

Majid Hosseini
Ioannis Karapanagiotis *Editors*

Materials with Extreme Wetting Properties

Methods and Emerging Industrial
Applications



Springer

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ISBN 978-3-030-59564-7

ISBN 978-3-030-59565-4 (eBook)

<https://doi.org/10.1007/978-3-030-59565-4>

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The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

This book aims at identifying novel advanced materials of extreme wetting properties (MEWP) for practical, industrial applications. The state-of-the art superhydrophobic, superhydrophilic, superoleophobic, superoleophilic, and superomniphobic materials, which are MEWP, with respect to their technological and emerging industrial applications are discussed in this book. MEWP offer new perspectives providing numerous potential applications. Biomimetics, super-hydrophobic/oleophobic, and water/oil-repellent surfaces can be used, for instance, in automobiles, ships and aircrafts, microelectronics, textiles, biomedical devices and implants, devices in renewable energy systems, construction sites and buildings, and in other applications relevant to self-cleaning, friction reduction, oil–water separation, water harvesting and desalination, drug delivery, anti-icing, anti-corrosion, and anti-bacterial methods. Hence, these advanced MEWP have the potential to lead to a new generation of products and devices with unique properties and functionalities. Despite the large scientific progress on MEWP, there are still some obstacles which have to be solved to make these materials available for real-life applications. For example, the durability of the surfaces of MEWP is clearly a main obstacle. Recent advances on the production strategies of MEWP have improved their durability and sustainability, thus offering the possibility for industrial exploitation. MEWP with wettabilities ranging from superhydrophobicity to superhydrophilicity provide promising avenues for several important applications, which sometimes are crucial for humankind, for example, water harvesting. In principle, MEWP can improve the capacity of fog catchers and membranes. Friction reduction and antifouling are crucial issues for maritime transport. Blood-repellent surfaces can become extremely useful in medicine. Self-cleaning surfaces are useful for textiles, buildings (and windows), automobiles, and essentially for any surface exposed to the outside conditions, including solar panel surfaces. Anti-icing materials can have an enormous impact in aerospace and wind power industry. Microfluidics and microelectronics devices can benefit from biomimetics materials with tuned wetting properties. This book discusses the aforementioned potential applications of MEWP, along with the large variety of other potential applications of MEWP, thus providing new ideas to scientists and engineers for further exploitation of these novel materials. Moreover,

the entire spectrum of recent technological developments, current research progress, most advanced methodologies, future outlook, and modern trends in the applications of MEWP are discussed in a consistent approach.

Chapter “[Superhydrophobic Textiles Using Nanoparticles](#)” presents a brief review of methods devised to impart superhydrophobicity to textiles using nanoparticles, combined with other materials, as hydrophobing agents. This chapter also discusses superhydrophobic textiles that show simultaneously superoleophobicity and/or anti-microbial/bacterial activity and highlights important properties influencing the textile industry (e.g., durability, transparency, UV-shielding, and air permeability). Finally, the application of treated textiles with extreme wetting properties in water cleaning and harvesting is also highlighted in this chapter.

Chapter “[Self-Recovery Superhydrophobic Surfaces](#)” provides an overview of the progress of self-recovery superhydrophobic surfaces, with a particular focus on the status of current fabrication processes and possible applications. It then continues by introducing certain applications of superhydrophobic surfaces processing enhanced durability. In addition, an outlook on future fabrication techniques for creating robust and durable superhydrophobic surfaces is presented in this chapter.

Chapter “[Structured Surfaces with Engineered Wettability: Fundamentals, Industrial Applications, and Challenges for Commercialization](#)” discusses recent developments in wettability-engineered surfaces for industrial applications, focusing on their different strategies or methods and unique competitive advantages, along with their current or future markets. This chapter also highlights the main technological challenges for commercialization of the wettability-control technologies. Moreover, the fundamentals of engineered wettability for its classification, control, and fabrication are summarized in this chapter.

Chapter “[Superhydrophobic Polymer/Nanoparticle Hybrids](#)” describes the role of various polymers and nanoparticles that are adopted to achieve superhydrophobicity and their wider usage in various applications. This chapter also highlights the role of natural and bio-polymers, synthetic polymers, and conducting polymers as well as various metal nanoparticles to prepare organic-inorganic hybrid materials used for superhydrophobic coatings. The chapter discusses the advantages of polymer/nanoparticle hybrids for superhydrophobic coatings as properties of both polymers and nanoparticles are present in a single body. Additionally, obtaining durable, stable, and robust surface properties by using the polymer/nanoparticle composite coatings on a wide variety of substrates is discussed. Finally, this chapter has considered various monomers and polymers for the development of stable superhydrophobic surfaces.

Chapter “[Nanoengineered Surfaces as a Tool Against Bacterial Biofilm Formation](#)” focuses on approaches based on nanoengineered abiotic surfaces with the aim of hindering or preventing biofilm-associated bacterial infections. Due to the difficulty associated with bacterial biofilm eradication, the development of approaches based on inhibition of biofilm formation is impactful and relevant. The chapter discusses strategies for the production of new materials with minimal bacteria-substrate contact area, considering adhesion stage as the target of these approaches and the fact that the contact area is a key factor. Moreover, the chapter

highlights superhydrophobic materials as attractive materials due to their micro- and nanodomains achieved through nanoengineering processes.

Chapter “[Non-fluorinated Superhydrophobic Surfaces: A New Scenario for Sustainable Applications](#)” deals with challenges and opportunities of non-fluorinated superhydrophobic surfaces (nFSHS) that might be considered in various applications such as oil–water separation (and their stabilized emulsions) or as a corrosion barrier in metallic surfaces. The chapter also discusses non-fluorinated superhydrophobic surfaces that may contribute to a new generation of high-performance functionalized coatings with sustainable synthesis and treatment strategies. The authors discuss different strategies for producing nFSHS, considering environmental and sustainable concepts such as environmentally friendly reactants or methods, the durability of nFSHS in front of abrasion, as well as their environmental applications such as oil–water separation and corrosion prevention.

Chapter “[Hydrophobized Granular Materials for Ground Infrastructure](#)” reviews recent research on hydrophobized granular materials for ground infrastructure including sample preparation, characterization, properties, and applications of hydrophobized granular materials. This chapter also discusses the specific challenges associated with the different methods of synthesizing granular materials to achieve the desired level of hydrophobicity, their eventual characterizations, as well as their engineering properties. The hydrophobization of soils allows for a more sustainable approach to be used in ground infrastructure. Moreover, the chapter provides a theoretical background and methods, as relevant to granular materials, reviews the physical and chemical properties of hydrophobic coatings as well as the hydraulic and mechanical properties of hydrophobized coated particles, and addresses some constraints of these new materials (durability) and potential applications in infrastructure (slopes).

Chapter “[Superhydrophobic Metal Surface](#)” highlights different synthesis techniques of superhydrophobic coatings for metallic bodies and fabrication process of superhydrophobic metal surfaces, their properties, and applications. The chapter also discusses different long-term problems associated with metal surfaces such as corrosion, icing, the reasons behind these problems, and different traditional methods used to overcome these problems and their limitations. The authors also provide information about different models on superhydrophobicity and the factors that are essential for development of artificial superhydrophobic metal surfaces. Finally, this chapter gives a brief discussion about the various techniques that have been reported for the synthesis of superhydrophobic metal surfaces and their unique properties in multiple fields.

Chapter “[Extreme Wetting Properties of Liquid Metal](#)” presents gallium/indium-based liquid metal, a kind of newly emerging functional metal materials with fluid state at room temperature. The authors highlight many complex functionalities of gallium/indium-based liquid metal such as special wettability, unconventional maneuverability, excellent fluid mechanics performance, and robust electrical conductivity. The authors also systematically interpret the mechanisms and applications of liquid metal enabled from wettability. The chapter also emphasizes the surface/

interfacial characteristics and the motion under stimulation, which is believed to have uncovered a new conception of transformable metal.

This chapter suggests that inspired by its special wettability, liquid metal droplet is driven in solution and transforms in atmosphere environment. The authors also review the application of liquid metal in printing electronics, as its wettability is changed and the form is transferred from liquid state into semisolid state by oxidation, foreign metal doping, buffer materials, and so on, which is easily printed on various base materials surfaces. The chapter emphasizes that by adjusting the wettability, liquid metal could fulfill many other special functions.

Chapter “[Superhydrophobic and Self-Cleaning Coatings for the Protection of the Cultural Heritage: A Case Study Using TiO₂ Nanoparticles](#)” discusses concepts of superhydrophobicity and self-cleaning induced by photocatalysis and reviews some crucial aspects related to the wettability of solid surfaces. It also gives a brief overview of the use of superhydrophobic and photocatalytic nanomaterials for the protection of cultural heritage. The chapter also presents a case study using TiO₂ nanoparticles. The chapter suggests that the useful properties of TiO₂ nanoparticles can lead to the production of very effective products for the conservation of natural stone.

Chapter “[Hydrophobic Carbon Soot Nanostructure Effect on the Coatings](#)” presents the effects of hydrophobic soot nanostructure on a coating. In particular, a one-component polyurethane air-drying system was stirred with 646 solvent at 20 °C using a pulsed ultrasonic mixer. Then, the dispersed hydrophobic carbon soot contained in the resulting mixture led to the formation of a hydrophobic coating, which possessed thixotropic properties, normal dispersion, and adhesion ability for different surfaces such as paper, metal, wood, and tile. The authors have synthesized nanostructure of soot using an isobutene-propane-butane combustion mixture with an application of 1 kilovolt (kV) electric field to the chamber. The chapter shows that the addition of carbon soot to the coating improved the hydrophobicity of wood, tile, metal, and paper surfaces. The authors also report that the mixing of polyurethane with hydrophobic soot in an ultrasonic homogenizer resulted in obtaining two hydrophobic coatings: coating-2 and coating-3. These coatings had good thixotropic properties which make the application of paint on wood, tile, paper, and metal surfaces efficient.

