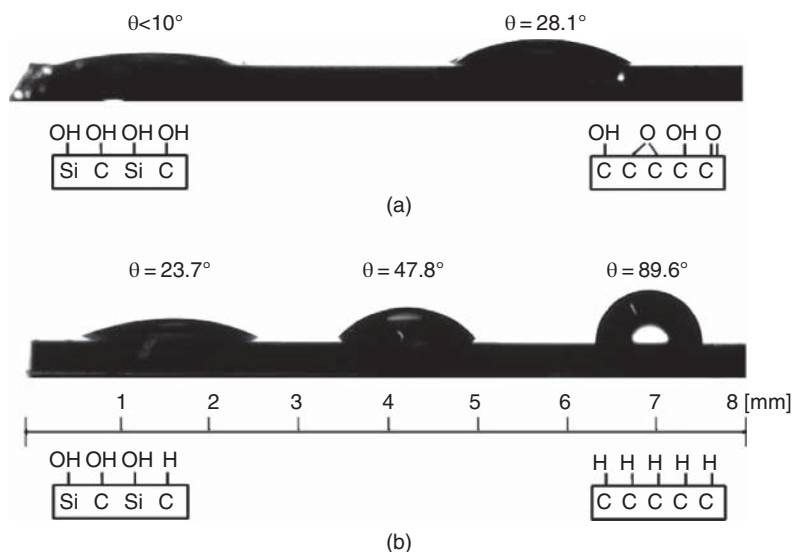


Figure 6.24 Couple-charge device (CCD) camera images of water drops in contact angle measurements of gradient films after (a) oxidation and (b) H-treatment from pure β -SiC (left side) to pure diamond (right side) [82]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

concentration of surface bonds versus f_{diamond} and the fluorescence emission intensities versus f_{diamond} . On the other hand, the diamond surface is terminated with OH and O groups and possesses lower γ_s^{AB} and γ_s^- than OH-terminated SiC. There is a weaker binding of the H_2O network to the surface, because the hydrogen bonding between O and the H_2O network is weaker than that between OH and the H_2O network. Thus the protein can displace the interphase water more easily and interact with O and OH terminations on the diamond surface. Figure 6.25c shows that with increasing C–O–C (on diamond) concentration, there was more protein adsorbed on the oxidized gradient surface. This suggests that the displacement of interphase water needs less energy at the diamond surface (lower $\Delta G_{\text{dehydration}}^0$). Therefore, G_{ads}^0 is lower on diamond than on SiC, resulting in preferential protein adsorption on diamond.

Proteins prefer to adsorb on SiC on the H-treated composite film. As discussed above, the H-terminated diamond surface is apolar. Hydrogen bonding with the protein or the H_2O network cannot occur on this surface, thus no adsorption of protein occurs. On the other hand, the surface of SiC consists of both OH and H bonds. On this SiC surface, the H_2O network is bound to the surface through hydrogen bonding (see Figure 6.25d). However, the H_2O network above the H-treated SiC is less strongly bound to the surface than above the oxidized SiC surfaces. Figure 6.25e,f show that there was more protein adsorbed on the H-treated gradient surface with increasing OH (on SiC) and $\text{Si}_3\text{C-H}$ concentration, suggesting that the $\text{Si}_3\text{C-H}$ lowered $\Delta G_{\text{dehydration}}^0$. Finally, G_{ads}^0 is lower on SiC than on diamond, resulting in preferential protein adsorption on SiC. This work shows that diamond/ β -SiC composite gradient film can be used to control protein adsorption, which is important for biomedical applications, such as materials for implants to direct cell migration, and substrates for biosensors.

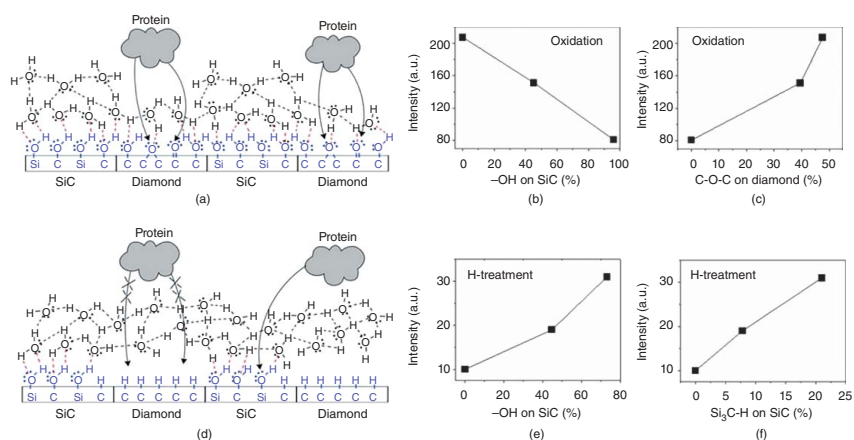


Figure 6.25 Proposed schematic of protein adsorption on (a) oxidized and (d) H-treated diamond/β-SiC composite films. Fluorescence emission intensities of albumin^{ITR} adsorbed on (b, c) oxidized and (e, f) H-treated gradient film versus different concentrations of surface bonds. The concentration of -OH consists of Si-O and C-O concentration on β-SiC [82]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

6.6.4 Diamond Networks

Porous materials have super large “extra spaces” and surface areas compared with their bulk flat materials, and therefore draw great attention from material scientists, chemists and biochemists. Moreover, to fabricate a porous structure from diamond to take advantage of its superlative physical qualities is very important, but challenging, and may involve complex templates or expensive dry etching processes [68, 69]. In this context, we demonstrate a new and controllable method to fabricate a so-called “diamond network” with three-dimensionally interconnected pores, on the basis of diamond/ β -SiC composite films [70]. Such a network allows the porous diamond to possess a high permeability in liquid media and combines the unprecedented physical/chemical properties of diamond and the advantages of porous structures. Tunable pore volume of the networks, namely porosity, ranging from 15% to 68% was achieved and resulted in a significant enhancement of their surface areas. For instance, a surface area enhancement of ~ 490 -fold was achievable for a diamond network with a $3.0\ \mu\text{m}$ thickness, in comparison with a flat nanocrystalline diamond film. Further electrochemical characterization indicates that the diamond networks possess similar electrochemical properties (i.e. electrochemical working potential and redox activities) to those of bulk diamond.

Figure 6.26a schematically shows the method to selectively remove the β -SiC phase from the composite film and leave the diamond phase. It is realized through wet-chemical boiling with a solution of HF and HNO_3 . During the etching process, the following reactions take place continuously [71, 72]:



According to the literature and experiments, the etching behavior of β -SiC is crystallinity-dependent [72]. To achieve an efficient and full removal of the β -SiC phase, a diamond/ β -SiC composite film system with a nanocrystalline β -SiC phase was chosen as the starting material for the fabrication of diamond networks. The supporting Si substrate was quickly removed in the first minute of the etching process. A freestanding diamond network sized $1 \times 0.5\ \text{cm}^2$ obtained with this method is shown in Figure 6.26b. Such freestanding films are transportable, yet a thin film such as $4\ \mu\text{m}$ might break when bearing force during processes. In this regard, materials such as diamond or single crystalline SiC with higher etching resistivity have been used for the deposition of the composite films, and diamond networks directly with substrate support after etching have been obtained. Figure 6.26c shows the SEM image of one diamond/ β -SiC nanocomposite film applied to the fabrication of the diamond network in Figure 6.26b. The film contains bright and dark regions corresponding to nanometer-sized diamond and β -SiC crystals, respectively, due to the different secondary electron yields of diamond and β -SiC [73]. This film underwent a 72-hour etching process to obtain the diamond network. Figure 6.26d,e depicts SEM images of the final structure of the diamond network from a side view and a top view. The thickness of this diamond network is about $4\ \mu\text{m}$. Because of the random growth of β -SiC phases, the pores are homogeneously distributed in the film but without uniform

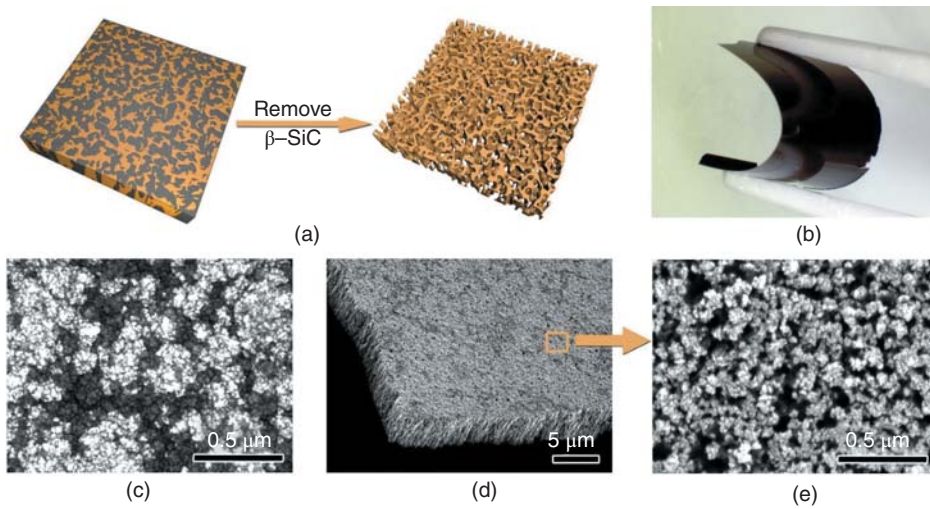
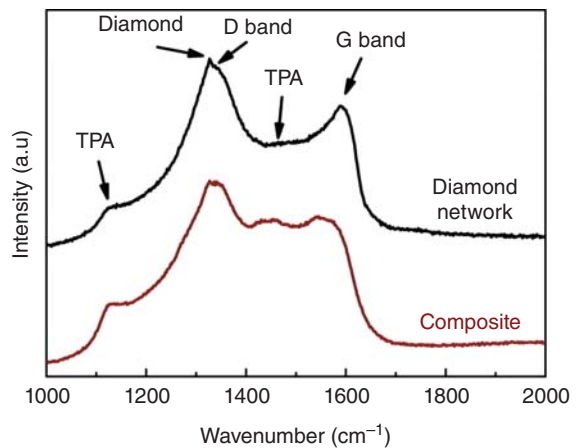


Figure 6.26 (a) Illustration of fabricating a diamond network from the composite film: the gray phase (β -SiC) is removed, leaving a yellow porous phase (diamond). (b) An optical photo of a flexible freestanding diamond network film. (c) SEM surface images of a nanocrystalline diamond/ β -SiC composite film deposited with a TMS/ CH_4 ratio of 1.5%. (d) Diamond network fabricated by etching the β -SiC phase from composite film shown in image (c). (e) High-magnification SEM images of the surface of the film shown in image (d) [83]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

size and shape. Nevertheless, the size of all the pores is tens of nanometers, suggesting that this diamond network can be classified as a macroporous material [74].

The Raman spectra of a diamond/ β -SiC nanocomposite film before (Figure 6.26c) and after the etching process (Figure 6.26e) are shown in Figure 6.27. The Raman signal of the β -SiC phase could not be distinguished in the carbon-rich atmosphere because of its poor crystallinity [73]. In both of the samples, peaks at 1332 cm^{-1} (corresponding to diamond), at ~ 1150 and $\sim 1460\text{ cm}^{-1}$ (corresponding to trans-polyacetylene, TPA), and at ~ 1350 and $\sim 1520\text{ cm}^{-1}$ (corresponding to D band and G band of amorphous carbon,

Figure 6.27 Raman spectra of the composite film and the diamond network [83]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.



respectively) are present. The strong D and G bands and the existence of the TPA Raman peak strongly indicate that the diamond phase is composed of nanocrystalline diamond, which is in good accordance with the SEM observations (Figure 6.26c,e) [75]. Moreover, the similarities of the Raman spectra before and after etching implies that the structure of the diamond phase in the film was not changed during etching. A slight change in the relative intensities of the above peaks is probably due to the alteration of the diamond fraction in the film before and after etching. This is because the amorphous phase and TPA existing in the grain boundaries of the SiC region were removed during the etching process, leading to the reduction of their Raman signal in the diamond network.

While fabricating porous materials, especially networks, the tunability of porosity always needs to be undertaken with particular care. Figure 6.28a–c show SEM images of diamond networks with different porosities, which are fabricated from three composite films deposited with different diamond/ β -SiC ratios. The pores are irregularly shaped for all produced diamond networks, and the pore size and total porosity are greatly different between samples. The pore size increases from tens of nanometers to hundreds of nanometers with an increase of TMS/ CH_4 ratios from 0.8% to 2.2%. The porosity

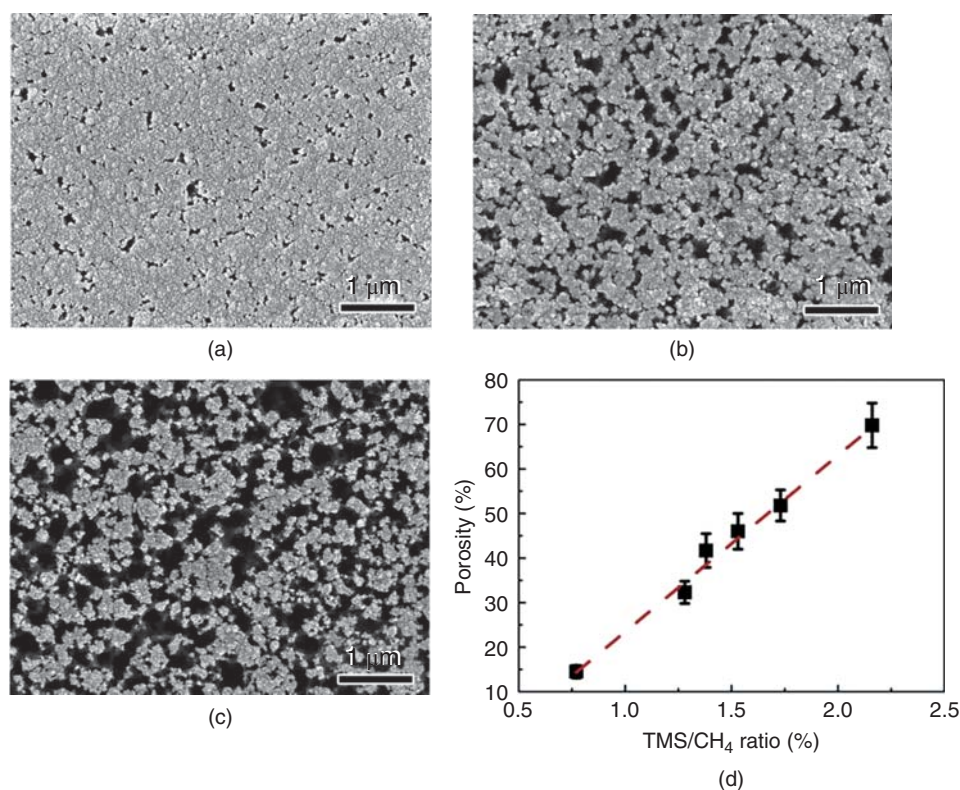


Figure 6.28 SEM surface images of diamond networks having different porosities fabricated from composite films deposited with TMS/ CH_4 ratios of (a) 0.8%, (b) 1.3%, and (c) 2.2%. (d) Plot of the porosity of the diamond networks as a function of the TMS/ CH_4 ratios used for the deposition of composite films [83]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

of diamond networks can be estimated by evaluating the volume fraction of the β -SiC phase in the diamond/ β -SiC composite film. As the growth of diamond/ β -SiC composite films is a competitive process, an equilibrium between the diamond and β -SiC phases can be quickly established after the initial nucleation stage (within 100 nm thickness) [13]. The diamond/ β -SiC ratio in the composite film will remain constant throughout the deposition process if the TMS/ CH_4 ratio and other conditions are constant. This allows us to get an estimate of the volume fraction of β -SiC by measuring the β -SiC ratio on the surface of the composite films. In this way, the porosities were estimated to be 15%, 30%, and 68% for the diamond networks shown in Figure 6.28a–c, respectively. Figure 6.28d shows a wide-range tunability of diamond network porosity ($\sim 15\%$ to $\sim 68\%$), as all the porosities increase linearly with increased TMS/ CH_4 ratio during deposition.

Yet, the above-mentioned diamond networks are undoped. It is well-known that, owing to their large surface area, one promising application of porous materials is as electrodes for electrochemical applications like supercapacitors, catalyst support, batteries, and so on. To adopt diamond networks for such applications, we introduced trimethylborane (TMB) during deposition, and applied a B/C ratio of 3000 ppm in the gas phase to achieve a nanocrystalline composite film with a similar structure to that of the undoped composite films. With a relatively low doping level, a sheet resistance lower than $300 \Omega \text{ cm}^{-2}$ was obtained for all the films. This value suggests their suitability as electrodes for electrochemical applications. Also prior to the composite films, a $\sim 800 \text{ nm}$ boron-doped diamond layer was used as a current-collecting layer, thus preventing leakage of electrolyte on the substrate.

The electrochemical properties of two boron-doped diamond networks with two different porosities of 16% (DN16) and 64% (DN64) were studied. The thickness of the boron-doped diamond networks is $3 \mu\text{m}$. Figure 6.29a shows their cyclic voltammograms in $0.1 \text{ M H}_2\text{SO}_4$, along with that of the flat nanocrystalline diamond film. The currents at 0.15 V are 0.052 , 8.33 , and $25.5 \mu\text{A}$ for the flat diamond film, DN16, and DN64, respectively. The electrochemical background (or capacitive) current is known

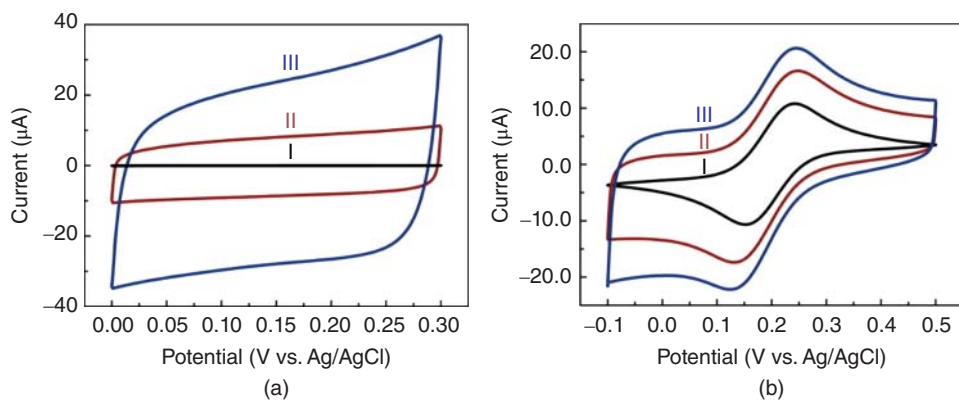


Figure 6.29 Electrochemical properties of a flat diamond film (I), DN16 (II), and DN64 (III). (a) Cyclic voltammetry in $0.1 \text{ M H}_2\text{SO}_4$ at a scan rate of 0.1 V s^{-1} . (b) Cyclic voltammetry in $1.0 \text{ mM [Fe(CN)}_6\text{]}^{3-/4-}$ in 0.1 M KCl at a scan rate of 0.1 V s^{-1} [83]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

to be proportional to the active surface area in contact with the electrolyte solution [76]. Assuming that the specific capacitance of diamond does not alter before and after wet-chemical etching, the effective surface areas of DN16 and DN64 are ~ 160 and ~ 490 times higher than that of the flat nanocrystalline diamond film. Yet the potential of its surface area enhancement may not be fully reflected by the measurements. The diamond networks measured here are half-closed. The air can still partially seal pores and stop the diffusion of the electrolyte into the pores, even though the pores are in the macroporous range and the surface is hydrophilic after etching.

The normalized surface areas with thickness of the diamond network is higher than that of other porous diamond films such as diamond foam, and diamond/carbon nanotubes (CNTs) from the literature [77, 78]. Moreover, the double layer capacitance of DN64 was calculated as 13.7 F g^{-1} or 17.3 F cm^{-3} at a scan rate of 100 mV s^{-1} , which is of the same order as that of carbon aerogel (77 F cm^{-3}) [79] and microporous carbon (80 F cm^{-3}) [80]. After further optimization and proper decoration with other materials (i.e. MnO_2 , NiO , V_2O_5 , etc.), diamond-network-based supercapacitors can be constructed with a high power density and a long lifetime.

6.7 Conclusions and Future Aspects

Diamond/ β -SiC composite films have been successfully synthesized through MWCVD and HFCVD processes. To date, good control of the crystallinity, orientation and phase distribution has been achieved. The films show good adhesion to the cutting tool materials and have drastically improved their lifetime. The surface status of the composite film has been systematically studied, and shows high potential in biological applications. Diamond/ β -SiC composite gradient film can be used to control protein adsorption. In this context, a composite film-based DNA sensor is fabricated, and diamond networks based on diamond/ β -SiC composite films are studied. However, to fully explore the potential of the composite films, it would be helpful to address the following aspects of diamond/ β -SiC composite film systems in future studies.

The achievement in the controlled synthesis of composite films offers us the possibility of designing the growth of composite films with complex 3D structures to improve the toughness and wear resistance of diamond films on various substrates. However, to obtain these structures, a high resolution is needed in the selective growth of diamond or likewise β -SiC on a surface, along with the ability to define and steer the structural properties such as grain size and possibly the crystallographic orientation of the phase(s) growing at the selected spot(s) and throughout the deposition process. This requires a deep understanding of the growth process, especially at high microwave power densities, which induce the selective growth of the composite films. At the same time, a systematic analysis of the film/substrate interface and diamond/ β -SiC boundary under different loadings or environments is also of great importance.

The successful growth of patterned composite films opens the door to numerous composite film-based electronic device applications. In this regard, doping of the composite film is essential. As diamond and β -SiC can both be easily doped by boron to a high level, boron is expected to be a good dopant. Nitrogen would be another promising candidate – β -SiC can be easily doped with nitrogen, whereas nitrogen doping of diamond is known to be difficult. By employing nitrogen as the dopant, the selective

doping of β -SiC in the composite film, leaving the diamond phase undoped, will be possible. This opens the possibility of producing a conductive β -SiC electrode embedded in insulating diamond film. Combined with the good stability of both diamond and β -SiC, such electrodes would be very suitable for harsh environment applications as well as biosensor applications. Nevertheless, the influence of the addition of boron- or nitrogen-containing species on the co-deposition of diamond and β -SiC is still unknown and requires systematic study. For example, it will affect the growth rate and defect evolution of diamond and β -SiC crystals, which might result in the disappearance of either phase in the composite film. Moreover, when boron is employed, owing to the great disparity in the volume of methane and TMS in the gas phase, the doping level of diamond and β -SiC phases would also be different in the composite films.

Composite films have been successfully applied to the fabrication of a DNA biosensor via the linkage of allylamine. However, the linkage of allylamine onto diamond and β -SiC is expected to have different reaction rates, owing to its different reactivities with diamond and β -SiC. Therefore, it is reasonable to expect that before allylamine fully covers one phase, its full coverage of the other phase will already have been achieved and the cross-polymerization of allylamine already begun. As a result, inhomogeneity of the surface amine layer exists, and this will have a strong impact on the electrical detection of biomolecules. If the amine layer coverage is low, the signal from the DNA hybridization will possibly be too low for detection. If the amine layer coverage, on the other hand, is too high or even cross-polymerized, the electric response of the DNA hybridization event will be blocked. Therefore, special attention will have to be given to achieving a relatively homogeneous amine layer on the composite film surface. Surface wettability studies of the composite films show that the H-termination of the diamond surface and the OH-termination of the SiC surface are possible simultaneously. Different surface terminations allow for selective surface reactivity with respect to the diamond and SiC phases. For example, the OH-terminated SiC surface reacts with organosilanes, while the H-terminated diamond is not able to do so. Consequently, it is possible to exploit the selective functionalization of diamond and SiC by utilizing two different functional groups (i.e. diamond-NH₂, SiC-COOH), respectively. These functional groups are, in turn, able to react and link with two different kinds of DNA featuring different end groups, respectively. Due to the homogeneous distribution of diamond and SiC phases in the composite film, the detection range of the biosensor chip would be doubled. In order to achieve this, a strategy will have to be evaluated which allows the functionalization of one phase while leaving the other phase unaffected. However, this still requires additional dedicated research.

Diamond/ β -SiC composite gradient films were synthesized by careful manipulation of the sample position during the HFCVD process. The diamond/ β -SiC ratio gradually changed from pure diamond to pure β -SiC along the length of the sample. β -SiC is OH-terminated after oxidation, but OH-/H-terminated after H-treatment, while diamond is O-/OH-terminated after oxidation, but H-terminated after H-treatment. The surface chemistry could be controlled by different diamond/ β -SiC ratios and surface treatments. According to confocal fluorescence microscopy, proteins were preferentially adsorbed corresponding to the distribution of diamond and β -SiC in the composite film, thus proteins preferred to adsorb on diamond surfaces rather than β -SiC after oxidation. On the other hand, proteins preferentially adsorbed on β -SiC surfaces rather than on diamond after H-treatment. The mechanism of preferential protein adsorption was

discussed by considering the hydrogen bonding of the water self-association network to OH-terminated surfaces and the change of the polar surface energy component, which was determined together with the other thermodynamic surface free energy components according to the van Oss method, respectively, on the basis of static contact angle measurements of various probe liquids. This work shows that diamond/ β -SiC composite gradient film can be used to control protein adsorption, which is important for biomedical applications, such as materials for implants to direct cell migration and substrates for biosensors. But more study has to be carried out in order to observe the behavior during biosensor applications.

Diamond networks, the porous diamond with both vertically and horizontally interconnected pores, have been fabricated using a simple template-free approach. Experimentally, it was conducted by selective removal of the β -SiC phase from diamond/ β -SiC composite films. The etching rate was determined to be $\sim 50 \text{ nm h}^{-1}$. The porosity has been designed through varying the ratios of the β -SiC phase in the composite during preparation of composite films. The porosities were tunable in the range of 15–68%. Electrochemical analysis reveals that diamond networks maintain the excellent electrochemical properties of diamond, regardless of their different porosities. For a $3 \mu\text{m}$ thick diamond network with a porosity of 64%, a surface area enhancement of ~ 490 -fold has been achieved. Compared with other template-based methods, it reduces the complexities and costs of fabrication, which is favorable for industrial application and beneficial for its further translation. These diamond networks are promising candidates for applications in the fields of water filtering, supercapacitors, catalyst supports, and so on. Furthermore, by introducing a bias-assisted composite film deposition, the distribution of the β -SiC phase in the film can be further controlled to achieve a nanometer-scale distribution. In this case, diamond networks with nanometer-sized pores may even be possible, and its application in lithium-free batteries or biofiltrations may be evoked. However, the long etching duration could be a drawback of the current approach, which requires further investigation to explore a more efficient etching process. Also, more details will be required in the future regarding its local functionalization as well as its size/shape-related properties.

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7

Diamond/Graphite Nanostructured Film: Synthesis, Properties, and Applications

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7.1 Introduction

Carbon-based nanostructures with outstanding and unique structural characteristics and properties are now the focus of the most active areas of research in recent decades. Besides diamond, graphite, carbon nanotubes [1], fullerene [2], and graphene [3], innovative hybrid sp^3 -C and sp^2 -C architectures have attracted growing scientific interest owing to extraordinary mechanical properties and high conductivity without doping coexisting in the films. Bottom-up crystalline hybrid sp^3 -C diamond(D)/ sp^2 -C graphite(G) nanostructured film was first reported in 2007 via microwave plasma-enhanced chemical vapor deposition (MPCVD) in an $Ar/CH_4/H_2/N_2$ mixture [4]. The hybrid nanostructures consist of a diamond nanowire core of 5–6 nm in diameter encased into graphite of a certain thickness. Arenal et al. [5] also obtained hybrid D/G nanowires after adding more than 10% N_2 into $Ar/N_2/CH_4$ feed gases, which revealed that the graphite sheath surrounding the diamond provides the electrical transport path responsible for the electrical conductivity. This kind of conductive D/G nanostructure has been developed using different gas mixtures including $Ar/CH_4/H_2/N_2$ [6, 7], N_2/CH_4 [8–12] and $Ar/N_2/CH_4$ [13]. Nitrogen gas incorporation was proved to be a decisive factor for the growth of the hybrid sp^3 and sp^2 carbon materials. Nowadays, D/G nanostructured film can be found as a suitable material for biosensors [8, 10, 14], electron field emission [11, 15, 16] in harsh environments, and protective wear-resistant coating [17–19]. In this chapter, we review hybrid D/G core-shell nanostructured films grown in CH_4 and H_2 source gases without N_2 addition using a plasma-enhanced chemical vapor deposition (CVD) system. To the best of our knowledge, the D/G nanostructure film, prepared without nitrogen or argon involved in microwave plasma, has not yet been reported by other groups. Herein, Surface morphology, carbon phase distribution and microstructure have been comprehensively studied by field emission scanning electron microscope (FE-SEM), Raman spectrometer and transmission electron microscope (TEM). The growth mechanism was studied in depth, and a D/G nanostructured film deposition

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process is proposed in this review. It is noteworthy that good mechanical, electrical and electrochemical properties coexist in the hybrid D/G nanostructure films obtained in the absence of N_2 . It shows great potentials in applications such as sealing rings, rolling bearings, tracing heavy metal ion detection, and biosensors.