Chapter “[Laser Surface Engineering for Boiling Heat Transfer Applications](#)” demonstrates how nucleate boiling enhancement can be achieved on surfaces with various wetting properties and specific micro/nano topographical features, fabricated using a straightforward, robust, and scalable laser texturing approach. The chapter discusses the basics of nucleate boiling and how it is affected by surface wettability, provides a fundamental background of laser surface engineering and its ability to achieve extreme wetting properties, and finally demonstrates the applicability of the laser-textured surfaces in enhancing and controlling nucleate pool boiling of different fluids. In other words, this chapter introduces direct laser texturing as an emerging technology to produce surfaces with different wetting properties and

morphological features. The chapter also explains how laser surface engineering can be used to decrease the influence of the surface wettability on the key boiling heat transfer parameters and – in this way – to ensure a more stable heat transfer process by utilizing functionalized surfaces. With an emphasis on the results obtained by the authors, the capabilities of surfaces functionalized by nanosecond-laser pulses to enhance saturated nucleate pool boiling with water and other fluids are demonstrated in this chapter.

Chapter “[Optimal Design of Flexible Micro Multi-level Topographies for Enhancing Durability of Superhydrophobic and Icephobic Functions](#)” presents a novel principle for designing robust and stable micro-/nano-structured surface for preventing stress concentration in the loading test. The chapter discusses the role of durability as one of the most significant parameters for the application of superhydrophobic and icephobic materials: having a favorable mechanical property of micro-/nano-topography is the key factor for robust superhydrophobicity, self-cleaning, and anti-icing property. Based on the earlier discussions, the authors highlight several factors for enhancing the durability of topography and maintaining functions, that is, flexibility, the shape and size of micro-topography, and multi-level. Furthermore, it is stated that the optimal design of flexible micro multi-level topographies could transform themselves under loading, which not only reduces the stress concentration, but also enhances the flexibility and self-recovery property. This provides a new strategy for designing reliable mechanics models in different systems.

Chapter “[Superhydrophobic Coatings for Marine Corrosion Protection](#)” deals with superhydrophobic coatings for inhibiting corrosion from marine atmosphere and seawater environment. The chapter proposes to set the standard for evaluating superhydrophobic coatings to propel their practical usage for corrosion inhibition. Moreover, the upgrading strategy is also proposed in this chapter for developing the further versatile coating for corrosion inhibition.

Chapter “[Investigation of Conditions for the Creation of Hydrophobic Sand](#)” presents a method for producing hydrophobic sand using silicone waste. In particular, the authors study the conditions for the formation of a water-repellent coating on the sand surface and the properties of the hydrophobic sand. The latter was produced using a hydrophobic agent which was obtained by the combustion of silicone waste. The obtained sand does not sink, but floats on water surface. Experiments demonstrated the ability of hydrophobic sand to not let water percolate, which enables it to be applied for preventing irrigation water from entering the lower soil layers and to separate the soil from saline groundwater. According to the authors, it was experimentally established that the suitable conditions for the creation of hydrophobic sand are met by the following: mixtures of the hydrophobic agent and sand in ratios of 1:100; 1.5:100; 2:100; and 3:100 were suitable for the creation of hydrophobic sand. The tests showed that the created sand remains absolutely dry for a long time without losing its hydrophobic properties over a period of months.

Finally, a number of people have helped make this book possible. We hereby acknowledge Ms. Anita Lekhwani, our executive editor at Springer Nature; Mr. Brian Halm, our project coordinator at Springer Nature; Mr. Michael Luby, our senior publishing editor at Springer Nature; Mrs. Sowmya Thodur, our production editor from SPi Global; Mrs. Shina Harshavaardhan, our project coordinator from SPi Global; Ms. Priyadharshini Natarajan, our project manager from SPi Global; Ms. Megan Rohm; and all contributors and reviewers; this book could not have been written without their contributions and support. We thank you all for the excellent work and assistance provided in moving this book project forward.

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About This Book

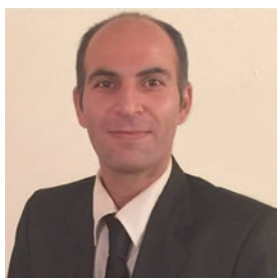
This book aims at identifying novel advanced materials of extreme wetting properties (MEWP) for practical, industrial applications. The state-of-the art superhydrophobic, superhydrophilic, superoleophobic, superoleophilic, and superomniphobic materials, which are MEWP, with respect to their technological and emerging industrial applications are discussed in this book. MEWP offer new perspectives providing numerous potential applications. Hence, these advanced MEWP have the potential to lead to a new generation of products and devices with unique properties and functionalities. Despite the large scientific progress on MEWP, there are still some obstacles which have to be solved to make these materials available for real-life applications. Recent advances on the production strategies, including methods and materials, of MEWP have shown that the durability and sustainability obstacles can be addressed, thus offering the possibility for industrial exploitation. MEWP with wettabilities ranging from superhydrophobicity to superhydrophilicity provide promising avenues for several important applications, which sometimes are crucial for humankind. This book also discusses a large variety of other potential applications of MEWP, thus providing new ideas to scientists and engineers for further exploitation of these novel materials. Moreover, the entire spectrum of recent technological developments, current research progress, future outlook, and modern trends in the applications of MEWP are discussed in a consistent approach.

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Superhydrophobic Textiles Using Nanoparticles



Ioannis Karapanagiotis and Majid Hosseini

1 Introduction

The wettability of a solid surface (i.e., the interaction between the solid and liquid water) is influenced by (i) the intermolecular interactions among water, solid, and vapor and (ii) the surface roughness of the solid. The intermolecular interactions are summarized by the Young equation which defines the inherent hydrophilic or hydrophobic character of a solid based on the contact angle (CA_Y) of a water drop on the smooth surface of the solid [1]: hydrophilic and hydrophobic surfaces correspond to $CA_Y < 90^\circ$ and $CA_Y > 90^\circ$, respectively. It is noteworthy, however, that recent reports suggested that 65° is a more appropriate critical value to define hydrophobicity and hydrophilicity [2, 3]. The significant effect of the solid surface's roughness on the measured, apparent CA has been recognized and described by Wenzel [4] as well as Cassie and Baxter [5]. The Wenzel model predicts that surface roughness can lead to complete wetting (superhydrophilicity, $CA < 5^\circ$) or non-wetting (superhydrophobicity, $CA > 150^\circ$) state for solids with $CA_Y < 90^\circ$ and $CA_Y > 90^\circ$, respectively. According to the Cassie-Baxter model, surface roughness promotes only the hydrophobic character of a surface.

CA describes the contact of a water drop at equilibrium with a horizontal surface. The contact angle hysteresis (CAH), defined as the difference between the advancing contact angle (ACA) and the receding contact angle (RCA), is related to the force needed to start a drop moving over the surface [6]. Small CAH implies that a

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water drop moves easily on the surface, which is therefore considered as a water-repellent surface [7]. Consequently, when this surface is slightly tilted the drop rolls off, thus corresponding to small sliding angle (SA) and rolling angle (RA). In contrast, when water drop is pinned on a solid surface, then large CAH, SA, and RA are measured. For example, small and large CAH have been observed on the surfaces of the lotus leaf [8] and rose petal [9], respectively, whereas both biological surfaces exhibit superhydrophobicity corresponding to $CA > 150^\circ$. For non-reflective or macroscopically rough surfaces, the water shedding angle (WSA) was suggested as an alternative and more reliable technique to evaluate the wetting properties [10].

Superhydrophobicity ($CA > 150^\circ$) and water repellency ($CAH < 10^\circ$) are properties which are extremely useful for the textile industry. This interest is evident by relative articles published in the 1940s [11–13] and, more recently, by review articles which summarize methods to produce modified and non-wetting textiles and fabrics [14–19]. In principle, a textile surface is rough and hydrophilic. However, the inherent surface roughness of a textile is not enough to deliver superhydrophobicity which, moreover, should be typically promoted by a hydrophobization procedure. A widely adopted strategy to enhance the roughness of a surface is to deposit nanoparticles onto the surface. Hydrophilic nanoparticles and functionalized hydrophobic nanoparticles usually mixed with hydrophobic agents have been extensively used for textile treatment, as described in the present review.

The objective of this chapter is to provide an overview of the major methods suggested in the past to impart superhydrophobicity to textiles using nanoparticles. Superhydrophobicity is sometimes accompanied by superoleophobicity and/or antimicrobial/bacterial activity. As these two properties are extremely useful for the textile industry, the corresponding methods are reviewed in separate sections, that is, Sects. 3 and 4. Moreover, textiles with extreme wetting properties were often designed to be used as membranes for water-oil separation. These methods are discussed in Sect. 5. Finally, other properties which are reported by the reviewed literature and are important for practical applications (e.g., durability, transparency, UV shielding, air permeability, etc.) are mentioned in this discussion. It is stressed that reports which focus exclusively on textiles and fabrics are included in the present review. Consequently, nanoparticle-based methods which have been developed to achieve superhydrophobicity on model-glass and other surfaces and have the potential to be used for textile treatment are not reviewed herein.