7.2 Synthesis of the D/G Nanostructured Film

Simultaneous CVD synthesis of the D/G nanostructured film was achieved by adjusting CH_4/H_2 ratios in microwave plasma. The microwave power and the pressure in the chamber were held constant at 10 kW and 70 mbar, respectively, during the nucleation and growth process. The flow rate of H_2 was 400 sccm and the ratios of CH_4 were adjusted from 1% to 8%. During the process, the substrate holder was heated up to 1050°C measured by an infrared radiation thermometer. Prior to the CVD growth, n-type (100)-oriented silicon substrates were seeded in nanodiamond slurry to enhance the nucleation density. The surface morphology of the as-grown films was explored by means of FE-SEM (Zeiss-Super 55). The surface bonding structure and crystal quality of the deposited films were studied by Raman spectroscopy (Horiba HR Evolution) equipped with a 325 nm He-Cd laser as an excitation source. Spectra were recorded in the range of 1000–2000 cm^{-1} . The detailed microstructure and growth behavior of the samples were examined using a TEM (FEI Tecnai G2 F20).

Figure 7.1 shows the morphological evolution of the diamond films with different CH_4/H_2 ratios ranging from 1 to 8%. As can be seen, the methane concentration has an important impact on the diamond growth. When increasing the CH_4/H_2 ratio up to 7% in the plasmas, needle-like nanostructured clusters uniformly covered the substrate, instead of the granular crystals found at low methane levels. With a further increase of the methane concentration to 8%, the nanostructured clusters were clearly elongated on the surface. Therefore, the surface morphology of the films shows an obvious structural transformation from micrometer-sized diamond crystals to low-dimensional nanostructures with increasing methane concentration in the microwave plasmas. More importantly, it can be seen that the diamond nanostructures were prepared with only hydrogen and methane as the reactive gases, which has not yet been reported by other groups.

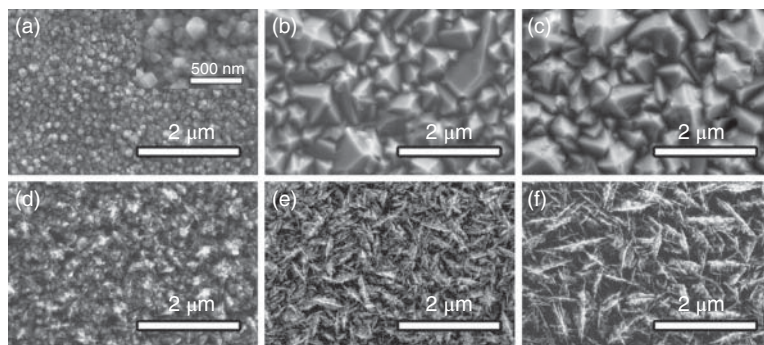
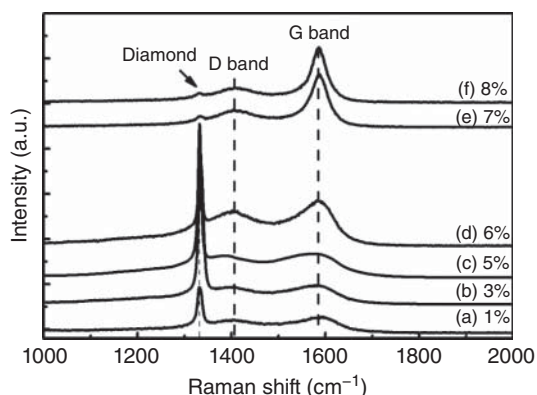


Figure 7.1 Plan-view FE-SEM images of diamond films grown on a silicon substrate in different ratios of CH_4/H_2 plasmas: (a) 1%; (b) 3%; (c) 5%; (d) 6%; (e) 7%; and (f) 8%, respectively [47]. Source: Reprinted with permission from Elsevier, Copyright 2016.

Figure 7.2 Raman spectra of diamond films grown on silicon substrate in different ratios of CH_4/H_2 plasmas: (a) 1%; (b) 3%; (c) 5%; (d) 6%; (e) 7%; and (f) 8%, respectively [47]. Source: Reprinted with permission from Elsevier, Copyright 2016.



The bonding characteristics of different types of carbon in hybrid nanostructured film prepared by a MPCVD system in a mixture of hydrogen and methane gas mixture were examined using Raman spectroscopy. Figure 7.2 shows the UV Raman spectra for the diamond films deposited with various methane concentrations from 1% to 8%. It is well known that the characteristic peak of sp^3 carbon (diamond) is located at $\sim 1332 \text{ cm}^{-1}$, and the Raman line at around 1580 cm^{-1} (G peak) reflects the mode of sp^2 -bonded carbon [20]. For the diamond films deposited with 1–6% CH_4 , a sharp peak at approximately 1332 cm^{-1} indicates a high-quality diamond phase. However, when the methane level increases up to 7% and 8%, the appearance of a strong G peak at 1585 cm^{-1} reveals the large amount of sp^2 carbon in the film, and the degradation of the diamond quality.

Figure 7.3a shows a cross-sectional TEM image of a hybrid D/G film deposited under an 8% ratio of CH_4/H_2 . The corresponding high-magnification TEM image as marked in the white rectangle is shown in Figure 7.3b. From electron diffraction (SAED) patterns of the selected area, the diffraction spots correspond to the diamond phase and the ring-shaped diffraction pattern indicates that the diamond grains are randomly orientated in this layer. Figure 7.3c shows the interface region between the diamond layer and the Si substrate, revealing an amorphous layer with a thickness of about 2 nm. The plane-view TEM image of the film is displayed in Figure 7.3d, showing diamond nanostructures were uniformly distributed in the film. These randomly oriented nanostructures have lengths of around 500 nm and a few nanometers in diameter. The SAED corresponding to the film is shown in the inset picture, which exhibits ring-shaped patterns, clearly demonstrating a random orientation feature. According to the SAED pattern, the lattice plane spacings are estimated to be 0.21, 0.12, and 0.11 nm, which are in accord with (111), (220), and (311) planes, respectively, of the diamond structure. An interplanar distance of 0.36 nm in the diffraction rings belongs to the (002) plane of the graphite phase. Hence, it indicates the coexistence of the diamond and graphite phases in the film. Therefore, from cross-sectional and plane-view TEM images, we can see that the film deposited at 8% CH_4/H_2 plasma consists of an amorphous layer, a diamond layer, and diamond/graphite composites. The hybrid D/G nanostructured film has been successfully synthesized without nitrogen or argon assistance. The growth process is discussed in the following paragraphs.

To undertake further detailed structural analysis of the D/G nanostructures, typical TEM images obtained from the sample are shown in Figure 7.4. The arrows in Figure 7.4a indicate the diamond nanostructures, which are 1 or 2 μm in length and

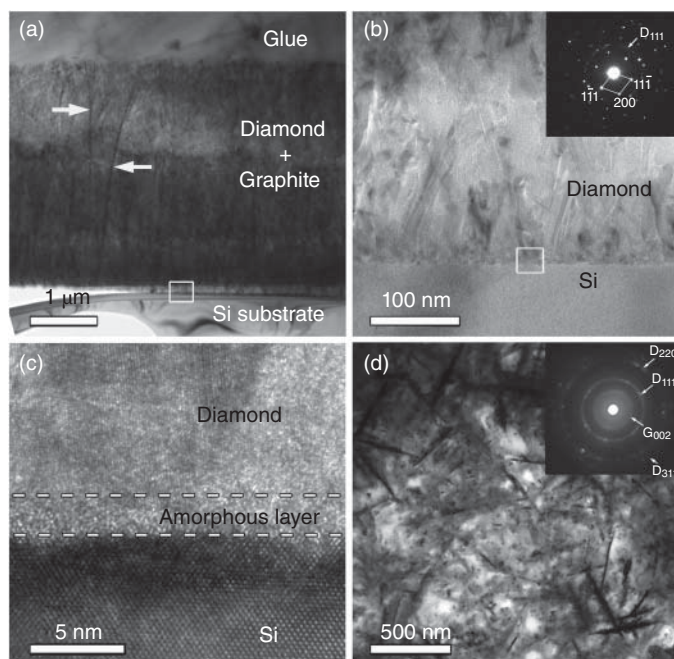


Figure 7.3 (a) Low-magnification cross-sectional TEM image of hybrid D/G film deposited under 8% ratio of CH_4/H_2 ; (b) High-magnification image of the white rectangle in (a), the inset shows the corresponding selected area electron diffraction patterns; (c) HRTEM image of the interface region of the white rectangle in (b); and (d) plane-view TEM image, the inset shows the corresponding selected area electron diffraction patterns [47]. Source: Reprinted with permission from Elsevier, Copyright 2016.

a few nanometers in diameter. High-resolution TEM was utilized for investigation of a single D/G nanostructure clearly illustrated in Figure 7.4b, where the diameter of the diamond nanorod is 6.5 nm. The lattice spacing of 0.21 nm corresponds to the diamond crystal planes, which shows that the diamond nanostructures orient along the (111) planes. The lattice spacing of 0.37 nm is indexed to be graphite (002) graphite planes, showing diamond nanostructures are encapsulated by a sheath of graphite phases. This diamond-core/graphite-shell structure also can be clearly distinguished by the dark-field observations from Figure 7.4c,d. In the dark-field image of graphite phase in Figure 7.4c, every two light lines correspond to the graphitic shell, while the dark-field image of the diamond phase shown in Figure 7.4d displays a bright line between two graphitic shells corresponding to the diamond core. Thus, the core-shell D/G nanostructures were verified to be successfully prepared by a microwave plasma enhanced CVD technique without N_2 addition.

7.3 Growth Mechanism of the D/G Nanostructured Film

In the previous CVD growth of diamond/graphite nanostructured films, nitrogen was demonstrated to play an important role in influencing the microstructures and the

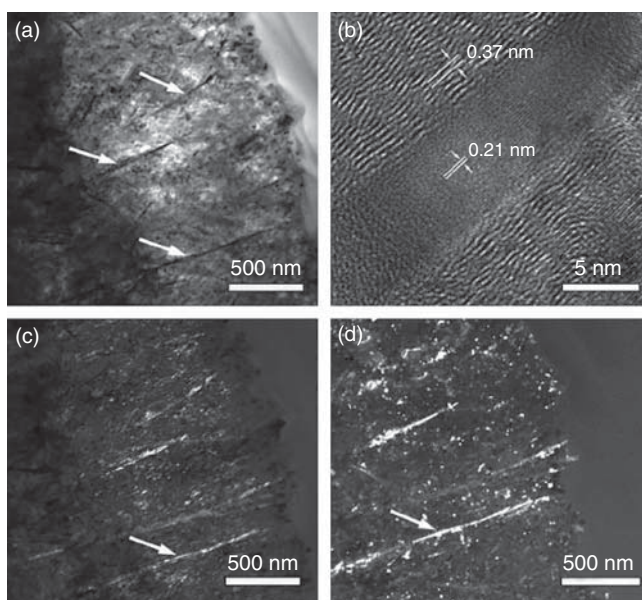


Figure 7.4 (a) Typical bright-field TEM image of hybrid D/G film deposited under 8% ratio of CH_4/H_2 ; (b) HRTEM image of a single D/G nanostructure, showing the diamond nanostructures encased into the graphite phase; (c) dark-field TEM image of graphite; and (d) dark-field TEM image of diamond [47]. Source: Reprinted with permission from Elsevier, Copyright 2016.

electrical characteristics of the diamond films. And nitrogen-related species such as CN or HCN contribute to the growth of diamond nanostructures [4]. In the present process, however, no nitrogen has been introduced into the chamber during film deposition. Thus, another mechanism must account for the formation of diamond nanostructures. From the above experimental results, the possible factor responsible for the synthesis of diamond/graphite nanostructures by MPCVD technique in mixed H_2 and CH_4 gas is the high methane concentration. Even though Rakha et al. [21] have clarified that the high level of methane is responsible for the formation of diamond nanostructures in Ar-rich microwave plasmas, the presence of argon also plays a role to enhance the nucleation rates and promote low-dimensional diamond growth. In the present study, only CH_4 and H_2 have been used as the reactive gases for the synthesis of the D/G nanostructures. Therefore, it is essential to conclude that the high concentration of methane produces the precursor species and radicals necessary for growth of the D/G nanostructured film.

When the methane concentration is relatively low, the hydrogen plasma produces preferential etching of non-diamond carbon from the film surface [22], increasing the quality of the diamond crystals, which in turn leads to the formation of columnar crystals related to the high CH_3 species concentration in the deposited films, as shown in Figure 7.1a–c [23, 24]. With the methane concentration gradually increasing to 6%, the micrometer-sized diamond crystals disappear. Instead, the amount of graphite phase significantly increases, attributing to the decrease of hydrogen, which was clarified by the obvious G peak in the Raman spectra (see Figure 7.2d). The formation rate of the sp^2 carbon phase is higher, and the atomic hydrogen is not able to totally etch them away. As

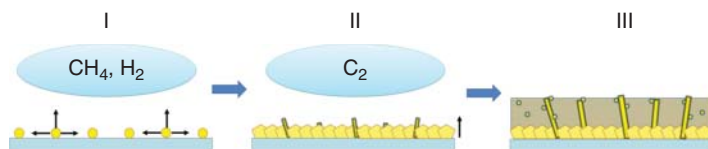


Figure 7.5 Schematic illustration of the growth process of the hybrid D/G nanostructures: (a) initial growth of pre-nucleation particles on the substrate; (b) continuous growth of diamond transition layer; (c) the formation of hybrid nanostructures adhered with diamond nanoparticles on the transition layer.

a result, certain sp^2 carbon remains on the diamond surface and serves as a secondary nucleation site. The secondary nucleation of diamond increases and finally leads to the decreased crystal size of diamond [25, 26]. When the methane concentration is even higher, the C_2 species is dominant in the reactive process instead of CH_3 or CH radicals, leading to the growth of elongated diamond nanostructures [27, 28]. However, it is different from the effect of the C_2 dimers with N_2 incorporation, attributing that the presence of CN species is mostly responsible for the anisotropic growth. Therefore, the addition of a high level of methane alters the growth mechanism of films, which creates favorable conditions for diverse growth rates of different crystal faces thus leading to the formation of diamond nanostructures. In other words, the growth of the diamond nanostructures is realized by only introducing high methane concentration in the plasmas. We can see a complete morphological evolution process from microcrystalline to nanocrystalline diamond and then into nanostructured film deposited in conventional CH_4 and H_2 mixtures, which has not been observed before. The present growth process may provide new understanding of the growth mechanisms of CVD diamond nanostructures.

According to the above discussion, a schematic illustration is shown in Figure 7.5 of the growth process of the hybrid diamond/graphite films with higher methane levels in hydrogen plasma. After the deposition starts, the random diamond seeds quickly expand to occupy the surface of the silicon substrate. With deposition time continuing, a continuous diamond layer forms due to the expansion of adjacent crystals, confirmed by TEM analysis shown in Figure 7.3. Subsequently, sp^2 carbon forms at the grain boundaries of diamond crystals due to the decrease of hydrogen, which improves the diamond growth along certain directions. Meanwhile, the C_2 species are dominant in the reactive process instead of CH_3 or CH radicals, and as a result the diamond nanostructures are formed on the diamond surface, as previously reported [27, 28]. Additionally, the remaining sp^2 carbon grows, surrounding the diamond nanostructure. Finally, owing to a high methane concentration, secondary nucleation is inevitable, which leads to the simultaneous formation of numbers of diamond nanoparticles on the surface of hybrid D/G nanostructure.

7.4 Properties and Applications of the D/G Nanostructured Film

7.4.1 Mechanical Properties

Three different D/G nanostructured films prepared at 6%, 7%, and 8% CH_4 levels were used for friction and wear tests carried out on a ball-on-disc type rotating friction tester

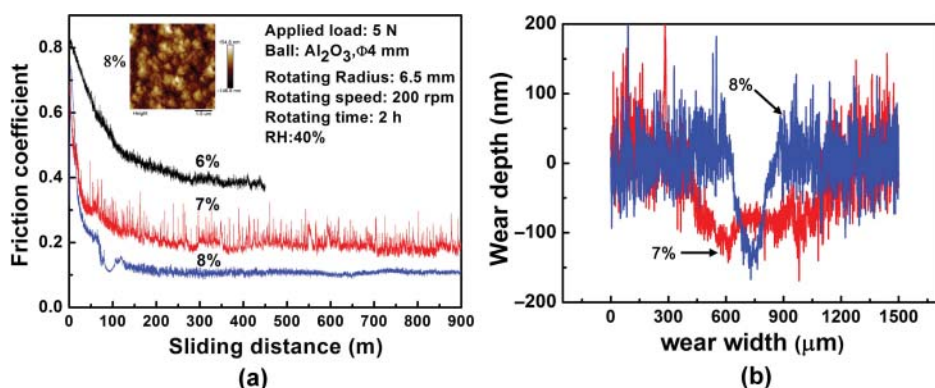


Figure 7.6 (a) Friction behavior of films deposited at 6%, 7%, and 8% CH₄ levels, rolling against an Al₂O₃ ceramic ball in air. The tests were done at room temperature and the relative humidity is $40 \pm 3\%$; (b) Surface profiles of the films deposited at 7% and 8% CH₄ content after the friction test [48]. Source: Reprinted with permission from Elsevier, Copyright 2016.

in ambient atmospheric conditions at room temperature with 40% relative humidity. The films were fixed on an Al₂O₃ ceramic ball with a diameter of 4 mm as a counterpart under an applied normal load of 5 N. A rotating radius of 6.5 mm and a rotational speed of 200 rotations per minute (rpm) corresponded to a sliding distance of ~ 980 m after two hours. The wear profiles of the samples were measured by a surface profilometer (Bruker, Dektak XT) using a diamond stylus tip with a radius of curvature of 2 μm. The wear rate of the film on the substrate was calculated using Archard's law ($K = VF_N^{-1}d^{-1}$, where K is the assumed linear wear rate, V is the volume worn, F_N is the applied load, and d is the total sliding distance). The influence of the methane level on the tribological behaviors of D/G films was studied, and the results are summarized in the Figure 7.6.

Figure 7.6a shows the curves of friction coefficient versus sliding cycles for the diamond/graphite films deposited at levels of 6%, 7%, and 8% CH₄ content against Al₂O₃ ceramic counter faces under a dry sliding environment. During the sliding testing, a slight vibration at the onset showed higher initial peaks, and subsequently the friction coefficients in the curve were in steady state for all of the D/G samples. The Al₂O₃ ceramic counter against the diamond film synthesized at the 6% methane level was severely worn at the beginning of the friction measurement, owing to the sharp diamond surface shown in Figure 7.1d. The steady-state friction coefficients for the films deposited at 6%, 7%, and 8% methane levels are 0.39, 0.19, and 0.10, respectively. The value of friction coefficient of 0.10 for the films in this study is attributed to the formation of the graphite phase with high methane level. Meanwhile, in comparison with the prior report, the friction coefficient is lower than that of the diamond film prepared by MPCVD in CH₄/H₂/N₂ plasma (~ 0.17) [29]. The wear tracks of the films prepared with 7% and 8% methane in hydrogen plasmas were determined three times, as shown in Figure 7.6b. It can be seen that a much broader wear track of about 820 μm was formed on 7% methane compared with ~ 310 μm of the film synthesized with 8% methane, revealing a larger wear loss for the film deposited at 7% CH₄ level. The depths of the wear tracks for both films are about ~ 150 nm. On the basis of the wear track dimensions, wear rates were calculated using Archard's law, giving 7.2×10^{-7} and 1.9×10^{-7} mm³ (N m)⁻¹, respectively. Inherently, D/G nanostructured films show low friction coefficients and

high wear resistance based on the unique surface chemical composition and optimal proportion of diamond and graphite in the composited film.

7.4.2 Electrochemical Properties

Electrochemical measurement experiments were performed with an Autolab workstation (PGSTAT302N) using a three-electrode system. The D/G film acted as a working electrode, with an geometric area of 0.053 cm^2 . An Ag/AgCl electrode and platinum wire served as the reference electrode and the counter electrode, respectively. The electrochemical responses of the D/G electrode deposited under 8% methane concentration were carried out in 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl and 1 mM ferrocene in 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) in CH_3CN solution. $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and ferrocene were redox mediators employed to probe the hybrid D/G electrode activity. 0.1 M sulfuric acid was used for the measurement of the electrochemical potential window. All aqueous solutions were prepared in Mill-Q water ($>18.2 \text{ M}\Omega \cdot \text{cm}$).

Figure 7.7 shows a cyclic voltammogram for the hybrid D/G nanostructured films measured in the 0.1 M H_2SO_4 solution. The potential windows of the different hybrid electrodes were evaluated. The potential window of the boron-doped diamond (BDD) electrode is also shown as a comparison. For the case of the hybrid diamond/graphite film with 7% methane, it barely shows any response, which is an indicator for slow kinetics on the electrode due to high sheet resistance ($10\text{--}100 \text{ k}\Omega/\text{square}$). A wide potential window of 3.1 V from -1.2 to 1.9 V vs. Ag/AgCl in 0.1 M H_2SO_4 solution with a low background current for the hybrid diamond/graphite film prepared with 8% methane is comparable to that of the B-doped diamond electrode, which is much wider than the exfoliated graphite electrode ($\sim 2.2 \text{ V}$) [30]. It is noted that the potential window range of the 8% sample in our work ($\sim 3.1 \text{ V}$) is wider than that fabricated in the presence

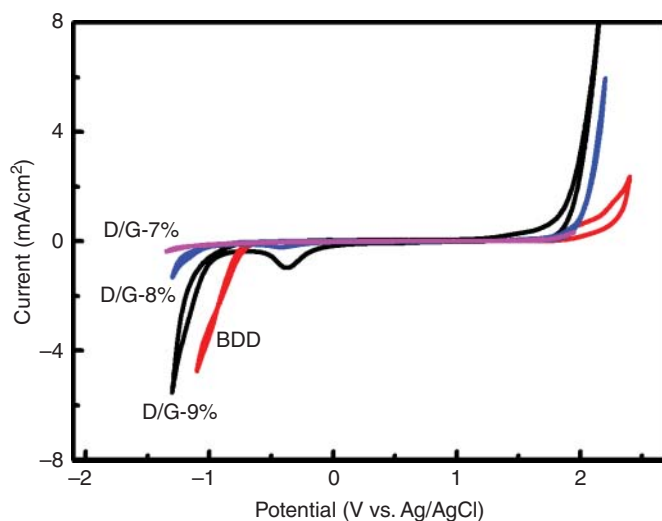


Figure 7.7 Potential windows of the D/G films grown under various methane concentrations (7%, 8%, and 9%) and B-doped diamond film (BDD) at a scan rate of 50 mV s^{-1} [48]. Source: Reprinted with permission from Elsevier, Copyright 2016.

of N_2 (~ 1.3 V) [3], due to the low quality of the diamond phase when a high nitrogen concentration (70% N_2 in reacting gas) is involved during the deposition process. The hybrid diamond/graphite film with 9% methane shows a narrower potential window range (from -0.8 to 1.7 V) and a higher background current ($\sim 60 \mu A cm^{-2}$), which is attributed to the decrease in diamond quality in the film, as demonstrated by the cathodic peak presented at around -0.5 V [31]. It was reported that the appropriate thickness of the graphite shell was responsible for the electrochemical reaction for the D/G nanostructures [32]. Hence, the D/G 8% film might be a suitable candidate for an electrode material.

Figure 7.8 shows the cyclic voltammograms of the D/G electrode prepared with 8% methane level in $[Fe(CN)_6]^{3-/4-}$ and ferrocene solutions to study the electrochemical reactivity at a scan rate varying from 10 to $200 mV s^{-1}$. The anodic peak potential (E_{pa}) was at 0.249 V (vs. Ag/AgCl), while the cathodic peak potential (E_{pc}) was at 0.176 (vs. Ag/AgCl). The anodic peak potential to cathodic peak potential separation (ΔE_p) for the diamond/graphite electrode at a scan rate of $10 mV s^{-1}$ is about $73 mV$ for $[Fe(CN)_6]^{3-/4-}$. The ΔE_p values increase with increasing potential scan rates, which indicates that the electrode process of the diamond/graphite electrode is a

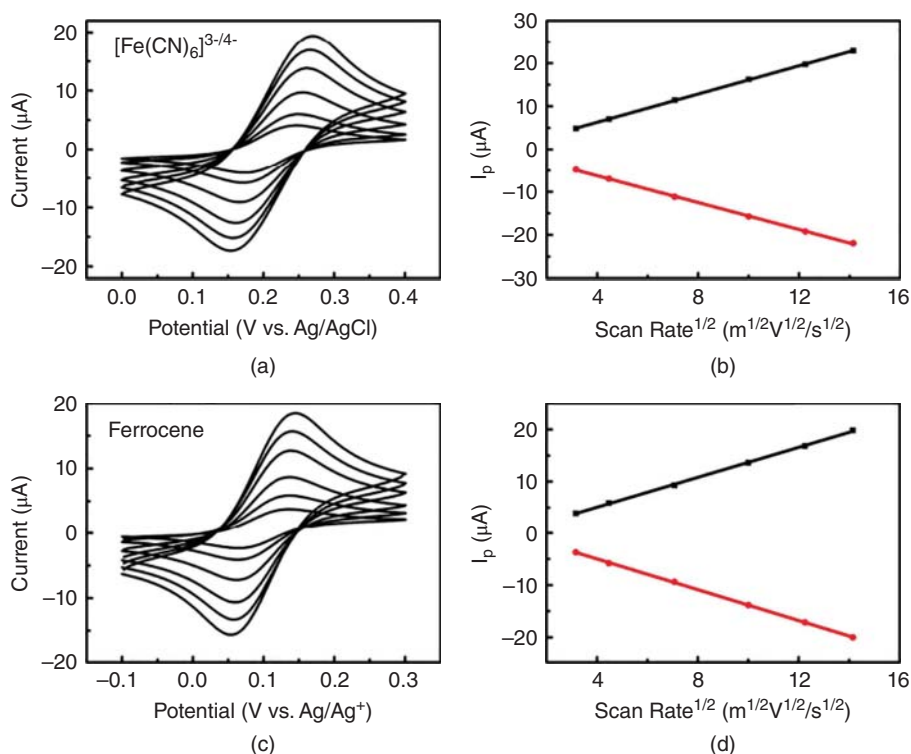


Figure 7.8 Cyclic voltammograms of a D/G electrode in $0.1 M$ KCl solution containing $1 mM$ $[Fe(CN)_6]^{3-/4-}$ (a), and $0.1 M$ TBABF₄ in CH_3CN solution containing $1 mM$ ferrocene (c), at different scan rates ($10, 20, 50, 100, 150$, and $200 mV s^{-1}$). Corresponding anodic and cathodic peak currents as a function of scan rates are shown in (b) and (d) [48]. Source: Reprinted with permission from Elsevier, Copyright 2016.

quasi-reversible reaction. Significantly, the ΔE_p value (73 mV in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couples) for the updoped diamond/graphite electrode herein is on a par with that of a high-quality B-doped diamond electrode. The ΔE_p is about 71 mV for ferrocene at a scan rate of 10 mV s^{-1} on the D/G electrode. The anodic to cathodic peak current ratio (I_{p_a}/I_{p_c}) is approximately 1.0 for both $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and ferrocene, indicating that the reduction and oxidation of the chemicals on the electrode happen at a similar electron transfer rate. The electrochemical response of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and ferrocene on the surface of the D/G electrode exhibits a linear relationship between the anodic or cathodic peak current and the square root of the scan rate with $r^2 \geq 0.999$ in both solutions, as shown in Figure 7.8b,d. Such a dependence on the scan rate indicates a typical mass-controlled process during electrochemical reactions. Therefore, the D/G nanostructured film shows a great potential as an electrochemical electrode with a wide potential window and quasi-reversible reaction, for applications such as electroanalysis and electrochemical sensors.

7.4.3 Hybrid D/G Film Electrode for the Detection of Trace Heavy Metal Ions

The electrochemical determination of heavy metal ions was performed using an Auto-lab workstation (PGSTAT302N) with a standard three-electrode system consisting of Ag/AgCl (3 M KCl) as a reference electrode, platinum wire as a counter electrode, and the 8%-D/G nanostructured film as the working electrode (geometric area = 0.053 cm^2). Copper and silver standard solutions were prepared from $\text{Cu}(\text{NO}_3)_2$ (99.999%) and AgNO_3 (99.999%) analytical-reagent grade salts supplied by Sigma-Aldrich and used without further purification. Solutions were freshly prepared using Milli-Q (Millipore Direct-Q 8 system) water with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$. The ion concentrations in copper and silver standard solutions are 10, 25, 50, 100, 200, 500, 800, and 1000 ppb. All experiments were carried out at room temperature.

Differential pulse anodic stripping voltammetry (DPASV) receives considerable attention as a rapid and effective technique compared with atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) or inductively coupled plasma mass spectrometry (ICPMS) [33, 34] for the detection of heavy metals at trace levels. In the DPASV approach, poisonous hanging mercury drop electrodes are normally used for the determination of trace heavy metal ions [35]. Therefore, a mercury-free DPASV technique has been developed, involving the use of carbon [36], gold [37], silver [38] and bismuth [39] films as promising electrodes. Due to the wide electrochemical potential window (wide cathodic and anodic potential limits), low background current, and high resistance to corrosion in extreme conditions compared with other electrodes, the environmental-friendly and feasible hybrid diamond/graphite film is a good alternative candidate for the Hg-based electrodes in ASV analysis of trace heavy metal ions.

Firstly, Ag and Cu metals were electrochemically deposited on the D/G electrodes in an acetate buffer solution containing 10, 25, 50, 100, 200, 500, 800, and 1000 ppb Ag^+ and Cu^{2+} solutions, respectively. Negative potential (-0.1 V for Ag^+ and -0.4 V for Cu^{2+}) was applied to the working electrode for three minutes to accumulate the corresponding metals on the surface of diamond/graphite films. Then differential pulse voltammetry was employed to strip the metal deposited on the working electrode back into the analyte solutions. Pulse amplitude and pulse width applied here were 50 mV and 50 ms, respectively. Finally, the working electrode was cleaned at an anodic

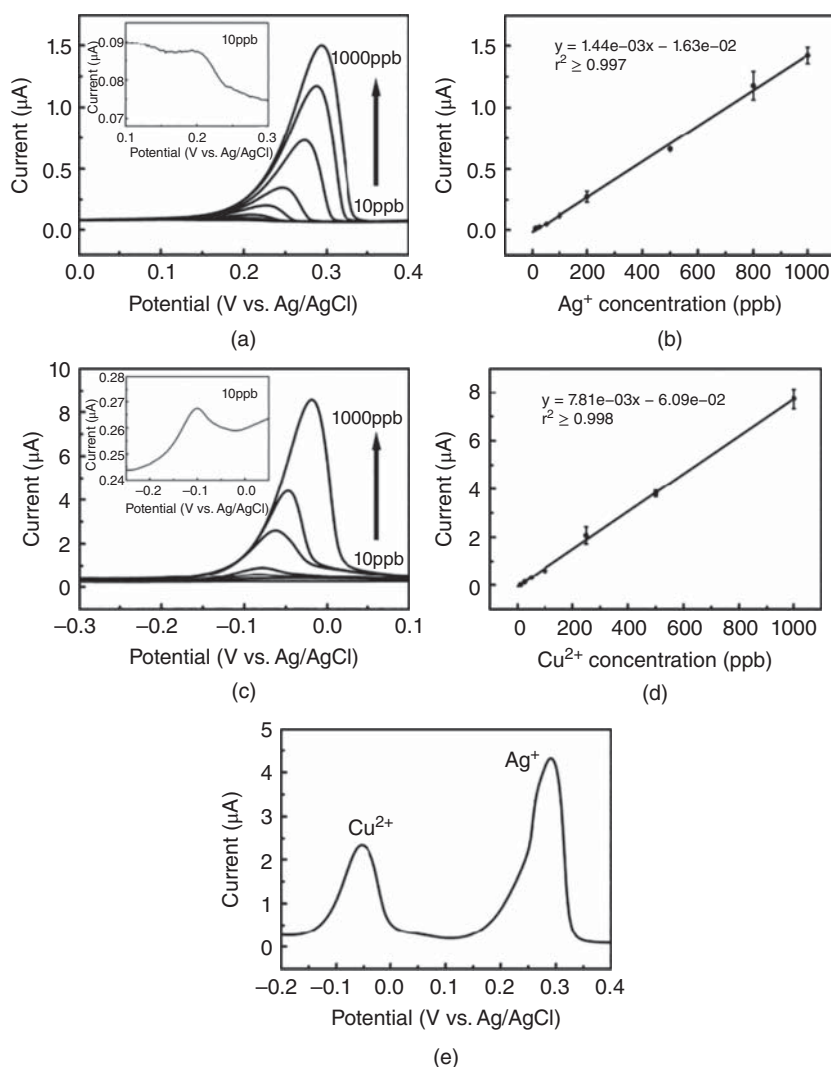


Figure 7.9 Anodic stripping voltammograms of silver (a) and copper (c) in heavy metal ion detection. Calibration plots for Ag^+ and Cu^{2+} are shown in (b) and (d). The error bars correspond to the standard deviation obtained from five measurements ($n = 5$). (e) The simultaneous determination of silver and copper ions in aqueous solutions. The scan rate is 20 mV s^{-1} [48]. Source: Reprinted with permission from Elsevier, Copyright 2016.

potential of 0.4 V for 3 minutes to remove the deposited species for further repeated use. Figure 7.9a,c shows the DPASV analytical characteristics for Ag^+ and Cu^{2+} determination on the D/G electrodes. The detection limit of Ag^+ is calculated to be 5.8 ppb, which cannot be detected by other electrodes due to the low anodic potential limits. The detection limit for Cu^{2+} is calculated to be 5.6 ppb, which is lower than that on the planar B-doped diamond (10 ppb) [40]. The corresponding calibration plots for Ag^+ and Cu^{2+} recorded at the optimum deposition potential and time are shown in

Table 7.1 Analytical performance of the hybrid D/G electrodes in the detection of Ag⁺ and Cu²⁺ [48].

Electrodes	Metal ions	Linear range (ppb)	Sensitivity (nA/ppb)	Correlation coefficient	Detection limit (ppb)	References
D/G	Ag ⁺	10–1000	1.44	0.997	5.8	This work
BDD	Ag ⁺	1–1000	9.12	—	1.0	[40]
D/G	Cu ²⁺	10–1000	7.81	0.998	5.6	This work
Hg-GC	Cu ²⁺	50–1000	31.4	—	50	[40]
Hg	Cu ²⁺	—	—	—	12	[49]
BDD	Cu ²⁺	10–1000	7.14	—	10	[40]
BDD	Cu ²⁺	7.7–100	40	0.998	—	[50]

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Figure 7.9b,d. The anodic peak currents show an excellent linear relationship ($r^2 \geq 0.997$ for Ag⁺ and $r^2 \geq 0.998$ for Cu²⁺) with the ion concentration over a wide range from 10 to 1000 ppb. The background currents of the diamond/graphite electrode in Ag⁺ and Cu²⁺ detection are ~ 1.5 and $\sim 4.7 \mu\text{A cm}^{-2}$, respectively, which are comparable with B-doped diamond electrodes [41]. The simultaneous determination of Ag⁺ and Cu²⁺ is also possible on the hybrid diamond/graphite electrode as shown in Figure 7.9e, showing a potential rapid measurement ability in the simultaneous detection of multi-metal trace ions. The trace Ag⁺ and Cu²⁺ detection performance of the hybrid diamond/graphite nanostructure electrode was compared with Hg, Hg-decorated glassy carbon (GC) and BDD electrodes, as shown in Table 7.1. One finds that the environmental-friendly D/G electrode shows obvious advantages over the traditional electrodes in aspect of detection limits and linear range. Thus, we have developed a novel biocompatible electrode with good sensitivity, selectivity, repeatability and reproducibility for anodic stripping voltammetric determination of trace silver and copper ions.

7.4.4 Hybrid D/G Film Electrochemical Biosensor for DNA Detection

A novel conductive diamond and graphite hybridized configuration was investigated as a DNA electrochemical sensor electrode in this work. By introducing amino groups (covalent biolinkers), we explore the possibility of using hybrid diamond/graphite films in biological applications as shown in Figure 7.10. The D/G based DNA biosensor was fabricated using electrochemical techniques. DNA used for detection was bought from TaKaRa Company, and the probe sequences are as follows: 5'-HS-C₆H₁₂-T₆-GCTTATCGAGCTTTCG-3'; complementary sequences: 5'-Cy5-CGAAAGCTCGATAAGC-3'; one-base mismatched sequences: 5'-Cy5-CGAATGCTCGATAAGC-3'; four-base mismatched (non-complementary) sequences: 5'-Cy5-CGAATTGCTCCTTAAGC-3'. To introduce biolinkers-amino groups covalently, diamond/graphite films were firstly modified via electrochemical grafting and reduction. Cyclic voltammograms of electrochemical grafting of 4-nitrophenyl (C₆H₅-NO₂) groups onto the film are shown in Figure 7.10a. The grafting of the film surface was performed in dehydrated acetonitrile containing 5.0 mM 4-nitrobenzene diazonium salts and 0.1 M TBABF₄ as supporting electrolyte. The first cycle (the thicker line) shows an irreversible reduction peak centered about -0.17 V (vs Ag/Ag⁺), which

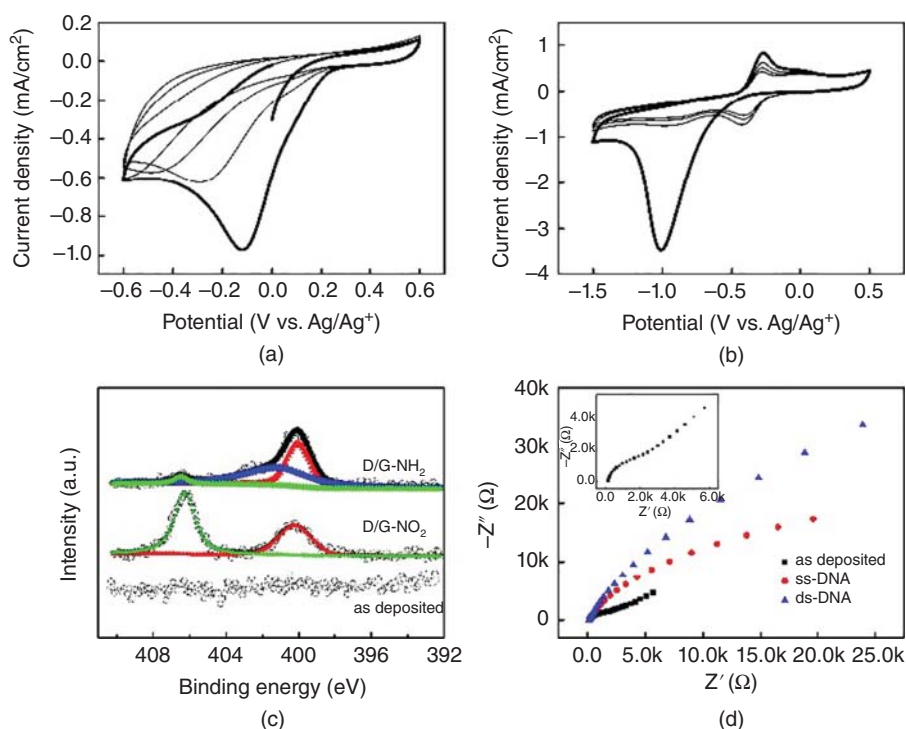


Figure 7.10 (a) Cyclic voltammograms of electrochemical grafting of nitrophenyl layers onto the surface of diamond/graphite film in 0.1 M TBABF₄ solution containing 5 mM 4-nitrobenzene diazonium salts, at a scan rate of 200 mVs⁻¹ and scanning range from 0.6 to -0.6 V (vs Ag/Ag⁺). (b) Cyclic voltammograms of the reduction of nitrophenyl film on diamond/graphite electrode in a solution (H₂O:EtOH = 9:1) containing 0.1 M KCl, at a scan rate of 100 mV s⁻¹. (c) XPS of the as-deposited, nitrophenyl modified (D/G-NO₂) and reduced (D/G-NH₂) films, respectively. (d) Electrochemical impedance of as-deposited, ss-DNA and ds-DNA functionalized diamond/graphite film in PBS solution (pH = 7.4) containing 1 mM Fe(CN)₆^{3-/4-}.

is close to the value for the grafting of C₆H₅-NO₂ groups onto hydrogen-terminated, boron-doped, single-crystalline diamond [42]. This is due to the reduction of diazonium salts, which generates active aryl radicals covalently bonded to the surface [43]. It was noticed that the peak current significantly decreases during the second scan and shifts to more negative potentials in subsequent cycles (the thinner lines). Such a phenomenon can be attributed to the formation of insulating C₆H₅-NO₂ layers on the film during the grafting process [41], which in turn block further electron transfer. Nevertheless, the cathodic peak is still observable even after four cycles. This behavior is different from that on the pure diamond surface. On single-crystalline diamond, this peak quickly disappears after only one cycle, while it decrease to zero on the ultra-nanocrystalline diamond electrode. So it indicates the formation of C₆H₅-NO₂ layers on the diamond surface is much faster than that on the D/G nanostructures. The reason might be that a greater proportion of radicals produced by reduction of the diazonium salts diffuses and reacts in the solution rather than attaches to the hybrid surface.

The diamond/graphite hybrid films modified with 4-nitrophenyl were then reduced in 0.1 M KCl in C₂H₅OH-H₂O (V/V = 1:9) solvent. During the first scan (Figure 7.10b),

an irreversible reduction peak appears at -1.01 V (vs Ag/AgCl). This cathodic wave is caused by an overall $6e^-$ two-step electrochemical reduction of 4-nitrophenyl to aminophenyl ($C_6H_5-NH_2$). During the process, hydroxyaminophenyl (C_6H_5-NHOH) is formed as an intermediate product [44]. In subsequent cycles, this reduction peak drastically diminishes, indicating that most of the $C_6H_5-NO_2$ groups are reduced in the first scan. During the anodic scan, reversible redox peaks appear at $E_{1/2} = -0.35$ V (vs Ag/AgCl), which results from the hydroxyaminophenyl/nitrosophenyl interconversion [45]. As a result, the reduction process of $C_6H_5-NO_2$ to $C_6H_5-NH_2$ during the cathodic scan is incomplete.

The above process can be further confirmed by x-ray photoelectron spectroscopy (XPS) measurements depicted in Figure 7.10c. On the bare surface of the diamond/graphite hybrid electrode, no N(1s) peak is observable. However, two peaks appear after grafting. The peak positioning at 406 eV corresponds to the $-NO_2$ group, which indicates the successful modification of the diazonium salts, while the peak locating at 400 eV is due to the reduction of the nitro group into amino group. After the reduction of $-NO_2$ groups, the peak at 406 eV decreases while the peak at 400 eV increases, implying that a significant amount of $-NO_2$ groups has been reduced to $-NH_2$ groups [46]. Nevertheless, the existence of the N1s (406 eV) peak indicates that the conversion is incomplete, which agrees with the cyclic voltammetry results shown in Figure 7.10b.

After the attachment of amino groups, probe DNA (ss-DNA) was further linked to the functionalized D/G nanostructures and hybridized with $5\text{ }\mu\text{M}$ complementary DNA to form double-stranded DNA (ds-DNA). As shown in Figure 7.10d, the biosensor based on functionalized D/G nanostructures was then measured by electrochemical impedance in PBS (pH = 7.4) solution containing $1\text{ mM Fe(CN)}_6^{3-/4-}$. The charge transfer resistance (R_{CT}) of as-deposited D/G nanostructures is $4.03\text{ k}\Omega$, while it significantly increases after immobilizing ss-probe DNA ($48.13\text{ k}\Omega$). This is due to the blocking effect of insulating organic films and the presence of ss-DNA. The R_{CT} of ds-DNA is even higher ($116.61\text{ k}\Omega$), caused by the increased rigidity of ds-DNA molecules [44]. Therefore, the performance of the biosensor can be improved through utilization of such novel hybrid D/G nanostructures.

7.5 Conclusions

Hybrid sp^3 -diamond/ sp^2 -graphite nanostructured film was successfully prepared in methane and hydrogen plasmas by microwave plasma enhanced chemical vapor deposition technique in this review. The sp^3 diamond nanostructures have a diameter of 6.5 nm encapsulated by a sheath of sp^2 graphite phase. The high concentration of methane produced C_2 species in the reactive process, instead of CH_3 or CH radicals, and C_2 species are responsible for the growth of D/G nanostructured film. The novel D/G nanostructured film deposited at 8% methane level not only shows good mechanical properties with a low friction coefficient of 0.1 and high wear resistance of $1.9 \times 10^{-7}\text{ mm}^3\text{ (Nm)}^{-1}$, but also displays a great potential as an electrochemical electrode with a wide potential window of 3.1 V and a typical quasi-reversible mass-controlled process in $[Fe(CN)_6]^{3-/4-}$ and ferrocene solutions contributed by the conductive sp^2 -carbon channel. Thus, a novel biocompatible electrode based on the D/G electrode has been developed for anodic stripping voltammetric determination of trace silver (5.8 ppb) and copper (5.6 ppb) ions with good sensitivity and selectivity.

Besides, the good performance in determination of DNA sequence has been verified using such novel hybrid D/G electrochemical DNA biosensor. Therefore, continued investigations into such innovative hybrid sp^3 -C and sp^2 -C architectures, owing to their extraordinary mechanical and good electrochemical properties, will achieve many of the desired applications.

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8

Carbon Nanodot Composites: Fabrication, Properties, and Environmental and Energy Applications

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8.1 Introduction

Carbon dots (C-dots) were first obtained during the purification of single-walled carbon nanotubes (CNTs) through preparative electrophoresis in 2004. Since then, wide attention has been focused on this kind of sp^2 hybrid carbon particle because of their good solubility and strong luminescence, for which they are referred to as carbon nanolights. During the past ten years, much progress has been achieved in the synthesis, structure and property studies, and applications of C-dots. The family of C-dots encompasses several types of carbon-based fluorescent nanoparticles (NPs). The group defined as C-dots is quite general and can be further divided into different subgroups, namely, very tiny carbon nanoparticles, graphene quantum dots, graphitic carbon quantum dots, amorphous carbon dots, and polymer dots. In general, we can define C-dots as spherical-like carbon-based objects (and/or graphite fragments) with dimensions below 10 nm. C-dots, with their fascinating properties, have gradually become a rising star due to their benign, abundant, and inexpensive nature. Compared with traditional semiconductor quantum dots and organic dyes, photoluminescent C-dots are superior in terms of high (aqueous) solubility, robust chemical inertness, simple modification and high resistance to photobleaching. The superior biological properties, such as low toxicity and good biocompatibility, give C-dots potential applications in bioimaging, biosensors, and biomolecule (drug) delivery. The outstanding electrochemical properties of C-dots as electron donors and acceptors, causing chemiluminescence and electrochemical luminescence, endow them with wide potentials in optoelectronics, catalysis and sensors. The rich photoluminescence (PL) and photochemical properties of C-dots also make them efficient catalysts (such as photocatalysts for selective oxidation, light-driven acid-catalysis and hydrogen-bond catalysis) and very active additives commonly used in energy devices (solar cells (SCs), photo-electronic water-splitting cells, batteries and supercapacitors) for improving performance. Another important property is the tailorable surface chemistry of C-dots that facilitates their functionalization and integration with other functional materials. Recently, some reviews have introduced the properties of C-dots and focus on their recent applications in biosensing, bioimaging, optoelectronic devices and sensors.

Novel Carbon Materials and Composites: Synthesis, Properties and Applications, First Edition.

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Here, we will give some in-depth discussion and understanding of the properties of C-dots, and discuss recent progress in their applications in nanocatalysis, sensing, environmental and new energy fields. We hope this review will provide some critical insights to inspire more exciting work on C-dots for environmental and energy applications in the near future.

8.2 Synthesis, Structure, and Properties

8.2.1 Synthesis of C-dots

Here we simply summarize the typical C-dots developed in the last decade, and more technological details about them can be found in recent reviews [1–7]. The preparation methods for C-dots can be roughly classified into “top-down” and “bottom-up” approaches. The top-down routes are implemented via either physical or chemical techniques, with the latter being more popular. Typically, the top-down methods include electron beam lithography, laser ablation, acidic exfoliation, electrochemical oxidation, microwave-assisted hydrothermal synthesis, and so on. The top-down routes for the preparation of C-dots have the advantages of abundant raw materials, large-scale production and simple operation. A simple electrochemical approach was recently reported by the Kang group for the large-scale synthesis of high-quality C-dots with high purity, using only pure water as an electrolyte without any other chemical additives (see Figure 8.1) [2]. The obtained C-dots feature a highly crystalline nature and excellent aqueous dispersibility. C-dots can also be prepared through bottom-up routes, including solution chemistry, cyclodehydrogenation of polyphenylene precursors, carbonization of some special organic precursors, or the fragmentation of suitable precursors. The bottom-up methods offer the exciting opportunities to control C-dots with well-defined molecular size, shape, and thus properties. Nevertheless, these methods always involve complex synthetic procedures, and the special organic precursors may be difficult to obtain. In any case, C-dot preparation has three notable problems: (i) carbonaceous aggregation during carbonization, which can be avoided by using electrochemical synthesis, confined pyrolysis, or solution chemistry methods; (ii) size control and uniformity, which is important for uniform properties and mechanistic study, but can be optimized via post-treatment, such as gel electrophoresis, centrifugation, and dialysis; and (iii) surface properties that are critical for solubility and selected applications, which can be tuned during preparation or post-treatment. For applications, it is important to control the sizes of C-dots to get uniform properties. Many approaches have been proposed to obtain uniform C-dots during preparation or post-treatment. In most of the reports, the as-synthesized C-dot fragments were purified via post-treatments like filtration, dialysis, centrifugation, column chromatography and gel-electrophoresis. Surface modification is a powerful method to tune the surface properties of materials for selected applications. There are various approaches for functionalizing the surface of C-dots through the surface chemistry or interactions, such as covalent bonding, coordination, π - π interactions, and so on. Doping is a widely used approach to tune the PL and related optical properties of C-dots [1–7]. Last, but most important, methods for large-scale preparation of C-dots are highly desirable for practical applications. Recently, the gram-scale synthesis of single-crystalline

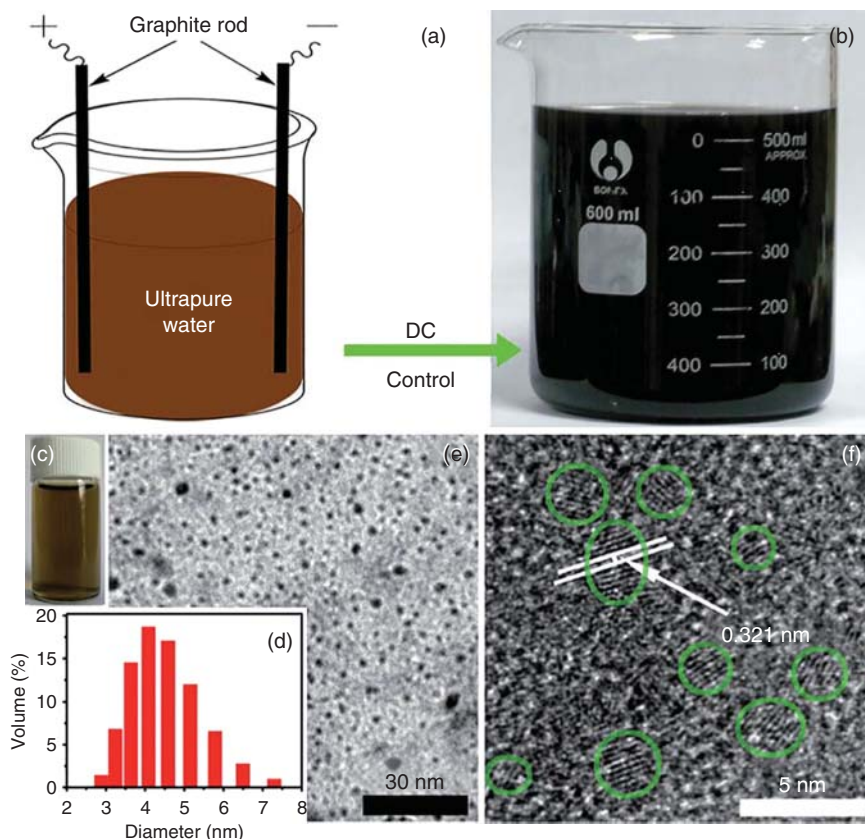


Figure 8.1 (a) Reaction equipment for the preparation of C-dots; digital image of C-dots solution, (b) before treatment, (c) after treatment; (d) dynamic light scattering (DLS) histogram of C-dots; (e) TEM and (f) HRTEM images of C-dots [2]. Source: Reprinted with permission from RSC publishers, Copyright 2012.

C-dots was demonstrated by a simple molecular fusion route under mild and green hydrothermal conditions. Alternatively, C-dots can be fabricated in large scale from various types of coals, based on the one-step wet-chemical route [8, 9].

8.2.2 Composition and Structure

In general, the average size of C-dots is mostly below 10 nm and dependent on the preparation methods. C-dots reported so far are always partially oxidized and therefore bear hydroxyl, epoxy/ether, carbonyl and carboxylic acid groups on the surfaces. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) methods are commonly adopted to analyze their composition. The crystalline nature of C-dots can be investigated through X-ray diffraction (XRD), Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM). Both (002) interlayer spacing and (100) in-plane lattice spacing exist in C-dots, and the former has been widely studied. The interlayer spacing of C-dots depends strongly on their degree of oxidation, because the anchored hydroxyl, epoxy/ether, carbonyl and carboxylic acid

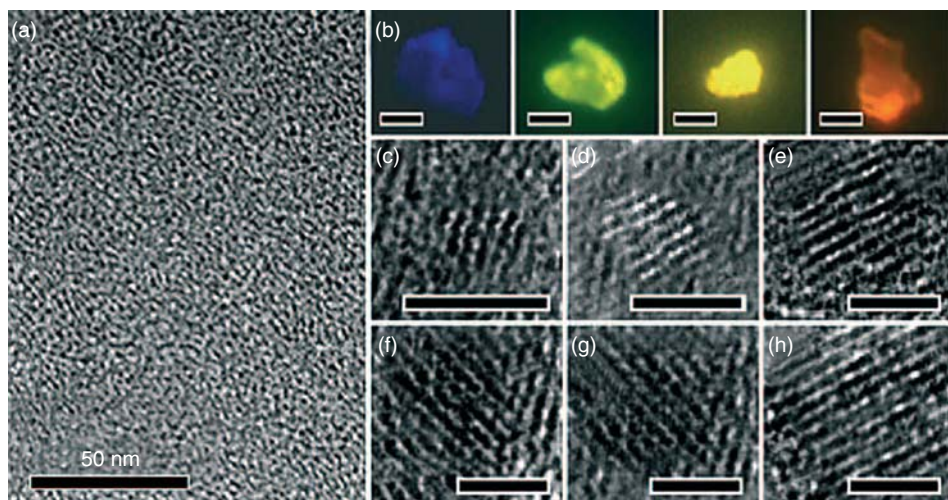


Figure 8.2 (a) TEM image of C-dots with diameters under 4 nm; (b) fluorescent microscopy images of C-dots with an excitation wavelength of 360 nm (scale bar: 50 nm); (c–h) HRTEM images of typical C-dots with different diameters (scale bar is 2 nm) [7]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2010.

groups can increase the interlayer spacing. Raman spectroscopy is a powerful and non-destructive tool for the characterization of C-dots. The G band in the Raman spectrum is assigned to the E_{2g} vibrational modes of the aromatic domains, whereas the D band arises from the breathing modes of the graphitic domains. The intensity ratio (I_D/I_G) of the “disordered” D to crystalline G band is used to compare the structural order between crystalline and amorphous graphitic systems. The I_D/I_G values of C-dots vary significantly depending on the preparation methods. The HRTEM images of C-dots feature two kinds of lattice fringes, namely (002) interlayer spacing (see Figure 8.2) and (110) in-plane lattice spacing. Similar to the XRD pattern, the former centered at 0.34 nm is observed for C-dots prepared by acidic oxidation from carbon black, microwave-assisted method, and electrochemical cutting method. The in-plane lattice spacing centered at 0.24 nm is observed for C-dots synthesized via a microwave-hydrothermal protocol, amino-hydrothermal method, K intercalation, acidic oxidation from carbon fibers, and photo-Fenton reaction, while the 0.21 nm spacing is observed from C-dots via hydrothermal cutting strategy and glucose carbonization method. Moreover, C-dots are not always crystalline; amorphous C-dots have also been prepared via hydrothermal methods and citric acid carbonization [1–7].