2 Superhydrophobic Textiles

The important results achieved in literature, which is described next, are summarized in Table 1. The fundamental property of interest is superhydrophobicity which was induced to textiles by nanoparticle-based coatings. The type and the size of nanoparticles which were used to treat the textiles are provided in Table 1. In some reports, the sizes of the nanoparticles are not described. In most of these reports, nanoparticles were produced via chemical reactions and deposited in situ on the

Table 1 Nanoparticles and other materials which were used to coat various textiles and to induce superhydrophobicity (SH). Other properties which were evaluated according to relative tests are indicated as follows: *DUR* durability, *TRA* transparency, *UVS* UV shielding, *APE* air permeability

Particle (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	Others	Ref.
SiO ₂	Poly(glycidyl methacrylate) and poly(styrene- <i>b</i> -(ethylene-co-butylene)- <i>b</i> -styrene)	Polyester	✓		[20]
CaCO ₃ (100 nm–200 nm), Ag (52–105 nm) with grafted PS, SiO ₂ (50–150 nm) with grafted PS	- For CaCO ₃ : poly(styrene- <i>b</i> -(ethylene-co-butylene)- <i>b</i> -styrene) - For Ag and SiO ₂ : poly(glycidyl methacrylate) and poly(2-vinylpyridine) matrix	Polyester	✓		[21]
SiO ₂ (50–150 nm)	TEOS and tridecafluorooctyl triethoxysilane (FAS)	Polyester, cotton, wool	✓		[22]
SiO ₂ (50–600 nm)	TEOS with one of the following: tridecafluorooctyl triethoxysilane, methyl triethoxysilane, phenyl triethoxysilane, octyl triethoxysilane, hexadecyltrimethoxysilane	Polyester, cotton, wool	✓	DUR	[23]
SiO ₂ (70 nm)	3-Aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, stearic acid, and 1 <i>H</i> , 1 <i>H</i> , 2 <i>H</i> , 2 <i>H</i> -perfluorodecyltrichlorosilane	Cotton	✓		[24]
SiO ₂ (70 nm)	3-Aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, stearic acid, and 1 <i>H</i> , 1 <i>H</i> , 2 <i>H</i> , 2 <i>H</i> -perfluorodecyltrichlorosilane	Cotton	✓	DUR	[26]
TiO ₂	Stearic acid, 1 <i>H</i> , 1 <i>H</i> , 2 <i>H</i> , 2 <i>H</i> -perfluorodecyltrichlorosilane	Cotton	✓	UVS	[27]
SiO ₂ (7 nm)	Poly(alkyl siloxane) or poly(methyl methacrylate)	Silk	✓		[28]
SiO ₂ (7 nm)	Mixture of silanes and siloxanes	Cotton	✓	TRA	[29]
SiO ₂ (10–50 nm)	PDMS, octyltriethoxysilane, and 3-aminopropyltriethoxysilane	Wool	✓	DUR	[30]
SiO ₂ (143 nm), SiO ₂ (378 nm)	Water-repellent agent (KF255)	Cotton	✓		[33]

(continued)

Table 1 (continued)

Particle (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	Others	Ref.
SiO ₂ (52 nm)	Hexadecyltrimethoxysilane	Cotton	✓	DUR, TRA, APE, mechanical properties	[34]
SiO ₂ (68 nm)	Poly(acrylic acid) and poly(allylamine hydrochloride)	Cotton	✓	DUR, buoyancy	[35]
Fe ₃ O ₄ (~10 nm)	Tridecafluorooctyl triethoxysilane	Cotton, polyester	✓	DUR (in magnetic field), coating removal	[36]
SiO ₂ (120–400 nm)	Stearyl acrylate/perfluorooctyl ethane/epoxy-modified polysiloxane	Cotton	✓	DUR	[37]
SiO ₂ (various sizes, 10–400 nm)	Fluorochemical (Rucostar EEE)	Polyester	✓		[38]
SiO ₂ (various sizes, 10–400 nm)	Fluorochemical (Rucostar EEE)	Polyester	✓	APE, mechanical properties	[39]
ZnO (continuous film with particulate morphology)	–	Cotton, polyester	✓		[40]
Ag (100–200 nm)	Glucose and 1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecanethiol	Polyester	✓	DUR	[41]
SiO ₂ (various sizes, 80–170 nm)	Tridecafluorooctyl triethoxysilane	Polyacrylonitrile	✓	APE, porosity	[42]
SiO ₂ (100 nm)	(Heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethylchlorosilane	Polyester	✓	TRA	[43]
SiO ₂ (22 nm and 150 nm)	PDMS and tridecafluorooctyl triethoxysilane	Polyester, cotton, wool	✓	DUR, APE	[44]
SiO ₂	–	Electrode (yarn SFY750)	✓	Conductivity	[45]
Ag (100–200 nm)	3-Aminopropyltrimethoxysilane	Cotton	✓	UVS, antistatic	[46]
ZnO nanorods	Octadecyltrimethoxysilane	PET	✓		[47]
ZnO hexagonal prism crystallites with 20–500 nm diameter and up to 1 mm in length	–	Polyester, poly(lactic acid), polyamide, hemp	✓		[48]

Particle (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	Others	Ref.
TiO ₂	Tetra(4-carboxyphenyl)porphyrin and trimethoxy(octadecyl) silane	Cotton	✓	DUR, UVS (light), self-cleaning by photocatalysis	[49]
SiO ₂ (100–150 nm for the functionalized particles)	Butyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, and dodecafluoroheptyl methacrylate	PET	✓		[51]
SiO ₂ (15 nm)	Functionalized according to Refs. [25, 26], hexadecyltrimethoxysilane and EDTA	Cotton	✓	DUR	[52]
Fluoropolymer/SiO ₂ (120 nm)	Butyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, dodecafluoroheptyl methacrylate, and vinyl trimethoxy silane	Polyester	✓		[53]
SiO ₂ (20 nm) and other produced by sol-gel	Polyurethane, n-dodecyltrimethoxysilane	Polyester	✓	APE	[54]
SiO ₂ (161 nm)	ZnO and sodium stearate	Nylon	✓	DUR, UVS	[55]
SiO ₂ (100–110 nm)	Hexadecyltrimethoxysilane, stearic acid, triethoxyoctylsilane, combinations of the above	Cotton	✓	Stain repellency	[57]
SiO ₂ (16 nm)	Trichlorododecylsilane	Cotton	✓	DUR, TRA	[58]
SiO ₂	Poly(styrene-block-butadiene-block-styrene)	PET	✓	DUR, APE	[59]
TiO ₂ (150 nm)	2-Hydroxy-4-n-octoxybenzophenone, fluorinated acrylic copolymer	Polyacrylonitrile/polyurethane	✓	DUR, UVS, moisture breathability	[60]
ZnO (30–45 nm)	Commercial fluorocompound (FABGUARD-ET)	Polyester	✓	APE, drag force	[61]
Polyesteracrylate and vinyl-modified SiO ₂ core-shell (200 nm)	Vinyl trimethoxy silane, sodium dodecyl benzene sulfonate, butyl acrylate, methyl methacrylate, hydroxyethyl acrylate, dodecafluoroheptyl methacrylate	Textile	✓	DUR	[62]
TiO ₂	(3-Mercaptopropyl)triethoxysilane, hexafluorobutyl methacrylate	Cotton	✓	DUR	[63]
Ag	1H,1H,2H,2H-perfluorodecanethiol	Commercial Kevlar fiber	✓	DUR, conductivity	[64]

(continued)

Table 1 (continued)

Particle (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	Others	Ref.
Al ₂ O ₃ (13 nm)	Polyvinylidene fluoride	Electrospun polyvinylidene fluoride	✓	DUR, air gap membrane distillation	[65]
TiO ₂ (9 nm)	PDMS	Cotton	✓	DUR, UVS, self-cleaning by photocatalysis	[66]
Cellulose nanofibers	Octadecylamine and glutaraldehyde	PET	✓		[68]
TiO ₂	(Heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane	Cotton	✓	DUR, self-cleaning by photocatalysis	[69]
ZnO nanorods (with 70–160 nm diameter and 0.9–1.3 µm in length)	n-Octadecanethiol	Silk	✓	DUR, TRA, UVS, APE	[70]
Fe ²⁺ grafted	Polydopamine	Silk	✓	DUR, UVS, flame retardancy	[71]

textile substrates. Apart from the nanoparticles, other materials were used for the functionalization/modification of the nanoparticles and for the textile treatment. These materials are included in Table 1 which, moreover, describes other properties of the treated textiles, such as durability, transparency, UV shielding, and air permeability, whenever they are applicable.

In their early work, Ramaratnam et al. deposited poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) on poly(ethylene terephthalate) (PET) fabric covered with epoxidized silica (SiO_2) nanoparticles which were prepared using poly(glycidyl methacrylate) [20]. Deposition was applied via dip coating. Superhydrophobicity was achieved, as revealed by the large CA ($>150^\circ$) of resting water drops on the treated PET. A self-cleaning scenario was then demonstrated [20]. These results provided the basis for another report. In particular, the goal of the next work by Ramaratnam et al. was to induce superhydrophobicity to polyester fabrics, using three different nanoparticles [21]. Calcium carbonate (CaCO_3) nanoparticles were mixed with poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene). Combinations of polystyrene grafted layers with silver (Ag) and SiO_2 nanoparticles were embedded in a poly(glycidyl methacrylate) and poly(2-vinylpyridine) matrix. Silicon wafers were used as a model substrate for flat surfaces, whereas films were produced on polyester fibers which showed superhydrophobic properties. The effect of the concentration and the shape of the nanoparticles on the wetting properties were investigated in detail and brief, respectively [21].