8.2.3 Properties

8.2.3.1 Absorption

C-dots typically show strong optical absorption in the UV region, with a tail extending out into the visible range. There may be some absorption shoulders attributed to the π – π^* transition of the C=C bonds, the n – π^* transition of C=O bonds, and/or others. Moreover, C-dots prepared via different methods also show different absorption behaviors and absorption peak positions. Furthermore, the variation of oxygen content

was reported to play an important role in deciding the absorption peak position of C-dots [1–7].

8.2.3.2 Photoluminescence

C-dots prepared via different approaches can emit PL with different colors, including UV, blue, green, yellow, red, and the near-infrared (NIR) region. Typically, the luminescence mechanism may derive from intrinsic state emission and defect state emission. However, the exact mechanism of PL for C-dots remains unsettled. The luminescence has been tentatively suggested to arise from excitons of carbon, emissive traps, quantum confinement effects, aromatic structures, oxygen-containing groups, free zigzag sites, and edge defects. A widely accepted mechanism for luminescence emission from C-dots needs more systematic investigation. In any case, the PL of C-dots should be attributed to either a combining effect or competition between intrinsic state emission and defect state emission. C-dots prepared via various methods probably exhibit distinct PL mechanisms, which lead to different dependences of their PL on size, excitation wavelength, pH, solvent, concentration, and so on. The quantum yield (QY) of C-dots varies with the fabrication method and the surface chemistry involved. As for the unpassivated C-dots prepared via stepwise solution chemistry and microwave-assisted acidic oxidation, respectively, QYs ranging between 2% and 30% are observed. The C-dots commonly contain carboxylic and epoxide groups, which can act as the non-radiative electron–hole recombination centers. Therefore, the removal of these oxygen-containing groups may improve the QY, either by reduction or surface passivation. Recently, a significantly enhanced QY of ~72% is the highest value for C-dots (see Figure 8.3) in solution reported so far [10].

8.2.3.3 Photoinduced Electron Transfer Property

The PL emission from a C-dots solution could be efficiently quenched in the presence of either electron acceptors such as 4-nitrotoluene and 2,4-dinitrotoluene or electron donors such as N,N-diethylaniline. Namely, the photoexcited C-dots are excellent as both electron donors and electron acceptors. The PL of C-dots can also be quenched efficiently by surface-doped metals through disrupting the excited state redox processes. Significant PL quenching was also observed in the C-dots–GO system, which was attributed to the ultrafast electron transfer (ET) from C-dots to GO. These photoinduced electron transfer properties of C-dots as an electron donor/acceptor may offer new opportunities for light energy conversion, catalysis and related applications, as well as mechanistic elucidation [1–7].

8.2.3.4 Electrochemiluminescence

Zheng and coworkers reported a simple and effective method for preparing water-soluble C-dots with electrochemiluminescence (ECL) activity by applying a scanning potential to graphite rods, and presented observations on the ECL behavior during and after the preparation of C-dots (see Figure 8.4) [11]. The ECL emission (maximum emission at 535 nm) of C-dots was observed when the potential was cycled between +1.8 and –1.5 V. The ECL mechanism of C-dots was suggested to involve the formation of excited-state C-dots (R^*) via electron-transfer (ET) annihilation of negatively charged (R^-) and positively charged (R^+) C-dots [12]. Zheng and coworkers also reported another ECL system consisting of C-dots and sulfite SO_3^{2-} , in which

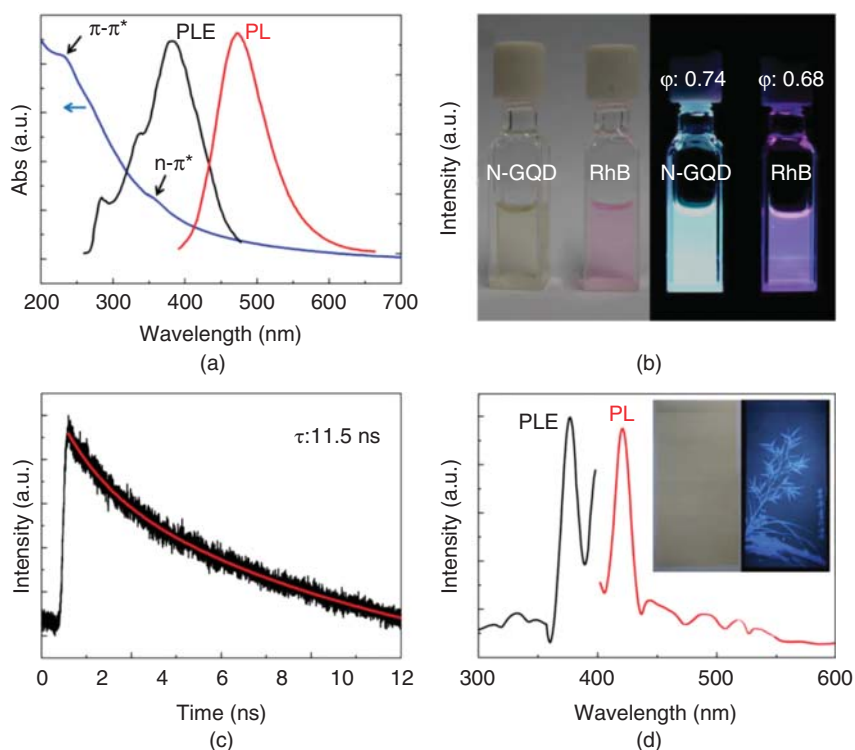


Figure 8.3 (a) UV-vis absorption, PL ($\lambda_{\text{ex}} = 400 \text{ nm}$) and PLE ($\lambda_{\text{ex}} = 500 \text{ nm}$) spectra of C-dot aqueous solution. (b) Photographs of C-dot aqueous solution and RhB ethanol solution with the same mass concentration ($10 \mu\text{g ml}^{-1}$) under visible light (left) and 365 nm UV light (right). (c) PL decay curves of C-dots measured at room temperature and excitations at 400 nm. (d) PL and PLE spectra of C-dots in solid state; inset: photo of bamboo drawing with C-dot ink under visible light (left) and 365 nm UV light (right). In this figure, the N-GQDs are the C-dots [10]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2015.

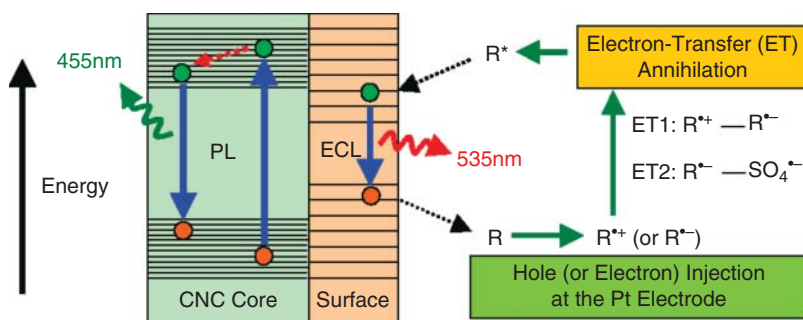


Figure 8.4 Schematic illustration of the ECL and PL mechanisms in C-dots (in this figure, CNCs are the C-dots). R^{*+} , R^{-} , and R^{*} represent negatively charged, positively charged, and excited-state C-dots, respectively [11]. Source: Reprinted with permission from American Chemical Society, Copyright 2009.

SO_3^{2-} as a new ECL coreactant can significantly enhance the cathodic ECL signal of C-dots [11].

8.2.3.5 Proton adsorption

The surface functional groups of C-dots, such as $-\text{OH}$, $-\text{COOH}$, and $-\text{C}=\text{O}$, help to draw H^+ closer to C-dots, which favors enhancing the adsorption capacity. On account of the excellent water solubility of C-dots, the adsorption experiments were conducted using a dialysis method [13]. The amount of adsorbed H^+ (based on HCl) was about $10\text{--}24\text{ mg g}^{-1}$ for C-dots. The equilibrium of sorption was further evaluated by the two well-known models of Langmuir and Freundlich isotherms. The Langmuir isotherms for C-dots, with higher correlation coefficients than that of the Freundlich isotherm model, indicated that monolayer adsorption of H^+ takes place on the homogeneous surface of C-dots. Moreover, the adsorption is favorable and rather irreversible. Since calculated correlation coefficients are closer to unity for a pseudo-first-order kinetic model than a pseudo-second-order kinetic model, the present sorption systems follow predominantly the first-order rate model [13–16].

8.2.3.6 Toxicity

The toxicity of C-dots is a natural concern for potential bioapplications. C-dots are variously reported to have low toxicity [17]. Tao et al. demonstrated that C-dots could serve as fluorescent probes for in-vivo imaging in live mice by using a wide range of excitation wavelengths, with excellent signal-to-background separation under NIR excitation. They further studied the in-vivo biodistribution of C-dots by a radiolabeling method. After intravenous injection, the C-dots exhibit high accumulation in the reticuloendothelial system as well as in the kidney, and they are gradually excreted via both renal and fecal pathways. Importantly, it was observed that C-dots at a dose of 20 mg kg^{-1} appeared to be safe for the treated animals over a period of three months, as evidenced by the systematic time-course blood chemical analysis and complete blood panel and histological analyses (see Figure 8.5) [17]. However, Markovic et al. demonstrated that the defects and free radicals of C-dots could result in the generation of singlet oxygen. An in-vitro photodynamic cytotoxicity study showed that photoexcited C-dots could cause programmed cell death via apoptosis and autophagy. Fortunately, this feature could be exploited in photodynamic therapy [18, 19]. Wu et al. investigated the cytotoxicity of C-dots in detail, prepared through a photo-Fenton reaction of GO [20]. The cytotoxicity of C-dots was lower than that of GO sheets, which can be proven by the effects on cell viability, internal cellular reactive oxygen species levels, damage to mitochondrial membrane potential, and cell cycle. The toxicity of C-dots did not significantly increase with increasing concentration.

8.3 C-dot-based Functional Nanocomposites

8.3.1 C-dots in Mesoporous Structures

Several examples of C-dots in mesoporous silica particles have been reported for bioimaging or drug delivery [21]. Different strategies have also been developed for the fabrication of mesoporous silica particles with C-dots; they differ both by the

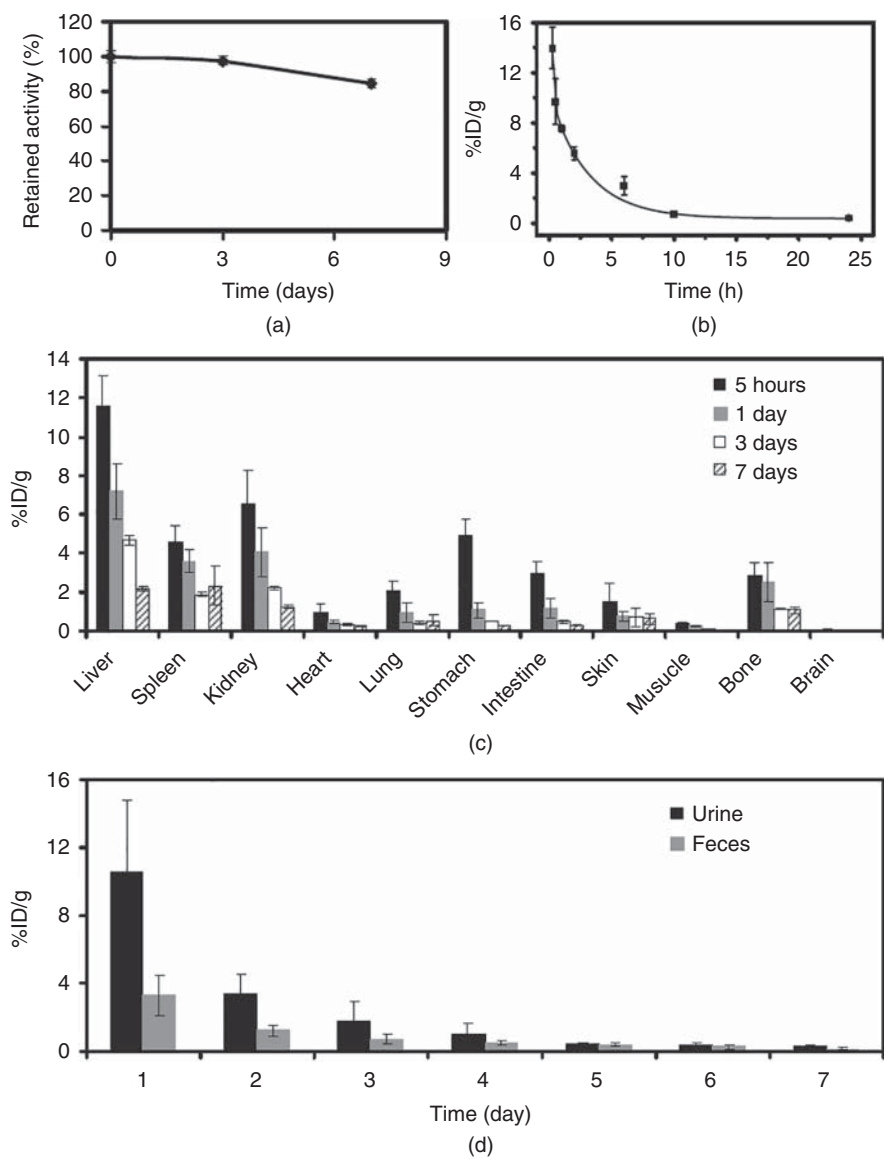


Figure 8.5 (a) The radiolabeling stability curve of C-dots in mouse plasma at 37°C. (b) The blood circulation curve of C-dots. (c) Time-dependent biodistribution of C-dots in female Balb/c mice. (d) Distribution of C-dots in urine and feces of Balb/c mice collected by metabolism cages. Error bars were based on standard deviations of four mice per group [17]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2012.

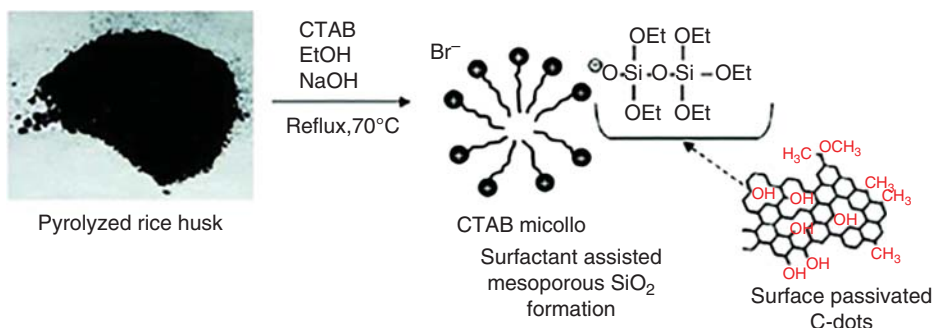


Figure 8.6 Schematic showing CTAB-assisted synthesis of meso-SiO₂ and attachment of C-dots to form the meso-SiO₂/C-dot complex [2]. Source: Reprinted with permission from RSC publishers, Copyright 2012.

matrix synthesis and the method for entrapping the carbon dots in the porous silica particle. Basically, two synthesis routes can be recognized; the first one is the so-called “one-pot” approach, which allows formation of the mesoporous silica matrix and incorporation of the C-dots in a single step. The second route, instead, allows addition of C-dots to pre-fabricated silica mesoporous particles. There is also a wide choice of methods for adding the C-dots; they can be capped on the particle surface, or embedded in the pores, or even onto the pore walls. The best strategy depends on the desired application; in theranostic applications, for instance, the mesoporous particles become an interactive platform with a multifunctional role, such as an environment sensitive gate [21]. A quite original one-pot method to preparing mesoporous silica nanoparticles containing C-dots is using rice husk as a precursor both for silica and the C-dots [2, 21] (see Figure 8.6). Rice husk is, in fact, rich in silica and carbon, and mixing a pyrolyzed powder with an ionic surfactant (cetyltrimethylammonium bromide, CTAB) gives a SiO₂-C-dots nanodispersion in water with strong fluorescence [22]. Similar systems for theranostic applications have been obtained by different routes such as forming the C-dots in the silica matrix by suitable precursors. One example of such precursors is given by carbohydrates such as glycerol, glycol, glucose and sucrose, which have been used to produce emissive C-dots [23]. A similar experiment has been reported in another study where MCM-41 silica particles have been loaded with C-dots and Doxorubicin; in this case, however, the C-dots played a more sophisticated role because they also served as caps to entrap the Doxorubicin molecules within the mesopores [24]. The versatility of a mesoporous material as a functional platform can be fully exploited by increasing the number of active species in the matrix. Previous examples have shown that combining the C-dots fluorescence with mesoporous silica particles allows the production of relatively simple and effective devices with combined properties, such as drug release and bioimaging. These properties can be enhanced by taking advantage, as previously underlined, of the open porosity. One main issue is increasing the fluorescence of C-dot-SiO₂ particles, which, however, can be achieved using the metal-enhanced fluorescence effect. Silica mesoporous particles containing both Ag and C-dots within the pores have been synthesized through a “one-pot” route, which produced a 3.4-fold enhancement of luminescence intensity [25]. In the above examples, the C-dots have been capped on silica mesoporous particles or embedded

into the pores. Alternatively, they can be anchored on the mesopore walls. This material has been prepared by reacting methoxysilyl-modified carbon dots (Si-C-dots) [26] with tetraethyl orthosilicate and organic template (CTAB) [27]. The mesopores have been used as hosts for analyte-sensitive molecules, while the C-dots in the silica backbone are the reference species. This allows construction of a pH ratiometric sensor. In fact, if the C-dots emission spectrum overlaps the excitation spectrum of the guest dye, fluorescent resonance energy transfer (FRET) occurs [28, 29]. A ratiometric sensor for the detection of Hg^{2+} ions has been realized using a Rhodamine 6G derivative as the Hg^{2+} sensitive dye. Zinc oxide mesoporous films containing C-dots have also been synthesized by a one-pot route using a fluorosurfactant as a templating agent [30]. The 3D PL maps show a complex trend that has been attributed to energy transfer involving dipole interactions and reabsorption between ZnO and C-dots, and the formation of surface defects in the inorganic oxide structure [30].

8.3.2 C-dots in Polymers

Luk et al. reported a simple, low-cost chemical oxidation polymerization process for preparing a polyaniline (PANI)–C-dots composite [31]. They have also demonstrated tunable PL and hysteresis behaviors for C-dots embedded in a PANI matrix. The controllable electrical and optical properties in the composite films are explained by the charge trapping sites located at the surface states induced by the functional groups. Mosconi et al. have proposed some convenient routes to produce hybrid-polymers (these polymers include polyamide, polyureaurethane, polyester, and polymethyl-methacrylate) with covalently enclosed or confined N-doped C-dots (see Figure 8.7) [32]. These hybrid materials can be easily prepared and processed to obtain macroscopic objects of different shapes, such as fibers, transparent sheets, and bulky forms, where the characteristic luminescent properties of the native N-doped C-dots are preserved. They also explore the potential use of these hybrid composites to achieve photochemical reactions such as those of photoreduction of silver ions to silver nanoparticles (under UV light), the selective photo-oxidation of benzyl alcohol to benzaldehyde (under visible light), and the photocatalytic generation of H_2 (under UV light). In this field, Xie and Liu et al. also report organic–inorganic hybrid functional C-dots gel glasses, in which the QY of C-dots were increased sharply (QY over 80%) [33].

8.3.3 C-dots as Building Blocks for Mesoporous Structures

As a result of their tiny size, highly crystalline nature (fragments of graphite) and functionalized surface, C-dots could be regarded as subunits for carbon materials, allowing the construction of mesoporous carbon (MC) without templates. Zhou et al. reported a template-free method of preparing MCs with a high specific surface area ($183.6 \text{ m}^2 \text{ g}^{-1}$) and uniform pore size distribution (5 nm) from C-dots via one-step calcination (see Figure 8.8) [34]. In comparison with previous techniques, there are two advantages of the C-dots annealing approach: (i) the synthesis procedure is fairly simple, requiring neither pre-synthesis of the templates nor additional filtration; (ii) the approach is mild, cheap and capable of large-scale production of MCs. Han et al. also developed a simple hydrolytic process for the preparation of C-dots/ SiO_2 nanocomposites with a pore size of about 5.8 nm [35]. These C-dots/ SiO_2 porous nanocomposites show high

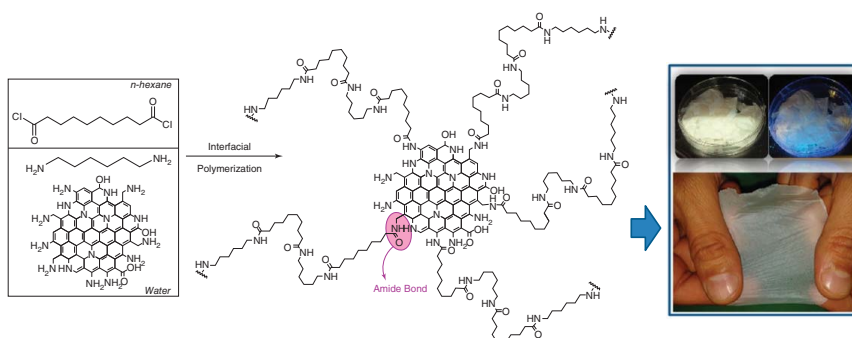


Figure 8.7 Top: Two-phase synthesis of nylon-6,6/N-doped C-dots hybrids and the related, macroscopic, electrospun material. Bottom: (a) SEM image of electrospun fibers from pristine nylon. (b–d) SEM images of electrospun fibers from nylon/N-doped C-dots hybrid materials obtained by use of increasing amounts of N-doped C-dots (5, 50, and 100 w/w%, respectively, referred to 1,6-hexamethylene-diamine). (e) TEM image of 100 w/w% (referred to 1,6-hexamethylene-diamine) nylon-6,6/N-doped C-dots electrospun fibers. In this figure, CQDs are C-dots [32]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

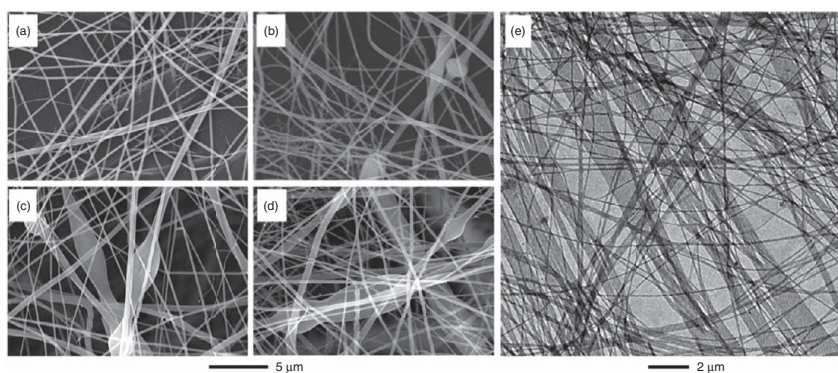


Figure 8.7 (Continued)

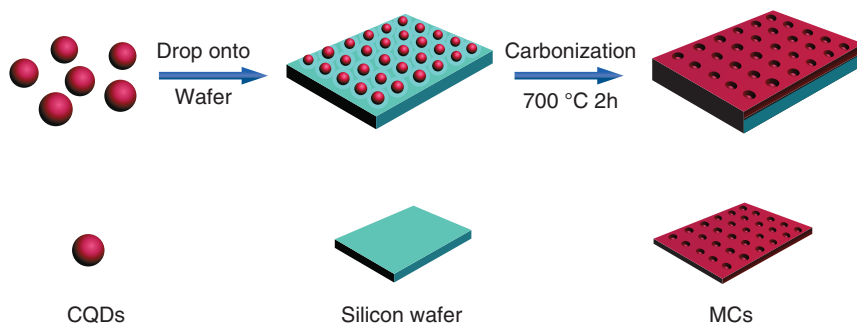


Figure 8.8 Schematic representation of the preparation process for MCs from C-dots. In this figure, CQDs are the C-dots [34]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

catalytic activity (31.73% conversion based on cis-cyclooctene and 89.13% selectivity for 2-hydroxycyclooctanone) for the selective oxidation of cis-cyclooctene under visible light irradiation, with tert-butyl hydroperoxide (TBHP) as a radical initiator and oxygen (in air) as an oxidant at 80°C. Yang et al. further reported the simple fabrication of porous Co/N/C by pyrolysis of VB₁₂ and C-dots [36]. It is noted that the doping concentrations of Co and N can be finely tuned from 0% to 3.68% and 0% to 5.88%, respectively. Particularly, Co/N/C containing 1.12% Co and 2.92% N prepared at 700°C exhibited the best electrocatalytic activity and selectivity for the oxygen reduction reaction (ORR) in both alkaline and acid media.

8.4 Catalysis Application

8.4.1 C-dots as Photocatalysts

Li et al reported that C-dots (1–4 nm) are effective NIR light-driven photocatalysts, which can catalyze the efficient oxidation of benzyl alcohol to benzaldehyde with high conversion rate (92%) and selectivity (100%) in the presence of H₂O₂ as oxidant (see Figure 8.9) [37]. The catalytic activity of C-dots is dependent on their photocatalytic activity for H₂O₂ decomposition and NIR light-induced electron transfer properties. Under the NIR light irradiation, the C-dots' photo-induced electron transfer ability (especially as strong electron donors) protects the first-step product (benzaldehyde) from overoxidation by the photoelectron reductive environment [38], thus yielding the high selectivity (100%) to benzaldehyde. The scope of reactivity of the aforementioned C-dots catalyst was further explored by Kang and coworkers (unpublished) using a variety of derivatives of benzyl alcohol under the same conditions of NIR light irradiation. Those derivatives could also produce oxidized aldehydes in high conversions and selectivities, with H₂O₂ as oxidant and NIR light irradiation.