Wang et al. produced superhydrophobic coatings with CA $> 170^\circ$ and SA $< 7^\circ$ using a silica sol solution which was prepared by co-hydrolysis and condensation of two silane precursors, tetraethyl orthosilicate (TEOS) and tridecafluorooctyl triethoxysilane (FAS) [22]. Treated polyester fibers showed a particulate surface, as revealed in Fig. 1. Particles had average size of 50–150 nm and aggregated randomly over the coated area. The FAS/TEOS ratio played a critical role in the wetting properties: CA increased with the increase of the FAS/TEOS ratio from 1:100 to 1:10 (mol/mol). Further increase in the FAS/TEOS ratio slightly reduced the CA value. The sol solution can be easily coated onto various substrates, by dipping, spraying, or spin coating [22]. It was noted that similar results were obtained for other treated materials including wool and cotton. In a following study, the same group [23] prepared five different coating solutions by co-hydrolysis/co-condensation of TEOS with an organic silane of one of the five following materials: FAS, methyl triethoxysilane (MTES), phenyl triethoxysilane (PhTES), octyl triethoxysilane (OTES), or hexadecyltrimethoxysilane (HDTMS) [23]. Coatings were applied on polyester, wool, and cotton. The best results, corresponding to high CA ($>150^\circ$) and low SA ($<15^\circ$), were obtained with the FAS, PhTES, and HDTMS treatments. For several treated fabrics, extreme results were obtained. For instance, the water CA and SA on polyester coated by TEOS-HDMS were 170° and 6.4° , respectively. In order to improve the coating adhesion, a third silane containing 3-glycidoxypropyltrimethoxysilane (GPTMS) was included in the coating synthesis. Superhydrophobicity was affected, as GPTMS induced smaller CAs and larger SAs, but the non-wetting state was maintained for most treated fabrics as evidenced by CAs which were typically $>150^\circ$. Treated polyester and cotton showed good

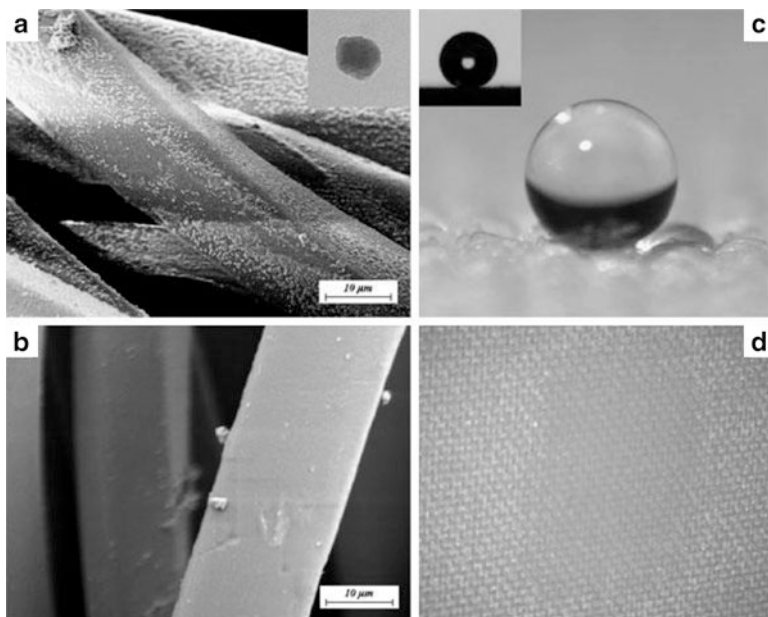


Fig. 1 SEM and photographic images of the polyester fabrics, (a) and (c) after superhydrophobic treatment, (b) and (d) the untreated pristine fabric (Reprinted with permission from [22], Copyright Royal Society of Chemistry)

washing durability which was evaluated according to the method specified in Australian Standards (AS 2001.1.4).

Xue et al. produced SiO_2 nanoparticles (70 nm) [24] according to the Stöber method [25]. Two types of nanoparticles were produced, as SiO_2 nanoparticles were subjected to amino functionalization and epoxy functionalization. Cotton textiles were impregnated in the functionalized SiO_2 nanoparticle sols, followed by hydrophobization with stearic acid and 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane which were used separately or in combination. Consequently, several combinations of coating formulations were tested for cotton treatment. Superhydrophobicity was induced in the cotton textiles depending on the type of nanoparticle functionalization and hydrophobization process [24]. The wetting properties were characterized only by measuring CA [24]. In a subsequent study, CA and RA angles were measured on cotton textiles which were treated by Xue et al., using a similar process [26]: cotton textiles were treated with an epoxy-functionalized and amino-functionalized SiO_2 nanoparticle solution. After hydrophobization, the treated textiles yielded very large CA (170°) and small RA (3°) of water drops. The robustness of the superhydrophobic and water-repellent textiles was tested using a sonication bath in ethanol [26]. Furthermore, the same group [27] produced titania (TiO_2) nanoparticles using tetrabutyl titanate and acetic acid [27]. Nanoparticles were used to generate a dual-size surface roughness onto cotton, followed by hydrophobization with stearic acid, 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane, or their

combination. The effect of the relative concentrations of the various chemicals, used to treat cotton, on the wetting properties were investigated. Best selections resulted in very large CA ($>160^\circ$) of water drops. Moreover, the incorporation of TiO_2 particles resulted in good UV shielding [27], as indicated in Table 1.

Manoudis et al. developed a method which was not substrate limited and scalable to large areas: SiO_2 nanoparticles were added in a polymer solution (e.g., poly(alkyl siloxane) or poly(methyl methacrylate)) [28]. The suspension was sprayed onto various surfaces, including silk textiles. The polymer played the role of the (i) binder and (ii) low surface energy agent, whereas nanoparticles led to the formation of microscale clusters with nanostructures, which induced a surface roughness at the micrometer and nanometer scale. The resulting composite polymer-nanoparticle films exhibited superhydrophobic and water-repellent properties which could be interpreted using the Cassie-Baxter model, provided that an appropriate, elevated particle concentration was added to the polymer solution. The extreme wetting properties were evidenced by appropriate measurements: CA $>150^\circ$ and CAH $<6^\circ$ [28]. In a follow-up investigation [29], it was shown that the method was successfully applied to treat cotton using a waterborne polysiloxane material as a polymer binder, thus replacing the harmful solvent-based polymers [29]. The color of the cotton was practically not affected by the polysiloxane- SiO_2 coating.

Zhang and Lamb devised a method of modifying the wettability of wool textiles by chemically binding in situ generated SiO_2 nanoparticles onto the fiber's surface [30]. The SiO_2 -based superhydrophobic modifier was produced according to patented procedures [31, 32] using TEOS, methyltrimethoxysilane (MTMS), and some other silanes/siloxanes described in Table 1. Treated wool exhibited large CA ($>165^\circ$) and small SA ($<7^\circ$), thus corresponding to superhydrophobicity and water repellency. Superhydrophobicity was maintained after 3 times of accelerated washing which was equivalent to 15 times of standard laundry wash [30].

Cotton fabrics were treated by Bae et al., using SiO_2 nanoparticles [33] which were synthesized by the Stöber method [25]. SiO_2 nanoparticles of two sizes (143 and 378 nm) were produced and used to treat cotton. A commercial water-repellent agent was used for post-treatment [33]. The effect of the concentration of the repellent agent on the CA of the treated fabrics was investigated. The results showed that marginal superhydrophobicity with high CA ($>140^\circ$ —almost 150°) can be achieved using any of the three treatments: SiO_2 (143 nm) + agent, SiO_2 (378 nm) + agent, and pure agent (no SiO_2). However, a lower concentration of water-repellent agent is needed when the cotton fabrics are covered by a SiO_2 nanoparticle layer [33].

Gao et al. prepared SiO_2 sols using an alkaline hydrolysis of TEOS in a NH_4OH ethanol solution [34]. A series of samples corresponding to different SiO_2 particle sizes (30–71 nm) were prepared by changing the NH_4OH concentration. The sols were used to treat cotton and polyester fabrics which were then coated by hydrolyzed hexadecyltrimethoxysilane (HDTMS). The effect of the NH_4OH concentration on the wetting properties of the treated fabrics was investigated. Superhydrophobicity was achieved only for treated cotton with a CA as high as 155° which was obtained with a sol with average nanoparticle size of 52 nm. The durability of the fabricated coating was tested, and it was found that after 30 washing

cycles, the CA of treated cotton fabric decreased from 155° to 95° . On the other hand, the treatment of the cotton fabric caused a small reduction in the fabric's tensile strength ($<10\%$) and practically no changes in fabric whiteness or air permeability.

Zhao et al. achieved imparting superhydrophobicity to cotton fabrics via electrostatic layer-by-layer assembly of polyelectrolyte/SiO₂ nanoparticle multilayers [35]. Nanoparticles with an average size of 68 nm were produced by TEOS according to the Stöber method [25]. Cotton fabrics were coated by multilayers after treatment with poly(acrylic acid), poly(allylamine hydrochloride), and SiO₂. Coated fabrics were finally treated with a fluoroalkylsilane. CA $> 150^{\circ}$ was easily obtained even with the deposition of one multilayer. However, low CAH ($<10^{\circ}$) was only achieved for the cotton fabrics assembled with five multilayers or more. The superhydrophobic cotton fabric showed (i) a reasonable durability to withstand at least 30 machine washing cycles and (ii) a remarkable buoyancy which was demonstrated using a miniature boat made with the fabric [35].

Fang et al. reported the production of superhydrophobic coatings using iron oxide (Fe₃O₄) magnetic nanoparticles functionalized with fluoroalkyl silica [36]. The 10 nm-sized synthesized nanoparticles were deposited under a magnetic field on various substrates, including cotton and polyester. The nanoparticles, agglomerated to larger structures with diameters in the range from 30 to 100 nm, protruded from the surface and formed superhydrophobic coatings corresponding to high CA ($>160^{\circ}$). The developed method is not substrate limited. Moreover, the coatings were very stable under the influence of a magnetic field, but they could be removed (e.g., by ultrasonication) to restore the original surface features of the substrates [36].

Hao et al. synthesized a fluoroalkylsiloxane polymer with reactive epoxy group, hydrophobic perfluoroalkyl group, and hydrophilic polyether [37]. Cotton fabrics were first coated with SiO₂ nanoparticles (120–400 nm) and then with the polymer which had the role of the hydrophobic agent. The SiO₂ nanoparticles created the appropriate surface roughness to reach superhydrophobicity with CA $> 155^{\circ}$. Moreover, the fabricated coating showed relatively good washing durability, as CA still remained $>100^{\circ}$ after 20 times of soaping operations [37].

The method to roughen the surface of a fabric using SiO₂ nanoparticles was employed by Mazrouei-Sebdani et al. and was compared with an alternative route based on the aminolysis of the polyester fibers [38]. Furthermore, treatment of polyester with a fluorochemical (Rucostar EEE) was included in the study [38]. In particular, various treatments were applied on the polyester fibers: (i) coating with the fluorochemical, (ii) coating with the fluorochemical and nanoparticles, (iii) aminolysis and coating with the fluorochemical, and (iv) aminolysis and coating with the fluorochemical and nanoparticles. Four sizes of SiO₂ nanoparticles were included in the study involving coating with the fluorochemical and nanoparticles: 10–20 nm, 40–50 nm, 100–200 nm, and 300–400 nm. It was shown that the SA decreased gradually when the nanoparticle size increased and/or the nanoparticle concentration decreased. Samples treated with the large nanoparticles (300–400 nm) revealed SA $< 15^{\circ}$. The best result (smallest SA = 12.5°) was accomplished by 0.4% (dry add-on) nanoparticles with a size of 300–400 nm. The small SA was attributed

to the introduction of double roughness with the original roughness appearing from the fabric structure itself and the next from the layer of the nanoparticles. In the study involving aminolysis and fluorochemical/nanoparticles coating, it was shown that aminolysis created proper roughness so that there was no necessity to use the nanoparticles. However, the self-cleaning effect was more pronounced in the nanoparticle-treated samples compared to the aminolyzed samples [38].

A similar study was published using the same materials (i.e., Rucostar EEE and SiO₂ nanoparticles) to treat polyester [39]. Wetting properties were evaluated by measuring the SA and carrying out the 3 M water-oil repellency test. The results led to the conclusion that the larger the nanoparticle size (i.e., 300–400 nm), the lower the SA. Moreover, it was shown that water repellency, described by SA < 10°, can be achieved if the polyester fabric is subjected to a moderate alkaline hydrolysis and coated by the fluorochemical and SiO₂ nanoparticles or only by the fluorochemical. Consequently, it was shown that the use of SiO₂ nanoparticles is not necessary to achieve water repellency. Finally, the treatment did not induce any adverse effect on the sample's tensile strength, abrasion resistance, or permeability to air.

Popescu et al. functionalized cotton and polyester fabrics with zinc oxide (ZnO) thin films and nanoparticles by pulsed laser deposition [40]. The number of applied pulses was the control parameter used to produce either a film or particle deposition type. Depending on the deposition ambience, different wetting properties were obtained in the treated fabrics. The wettability of thin films changed from hydrophilic when deposited in an oxygen flux to superhydrophobic (157°) when obtained in vacuum, whereas the wettability of the nanoparticles changed from hydrophilic when deposited in an oxygen flux to hydrophobic (120°) when obtained in vacuum. These changes in the wetting behaviors were assigned to the differences in microstructure features and surface electrical charging. It was reported that the superhydrophobic film showed a particulate surface morphology and consisted of grains of ~140 nm, with very small crystallites of a maximum 10 nm [40].

The goal of Zhu et al. was to produce durable and mechanically stable superhydrophobic polyester fabrics [41]. Ag was attached on polyester samples through a chemical process. Polyester fibers were thus covered with an Ag layer composed of particles in the range of 100–200 nm. The particles formed larger aggregates generating a dual surface texture. The coated fabrics were superhydrophilic. However, after a surface fluorination post-treatment (with 1H,1H,2H,2H-perfluorodecanethiol), the surface of the treated polyester became superhydrophobic, displaying a large CA (158°) and a small SA (5°). An intermediate treatment step with glucose was applied after the nanoparticle deposition and before fluorination. The mechanical durability of the superhydrophobic surface was assessed by the scratch test which is illustrated in Fig. 2a. The variation in the values of both the CA and SA of water drops on the coated fabric surface with abrasion cycles is shown in Fig. 2b. CA drops with abrasion, but it remains >150° after 30 abrasion cycles. SA increases with abrasion, but it remains <20° after 30 abrasion cycles. It was suggested that the enhanced mechanical resistance may result from a strong physical absorption interaction between the Ag particles and the fibrous substrate [41]. Finally, it was shown

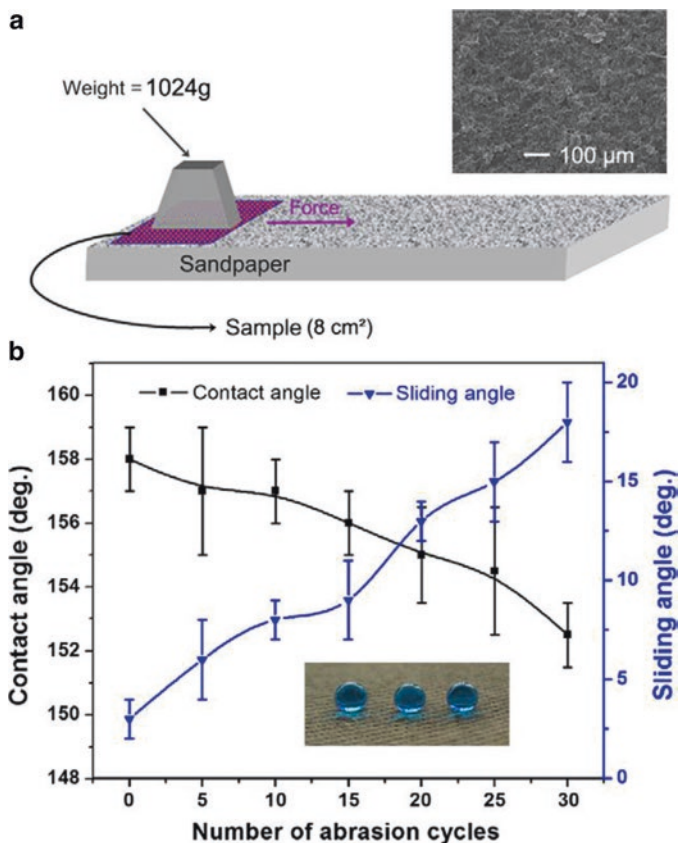


Fig. 2 (a) Schematic illustration of the scratch test employed to evaluate the mechanical durability of the superhydrophobic surface of polyester fabric: sandpaper (1200 mesh) served as an abrasion surface, with the superhydrophobic fabric to be tested facing this abrasion material. While a pressure (13 kPa) was applied to the fabric, the fabric was moved back and forth with a speed of 3 cm/s. The inset is the FESEM image of the sandpaper; (b) CAs and SAs as a function of number of abrasion cycles for the fabric surface. The inset highlights that the fabric surface can repel water after abrasion test (Reprinted with permission from [41], Copyright Elsevier)

that a damaged fabric surface can regain its superhydrophobic properties by repeating the aforementioned facile treatment process [41].

SiO₂ nanoparticles were produced by Fang et al., through hydrolysis-condensation of silane under alkaline conditions [42]. Particle size and concentration were controlled by the reaction time. For example, the particle size increased from roughly 80 to 170 nm after 1 hour of reaction. Likewise, an increase in nanoparticle concentration was noticed with the reaction time. Electrospun polyacrylonitrile nanofiber membranes were dip-coated in the SiO₂ coating solution and were treated with a fluorinated alkyl silane. The wetting properties of the treated polyacrylonitrile fibers were controlled by the SiO₂ nanoparticle loading which in turn was affected by the

nanoparticle concentration and size in the coating's solution. It was reported that increased particle loading led to high surface roughness. When the SiO_2 nanoparticle loading was roughly $>15\%$ of the weight of the polyacrylonitrile membrane, the resulting coating obtained superhydrophobic properties with $\text{CA} > 155^\circ$ and $\text{SA} < 20^\circ$. Finally, it was shown that air permeability decreased with the treatment; however it did not affect the porosity of the treated membranes [42].

Xu et al. prepared fluoro-functionalized SiO_2 nanoparticles using (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane [43]. When spin coating the hydrophobic nanoparticles onto various surfaces, including polyester fabric, the surface exhibited superhydrophobic properties as evidenced by the large ACA (150°) and small RA ($<5^\circ$) of water drops. In contrast, dip coating did not give extreme wetting properties. Finally, the spin-coated superhydrophobic film was also highly transparent with greater than 95% transmittance in the visible region.

Zhou et al. developed a method to treat polyester fabrics and to address the usual low washing and abrasion durability of superhydrophobic textiles [44]. The coating material consisted of polydimethyl siloxane (PDMS), fluorinated alkyl silane-functionalized SiO_2 nanoparticles, and an additional amount of fluorinated alkyl silane, as described in Table 1. Coated fabrics exhibited extreme superhydrophobicity and water repellency with $\text{CA} = 171^\circ$ and $\text{SA} = 2^\circ$, raised by a two-length scale particulate morphology developed on the fiber surface. These extreme wetting properties were achieved using SiO_2 nanoparticles of two sizes (22 nm and 150 nm) mixed with a weight ratio (NP22/NP150) of 2:1. Treated fabrics showed excellent washing and abrasion durability which were evaluated under extreme conditions following the AATCC Test Method 61-2006 test No 2A and the Martindale method, respectively. Coated fabrics could also withstand a strong acid and base as well as boiling water, coffee, and orange juice without losing their stain resistance. Finally, the breathability of the fabrics was not substantially hindered upon treatment. It was demonstrated that although the method was originally devised to treat polyester fabrics, it can be also used to treat other fibrous materials such as cotton and wool.

In the interesting report of Martinez-Tabares et al. [45], SiO_2 nanoparticles produced by hydrolysis and condensation of TEOS were sprayed and deposited on a textile-flexible electrode which was attached in a T-shirt. The developed hardware allowed ambulatory electrocardiogram monitoring. As the textile electrode should conduct electricity and should not absorb water, the purpose of using the SiO_2 coating was to preserve conductivity and impart superhydrophobicity. Both properties were achieved as CA was $>150^\circ$ and the electrical resistivity remained $<5 \Omega\cdot\text{cm}$ [45]. Flexible sensors and electrodes can be very useful for telemedicine applications.

A microwave-assisted synthesis of Ag nanoparticles on cotton fabric which was modified with 3-aminopropyltrimethoxysilane (APTMS) was developed by Guo et al. [46]. The coated fabric possessed superhydrophobic properties ($\text{CA} > 150^\circ$), excellent protection of UV radiation (ultraviolet protection factor = 396.5), and anti-static properties. Finally, it was shown that the APTMS pre-treatment improved the adhesive strength between Ag coatings and cotton fabric [46].