C-dots (5–10 nm) have strong photo-induced proton-generating capacity in solution under visible light irradiation (see Figure 8.10) [39]. The catalytic activity of 5–10 nm C-dots is strongly dependent on illumination intensity and reaction temperature. As a light-driven acid-catalyst, C-dots can catalyze a series of organic reactions (esterification, Beckmann rearrangement and Aldol condensation) with high conversion efficiency in water solution under visible light irradiation. 5–10 nm C-dots were produced from a

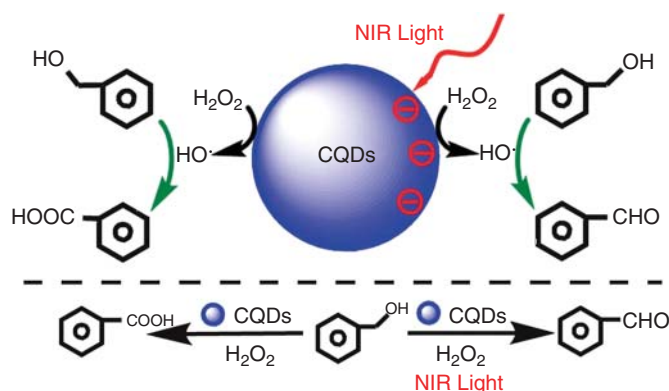


Figure 8.9 The proposed mechanism for highly selective oxidation of benzyl alcohol to benzaldehyde catalyzed by C-dots under NIR light irradiation. In this figure, CQDs are the C-dots [37]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

graphite rod by the electrochemical method in pure water. The reversible temperature- and concentration-dependent photo-proton generating ability can be attributed to the light-induced structure interconversion of the functional groups on the C-dots surface. The proton generation mechanism of C-dots under visible light irradiation is as follows. The hydroxyl group of C-dots dissolved in water releases a free proton (or H₃O⁺) under visible light irradiation. The intermediate produces another proton (hydrolyzed to H₃O⁺) from reaction of the C=O group with H₃O⁺. After the O in C=O links with HO⁻ by supramolecular interaction, the intermediate with the epoxy group is obtained under visible light irradiation. A series of reactions (esterification, Beckmann rearrangement, Aldol condensation) needing acid as a catalyst was performed by Li and coworkers to study the photo-induced proton-generating property of C-dots and reference samples (small-sized C-dots of 1–4 nm, graphite particles) [7]. The catalytic activities of C-dots in aqueous solution are attributed to the remarkable visible light-induced proton-generating capability associated with the oxygen-containing functional groups of C-dots.

C-dots are considered as good H-bonding catalysts because of their rich photochemical properties and functional carboxylic and hydroxyl groups [40]. As heterogeneous nanocatalysts for H-bond catalysis, C-dots showed good photo-enhanced catalytic abilities (89% yield when 4-cyanobenzaldehyde is used) in aldol condensation. A series of catalytic experiments confirmed that the catalytic activity of C-dots can be effectively enhanced by visible light, which may be attributed to their photo-induced electron-accepting properties. For the aldol condensation, 5 nm C-dots had the most satisfying photocatalytic performance for this H-bond catalysis reaction, which can be attributed to the highest electron-accepting ability when compared with other C-dots (with size >10 nm and <4 nm). Further, catalytic control experiments confirmed that the efficient electron-accepting properties of C-dots strengthened the O–H bond and activated the C=O bond of the 4-cyanobenzaldehyde, accelerating the aldol condensation.

Sahu and coworkers reported that functionalized C-dots with gold or platinum coatings can be used as photocatalysts for the reduction of CO₂ (see Figure 8.11) [41, 42].

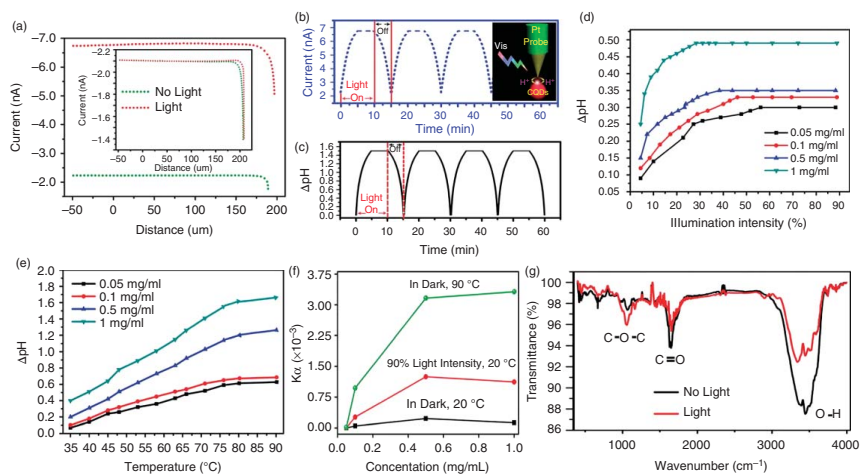


Figure 8.10 (a) Probe approach curves of a glassy carbon electrode modified by C-dots with and without visible light irradiation. Inset are the corresponding curves of the control sample (glass sheet). (b) Photocurrent responses of C-dots under visible light; inset shows the schematic of photocurrent measurement of photo-induced proton generation of C-dots: photo-generated protons can enhance the current at the Pt probe tip. (c) pH value responses of C-dots under visible light irradiation. (d, e) pH change versus illumination intensity and temperature for different C-dot concentrations (0.05, 0.1, 0.5, 1.0 mg ml⁻¹). (f) Dissociation constant (K_a) of different C-dot concentrations under different conditions (in the dark, 90% light intensity, and 90°C). (g) FT-IR spectra of C-dots with and without visible light irradiation. In this figure, CQDs are the C-dots [39]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

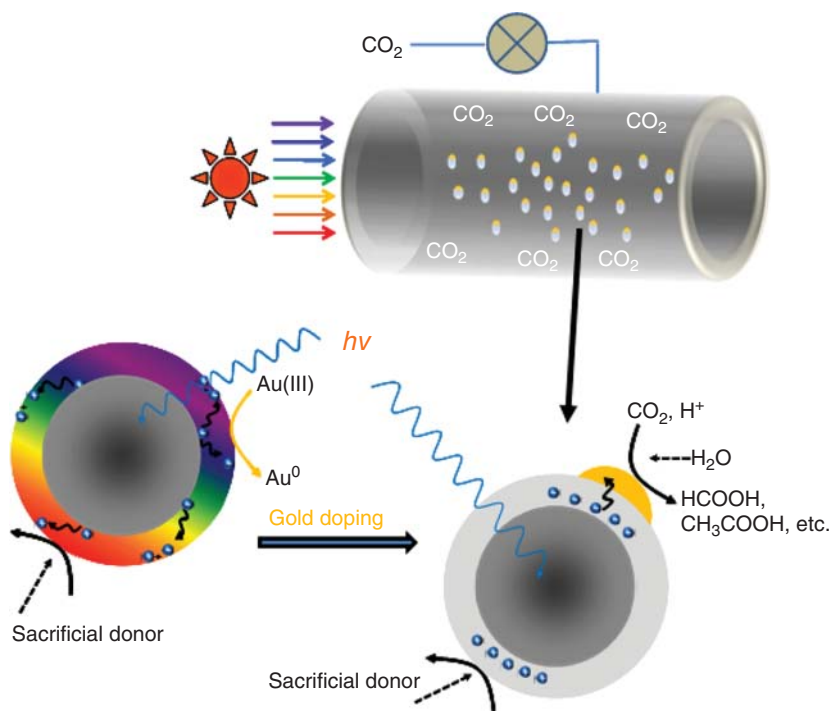


Figure 8.11 Cartoon illustration of (top) the high-pressure optical reactor. The lower left illustration shows photoreductive doping of the carbon dot with gold, completely quenching the dot-surface-based fluorescence, and the lower right shows the gold-doped C-dots as a photocatalyst for CO_2 conversion, where the doped gold was small in quantity, insufficient to form a shell, and likely random in terms of size and shape. The sacrificial electron donor was isopropanol added in some experiments, or PEG1500N molecules on the surface of the carbon dots in the absence of isopropanol [41]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

The photoreduction of CO_2 generally yields formic acid as a significant product. For the reduction to formic acid only, the estimated quantum yield was 0.3%, which was likely lower than the overall quantum yield for the CO_2 conversion. For the platinum-coated photocatalysts in the CO_2 conversion reaction, under otherwise identical experimental conditions, the results were generally similar to those with the gold-coated ones described above, although more quantitative comparisons, including those for effects of varying amounts of metal coating, are still being pursued. The functionalized C-dots apparently served the function of harvesting visible photons to drive the photoreduction process, with the particle surface defects facilitating the charge separation by trapping the separated electrons and holes. In addition to the obviously important advantage of strong visible absorption, other distinctive features of the nanoscale carbon-based photocatalysts include their aqueous solubility for photoconversion under homogeneous reaction conditions, and the confinement of the photoinduced charge separation to the particle surface, thus facilitating more efficient electron harvesting by the coated gold or platinum as the cocatalyst in the CO_2 conversion. Beyond CO_2 photoreduction, the same functionalized C-dots with gold or platinum coatings could be used as photocatalysts for H_2 generation from water [43, 44]. Fernando and coworkers also

highlighted the C-dots by focusing on their synthesis, their photoexcited state properties and redox processes, and their applications as photocatalysts in visible-light carbon dioxide reduction and in water-splitting, as well as on their mechanistic similarities and differences [45].

Teng and coworkers synthesized nitrogen-doped C-dots as the photocatalyst for overall water-splitting [46–48]. The nitrogen-doped C-dots exhibited both p- and n-type conductivities. The diode configuration resulted in an internal Z-scheme charge transfer for effective reaction at the C-dots interface. Visible light (>420 nm) irradiation of the C-dots resulted in simultaneous H_2 and O_2 evolution from pure water at an $H_2:O_2$ molar ratio of 2:1. An energetic band bending was present at the interface between semiconductor and solution, and a p–n type photochemical diode configuration, mimicking the biological photosynthesis system, provided a favorable situation to accomplish vectorial charge displacement for overall water-splitting. This N-doped C-dots photocatalyst consisted of nitrogen-doped graphene sheets stacked into crystals, with oxygen functional groups on the crystal surface. The bandgap of the nitrogen-doped C-dots was approximately 2.2 eV, and was capable of absorbing visible light to generate excitons. This nitrogen-doped C-dots construction resulted in the formation of p–n type photochemical diodes, in which the n-conductivity was caused by embedding nitrogen atoms in the graphene frame, and the p-conductivity by grafting oxygen functionalities on the graphene surface. Visible-light illumination of nitrogen-doped C-dots suspended in pure water resulted in the evolution of H_2 and O_2 at a molar ratio of approximately 2:1. The p- and n-domains were responsible for the production of H_2 and O_2 gases, respectively. Nitrogen-free C-dots with p-type conductivity catalyzed only H_2 evolution under irradiation, proving that the band bending in the p-type domains was favorable for electron injection to produce H_2 . Likewise, NH_3 -treated nitrogen-doped C-dots showed n-type conductivity and catalyzed only O_2 evolution (see Figure 8.12). Yeh and coworkers also synthesized other nitrogen-doped C-dots by thermally treating graphene oxide sheets in NH_3 with subsequent ultrasonic exfoliation. Nitrogen doping in C-dots synthesis repaired the vacancy-type defects of GO and introduced n-type conductivity to compensate for the unbalanced charges on p-type GO, thereby suppressing leaks of photogenerated charges. When deposited with Pt as the cocatalyst, this kind of nitrogen-doped C-dot exhibited high activity in H_2 generation with an apparent quantum yield (AQY) of 12.8% under monochromatic light (420 nm) irradiation. The high activity of the iNGO-QDs sample could be attributed to the synergistic effect of the oxygen and nitrogen functionalities in facilitating charge separation and transfer [47, 48].

8.4.2 C-dots as Electrocatalysts

N-doping is also demonstrated to significantly affect the properties of the C-dots, including the emergence of size-dependent electrocatalytic activity for the ORR [1–7]. For technological relevance in clean energy production, like fuel cells and clean fuel production, ORR and its reverse reaction (oxygen evolution reaction, OER) are at the center of intensive research. Because of the sluggish kinetics of ORR, electrocatalysts are usually used to improve the kinetics of ORR, of which platinum was the “state-of-the-art.” Unfortunately, the formidably high cost of platinum-based electrocatalysts has prompted researchers to look for non-platinum-based electrocatalysts for ORR, aiming at achieving comparable or even better electrocatalytic efficiency

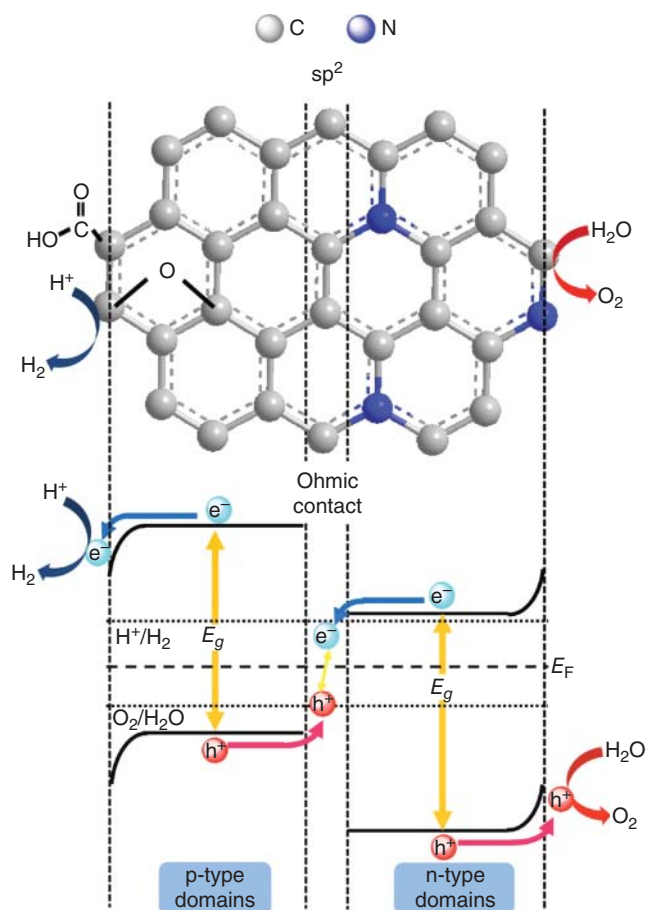


Figure 8.12 The diode consists of p- and n-type domains, connected through the sp^2 clusters as an ohmic contact. Illumination on the diode system results in recombination of majority carriers at the sp^2 clusters to produce useful electron-hole pairs at the semiconductor-water interfaces. The band bending of the p-type domains at the semiconductor-water interfaces is analogous to Photosystem I for electron injection to produce H_2 . The band bending of the n-type domains at the semiconductor-water interfaces is analogous to Photosystem II for hole injection to produce O_2 . This overall water-splitting reaction scheme for the graphene-based photocatalyst bears a remarkable similarity to biological photosynthesis [48]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2014.

as that of platinum-based electrocatalysts. The ultra-small size of C-dots, along with their high stability and good electrical conductivity, make them interesting contenders as electrocatalytic materials for ORR [43]. Previous investigations on graphene have indicated that doped nitrogen atoms in carbon materials, especially in the form of pyridinium moieties, play a critical role in enhancing their electrocatalytic activities toward ORR. One of the pioneering reports on the use of C-dots as electrocatalysts for ORR was provided by Maeda et al. [44]. They demonstrated that N-C-dots (N-doped C-dots) with oxygen-rich functional groups prepared via an electrochemical procedure were electrocatalytically active towards the electrochemical reduction of oxygen. The

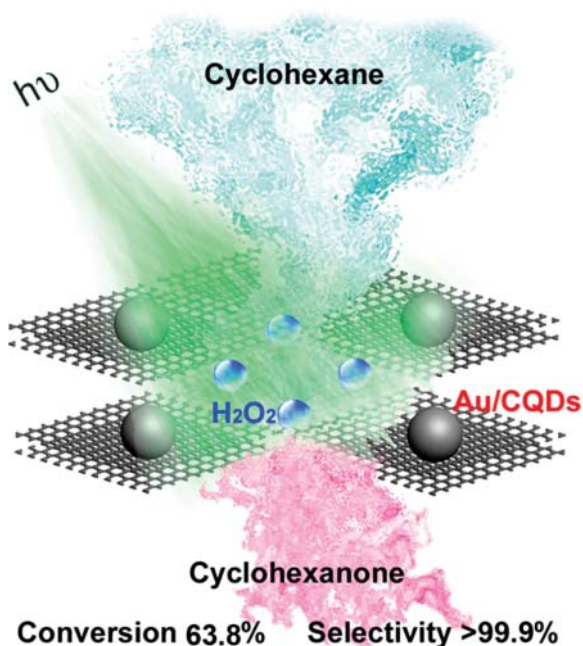
onset potential of ORR was found to be -0.16 V (vs. Ag/AgCl), which is close to that of commercial platinum-based electrocatalysts. Similar results were later obtained by Yan and coworkers and Liu et al. with N-C-dots synthesized by totally different procedures [49–59]. A comparison between nitrogen-free C-dots and the N-C-dots suggested that the electrocatalytic activity of the N-C-dots was indeed closely associated with the N-doping effect. In addition, the N-C-dots exhibited excellent tolerance to a possible crossover effect from methanol. First-principles investigations of the N-C-dots suggested that pyridinic and graphitic nitrogen were responsible for the observed electrocatalytic activity [60]. In another report, Liu and colleagues investigated the electrocatalytic activity of C-dots prepared from natural biomass – soy milk [25]. Similar to the N-C-dots, a much-enhanced electrochemical reduction profile of oxygen was obtained. Likewise, OER also suffers from sluggish kinetics and a high overpotential was required in order to drive OER at a reasonably high rate. Currently, the best electrocatalysts for OER are ruthenium- and iridium-based materials. Again, the formidably high cost of these materials has urged researchers to search for alternative electrocatalysts that could offer high efficiency in OER and are yet readily available at low cost. Unfortunately, reasonably high electrocatalytic activity of C-dots toward OER has yet to be reported.

8.4.3 Photocatalyst Design Based on C-dots

8.4.3.1 Metal Nanoparticle/C-dots Complex Photocatalyst

Liu et al. reported the design of a tunable photocatalyst based on a composite of C-dots and metal nanoparticles for the selective oxidation of cyclohexane (see Figure 8.13) [61]. Significantly, the Au nanoparticles/C-dots (Au/C-dots) composite catalyst yielded oxidation of cyclohexane to cyclohexanone with 63.8% efficiency and >99.9% selectivity

Figure 8.13 Au/C-dots composites as a photocatalyst for selective oxidation of cyclohexane in the presence of H_2O_2 under visible light. In this figure, CQDs are C-dots [61]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.



in the presence of H_2O_2 under visible light at room temperature. In the process, the interaction between C-dots and Au NPs under visible light played a key role in the eventual high conversion and selectivity. The surface plasma resonance of Au NPs enhanced the light absorption of Au/C-dots composites. Under visible light, H_2O_2 was decomposed to the hydroxyl radical ($\text{HO}^\cdot$), which served as a strong oxidant for conversion of cyclohexane to cyclohexanone. Further, Ag nanoparticles/C-dots (Ag/C-dots) and Cu nanoparticles/C-dots (Cu/C-dots) composite photocatalysts were synthesized, and used to catalyze cyclohexane oxidation under the same conditions as the Au/C-dots system. Like the Au/C-dots system, Ag/C-dots and Cu/C-dots composites exhibited similarly good catalytic performance under purple light (conversion 54.0%, selectivity 84.1% for Ag) and red light (conversion 46.7%, selectivity 75.3% for Cu), which corresponded respectively to the surface plasma resonance of Ag and Cu nanoparticles. Given its diversity and versatility of structural and composition design, metal nanoparticles/C-dots composites may provide a powerful pathway for the development of high-performance catalysts.

8.4.3.2 C-dots/Ag/Ag₃PW₁₂O₄₀ Photocatalysts

In light of the remarkable photocatalytic properties of C-dots, the surface plasmon resonance (SPR) effect of metal Ag, and the photocatalytic hydrogen generation of polyoxometalates (POMs), the combination of C-dots, Ag, and POMs may be a unique approach to constructing a stable and efficient complex photocatalyst for solar water-splitting. Liu et al. reported the design and fabrication of C-dots/Ag/Ag₃PW₁₂O₄₀ nanocomposites, which served as photocatalysts for overall water-splitting in visible light (light absorption extends to 650 nm) without any electron acceptors or hole scavengers (see Figure 8.14) [62]. The estimated AQY was 4.9% at 480 nm [63, 64]. POMs played a key role for the water-splitting. PB (a reduced form of POM) could be formed under visible light irradiation in a complex system [65, 66]. The absorption of visible light happened at the Ag nanoparticles surface for the SPR effect, and then

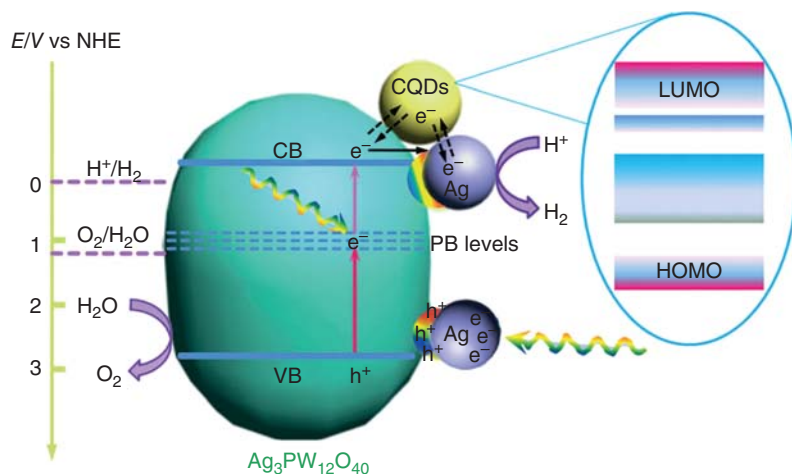


Figure 8.14 A proposed reaction mechanism for visible-light-driven water-splitting on C-dots/Ag/Ag₃PW₁₂O₄₀ nanocomposites. In this figure, CQDs are C-dots [62]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2014.

the absorbed photons would be efficiently separated into electrons and holes. Given the dipolar character of the surface plasmonic state of Ag nanoparticles, the electrons made in POM transfer to PB, which resulted from the one- and two-electron reduced, and the holes act as positive charge centers on the $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ surface [67, 68]. Also, PB could be further excited by visible light irradiation and electrons transferred to the conductive band of POM, as reported in the literature [69–71]. These non-tight-binding electrons in the intermediate energy levels acted as a “color center” in $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$, which could be transiently stabilized and further photoexcited to the conduction band of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ by photons in visible regions. On the other hand, the photoexcited electrons in the conduction band of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ were thermodynamically feasible for water reduction. The Ag nanoparticles here play two vital roles in the enhanced photocatalytic water-splitting efficiency: (i) the strong SPR-induced electric fields localized nearby at the Ag/ $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ interfaces can cause electron generation and enhance the separation efficiencies of electron–hole pairs in $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ [72]; (ii) the electrons in the conduction band of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ can be injected into the contractile Ag nanoparticles, which act as an electron buffer and catalytic site for hydrogen generation. The insoluble C-dots layer on the surface of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ effectively protects $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ from dissolution in aqueous solution, thus enhancing the structural stability of C-dots/ $\text{Ag}/\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ during the photocatalytic processes. Also, the C-dots with excellent charge-storing ability can act as an electron buffer to promote electron-extraction from the conduction band of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$, and thus decrease the electron–hole recombination rate in $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ and enhance the optical absorption of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ for the increased unoccupied occupiable-states in the conduction band of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ [73, 74]. Finally, C-dots could accelerate electron transport due to their photo-induced electron transfer property.

8.4.3.3 C-dots/ TiO_2 Photocatalysts

As one of the most popular photocatalysts, TiO_2 has been used in the removal of organic pollutants and in the generation of H_2 through water-splitting. However, a major drawback in its photocatalytic efficiency resides in its ineffective utilization of visible light as an irradiation source. Because the bandgap of bulk TiO_2 lies in the UV region (3.0–3.2 eV), less than 5% of sunlight is utilized by TiO_2 . TiO_2 –C-dots nanocomposites are able to completely degrade dye under visible light irradiation [7]. Apart from harvesting visible light and converting it to shorter wavelength light through upconversion, which in turn excites TiO_2 to form electron–hole pairs, it is believed that the C-dots in the nanocomposites facilitate the transfer of electrons from TiO_2 and the electrons can be shuttled freely along the conducting paths of the C-dots, allowing charge separation and stabilization, hindering recombination, and thereby generating long-lived holes on the TiO_2 surface. The longer-lived holes then account for the much-enhanced photocatalytic activity of the TiO_2 –C-dots nanocomposites. But more work is needed to improve the lifespan of the above-mentioned photocatalysts before they can be employed in practical scenarios. Yu et al. [75] also reported that C-dots/P25(TiO_2) exhibited improved photocatalytic H_2 evolution under UV-vis and visible light irradiation without loading any noble metal cocatalyst, compared with pure P25 (commercial titanium dioxide). Under UV-vis light irradiation, C-dots act as an electron reservoir to improve the efficient separation of the photoinduced electron–hole pairs of P25. However, under visible light irradiation, C-dots act as a

photosensitizer to sensitize P25 into a visible light response “dyade” structure for H₂ evolution.

Tian et al. [76] reported the UV-vis–NIR broad spectrum active photocatalytic properties of C-dots/hydrogenated TiO₂ (H-TiO₂) nanobelt heterostructures. The improved UV and visible photocatalytic properties could be attributed to improved optical absorption, charge carrier trapping, and hindering of the photogenerated electron–hole recombination of oxygen vacancies and Ti³⁺ ions in TiO₂ nanobelts created by hydrogenation. The NIR photocatalytic activity was from photoinduced electron transfer, electron reservoir, and upconverted PL properties of C-dots, which could absorb NIR light and convert into visible light, and transfer to visible photocatalytic active H-TiO₂ nanobelts.

8.4.3.4 CDs/Ag₃PO₄ Photocatalysts

Considering the properties of C-dots and the limitations of the Ag₃PO₄ photocatalytic system, the combination of C-dots and Ag₃PO₄ may be regarded as an ideal strategy to construct stable and efficient complex photocatalytic systems (such as C-dots/Ag₃PO₄ and C-dots/Ag/Ag₃PO₄ photocatalysts) [62, 73]. The key roles of C-dots in the complex photocatalysts have been soundly investigated. The C-dots layer on the surface of Ag₃PO₄ and Ag/Ag₃PO₄ particles can effectively protect Ag₃PO₄ from dissolution in aqueous solution. The unique photoinduced electron transfer properties of C-dots could make Ag₃PO₄ avoid photocorrosion. The upconverted PL property of C-dots make the C-dots/Ag₃PO₄ and C-dots/Ag/Ag₃PO₄ complex systems effectively utilize the full spectrum of sunlight to greatly enhance the photocatalytic activity. Moreover, C-dots can act as an electron reservoir to hinder the chance of recombination of electron–hole pairs. More interestingly, the existence of Ag accompanied by SPR could further enhance the utilization of sunlight and formation of electron–hole pairs [73].

8.4.3.5 CDs/Cu₂O Photocatalysts

It has been reported that C-dots/Cu₂O photocatalytic systems could harness (N)IR light to enhance photocatalytic activity based on the collective effect of the superior light-reflecting ability of Cu₂O protruding nanostructures and the upconverted PL property of C-dots. When the C-dots/Cu₂O composite photocatalyst was illuminated, the protruding nanostructures allowed multiple reflections of (N)IR light among the vacant spaces between these protruding particles, which could make better use of the source light and therefore offered improved photocatalytic activity [74]. On the other hand, C-dots can absorb (N)IR light (>700 nm), and then emit shorter-wavelength light (390–564 nm) as a result of upconversion, which in turn further excites Cu₂O to form electron–hole (e[−]/h⁺) pairs. The electron–hole pairs then react with the adsorbed oxidants/reducers (usually O₂/OH[−]) to produce active oxygen radicals (e.g. ·O₂, ·OH), which subsequently cause the degradation of organic dye (MB, Methylene blue). Significantly, when C-dots were attached on the surface of Cu₂O, the relative position of the C-dots band edge permitted the transfer of electrons from the Cu₂O surface, allowing the charge separation, stabilization, and then hindering e[−]/h⁺ pair recombination. The electrons could be shuttled freely along the conducting network of C-dots, and the longer-lived holes on the Cu₂O then accounted for the higher activity of the composite photocatalyst. In addition, for organic pollution degradation, the p–p

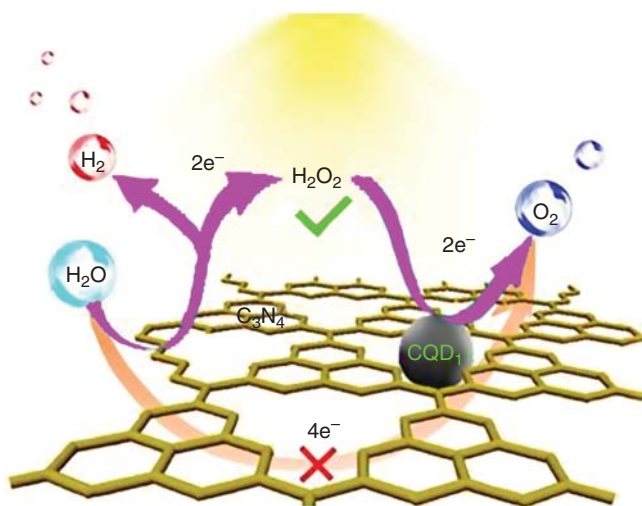


Figure 8.15 The proposed reaction mechanism for visible-light-driven water-splitting by C-dots- C_3N_4 [77]. Source: Reprinted with permission from AAAS publishers, Copyright 2015.

interaction between conjugated structures of C-dots and the benzene ring of MB was beneficial to the enrichment of MB on the surface of C-dots/ Cu_2O composite [74].