Nanorods of ZnO were grown on fibers of PET by Ashraf et al. [47] following a three-stage process. First PET was subjected to plasma treatment to generate polar

groups. Then a seed solution, made of zinc acetate dihydrate and granulated sodium hydroxide, was applied on the plasma-treated PET fabric. Finally, the nanorods were grown using zinc nitrate hexahydrate and hexamethylenetetramine. Samples with different seed concentrations were realized for detailed studies. The as-prepared fabrics were hydrophilic, whereas with increased seed concentrations, they became superhydrophilic. The wetting properties switched to hydrophobicity upon treatment of the fabrics with octadecyltrimethoxysilane. Using carefully selected seed concentrations and the vapor deposition method for hydrophobization, superhydrophobicity was achieved with high CA ($=158^\circ$) and very low SA ($=1^\circ$).

Using various materials (e.g., zinc nitrate, dimethylamine borane, SnCl_2 , and PdCl_2), electroless deposition was successfully applied by Frunza et al., in developing crystalline particles of ZnO onto polyester and other fabrics such as poly(lactic acid), polyamide, and hemp [48]. Treatment led to the formation of hierarchical roughness structures which generated superhydrophobicity with CA $> 150^\circ$.

Afzal et al. produced a colloidal anatase TiO_2 sol using titanium tetraisopropoxide [49], according to a previously published procedure [50]. Cotton was coated with TiO_2 and then treated with meso-tetra(4-carboxyphenyl)porphyrin and trimethoxy(octadecyl)silane. Treated cotton exhibited dual functionality including superhydrophobicity and visible-light photocatalysis. The former was demonstrated by the large CA ($=156^\circ$) of water drops and the latter by the degradation of methylene blue under visible-light irradiation. Superhydrophobicity was maintained after ten washing cycles and after exposing the coated cotton to visible irradiation for a prolonged time (30 h).

Xu et al. prepared nanocomposite coatings which consisted of vinyl SiO_2 nanoparticles, produced using vinyl trimethoxy silane, and a fluorinated acrylic polymer, produced using various acrylate monomers and a fluoroacrylic monomer [51], as summarized in Table 1. The coating was deposited on polyester (PET) fabrics. The wetting properties were evaluated by measuring the CA and the WSA of water drops and spray testing (AATCC Test Method 22-2005). The results were as follows: CA = 152° and WSA = 12° for 5 and 15 μL water drops, respectively, whereas the water repellency rating was 95. The results were achieved due to the synergistic effect of the rough surface structure provided by the SiO_2 nanoparticles and the low surface energy caused by the fluorinated polymers.

Abbas et al. [52] adopted previously published procedures [24, 26] to produce amino- and epoxy-functionalized SiO_2 nanoparticles. Cotton textiles were impregnated in the sols of the functionalized SiO_2 nanoparticles and in a solution of hexadecyltrimethoxysilane. Another step was added to improve the durability of the prepared superhydrophobic fabrics by using ethylenediaminetetraacetic acid (EDTA). The modified cotton fabrics exhibited superhydrophobicity with CA = 160° and SA = 4° . It was shown that EDTA offered enhanced washing durability.

A fluoropolymer/nano-silica nanocomposite was synthesized by Xu et al. [53] and applied to coat flexible polyester fabrics. Vinyl silica hydrosols were prepared by a sol-gel method using vinyl trimethoxy silane as the precursor in the presence of the non-ionic/anionic composite surfactant. The nanocomposite was synthesized

by seeded semi-continuous emulsion polymerization using butyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, and dodecafluoroheptyl methacrylate. The effects of the various ingredients on the properties of the nanocomposite were investigated. A dual-size surface topography was achieved on the surface of the coatings which resulted to CA of 152° and WSA of 12° .

A one-step sol-gel electrospinning method was developed by Jin et al., using TEOS and acetic acid which reacted to produce primary SiO_2 nanoparticles [54]. Commercial hydrophobic silica nanoparticles were then added to the sol. The mixture was added to a polyurethane solution and was electrospun to form a superhydrophobic web with CA as high as 157° and WSA as low as 5° . The extreme wetting properties were achieved after post-treatment of the coated polyester with *n*-dodecyltrimethoxysilane. When the webs were laminated onto polyester fabrics, they maintained air permeability and water vapor transmission rate.

Teli and Annaldewar produced SiO_2 nanoparticles [55] according to a sol-gel method which was published previously [56]. SiO_2 nanoparticles were applied on nylon knitted fabric and were modified by in situ deposition of ZnO and sodium stearate. The coated nylon exhibited superhydrophobic properties (CA = 157°) by adjusting the concentration of sodium stearate appropriately. Furthermore, the ultra-violet protection factor reported for the coated nylon was >270 . However, superhydrophobicity was lost after washing treatment.

Manatunga et al. deposited hexadecyltrimethoxysilane (HDTMS), stearic acid (SA), triethoxyoctylsilane (OTES), and their mixtures/combinations on cotton fabrics that were first roughened using SiO_2 nanoparticles [57]. It should be noted that hydrophobization of cotton by HDTMS was previously reported by Gao et al. [34]. Cotton samples without nanoparticles were also treated by hydrophobic agents, but these samples did not show superhydrophobicity. Silica nanosol was prepared by adopting the Stöber method [25]. Almost all cotton samples treated with SiO_2 nanoparticles and the hydrophobic agents corresponded to CA $> 150^\circ$. In particular, the combination of HDTMS-OTES gave the highest CA ($=161.5^\circ$) and the lowest RA. The AATCC test method 193-2005 was carried out to further evaluate the water repellency of the treated fabrics showing the reduced surface tension of the fabrics treated with HDTMS-SA and HDTMS-OTES. Finally, good results were obtained for the water uptake and stain repellency tests.

Jeong and Kang used hydrophobic SiO_2 nanoparticles which were treated with trichlorododecylsilane [58]. Treated nanoparticles were added in methyl, ethyl, and propyl alcohol. The three suspensions were sprayed onto cotton. The effects of the alcohol medium on the structure and therefore the wettability of the treated cotton were investigated. Low CAH ($<10^\circ$) was achieved for the methanol-based suspension which was accompanied by extremely high CA ($\sim 170^\circ$). The durability of treated cotton, however, was poor as superhydrophobicity was lost after washing treatment. Finally, no difference in the colors of untreated and coated cotton was noticed.

PET was the target material for Meng et al. [59] who treated the textile by combining spraying and non-solvent vapor-induced phase separation. A star-shaped copolymer of poly(styrene-block-butadiene-block-styrene) was sprayed onto the

fabric. The effect of the vapor atmosphere on the morphology and wettability of the resulting coating was investigated. The best results were obtained in an ethanol vapor atmosphere. In order to improve the suggested coating, hydrophobically modified fumed SiO_2 nanoparticles were added in the initial solution. The effect of the relative mass ratio of polymer/HMFS on CA and SA was investigated. High CA ($>150^\circ$) and low SA ($<5^\circ$) were achieved. The chemical and thermal stability of the coated textiles were excellent, whereas abrasion testing (mechanical stability) led to the reduction of CA which still remained above 140° . Finally, water vapor permeation through the coating film was checked indicating satisfactory breathability.

Xu et al. fabricated multifunctional textile membranes consisted of polyacrylonitrile, polyurethane, and TO_2 nanoparticles through electrospinning process [60]. To enhance UV resistance and water-repellent performance of the nanofibrous membranes, they were further treated with 2-hydroxy-4-n-octoxybenzophenone (UV531) and a commercial fluorinated acrylic copolymer acting as a water-repellent finishing agent. The effects of the relative amounts of the materials which were used to treat the textile membranes on their performance were revealed. An optimum recipe was obtained which gave the following results: superhydrophobic wettability with ACA of 152° , good UV resistance, modest waterproofness, and moisture breathability as well as mechanical robustness.

Norouzi et al. designed an experimental setup to measure the drag force in simulated swimsuits [61]. Polyester fabrics were coated by ZnO nanoparticles which were synthesized in situ using zinc nitrate and sodium hydroxide. A commercial water-repellent fluorochemical compound (FABGUARD-ET) was then applied to lower the surface energy. Optimum conditions for the fabric treatment led to the following results: very high CA of water drops ($>150^\circ$) and low SA ($<10^\circ$), i.e., superhydrophobicity was achieved; reduction of air permeability and breathability of the fabric with no discomfort noted by the wearer; and reduction of the drag force on treated fabric as high as 80%.

Feng et al. produced nanospheres with core-shell structure derived from polyestercrylate and vinyl-modified SiO_2 nanoparticles [62]. The latter were synthesized by vinyl trimethoxy silane with sodium dodecyl benzene sulfonate as a surface-active agent. Butyl acrylate, methyl methacrylate, hydroxyethyl acrylate, and dodecafluoroheptyl methacrylate were added gradually to form the final emulsion. The emulsion was applied on a textile leading to the formation of nanostructures with mean diameter of 200 nm which gave a large CA ($>150^\circ$). Superhydrophobicity was accompanied by oleophobicity. The Martindale standard abrasion test was applied and the results showed a deterioration of hydrophobicity of around 6%.

Yang et al. produced superhydrophobic cotton using a fluorinated TiO_2 sol [63] which was prepared according to a previously published procedure [27]. (3-Mercaptopropyl)triethoxysilane and hexafluorobutyl methacrylate were subjected to free radical polymerization, and the resulting polymer was used to fluorinate the TiO_2 nanoparticles. The nanocomposite was deposited onto cotton. Selection of the appropriate concentration for the fluoropolymer led to superhydrophobicity with CA of water drops of 153° and self-cleaning properties. Due to the

nanocomposite covalently bonded to the cotton fabric, the modified cotton displayed high resistance to organic solvents (DMF, THF, and others) and acidic solutions.