8.4.3.6 C-dots/ C_3N_4 Photocatalysts

The use of solar energy to produce molecular hydrogen and oxygen (H_2 and O_2) from overall water-splitting is a promising means of renewable energy storage. In the past 40 years, various inorganic and organic systems have been developed as photocatalysts for water-splitting driven by visible light. These photocatalysts, however, still suffer from low quantum efficiency and/or poor stability. Liu et al. [77] reported the design and fabrication of a metal-free carbon nanodot-carbon nitride (C_3N_4) nanocomposite, and demonstrated its impressive performance for photocatalytic solar water-splitting (see Figure 8.15). They measured quantum efficiencies of 16% for wavelength $\lambda = 420$ nm, 6.29% for $\lambda = 580$ nm, and 4.42% for $\lambda = 600$ nm, and determined an overall solar energy conversion efficiency of about 2.0%. The catalyst comprised low-cost, earth-abundant, environmentally friendly materials and showed excellent stability. Xia et al. [78] also reported that NIR light-induced H_2 evolution was realized by C-dots/ C_3N_4 metal-free photocatalyst. The considerable H_2 production at 808 nm and large promotion of the photocatalytic activity in both UV-vis and visible regions originated from the synergistic effect on spectral and electronic coupling of C_3N_4 nanosheets and C-dots.

8.4.3.7 C-dots/Enzyme Photocatalysts

Li et al. [79] demonstrated that enzyme catalytic activity could be modified by C-dots in the presence of visible light. They created porcine pancreatic lipase (PPL)/C-dots hybrids using a wet chemical method. When PPL/C-dots were irradiated by visible light (PPL/C-dots-Light), their activity was higher than that of free PPL (activity increased by $\sim 10\%$). When the light source was removed, the activity of PPL/CDs was lower than that of free PPL (activity decreased by $\sim 30\%$). Using Michaelis-Menten kinetics, they also confirmed that C-dots play the role of a non-competitive inhibitor. The addition

of visible light irradiation initiated C-dot-mediated structural changes to the PPL in PPL/C-dots hybrids, which improved the catalytic activity. The surface of C-dots contained many functional groups including amino groups, carboxyl groups, and hydroxyl groups, which allowed for easy adsorption of C-dots onto the surface of PPL to form PPL/C-dots hybrids. Li et al. [80] further fabricated the laccase/phosphate modification carbon dots (P-C-dots) hybrids and investigated the effect that P-C-dots and visible light had on the catalytic behavior of laccase. The catalytic activity of laccase/P-C-dots was higher than that of laccase (increase of about 47.7%). When the laccase/P-C-dots were irradiated by visible light (laccase/P-C-dots-Light), their catalytic activity increased by about 92.1% vs. laccase/P-C-dots hybrids. The functional groups of C-dots also played an important role in affecting the activity of laccase via the interaction between the phosphate group and T1 Cu in laccase.

8.4.4 Photoelectrochemical Catalyst Design Based on C-dots

TiO₂ is regarded as one of the most popular photoanode materials of photoelectrochemical (PEC) water-splitting devices owing to its high resistance to photocorrosion, physical and chemical stability, easy availability, and low cost. For efficient hydrogen generation under visible light, a good sensitizer should meet several criteria described as follows [81, 82]. First, it must be able to enhance the absorption of the solar spectrum for the host materials. Second, it should have suitable energy levels such that the photoexcited electrons in the highest occupied molecular orbital (HOMO) level or conduction band could be efficiently injected into the semiconductor acceptor's conduction band, and simultaneously the holes in the lowest unoccupied molecular orbital (LUMO) level or valence band could oxidize the reducing substances in the electrolytes. Third, it is favorable to have some specific functional groups on their surfaces which could make them easy and stable to attach to the surfaces of the semiconductor acceptor. Fourth, it should be resistant to corrosion or degradation in the practical operating conditions of PEC cells for the long term. Zhang et al. [82] reported that C-dots could be used as an alternative sensitizer for the PEC cells based on TiO₂ nanotube arrays (TiO₂ NTs) (see Figure 8.16). Under simulated sunlight illumination (100 mW cm⁻²), the photocurrent density of the C-dots sensitized PEC cell was four times higher than for the unsensitized cell at 0 V vs Ag/AgCl. The corresponding hydrogen production rate was determined to be about 14.1 μmol h⁻¹ for a C-dots sensitized TiO₂ NTs (C-dots/TiO₂ NTs) photoanode with Faradaic efficiency of nearly 100%. A sensibilization mechanism was proposed to illustrate the role of C-dots in the PEC cells. A photon with adequate energy could excite the electrons in the HOMO level, transferring to the LUMO level of C-dots. Afterwards, the excited electrons in the LUMO level of the C-dots were transferred to the conduction band of the contacted TiO₂ NTs and then transported to the counter electrode for the hydrogen evolution reaction (HER) along the TiO₂ NTs axial direction. The holes left in the HOMO level of the C-dots could oxidize the sacrificial reagent to complete a whole galvanic circle. Further studies also demonstrated that C-dots are effective sensitizers for the PEC photoelectrode based on various semiconductors, such as ZnO, CdSe, CdSe/TiO₂, and np⁺-Si [83–86]. Recently, Tang et al. [87] reported that a C-dots-coated BiVO₄ inverse opal (io-BiVO₄) structure showed dramatic improvement of PEC hydrogen generation. The io-BiVO₄ maximized photon-trapping through a slow light effect, while maintaining adequate surface area for effective redox reactions.

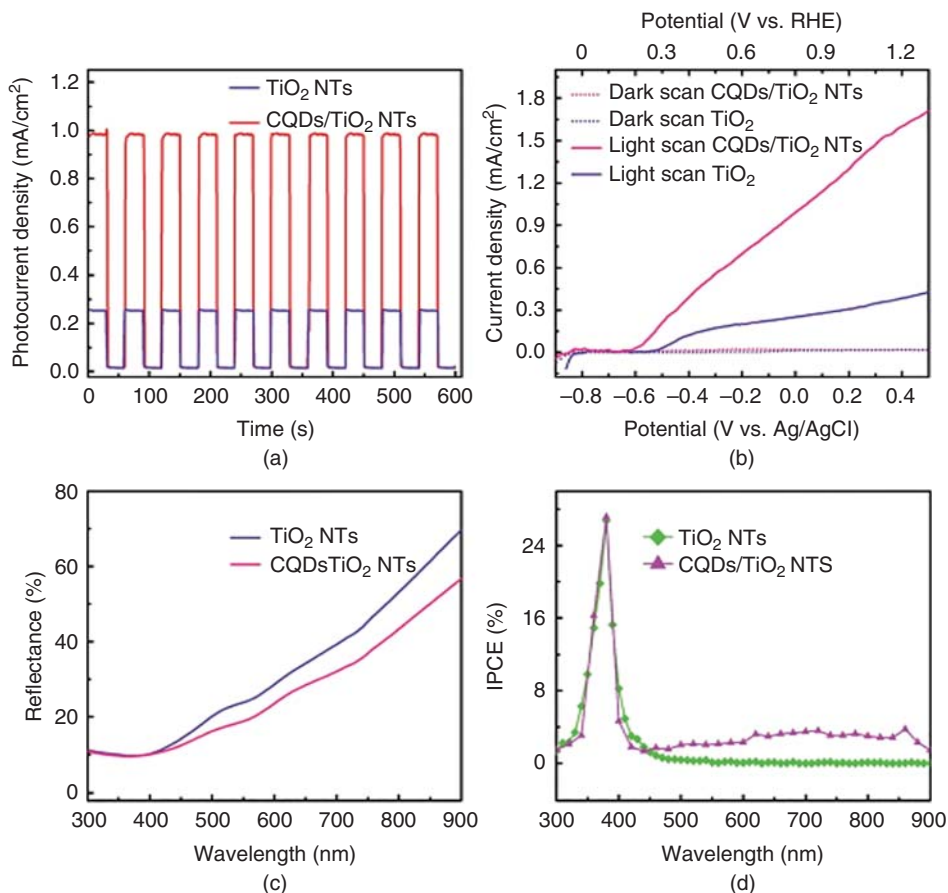


Figure 8.16 (a) The chopped-light current density versus time (J-t) curves of the TiO_2 NTs and C-dots/ TiO_2 NT photoanodes at 0 V vs Ag/AgCl. (b) Linear sweep voltammetric (J-V) curves of the two kinds of photoanodes under dark and simulated light illumination. (c) The diffused reflectance UV-vis spectra of the two types of TiO_2 NTs. (d) A comparison of the incident photon to current conversion efficiency (IPCE) spectra of the two photoanodes measured at 0 V vs Ag/AgCl. In this figure, CQDs are C-dots [82]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

C-dots were then incorporated into the io- BiVO_4 to further improve the photoconversion efficiency. Due to the strong visible-light absorption property of C-dots and enhanced separation of the photoexcited electrons, the C-dots-coated io- BiVO_4 exhibited a maximum photo-to-hydrogen conversion efficiency of 0.35%, which is six times higher than that of the pure BiVO_4 thin films. On the other hand, Martindale et al. [88] reported that C-dots were established as excellent photosensitizers in combination with a molecular catalyst for solar light-driven hydrogen production in aqueous solution (see Figure 8.17). The C-dots displayed activity in the visible region beyond $\lambda > 455$ nm and maintained their full photocatalytic activity for at least one day under full solar spectrum irradiation. A high quantum efficiency of 1.4% was recorded for the noble- and toxic-metal free photocatalytic system.

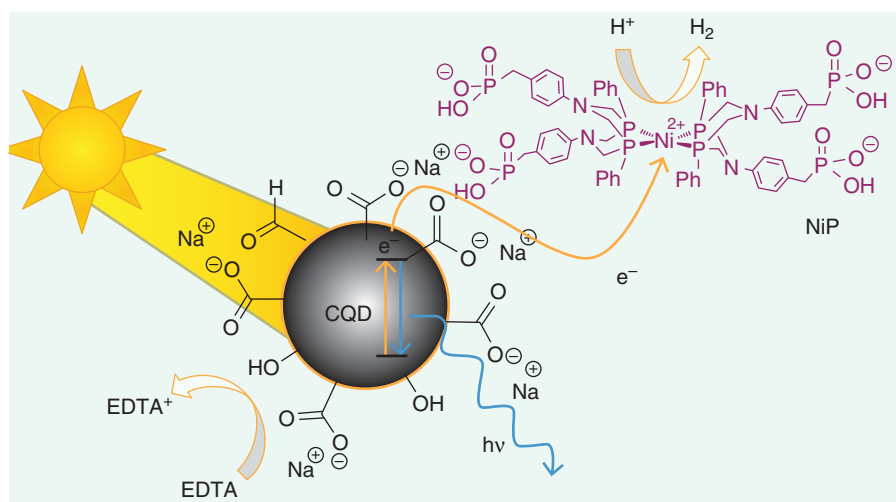


Figure 8.17 Representation of solar H_2 production using the hybrid C-dots–NiP system. Irradiation of photoluminescent C-dots results in the direct transfer of photoexcited electrons to the catalyst NiP with subsequent reduction of aqueous protons. The electron donor EDTA (ethylene diamine tetraacetic acid) carries out quenching of photoinduced holes in the C-dots. In this figure, CQDs are C-dots [88]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

8.4.5 Modulation of Electron/Energy Transfer States at the TiO_2 –C-dots Interface

Wang et al. showed a bias-mediated electron/energy transfer process at the C-dots/ TiO_2 interface for the dynamic modulation of optoelectronic properties (see Figure 8.18) [89]. Different energy and electron transfer states have been observed in the C-dot-decorated TiO_2 nanotubes (C-dots/TNTs) system due to the upconversion PL and the electron donation/acceptance properties of the C-dots layer. Specifically, five distinct electron/energy transfer states of the C-dots/TNTs system could be dynamically tuned by different pulse-bias treatments. When the negative bias applied to the C-dots/TNTs electrode was increased from -1 to -3 V, the positively charged C-dots would be attracted increasingly closer to TNTs, leading to a gradual reduction in interface impedance. At 0 and -1 V pulse-bias treatment, or high and medium interface impedance, photoexcited electrons of TNTs would favor transfer to the Pt electrode, and those of C-dots would favor a return to a low-energy state. Then the upconverted PL of C-dots would excite the TiO_2 , leading to higher incident photon to current conversion efficiencies, IPCE_{max} (optoelectronic conversion). At -2 V pulse-bias treatment, or low interface impedance, the symbiotic effect of upconverted PL of C-dots and a high electron transfer ability between TNTs and C-dots would lead to the highest IPCE_{max} (optoelectronic conversion), while at -3 V pulse-bias treatment, the interface impedance between TNTs and C-dots would be the lowest, and recombination of photoinduced electrons and holes of TNTs through a TiO_2 –C-dots– TiO_2 pathway be the highest, thus leading to the least upconverted PL and the lowest optoelectronic conversion. The present pulse-bias treatment method would enable the optoelectronic conversion logic phenomenon in the C-dots/TNTs nanosystem. Application of different

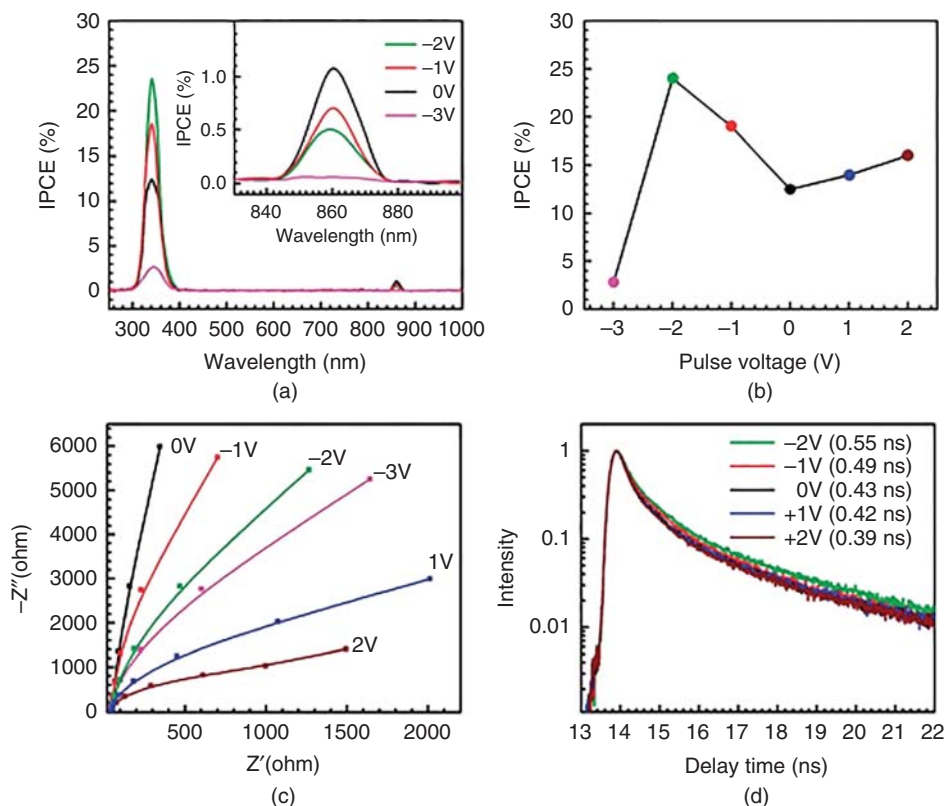


Figure 8.18 (a) IPCE spectra of C-dots-TNTs under different bias potential treatment from 0 V to 3 V. The inset shows the enlarged IPCE spectra in the range of 830–900 nm. (b) IPCE_{max} of a C-dots-TNTs electrode in 0.1 M Na₂SO₄ solution as a function of the applied pulse voltage treatment from 3 V to 2 V. (c) Nyquist plots of C-dots-TNTs collected at open circuit potential in the dark after pulse voltage treatment at 0, 1, 2, 3, 1, and 2 V, respectively. (d) Time-correlated single photon counting (TCSPC) of the C-dots-TNTs system after negative and positive pulse voltage treatment [89]. Source: Reprinted with permission from RSC publishers, Copyright 2013.

pulse-bias treatment could generate high, medium or low optoelectronic conversion efficiency. The IPCE of the electrode increased from 13.5% to 19% after -1 V pulse-bias treatment, and from 13.5% to 24% after -2 V pulse-bias treatment, but decreased from 13.5% to 2.5% after -3 V pulse-bias treatment. This phenomenon represented a simple logic function, which yielded a medium output at no bias (or low positive pulse bias), a high output at -2 V pulse bias, and a low output at -3 V pulse bias.

8.4.6 Electrocatalyst Design Based on C-dots

A C-dots/NiFe-layered double hydroxide (LDH) complex exhibited high OER electrocatalytic activity (with overpotential of ~ 235 mV in 1 M KOH at a current density of 10 mA cm^{-2}) and stability for oxygen evolution [90]. Its activity almost exceeded that of any previous Ni-Fe compound, and was even comparable to that of the lowest overpotential reported in Ni-Fe catalysts, 230 mV at 10 mA cm^{-2} for electrodeposited

Ni-Fe films [74, 87, 91]. This electrocatalytic property was primarily attributed to the NiFe-LDH phase, and further enhanced by strongly associating the LDH with C-dots, which possessed small size, excellent conductivity, rapid electron transfer, and electron reservoir properties. Specifically, the small size of the C-dots may provide a large specific surface area for more convenient electrocatalytic reactions. The rapid electron transfers from C-dots to NiFe-LDH on the surface could further improve the electrocatalytic activity. The surface functional groups on C-dots (such as carbonyl C=O) made the formation of C-dots/NiFe-LDH composites easier due to the strong electrostatic interactions (or generating new covalent bonds, such as C–O–Ni or C–O–Fe). In any case, synergistic effects between NiFe-LDH and C-dots afforded by direct integration of the NiFe-LDH nanoplates with the surface functional groups on C-dots contributed to the optimal OER activity of the C-dots/NiFe-LDH composite catalysts. Zhao et al. [92] also demonstrated that the carbon nanodots (phosphate-functionalized carbon nanodots, P-C-dots) modified cobalt phosphate (CoPi) composite (CoPi/P-C-dots) could serve as a high-efficiency OER catalyst in both neutral and alkaline conditions with low onset potential and high current density. Further, as reported by Yang et al. [93], a Ni nanoparticle/carbon quantum dot (Ni/C-dots) hybrid was synthesized and evaluated as an electrocatalyst for HER in a strongly alkaline medium (1 M KOH solution). The obtained Ni/C-dots hybrid showed good catalytic ability for HER, with an onset potential comparable to that of Pt wire and a low Tafel slope of 98 mV dec^{-1} , which may be attributed to the Ni–O–C interface between Ni NPs and C-dots. Samantara et al. [94] prepared a hybrid material composed of sandwiched reduced graphene oxide (rGO) and N,S co-doped carbon dots (N,S-C-dots). This composite exhibited dual performance as an electrode material for supercapacitors and fuel cell catalysts. Xu et al. [95] reported C_3N_4 @C-dots nanohybrids by a one-step hydrothermal treatment, and then further demonstrated the potential for energy conversion applications. The N,S-doped RGO/C-dots hybrids were demonstrated by Luo et al. [96] to have good catalytic properties as metal-free electrocatalysts, with long-term operational stability and tolerance to the crossover effects of methanol for oxygen reduction via a four-electron pathway in alkaline solution. There were also many reports on the electrocatalyst design based on C-dots and metal-free semiconductors (GO, C_3N_4 , microporous carbon nanospheres, and graphene nanoribbons). On the other hand, Favaro et al. [97] reported the synthesis of singly- and multiply-doped graphene oxide quantum dots via a simple electrochemical method with water as solvent. Chemical and structural properties of the obtained materials were investigated by photoemission spectroscopy and scanning tunneling microscopy analyses. The electrochemical activity toward the ORR of the doped graphene oxide quantum dots was studied by cyclic voltammetry and rotating disk electrode measurements (see Figure 8.19), showing a clear decrease of the overpotential as a function of the dopant according to the sequence: $\text{N} \sim \text{B} > \text{B}$, N . Moreover, assisted by density functional calculations of the Gibbs free energy associated with every electron transfer, they demonstrated that the selectivity of the reaction was controlled by the oxidation states of the dopants: as-prepared graphene oxide quantum dots followed a two-electron reduction path that leads to the formation of hydrogen peroxide, whereas after the reduction with NaBH_4 , the same materials favored a four-electron reduction of oxygen to water.

It should be noted that nitrogen (N)-doped carbon materials exhibit high electrocatalytic activity for the ORR, which is essential for several renewable energy systems. However, the ORR active site (or sites) is unclear, which retards further development of

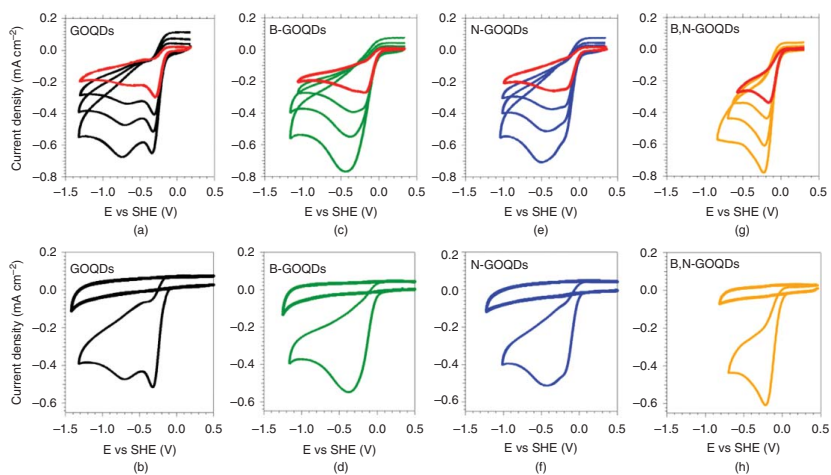


Figure 9.19 Cyclic voltammograms (CVs) of (a) pure C-dots, and (c) B-, (e), N-, and (g) B,N-C-dots in O₂-saturated 0.1 M KOH solution, at different potential scan rates (10, 20, 50, and 100 mV s⁻¹), and the corresponding CVs (b, d, f, h; scan rate 50 mV s⁻¹) acquired in Ar-saturated (thick curves) and O₂-saturated 0.1 M KOH solutions. In this figure, GOQDs are C-dots [97]. Source: Reprinted with permission from American Chemical Society, Copyright 2014.

high-performance catalysts. Very recently, Guo et al. [98] characterized the ORR active site by using newly designed graphite (highly oriented pyrolytic graphite, HOPG) model catalysts with well-defined p conjugation and well-controlled doping of N species. The ORR active site is created by pyridinic N. Carbon dioxide adsorption experiments indicated that pyridinic N also created Lewis basic sites. The specific activities per pyridinic N in the HOPG model catalysts were comparable with those of N-doped graphene powder catalysts. Thus, the ORR active sites in N-doped carbon materials were carbon atoms with Lewis basicity next to pyridinic N (see Figure 8.20).

8.4.7 Surface Modifications Towards Catalyst Design

Efficient electrocatalysts for OER and ORR are essential components of renewable energy technologies, from fuel cells to metal–air batteries [99–102]. Much progress has been achieved in the development of platinum-based electrocatalysts for ORR and iridium (or Ru)-based electrocatalysts for OER, so that they are regarded as the most effective catalysts for ORR and OER, respectively [103–107]. However, these electrocatalysts still do not meet the demands of large-scale commercialization because of their sluggish electron-transfer kinetics [108], poor durability [109], and high cost. Carbon nanostructures have notable merits including low cost, wide abundance, large surface areas, high electrical conductivity, and good stability [110–114]. Consequently, catalysts based on carbon nanostructures (doped with nitrogen, boron, phosphorus, iodine, fluorine, etc.) have attracted much attention in the past decade [115–119], particularly in improving their ORR and OER activity relative to that of commercial Pt/C and IrO₂/C [120–123]. Among efforts in carbon nanostructures for ORR and OER catalysts [124–127], a recent exciting development showed that a polymer co-doped with P and N (coined as N-P co-doped mesoporous nanocarbon (NPMC) foam) could serve as an efficient bifunctional electrocatalyst for both ORR and OER [128]. Liu et al. reported that carbon nanodots, via surface modification, could independently become either an ORR or OER electrocatalyst with unprecedented performance better than all previous catalysts, including NPMC [129, 130]. C-dots exhibit unique photo-induced electron transfer, PL, and electron reservoir properties [2, 3, 7, 131, 132]. They possess high catalytic activity for various reactions and can also serve as functional units for photocatalyst and electrocatalyst design [38, 73, 74, 77, 87, 90, 133]. Liu et al. [129] have demonstrated that C-dots after surface modification with amidogen and phosphorus species (NH₂-C-dots and PO₄-C-dots) respectively possessed outstanding OER and ORR electrocatalytic properties (e.g. activity), which were similar to or even better than iridium-based and platinum-based electrocatalysts (see Figure 8.21). Furthermore, superior electrocatalytic activity and stability were achieved by attaching Au nanoparticles to NH₂-C-dots and PO₄-C-dots, exceeding those of commercial catalysts (IrO₂/C and Pt/C) under visible light [129].

8.5 C-Dots for Sensing and Detection

8.5.1 PL Sensors

For sensing applications, various C-dot-based PL sensors have been fabricated with either a signal-off or signal-on process. Recently, Fan et al. [134] reported that doping

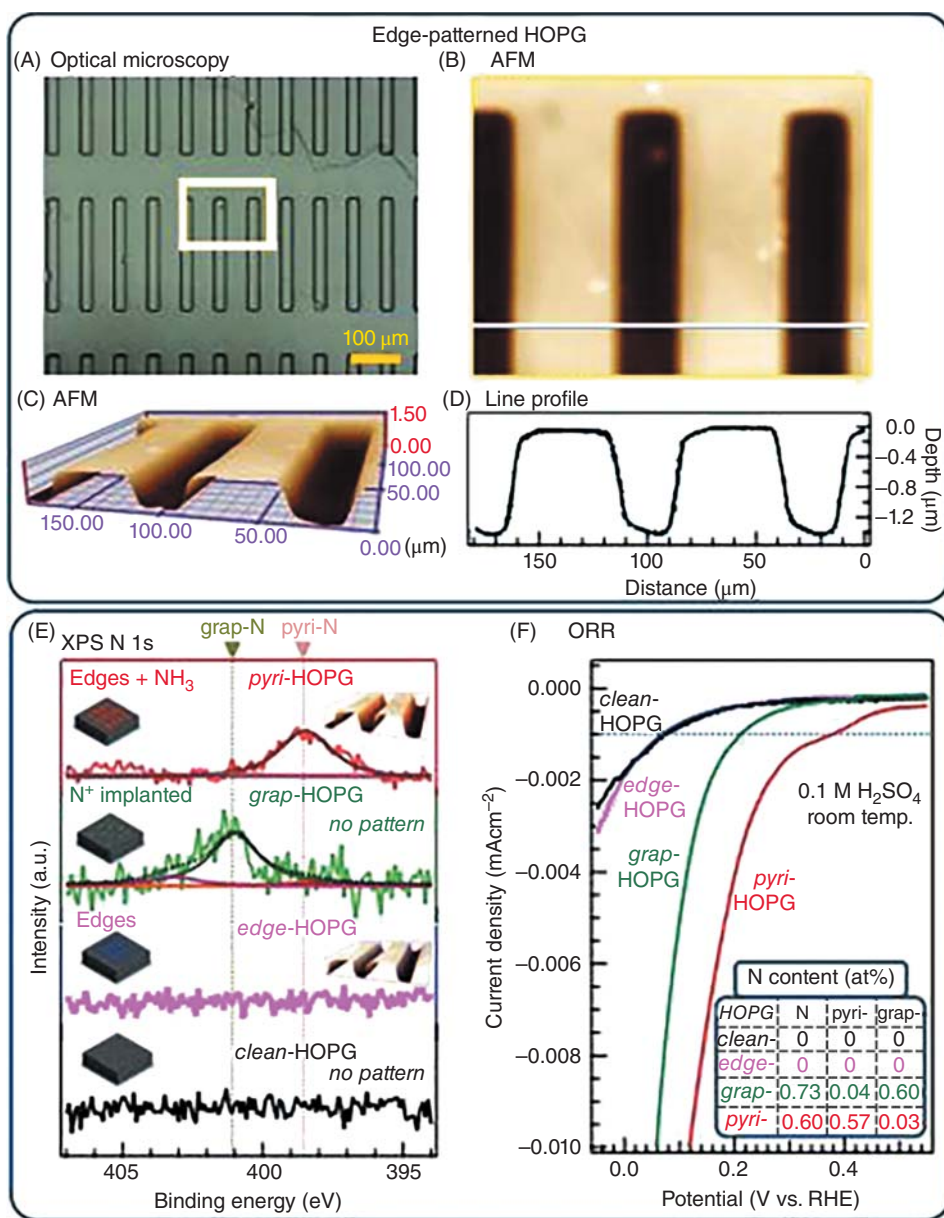


Figure 8.20 Structural and elemental characterization of four types of N-HOPG model catalysts and their ORR performance. (A) Optical image of patterned edge-N+-HOPG. (B) The AFM image obtained for the region indicated by the rectangle in (A). (C) Three-dimensional representation of (B). (D) Line profile of the AFM image obtained along the line in (B). (E) N 1s XPS spectra of model catalysts. (F) ORR results for model catalysts corresponding to (E). Inset in (F), nitrogen contents of the model catalysts [98]. Source: Reprinted with permission from AAAS publishers, Copyright 2016.

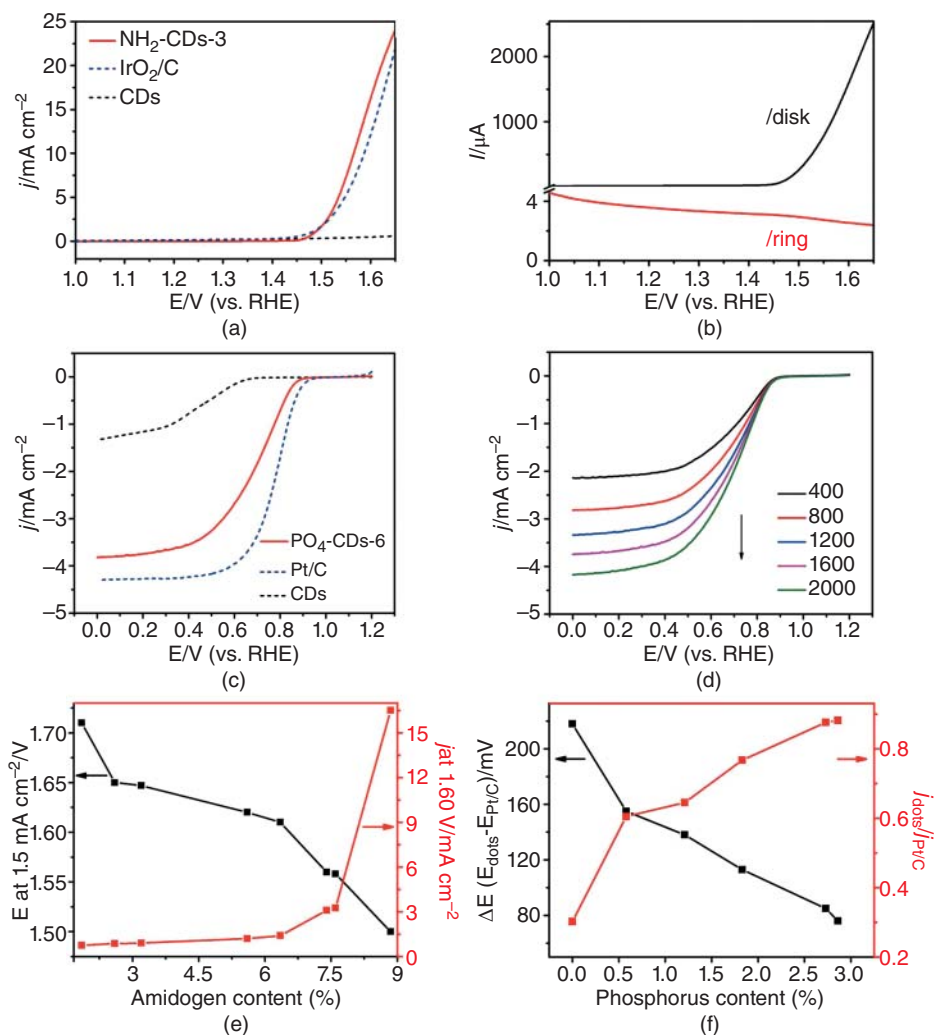


Figure 8.21 Electrocatalytic activities of $\text{NH}_2\text{-C-dots}$ and $\text{PO}_4\text{-C-dots}$. (a) Linear sweep voltammogram (LSV) curves of C-dots, $\text{NH}_2\text{-C-dots-3}$, and IrO_2/C (20 wt% of IrO_2 loading) in an N_2 -saturated 0.1 M KOH aqueous solution. (b) Steady-state voltammograms for the OER in N_2 -saturated 0.1 M KOH at the Pt disk-Pt ring electrodes applying a rotation rate of 1600 rpm. The Pt ring was biased at 1.51 V vs. the reversible hydrogen electrode (RHE). (c) LSV curves of CDs, $\text{PO}_4\text{-C-dots-6}$, and Pt/C in an O_2 -saturated 0.1 M KOH aqueous solution. (d) LSV curves of $\text{PO}_4\text{-C-dots-6}$ in an O_2 -saturated 0.1 M KOH aqueous solution. (e) Relationship between the amidogen contents and OER activities of the $\text{NH}_2\text{-C-dots}$ electrocatalyst (black line: the potentials required to achieve 0.15 mA cm^{-2} ; gray line: the current density at 1.60 V). (f) The relationship between phosphorus contents of $\text{PO}_4\text{-C-dots}$ and onset potentials (black line) and current densities (gray line) normalized to commercial Pt/C. In this figure, CDs are C-dots [129]. Source: Reprinted with permission from John Wiley & Sons Ltd, Copyright 2016.

C-dots with a S atom (S-C-dots) could promote the coordination interaction between Fe^{3+} and phenolic hydroxyl groups of S-C-dots, leading to significant PL quenching. Taking advantage of the PL quenching of C-dots, a turn-off sensor for Ag^+ and biothiol detection was developed by Ran et al. [134, 135]. He et al. reported a glucose biosensor via the PL quenching of hemin-functionalized C-dots [136]. According to the surface quenching states induced mechanism, 3-aminobenzenboronic acid functionalized C-dots were also used for glucose detection by Qu et al. [137]. In addition, Wang et al. developed a simple PL-off assay for the activity of protein kinase CK2 based on the selective aggregation of phosphorylated peptide-C-dot conjugates triggered by Zr^{4+} coordination [138]. Apart from the signal-off PL sensors described above, signal-on PL sensors have also been designed [139–142]. An aggregation-induced PL sensor for label-free detection of glucose was proposed by Zhang et al. [140]. In another study, Li et al. designed a glucose sensing system using anionic C-dots and a cationic boronic acid substituted bipyridinium salt [141]. Li et al. also demonstrated a label-free PL signal-on assay for the detection of trypsin based on cytochrome c (Cyt c)-induced self-assembled C-dots [142]. Wu et al. designed a PL turn-on sensor for sensitive biothiols and Hg^{2+} detection. Fan et al. demonstrated the use of B-CDs as PL turn-on sensors for detecting Al^{3+} [139]. Zhang et al. reported C-dots as a fluorescent sensing platform for the highly sensitive and selective detection of Fe^{3+} ions [143]. Li et al. [13] demonstrated that C-dots/tyrosinase (TYR) hybrids, as a fluorescent probe, were efficient, fast, stable and sensitive in the detection of levodopa (L-DOPA). It is worth mentioning that TYR did not require modification and immobilization, and the test results could be read as soon as the probe-sample incubation was completed. Moreover, the test results were comparable to those of the present clinical fluorescence and high-performance liquid chromatography (HPLC) methods [13]. Similarly, Li et al. also reported that the C-dots-laccase hybrids, which were sensitive, stable, and of low cost, gave precise detection of catechol and catechol derivatives [144]. Yang et al. established a FRET system for the determination of Zn(II) based on C-dots [145].

Notably, the C-dots synthesized through refluxing glucose could serve as efficient fluorescent probes for the convenient and sensitive detection of Norfloxacin (NOR) with a wide concentration range (see Figure 8.22) [146]. For C-dots, the fluorescence intensity enhanced gradually as the NOR concentrations increased. Under optimized conditions, the detection of NOR could be performed in the liquid phase and on solid substrate. This method has been used to detect NOR in real samples. A series of experiments suggested that the enhanced fluorescence should be attributed to the strong hydrogen bond interaction between C-dots and NOR. Compared with HPLC, this method was faster and simpler, with lower cost and higher sensitivity.

8.5.2 Electronic, Electrochemiluminescent and Electrochemical Sensors

Unlike the extensive applications of graphene in field-effect transistors, C-dots are mainly used in single electron transistor (SET)-based charge sensors [147–151]. As the bias voltage between the source and drain increases, an electron can pass through the island, then current flows, and charge detection is realized [148–151]. In addition to detecting charge in SETs, C-dots have also been applied to the construction of electronic sensors for the detection of humidity and pressure [152]. ECL emission was also observed from C-dots [153–157]. Yang et al. designed a sandwich-type

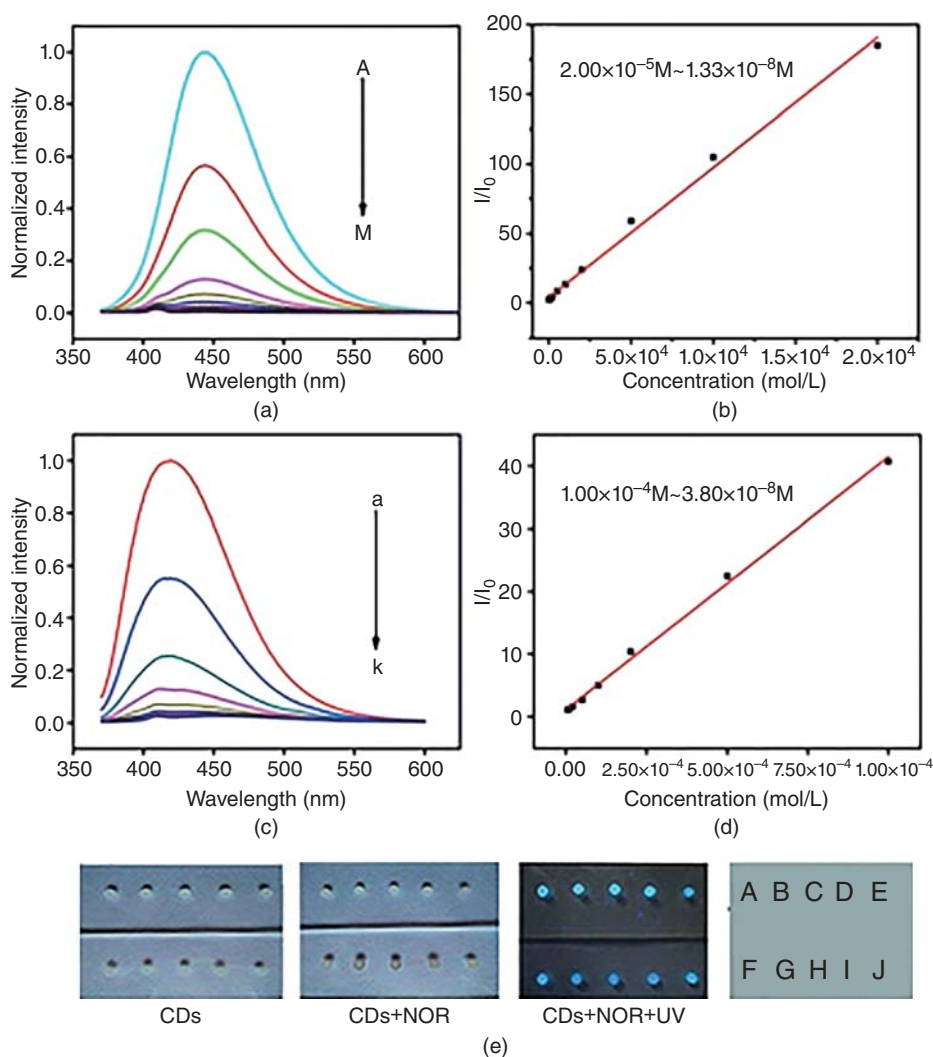


Figure 8.22 (a) Fluorescence spectra of C-dots with enhanced fluorescence using a series of NOR concentrations in phosphate buffer saline (PBS). C_{NOR} (0.01 μM) = (A) 2000; (B) 1000; (C) 500; (D) 200; (E) 100; (F) 50; (G) 20; (H) 10; (I) 5; (J) 3; (K) 2; (L) 1.33; and (M) 0. (b) The relationship between I/I_0 and NOR concentration. (c) Fluorescence spectra of the C-dots enhanced fluorescence using a series of NOR concentrations in PBS. C_{NOR} (0.01 μM) = (a) 10000; (b) 5000; (c) 2000; (d) 1000; (e) 500; (f) 200; (g) 100; (h) 50; (i) 5; (j) 3.8; and (k) 0. (d) The relationship between I/I_0 and NOR concentration. (e) Images of the C-dots and their responses to NOR solution with concentrations of 8.4×10^{-4} , 4.2×10^{-4} , 8×10^{-5} , 2×10^{-5} , 8×10^{-6} , 2×10^{-6} , 8×10^{-7} , 2×10^{-7} , 8×10^{-8} , and 0 mol/L (spots A–J, respectively) under visible and UV (at 365 nm excitation) light. In this figure, CDs are C-dots [146]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

ECL immunosensor by using gold–silver nanocomposite-functionalized graphene (GN-Ag–Au) as the sensor platform and C-dot-functionalized porous Pt/Pd nanochains (pPtPd) as the signal amplifier for the detection of a tumor marker (see Figure 8.23) [154]. Lu et al. constructed an ECL sensor via an electrochemiluminescence resonance energy transfer (ERET) between C-dots and gold nanoparticles (Au NPs) for DNA damage detection [155]. By combining intense ECL of C-dots and an aptamer technique, Lu et al. proposed a novel ECL aptamer sensor for measuring ATP [156]. In addition, Dong et al. presented an ECL sensor for the detection of H_2O_2 using hydrazide-modified C-dots [157]. On the other hand, the electrocatalytic performances of C-dots have been gradually recognized, allowing the use of C-dots as nanoprobe for electrochemical biosensors [158–161]. Due to their biocompatibility, large surface-to-volume ratio, and ease of modification, C-dots can be employed in electrochemical biosensors as nanocarriers [162–170].

8.5.3 C-dots for Humidity and Temperature Sensing

Zhang et al. reported the fabrication of a humidity sensing device based on C-dots film (see Figure 8.24) [171]. The conductivity of the C-dots film had a linear and rapid response to relative humidity. The sensing mechanism was proposed to be the formation of hydrogen bonds between carbon quantum dots and water molecules in the humid environment, which significantly promoted electron migration. In a control experiment, this hypothesis was confirmed by comparing the humidity sensitivity of candle soot (i.e. carbon nanoparticles) with and without oxygen-containing groups on the surfaces. As reported by Liu et al., N-doped C-dots, obtained from C_3N_4 and ethanediamine, emitted bright-blue fluorescence under UV light [172]. They were demonstrated to have good water dispersibility and excellent fluorescence properties, which were independent of ionic strength, pH, and time. Besides, the temperature-dependent fluorescence was also measured from 20 to 80°C. The fluorescence intensity decreased with higher temperature. Significantly, this process was reversible and the fluorescence could recover to the initial intensity with the temperature decreasing. For the present system, the thermal sensitivity of the PL intensity of N-doped C-dots is determined to be about $0.85\% \text{ } ^\circ\text{C}^{-1}$. The origin of this temperature-dependent PL sensing may be attributed to the synergistic effect of abundant oxygen-containing functional groups and hydrogen bonds (see Figure 8.25). Further, these N-doped C-dots are also demonstrated to have low cytotoxicity, and could be regarded as effective in-vitro and in-vivo nanothermometers in a biosystem [172].

8.6 C-dots for Solar Energy

In addition to being used as photocatalysts, C-dots have been capturing the attention of researchers as potential photosensitizers in solar cells [7]. For example, a C-dots–RhB– TiO_2 system showed that the C-dots effectively bridge the RhB molecules to the TiO_2 substrate by acting as a one-way electron transfer intermediary (see Figure 8.26) [132]. Compared with the RhB– TiO_2 system, the presence of C-dots significantly enhanced the photoelectric conversion efficiency by as much as seven times. In another report, a C-dots/ TiO_2 electrode was employed in a solar cell [89]. The photocurrent density was 2.7 times larger than that of pristine TiO_2 electrode under

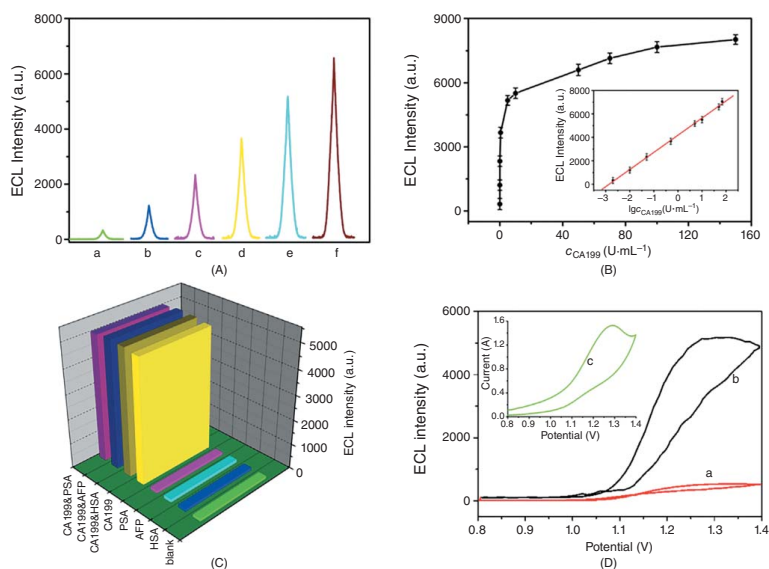


Figure 8.23 (A) ECL of the immunosensor at various concentrations of CA199 (U mL⁻¹): (a) 0.002, (b) 0.01, (c) 0.05, (d) 0.5, (e) 5, (f) 50. (B) Relationship between ECL and the CA199 concentration, each point being the average of 10 measurements. (C) The selectivity of the ECL immunosensor. (D) ECL-potential curves of (a) pure C-dots, (b) pPtPd@C-dots and cyclic voltammogram (inset) of pPtPd@C-dots on the electrode in pH 7.4 phosphate buffer saline (PBS) containing tissue plasminogen activator (TPA) [154]. Source: Reprinted with permission from Elsevier, Copyright 2014.

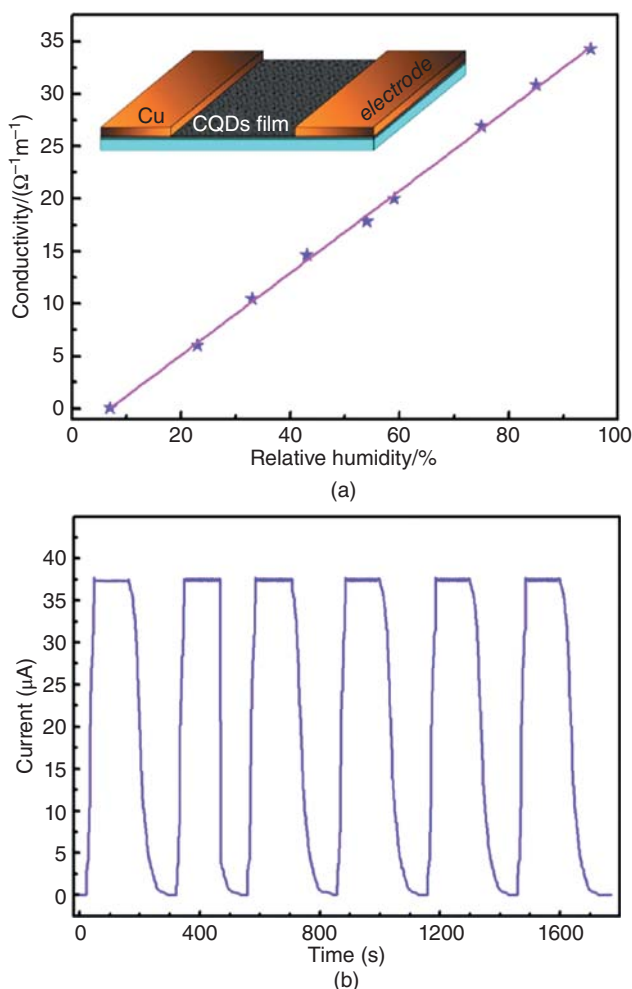


Figure 8.24 (a) The conductivity of the C-dots film as a function of the ambient relative humidity. (b) The response and recovery curve of the C-dot-based humidity sensing device. The curves were measured between 7% and 43% relative humidity at room temperature [171]. Source: Reprinted with permission from Elsevier, Copyright 2013.

visible light illumination. Enhanced performance of a solar cell was also obtained when N-C-dots were used as photosensitizers. Although the photo-to-electricity conversion efficiency of the above-mentioned solar cells is far from satisfactory, these findings definitely encourage more research in the application of C-dots in photovoltaic devices and photocatalyst design.

C-dots could play different roles as photoabsorption agents, sensitizers, and transporting layers, with efficiency varying from 0.1% to 9%. For example, C-dots/silicon nanowire array core-shell devices showed a conversion efficiency of 9.1%, which is comparable to that of Si-based hybrid solar cells (SCs) [173]. A similar structure was also employed by Gao et al., and a conversion efficiency of 6.63% was obtained [174]. Such improved performance compared with bare Si or graphene oxide hybrids could

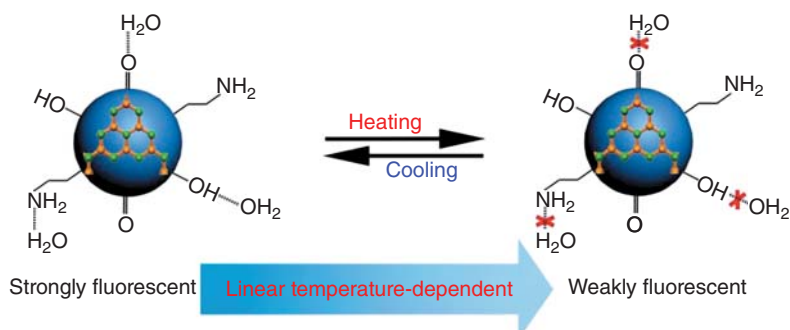


Figure 8.25 Schematic mechanism for the temperature-dependent fluorescence intensity of N-C-dots [172]. Source: Reprinted with permission from RSC publishers, Copyright 2014.

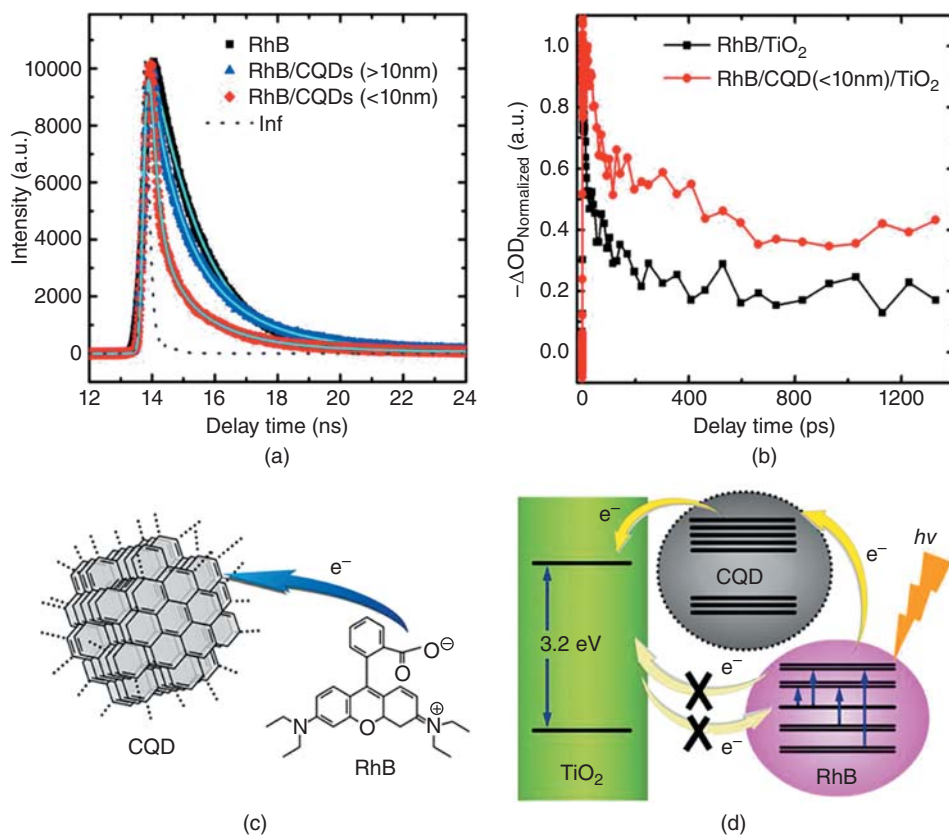


Figure 8.26 (a) Photoluminescence quenching of RhB and RhB/C-dots complex measured by time-correlated single photon counting (TCSPC) technique. (b) Ground-state bleaching recovery of RhB molecules in RhB/TiO₂ and RhB/C-dots/TiO₂ complex systems extracted from femtosecond transient absorption (TA) spectroscopy. (c) Scheme of electron transfer from RhB to C-dots. (d) C-dots serve as an electron transfer intermediary for bridging the photogenerated electrons and suppressing their recombination. In this figure, CQDs are C-dots [132]. Source: Reprinted with permission from American Chemical Society, Copyright 2013.

be explained by the special energy band structure of C-dots, which behaves as an electron blocking layer [174]. The size of the C-dots plays an important role in device performance, as shown by the open-circuit voltage (VOC) of the device increasing while the short-circuit current (JSC) decreases, with a decrease in size of C-dots. The quantum size effect accounts for the phenomenon that the heterojunction barrier increases with the decrease in size, and the barrier for hole transportation increases, resulting in an increase of VOC and decrease of JSC, respectively. In fact, to make the best of the photogenerated carriers, many approaches have been applied to facilitate the separation and to suppress the recombination of carriers. The interfaces between materials, layers and different units are very important for the enhancement of SCs. For example, ZnO nanorod arrays decorated with C-dots were prepared [175, 176]. Other kinds of solid-state solar cells have also been fabricated, combining inorganic quantum dots and C-dots [177, 178]. It turns out that facilitation of the charge propagation from C-dots and Förster resonance energy transfer improves the device performance greatly. All solutions processed by organic and dye-sensitized SCs can also benefit from the broad absorption, special band structure, and electron transportation ability of C-dots. Bao et al. fabricated a bulk heterojunction organic solar cell based on a composite layer of poly(3-hexylthiophene) (P3HT) and C-dots [179]. C-dots improved the charge transport through the active layer, and a photo-conversion efficiency of 1.28% was obtained; other groups have used such a structure without C₆₀ to fabricate organic solar cells [180, 181]. High VOC (1.6 V) and a conversion efficiency of about 1% can be obtained. Although the efficiency of these devices is still low compared with conventional organic solar cells, it is expected that C-dots can be promising alternatives to the expensive C₆₀ as electron acceptors.