Choi et al. developed a two-step process to produce highly conductive and water-proof fibers for advanced interconnector components in wearable textile electronics [64]. The first step was the formation of a flexible and conductive layer on the surface of commercial Kevlar fiber: poly(styrene-block-butadiene-block-styrene) was deposited onto the fiber, and Ag nanoparticles were produced and deposited in situ on the coated fiber using CF_3COOAg and $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$. The second step was the waterproof surface treatment of the conductive fiber by using self-assembled monolayer (SAM) reagents. Four reagents were investigated: 1-decanethiol, 1*H*, 1*H*, 2*H*, 2*H*-perfluorohexanethiol, 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyltrichlorosilane, and 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecanethiol (PFDT). The best results were obtained with the PFDT-treated conductive fiber which showed superhydrophobicity with CA of water drops $>150^\circ$ and self-cleaning properties; the least change of resistance in both water and acid; excellent operation of a LED over 4 h through partially immersed conditions; and mechanical durability, withstanding repeated folding deformation and washing processes.

Attia et al. fabricated a superhydrophobic membrane by a combined electrospinning/electrospray method that has the potential for membrane distillation applications [65]. A mixture of polyvinylidene fluoride and Al_2O_3 nanoparticles were sprayed on an electrospun base membrane made from polyvinylidene fluoride. A lab-made electrospinning device was used [65]. By adjusting the processing parameters, a hierarchical micro- and nanostructure was obtained on the surface of the membrane which resulted in a large CA ($>150^\circ$). Moreover, the values for liquid entry pressure and porosity were adequate for air gap membrane distillation applications. Long-term operation (30 h), mechanical, and thermal properties were evaluated.

Jiang et al. produced anatase TiO_2 sol and subsequently TiO_2 nanoparticles using titanium tetraisopropoxide [66], according to a procedure described in a previously published report [67]. Cotton was coated first by TiO_2 nanoparticles and then by PDMS. The relationship between the CA of water drops on coated cotton and PDMS concentration was studied, reaching a max CA of 154° . Treated cotton displayed excellent UV resistance and durability after immersion in solutions of different pH values and different organic solvents, whereas CA decreased to 146° after 30 laundering cycles, indicating desirable washing durability. Finally, the coated cotton textile displayed considerable photocatalytic activity by the decomposition of Oil Red O under UV exposure [66].

Roy et al. treated cellulose nanofibers with octadecylamine and glutaraldehyde [68]. The as-prepared material was used to coat various surfaces, including a PET surface which obtained superhydrophobic properties with a CA of water drops of 153° . Treated tissue paper and sponge (but not textile) were successfully tested for water-oil separation.

Yang et al. utilized a previously published procedure [67] to produce TiO_2 sol which was deposited on cotton and was subsequently modified using (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (F-17) [69]. The textile

surface showed self-cleaning, stain-resistant performance against various contaminants, attributed to the synergetic function of superhydrophobicity (CA $\sim 160^\circ$) and photocatalysis of the anatase TiO_2 nanoparticles. The durability of the treatment was tested by immersing the treated textiles in various organic solutions and by measuring the CA of drops with different pHs. Moreover, laundering durability was evaluated and it was shown that superhydrophobicity was maintained after 30 washing cycles.

Starting with zinc nitrate hexahydrate, Huang et al. developed ZnO nanorods on silk fabrics which were subjected to post-treatment using n-octadecanethiol [70]. Treated silk showed superhydrophobic and UV-blocking properties as evidenced by the high CA ($\sim 152^\circ$) and ultraviolet protection factor (>50). Mechanical and chemical durability were evaluated by abrasion and immersion in acidic and alkaline solutions. Finally, experimental results showed that the treatment method had slight effects on air permeability and the color of silk.

In the report published by Yan et al., silk was coated with polydopamine, and Fe^{2+} was grafted onto the fabric surface through a secondary reaction forming micro-/nanoparticles [71]. This chemical treatment, together with the developed rough structure of the surface, gave the silk fabric superhydrophobicity, flame retardancy, and UV shielding ability. The former was evidenced by the large CA ($>150^\circ$) and small SA ($<10^\circ$) of water drops and moreover by demonstrating the standard self-cleaning scenario. Superhydrophobic properties were resistant to 20 laundering cycles or 250 friction cycles. The vertical burning damage length was <12 cm revealing the flame-retardant properties of the silk, whereas the UV protection factor was >30 .

3 Superhydrophobic and Superoleophobic Textiles

Table 2 summarizes the materials and the combinations used to impart both superhydrophobicity and superoleophobicity to various textiles. Other useful properties of the treated textiles are indicated in the table. The reports included in Table 2 are discussed next.

In their pioneering work of 2007, Yu et al. set forth to impart enhanced hydrophobicity and oleophobicity to cotton [72]. Superhydrophobic/oleophobic states defined by CA of water and oil drops $>150^\circ$ were almost reached, as the corresponding reported angles were 145° and 131° , respectively. This result was obtained after treating cotton samples with SiO_2 nanoparticles prepared via alkaline hydrolysis of TEOS and a perfluorooctylated quaternary ammonium silane coupling agent. The former made the textile surface much rougher by introducing the SiO_2 nanoparticles, and the latter coupling agent on the top layer of the surface lowered the surface free energy. SiO_2 nanoparticles with different sizes were tested, ranging roughly from 110 to 200 nm. The larger nanoparticles gave the highest CAs described above [72].

Table 2 Nanoparticles and other materials which were used to coat various textiles and to induce superhydrophobicity (SH) and superoleophobicity (SO). Other properties which were evaluated according to relative tests are indicated as follows: *DUR* durability, *TRA* transparency, *UVS* UV shielding, *APE* air permeability

Particle used (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	SO	Others	Ref.
SiO ₂ (110–200 nm)	Perfluorooctylated quaternary ammonium silane	Cotton	✓ ^a	✓ ^a		[72]
SiO ₂ (500–2000 nm for the functionalized particles)	3-Aminopropyl-triethoxysiloxane, PDMS, and 1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecyltrichlorosilane	Cotton	✓	✓ ^a		[73]
SiO ₂ (100 nm), SiO ₂ (160 nm), SiO ₂ (220 nm)	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecyl trichlorosilane	Cotton	✓	✓		[74]
SiO ₂ (45 nm)	Tridecafluorooctyl triethoxysilane	Cotton	✓	✓		[75]
Fluorosiloxane precursor	–	Nylon	✓	✓		[76]
Al ₂ O ₃	Silicone oil	Cotton, polyester	✓ ^{a,b}	✓	DUR	[77]
SiO ₂ (7 nm)	Emulsion of alkoxy silanes and organic fluoropolymer	Silk	✓	✓	TRA, coating removal	[78]
SiO ₂	Dodecyltrimethoxysilane, perfluorodecyltrichlorosilane, and PDMS	PET	✓	✓	DUR, UVS	[79]

^aEnhanced hydrophobicity and/or oleophobicity were achieved

^bLow CAH but moderate CA

Hoefnagels et al. attached SiO₂ nanoparticles onto cotton fibers by covalent bonds [73]. Amine-functional SiO₂ nanoparticles were in situ synthesized following the Stöber method [25] and using TEOS and 3-aminopropyl-triethoxysiloxane (APS). The nanoparticles were covalently bonded to the cotton fibers which were subjected to post-treatment using PDMS and a perfluoroalkyl silane (Table 2). The best results were obtained when a two-step process was followed: first, SiO₂ particles were attached onto the cotton fibers, and then the particle-containing cotton textile was added to an APS solution. Treated cotton exhibited high CA (=155°) and small RA (=15°) for 10 µL drops of water which has a surface tension of 72 mN/m. The effect of the drop volume on the RA was investigated in detail. It was shown that the RA decreases with the drop volume. When a perfluoroalkyl chain was introduced to the SiO₂ particle surface, the superhydrophobic textile became highly oleophobic (almost superoleophobic), as demonstrated by contact angle measurements carried out using 15 µL drops of sunflower oil, which has a low surface tension of 33.0 mN/m. In particular, for oil drops a CA of 140° and RA of 24° were measured.

Leng et al. obtained both superhydrophobicity and superoleophobicity on cotton textiles as evidenced by CA and RA angle measurements which were carried out using water and hexadecane drops of various volumes [74]. The extreme wetting

properties were achieved by a multilength-scale roughness which was based on the woven structure of cotton, with an additional two layers of SiO_2 particles. The microparticles were in situ introduced on cotton fibers according to the Stöber method [25], and, furthermore, three different nanoparticles (100, 160, and 220 nm) were adsorbed by the cotton textiles by electrostatic attraction. Finally, the treated rough cotton textiles were subjected to perfluorination using 1*H*,1*H*,2*H*,2*H*-perfluorodecyl trichlorosilane. In general, large CAs and small RAs for both water and hexadecane drops were achieved. The largest CAs ($>150^\circ$) were achieved for the small-volume drops (5 μL), and the smallest RAs ($<13^\circ$) were recorded when drops of large volume (20 μL) were used for the measurements [74].

Pereira et al. produced mesoporous SiO_2 nanoparticles functionalized with a fluoro-silane (Table 2). The average size of the nanoparticles was ~ 45 nm [75]. The hybrid nanoparticles were incorporated onto cotton textiles through a condensation methodology between TEOS and the fluoro-silane. The effects of the molar ratio of fluoro-silane/TEOS on the surface morphology, and therefore the wetting properties of treated cotton, were investigated. The best results were obtained with a ratio of 1:5 as this recipe induced both superhydrophobic and superoleophobic properties on the treated cotton; CAs of both water and oil drops were $> 150^\circ$ [75].

Saraf et al. induced superhydrophobicity and superoleophobicity to hydroentangled nylon nonwoven fabric [76]. Typical nanoparticles, which are the target materials in this review, were not used for the treatment of the fabric. The latter was coated with a fluorosiloxane, which could self-condense forming nano- or microparticles and is therefore included herein. Grafting of the fluorosiloxane onto the fabric was achieved by a microwave-assisted process and a wet process. Extreme wetting properties were achieved with CA of water drops $>170^\circ$ and CA of dodecane drops $>150^\circ$. Interestingly, drops with volumes of 10 μL did not roll off any of the produced surfaces. However, for drops with volumes of 50 μL , RAs as low as 6° for water and 21° for dodecane were obtained.