C-dots were first applied in dye-sensitized solar cells (DSSCs) by Yan et al. [182]. However, limited efficiency was obtained, with a rather low current density of 200 $\mu\text{A cm}^{-2}$ because of the weak affinity between grapheme quantum dots (GQDs) and the TiO₂ surface. Such physical adsorption was detrimental to the charge injection due to the functionalization for covalent attaching and adjusting of band energy structure. A device with the same configuration was fabricated by employing nitrogen-doped C-dots (N-C-dots) [183]. In-situ hybridization of TiO₂ with C-dots, and a lowered work function induced by nitrogen doping, contribute to the improvement in device performance. A VOC of 0.46 V and a JSC of 0.69 mA cm^{-2} was obtained, with a conversion efficiency of 0.13%. Recently, DSSCs combined with dyes and C-dots (co-sensitizers) were fabricated and a high conversion efficiency was achieved [184, 185]. A type II alignment for TiO₂/C-dots/dye configuration was realized by tuning the electronic levels of C-dots, and such cascaded alignment of energy levels enhanced the charge separation and collection. Additionally, energy transfer from C-dots to dyes, because of the overlap between the PL of C-dots and absorption of dye, promotes the application of solar energy. Last but not the least, electron recombination to the redox couple is reduced because of the inhibition of the back-electron transfer to the electrolyte by the C-dots. Therefore, DSSCs exhibit an efficiency of 6.1%, higher than that of a device without C-dots by 19.6%. Organic/inorganic hybrid solar cells combined with metal oxides and organic semiconductors have also got the attention of researchers, while it remains a challenge to match the energy levels of the donor–acceptor system. Qin et al. demonstrated the insertion of C-dots in organic/inorganic layers or combination with organic semiconductors, which led to an enhancement of the power conversion efficiency (see Figure 8.27) [186, 187].

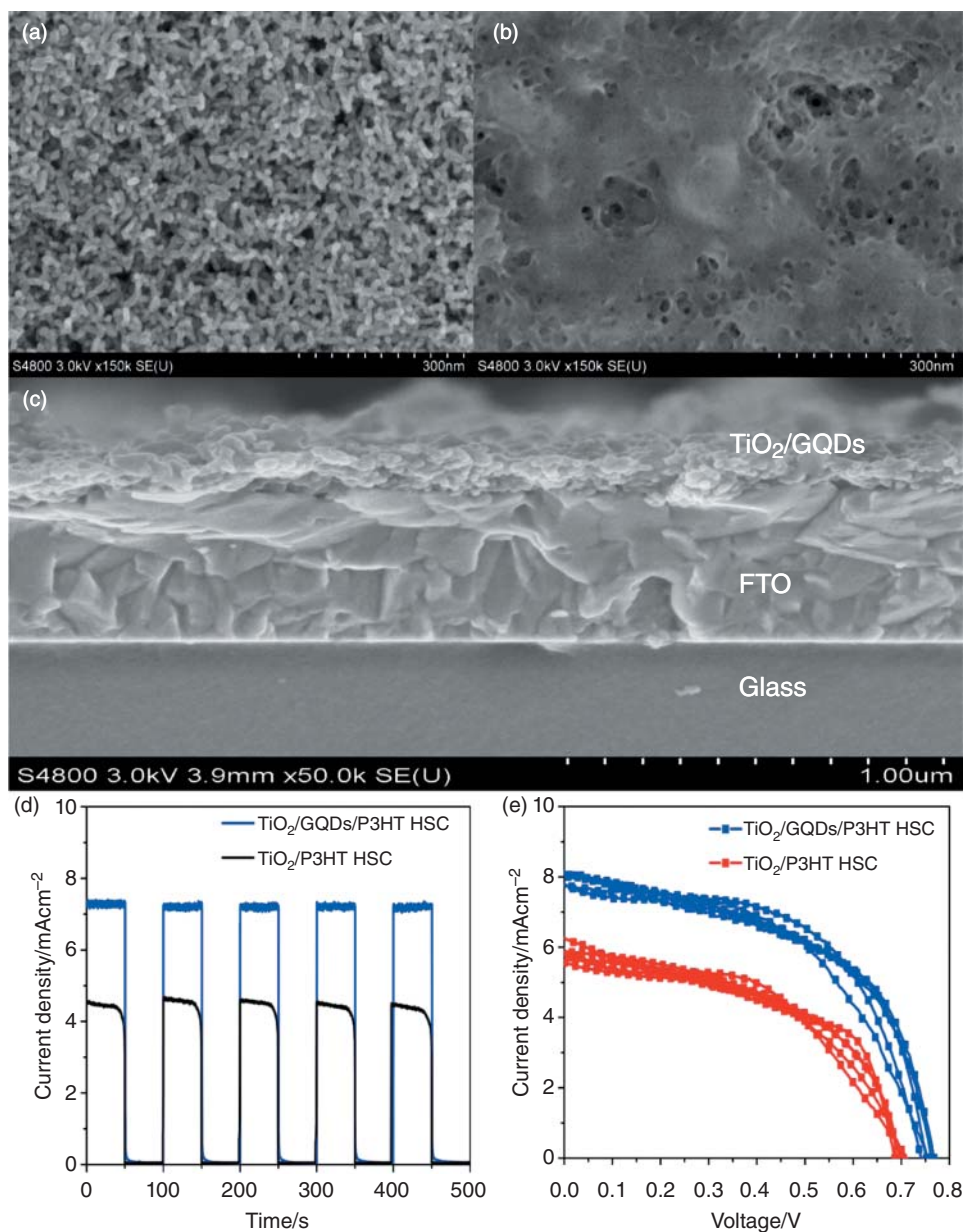


Figure 8.27 SEM images of TiO_2 (a) and $\text{TiO}_2/\text{C-dots}$ (b). (c) Cross-sectional SEM image of $\text{TiO}_2/\text{C-dots}$ blend film. (d) On-off switches by illuminating (100 mW cm^{-2}) and darkening (0 mW cm^{-2}). (e) $J-V$ curves of the HSCs with and without C-dots. In this figure, GQDs are C-dots [186]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

Huang et al. developed a conceptual device by employing poly-(3-hexylthiophene) (P3HT)/C-dots as electron donors/acceptors [188]. Wang et al. demonstrated that, in solution-processed small-molecule bulk-heterojunction solar cells, the C-dots improved light absorption and effective charge conduction, and then led to high-efficiency, solution-processed, small-molecule solar cells [189]. Zhu et al. reported a power conversion efficiency improvement of perovskite solar cells from 8.81% to 10.15% due to insertion of a C-dots layer between perovskite and TiO_2 [190]. Pan et al. prepared C-dots/p-type CuAlO_2 /n-type ZnO photoelectric bilayer film composites [191]. The enhancement of the photoconductivity was mainly attributed to C-dots with a unique upconverted PL behavior. In addition, the p–n junction structure and C-dots with the ability to accept electrons could help to separate the photogenerated electron–hole pairs to increase the carrier concentration further [191]. When C-dots were also introduced into active layers of polymer solar cells, the performance of doped devices obtained by Liu et al. was apparently improved, and the highest power conversion efficiency of 7.05% was obtained, corresponding to a 28.2% enhancement compared with that of the contrast device [187]. C-dots were demonstrated by Li et al. to be excellent hole transport layers in both polymer solar cells and small-molecule solar cells [192].

8.7 Application in Supercapacitors and Lithium-Ion Batteries

For the application of C-dots in supercapacitors, Hu et al. deposited C-dots onto aligned CNTs by an electrical method [193]. A capacitance of 44 mF cm^{-2} was obtained, exhibiting a more than 200% improvement over that of bare CNT electrodes. Considering the formation of micropores between C-dots and CNT scaffolds and neighboring C-dots, here the authors referenced the electric double-cylinder capacitor model [194]. Such a structure facilitated the amount and transportation of ions, resulting in high capacitance and stability. Similarly, C-dots and other carbon porous structures, such as graphene [195] and three-dimensional aerogel [196], were applied. At least 100% improvement was obtained, thanks to the high specific surface area and easy access and diffusion of ions. While capacitors used in the workplace may have higher energy, micro-supercapacitors applied in portable electronics are studied. A C-dot-based symmetric micro-supercapacitor was first prepared by Liu et al., using a simple electrodeposition method on interdigital gold electrodes [197]. The devices exhibited superior rate capability (1000 V s^{-1}) and excellent power response with a very short relaxation time constant in both aqueous and ion liquid electrolytes. A capability of 97.8% of its initial specific capacitance after 5000 cycles was obtained. Then an asymmetric device employing a conductive polymer, PANI, was prepared using a similar method [198]. First of all, PANI nanofibers were prepared through an electrochemical method, and then C-dots were electrodeposited on aligned PANI fibers. Such devices employing PANI and C-dots as the positive and negative active materials also show high rate capability and a short relaxation time constant of 115.9 ms. Compared with double layer capacitors, pseudocapacitors associated with redox reactions usually exhibit higher energy density. Clearly, a higher specific surface area and more atoms participating in the redox reactions will result in higher specific capacitance. Zhu et al. reported that a C-dots-decorated RuO_2 network exhibited a specific capacitance

of 460 Fg^{-1} and excellent rate capability [199]. Hassan et al. developed a simple and effective strategy using ultrasonication and chemical activation to generate activated C-dots with enriched edges, which showed PL similar in origin to their non-activated counterparts but distinctive in their higher intensity [200].

For the application of C-dots in lithium-ion batteries (LIBs), Zhu et al. have synthesized CuO/Cu/C-dots tri-axial nanowire arrays [201]. This is the first report of the application of C-dots in LIBs. The soft protection of C-dots showed greatly increased surface conductivity and the stability of a nanowire array structure. Compared with CuO/Cu composite structure, the triaxial nanowire electrodes achieved high initial coulombic efficiency (87%) and superior retention capability (high retention after 1000 cycles). The current collector, copper foam, also provided good conductivity for electrons because no binder was used. This method is suitable for the improvement of performance in other less stable materials such as VO_2 . C-dot-coated VO_2 arrays were fabricated via a similar method by the same research group [202]. The effect of C-dots is similar to that in supercapacitors, separating VO_2 nanobelts from each other and avoiding the agglomeration as well as minimizing the dissolution of active materials. The LIBs based on the above electrodes exhibit about 99% initial coulombic efficiency and 100% during the following cycles, and 36% capacitance is retained when the current density is increased from $1/3 \text{ C}$ to 120 C . Incredibly, such a structure delivers a retention of 94% of the original capacity after 1500 cycles at 60 C (see Figure 8.28). Jing et al. also demonstrated the fabrication of C-dot-coated Mn_3O_4 composite by a green alternating voltage electrochemical approach. The as-produced $\text{Mn}_3\text{O}_4/\text{C}$ -dots composite, utilized as an anode material for LIBs, demonstrates excellent electrochemical performance, showing an enhanced reversible discharge capacity of 934 mA h g^{-1} after 50 cycles at a current density of 100 mA g^{-1} , which is almost five times as much as that of pure Mn_3O_4 [203].

8.8 C-Dots Nanocomposite for Efficient Lubrication

Mechanical wear accounts for a third of present global energy consumption. Yet it still lacks an efficient lubricant to achieve simultaneous highly efficient lubrication and metal wear repair [204–207]. Huang et al. reported that the C-dots/ CuS_x nanocomposites show enhanced lubrication and worn metal surface repair abilities when used as additives [208]. They reported a simple method to obtain the C-dots/ CuS_x nanocomposites on a large-scale (about 250 g h^{-1}). The obtained C-dots/ CuS_x nanocomposites were uniform and monodisperse with a diameter of approximately 20 nm. C-dots possess a graphite-like multilayer structure, which can improve lubrication performance, while CuS_x with noninteger ratios exhibits high chemical activity (easy to form $\text{CuFe}_y\text{S}_{x-y}$ alloy with Fe) in oil. The antiwear properties of C-dots/ CuS_x nanocomposites in liquid paraffin (as additive) were evaluated with a four-ball machine at ambient conditions. The wear scar volume significantly decreased with an increase in the C-dots/ CuS_x nanocomposites. It indicates that C-dots/ CuS_x nanocomposites have significant antiwear effects as lubrication additives, which may be closely related to their small size, low melting point, and high reactivity [208]. The high oil solubility and stability of C-dots/ CuS_x nanocomposites in liquid paraffin can be readily transferred onto the contact zone of rubbing steel surfaces and deposited there to form a surface protective and lubricant layer, resulting in a reduced friction coefficient. Further experiments were carried out; the C-dots/ CuS_x

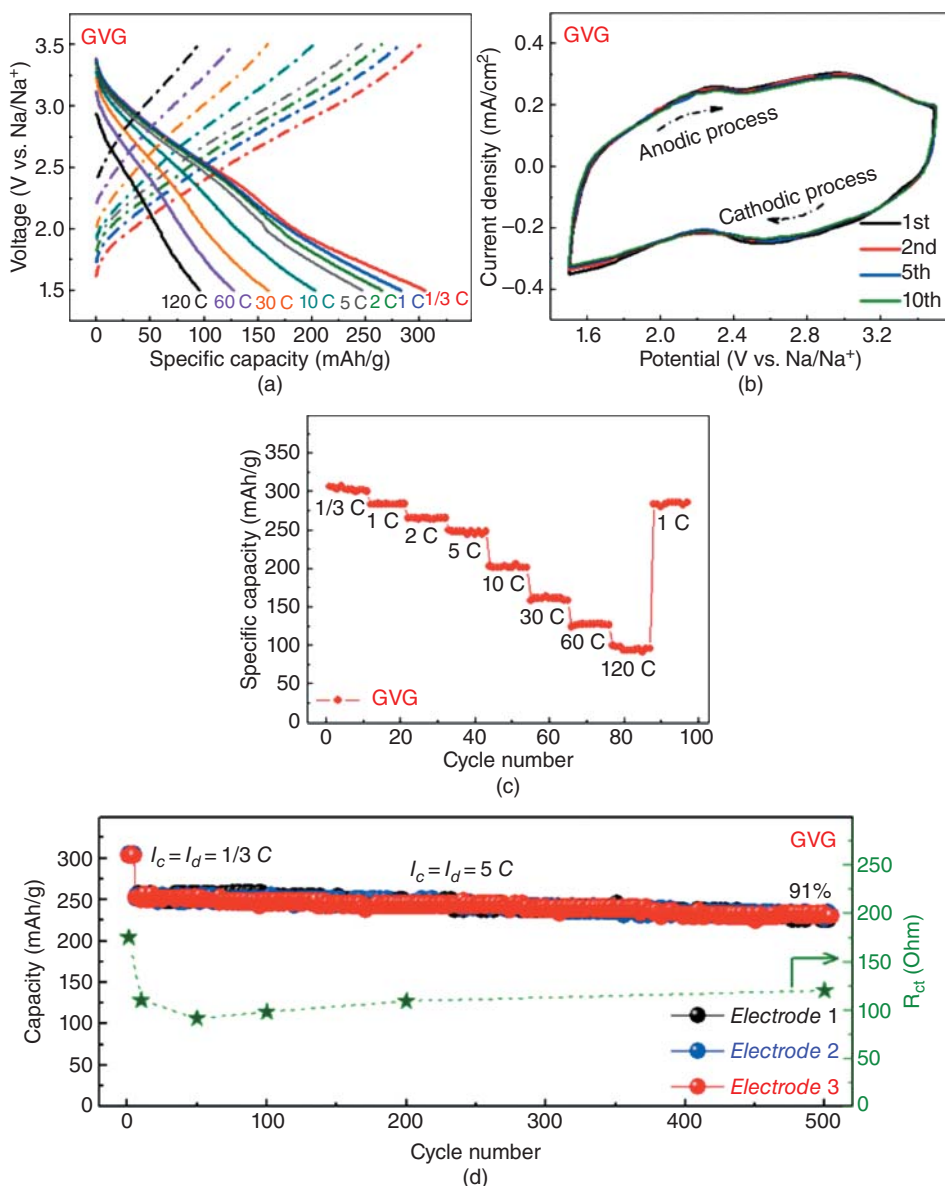


Figure 8.28 (a) Charge–discharge curves at different C rates ($1\text{ C} = 300\text{ mA g}^{-1}$). (b) CV curves at a scan rate of 0.3 mV s^{-1} . (c) Rate tolerance performance of the GVG electrode. (d) Cycling performance of three different GVG electrodes at 5 C for 500 cycles. The R_{ct} as a function of cycle number is also shown. (e) AC impedance plots at full-charge state after different cycles. The resistance is simulated using the same equivalent circuit $R_s(Q(R_{ct}Z_W))$ (inset in panel e) as used in LIBs. (f) Cycling performance of three different electrodes at 60 C for 1500 cycles ($1/3\text{ C}$ at first five cycles for activation). (g) Ragone plot based on the total mass of the whole electrode; the sloping lines indicate the relative time to get the charge in or out of the electrodes [202]. Source: Reprinted with permission from American Chemical Society, Copyright 2015.

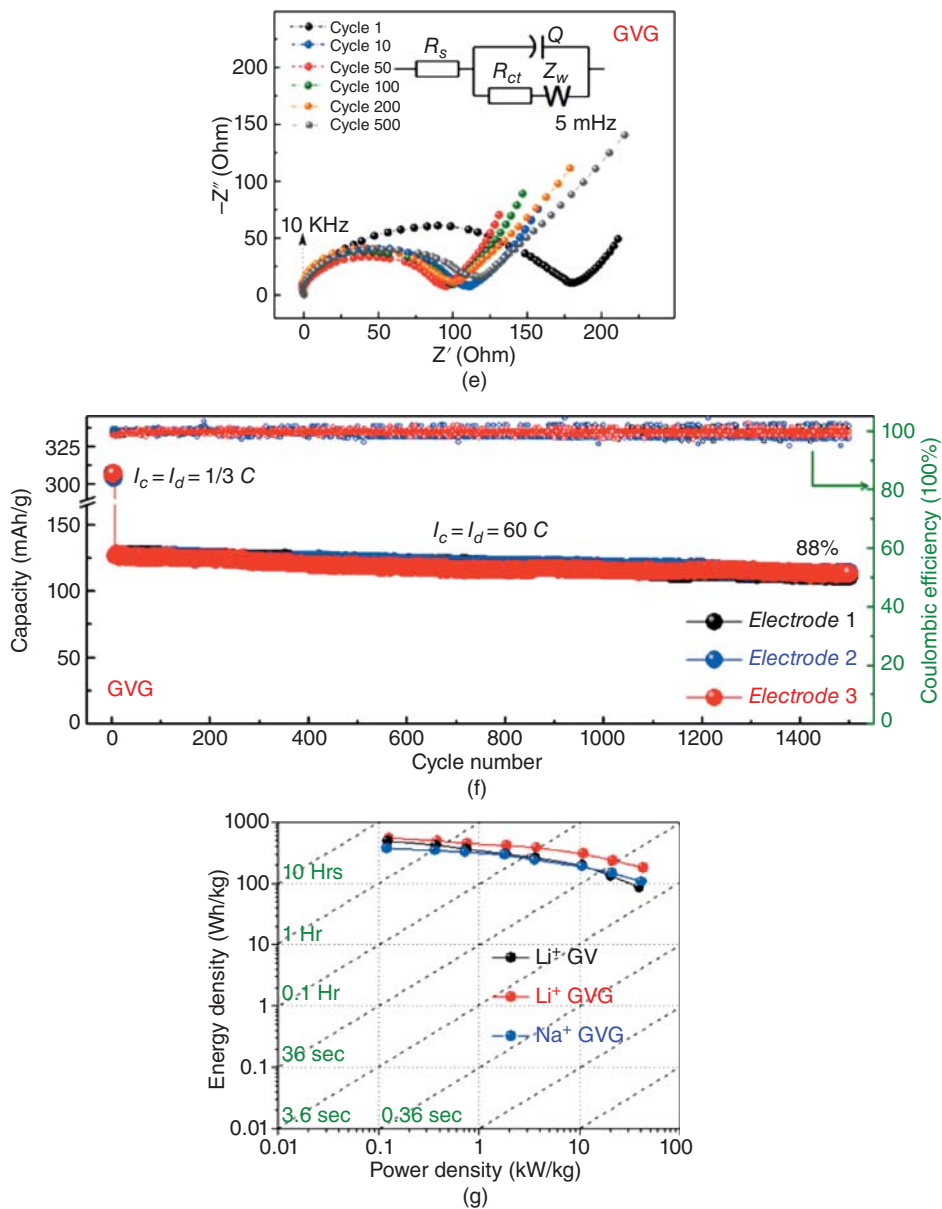


Figure 8.28 (Continued)

nanocomposites were loaded onto the surface of metal plates, and then these two metal plates underwent high-speed relative rotation. The worn surfaces analysis suggested that the Cu and S elements could uniformly append onto the surface of frictional couple of the carbon steel, which confirmed that C-dots/CuS_x nanocomposites could efficiently achieve the repair of a worn surface. The C-dots/CuS_x nanocomposites could efficiently combine with the substrate to form bonding and alloys, which was the key to enhanced

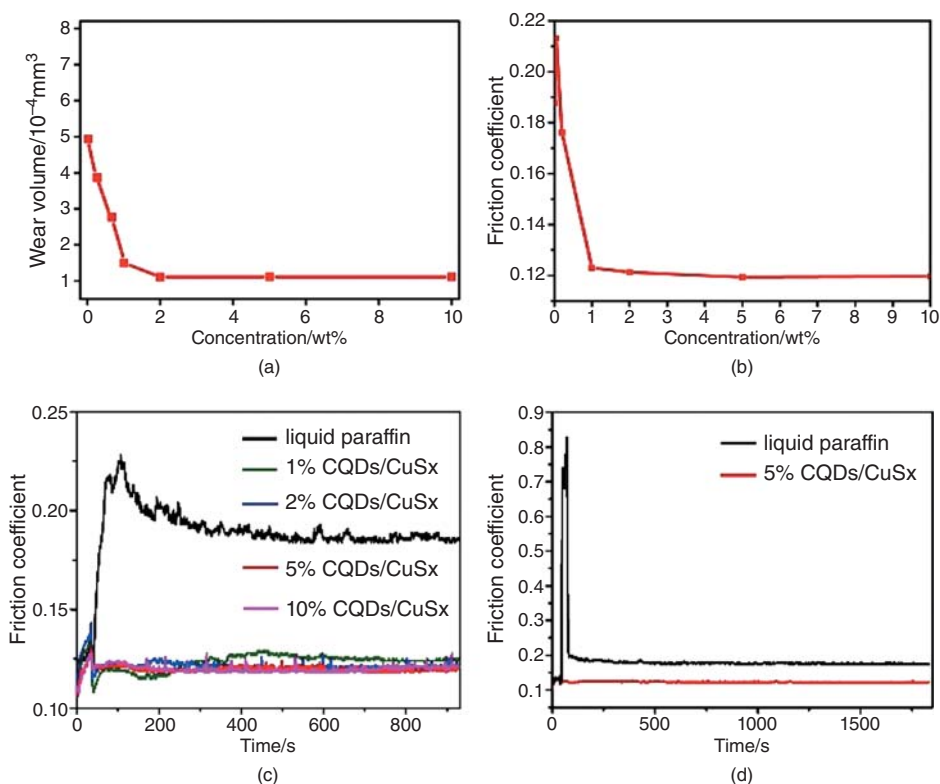


Figure 8.29 The variation of wear scar volume (a) and friction coefficient (b) with different contents of C-dots/CuS_x nanocomposites in liquid paraffin (four-ball, 100 N, 1450 rpm, and 15 minutes). (c) The relationship between friction coefficient and friction time (920 seconds) using C-dots/CuS_x nanocomposites with different contents (1, 2, 5, and 10 wt%) and liquid paraffin as additives (four-ball, 100 N, 1450 rpm, and 15 minutes). (d) The relationship between friction coefficient versus friction time (1850 seconds) with 5 wt% C-dots/CuS_x nanocomposites and liquid paraffin as additives (four-ball, 100 N, 1450 rpm). In this figure, CQDs are C-dots [208]. Source: Reprinted with permission from RSC publishers, Copyright 2015.

lubrication and restoration of strength in damaged areas. As stated by the authors, the CuS_x with a noninteger ratio exhibits high chemical activity, forming CuFe_yS_{x-y} alloys with Fe in oil easily [208]. More tests indicated that the C-dots/CuS_x nanocomposites not only enhanced the precision of machine tools, but could also repair them, thus prolonging the service life and reducing the cost. The C-dots/CuS_x nanocomposites showed distinct improvement in the engine repair test (Figure 8.29).

8.9 Outlook

In this chapter we have described the recent advances in the research on C-dots, focusing on their synthesis, properties, nanocomposites, and applications in catalysis, environmental and new energy. A variety of synthesis techniques already exist for producing C-dots of different characteristics. In the future, we expect the advent of

simpler and more robust synthetic routes and creative applications to better realize the potential of the increasingly important C-dot materials. New properties (such as fresh phosphorescence and upconverted PL), and how to tune these properties, are also challengeable for its ambiguous luminescent mechanism. The amorphous to nearly crystalline internal structure, nonquantitative surface structure and virtual size polydispersion may impede investigation of the luminescence mechanism. This problem will be solved through accurate synthesis, careful analysis, and intelligent consideration. C-dots as photocatalysts represent an attractive approach in the development of green chemistry, which may eventually lessen the burden of energy consumption, product cleanup and waste disposal. The immediate goal in this emerging area should be geared toward the discovery of photochemical solutions for increasingly ambitious synthetic goals. The long-term goals should be to improve efficiency and synthetic utility, and eventually to perform chemical synthesis under sunlight. Compared with other applications of C-dots, there have been fewer studies in the usability of C-dots as electrocatalysts for ORR and OER. In-depth theoretical and experimental studies are needed to delicately design C-dots-based electrocatalysts with desirable electrocatalytic activity and long-term operational stability. The combination of C-dot doping and C-dots-based nanocomposites with other nanomaterials may open up new avenues to systematically study the effects of structural parameters and chemical compositions on the catalytic performance of the electrocatalysts, thus leading to fundamental insights and practical applications. The potential of C-dots in the storage and transport of electrons impacted by light has yet to be exploited fully. C-dots also stand to have a huge impact in biosensing, environmental and energy applications. Their optical properties, such as tuning of emission colors, high quantum yield, and lack of blinking, enable them to be used in the development of nanosensors with high sensitivity. Engineering the surface chemistry, properties and functionalization of C-dots also provides a lot of scope for them to be incorporated into imaging and sensing. Research into the detection of toxic elements present in the environment by C-dots is also underway, relying on their energy-transfer capability. Their biocompatible nature allows them to be used in the analysis of biological samples and also in wastewater treatment, to deal with toxic chemicals. By surface and bandgap modification of C-dots via functionalization, we can expect to design novel functional systems from C-dots for green chemistry and energy issues. Carefully designed C-dots composites have the potential to expand the capabilities of next-generation energy storage and photovoltaic devices and sensors. The unique photoinduced electron transfer ability, as well as excellent light harvesting capability, makes C-dots an exceptional candidate for photovoltaic applications. Use of C-dots in optoelectronics is also of primary interest, as the production will be high and also cost-effective. Electronic devices like light-emitting diodes can be produced with improved brightness. Light energy conversion is also possible with C-dot solutions, which makes them a promising candidate for use in photovoltaic systems.

In the future, carbon dots will definitely brighten the lives of humans by paving the way to simplified bioimaging techniques, drug delivery systems, efficient optoelectronics, photovoltaic systems, optical sensors, and detectors. As this is a very new field, there is a lot of space for new discoveries, and much exploration is still needed. We believe that new physical and chemical properties will be found, and new applications and devices will be invented. As time progresses, many challenges might be faced, and at the same time lead to many more advantages which will help achieve a better future.

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