Damle et al. [77] developed several methods to treat cotton and polyester. The use of alumina (Al_2O_3) nanoparticles was included in one of the tested methods where nanoparticles were deposited onto the fabrics, which were subsequently lubricated by soaking in silicone oil. Relatively low CA of water drops were measured on treated fabrics which were on the order of 140° , but the slippery surfaces gave low CAH ($<10^\circ$). Attention was focused to investigate the wettability of the coated fabrics after physical contact with other objects. In particular, CAH of water drops on coated fabrics and the loss of the lubricant upon repeated pressurized contact with highly absorbent cellulose-fiber wipes were investigated. It was shown that the CAH on treated cotton remained $<20^\circ$ even after multiple contacts with the wipes but the polyester fabric had the water CAH increased to 30° . The measurements were also carried out using ethanol drops which gave low CAHs, but it was observed that ethanol wicked into the treated fabric after first contact with the wipes. Significant oil depletion near the fabric surface after contact with the wipes was observed and was the reason for the poor performance of the fabrics to repel ethanol.

Aslanidou et al. employed methods based on procedures which were previously developed [28, 29]. SiO_2 nanoparticles were mixed with a polymer binder which

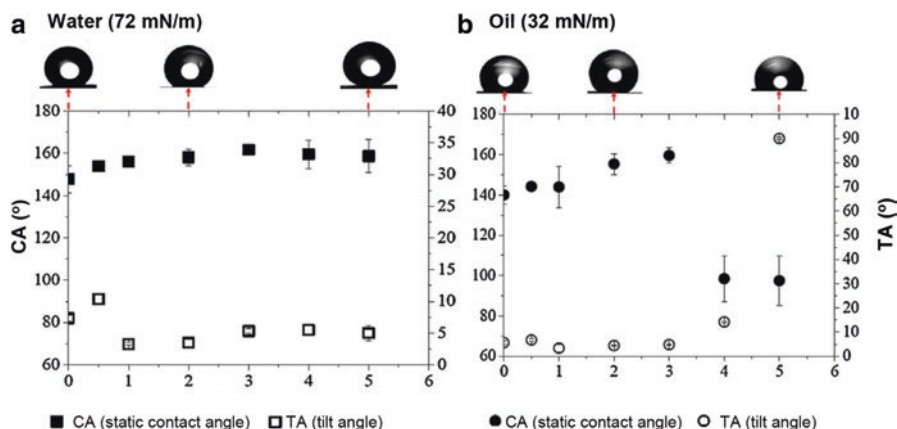


Fig. 3 Static (CA) and tilt (TA) contact angles of (a) water and (b) oil drops on coated silk vs the concentration of SiO_2 nanoparticles in the emulsion of alkoxy silanes and organic fluoropolymer which was used to coat silk. Photographs of selected water and oil drops on coated silk are included. Surface tensions of the tested liquids are provided in parentheses (Adapted with permission from [78], Copyright Elsevier)

originated from a water-soluble emulsion of alkoxy silanes and organic fluoropolymer. The produced coatings were used to treat silk [78]. The effect of the nanoparticle concentration on CA and SA of water and oil drops was investigated and the results are summarized in Fig. 3 [78]. Superhydrophobicity and water repellency are sustained by any surface corresponding to particle concentration $> 1\%$ w/w. However, superoleophobicity and oil repellency collapse at the concentration of 4% w/w, implying that the low surface tension oil drops sink into the rough surfaces, thus corresponding to a transition from the non-sticking, repellent state to the drop-pinned state [78]. According to colorimetric measurements, the produced coatings had practically no effect on the aesthetic appearance of dyed silk. Finally, it was shown that the applied coatings can be totally removed from the silk substrates using compressed carbon dioxide, either in supercritical or liquid state, mixed with a small amount of methanol.

Guo et al. treated PET fabrics using SiO_2 nanoparticles which were produced by an in situ Stöber reaction [25] of TEOS and dodecyltrimethoxysilane (DTMS), thus achieving both enhanced roughness and hydrophobization by the nanoparticles and DTMS, respectively [79]. The wetting properties of the treated fabrics were tested using drops of various liquids. It was shown that $\text{CA} > 150^\circ$ was achieved for drops of liquids with surface tensions greater than 40mN/m . To further improve liquid repellency, the SiO_2 -DTMS/PET fabrics were subjected to a second treatment process as they were coated with a mixed solution of perfluorodecyltrichlorosilane and PDMS. With this additional step, CA became $> 150^\circ$ for drops of liquids with surface tensions greater than 24mN/m . Moreover, it was reported that $\text{SA} < 10^\circ$ for liquids with a surface tension greater than 30mN/m . The superamphiphobic fabric

showed excellent chemical robustness, durability after repeated cycles of laundering and mechanical abrasion, as well as stability against UV radiation.

4 Superhydrophobic and Antimicrobial Textiles

In principle, superhydrophobicity and water repellency can promote antimicrobial/bacterial activity. Several research groups took advantage of this principle and designed methods for antimicrobial functionalization of various superhydrophobic textiles using nanoparticles and some other materials, as summarized in Table 3. Consequently, the proposed methods led to the production of multifunctional textiles.

The attention of Mahltig and Fischer was focused on parameters such as textile comfort (stiffness), water uptake, and air permeability [80]. Viscose and polyamide were dip-coated with various coatings. Enhanced hydrophobicity (CA $\sim 140^\circ$) was obtained when the textiles were treated with a sol which was prepared by hydrolysis of TEOS under addition of triethoxytridecafluorooctylsilane. For antimicrobial functionalization, another sol was prepared by hydrolysis of TEOS and Ag modification (Fig. 4). The biocidal activity was retained after ten washing procedures. Considering that with low concentrated coating solutions, a sufficient low stiffness, an acceptable decrease of air permeability, and an enhanced water uptake could be realized, it was suggested to use diluted coating solutions for textile treatment [80].

Ivanova and Philipchenko developed a method to design superhydrophobic and antibacterial textiles, using chitosan-based hydrophobic nanoparticles [81]. Nanoparticles of different sizes (62–67 nm) and surface charge were produced and sprayed onto cotton specimens which obtained a porous texture top layer. The size and surface charge of the nanoparticles were controlled by changing the concentrations of chitosan and an anionic fluorosurfactant (Table 3). The best results were reported for coatings which were prepared using chitosan nanoparticle dispersions with relative number of fluoroanions per elementary unit of chitosan $r = 0.9$ (corresponding to particle size of 63 nm). This sample corresponded to large CA (157°) and small RA (14°) and showed the best durability when in continuous contact with water drop and in washing procedures [81]. In a subsequent study, Ivanova et al. modified the above described method [81] to enhance the stability of the superhydrophobic state of chitosan-based coatings [82]. In particular, to ensure higher

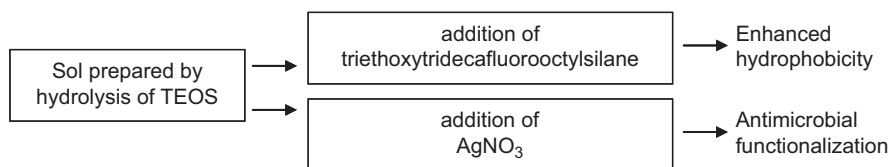


Fig. 4 Routes to treat viscose and polyamide and to achieve enhanced hydrophobicity and antimicrobial activity according to Ref. [80]

Table 3 Nanoparticles and other materials which were used to coat various textiles and to induce superhydrophobicity (SH), accompanied by antimicrobial/bacterial activity (AM). Superoleophobicity (SO) is indicated in a separate column. Other properties which were evaluated according to relative tests are indicated as follows: *DUR* durability, *TRA* transparency, *UVS* UV shielding, *APE* air permeability

Particle used (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	SO	AM	Others	Ref.
SiO ₂	Triethoxytridecafluorooctylsilane for SH property and Ag for AM property	Viscose, polyamide	✓ ^a		✓ ^b	Stiffness, water uptake, APE	[80]
Chitosan (62–67 nm)	CF ₃ (CF ₂) ₇ SO ₃ Li	Cotton	✓		✓	DUR	[81]
Chitosan (62–65 nm)	CF ₃ (CF ₂) ₇ SO ₃ Li and chlorodimethyl-1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecylsilane	Cotton	✓		✓	DUR	[82]
Ag (100–500 nm)	Octyltriethoxysilane	Cotton	✓		✓	DUR, UVS	[84]
TiO ₂ (20 nm)	MTP acrylate	Cotton/polyester blend, wool	✓		✓	UVS, mechanical properties were improved	[85]
SiO ₂ (7 nm)	Emulsion of alkoxy silanes and organic fluoropolymer, 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride	Silk	✓	✓	✓	DUR, TRA, APE	[86]
ZnO and TiO ₂	Organic-inorganic binder and fluorocarbon-based water repellent	Cotton	✓		✓	DUR, UVS	[87]
ZnO (crystallite size ~20 nm or lower)	Magnesium acetate tetrahydrate, monoethanolamine	Cotton	✓		✓	DUR, UVS	[88]
<i>Aloe vera</i> (40 nm)	Chitosan	Cotton	✓		✓	DUR, UVS	[89]
Ag (~40 nm)	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecanethiol	Viscose	✓		✓	DUR, APE, TRA	[90]
SiO ₂ (20–30 nm)	3-(Trimethoxysilyl) propyl-N, N, N-dimethyloctadecyl ammonium chloride and (3-glycidoxypropyl) trimethoxy-silane	Cotton	✓ ^a		✓	DUR, mechanical properties were improved	[91]

(continued)

Table 3 (continued)

Particle used (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	SO	AM	Others	Ref.
TiO ₂ (40 nm)	3-(Trimethoxysilyl) propyl-N, N, N-dimethyloctadecyl ammonium chloride and (3-glycidoxypopyl) trimethoxy-silane	Cotton	✓		✓	DUR, UVS, photocatalytic dye degradation	[92]

^aEnhanced hydrophobicity and oleophobicity were achieved

^bAntimicrobial activity and enhanced hydrophobicity were introduced using different treatments which were applied on different samples

stability of the final coatings in contact with aqueous medium and saturated vapors, an additional treatment step was added to replace the hydrophilic hydroxyl groups of the chitosan nanoparticles with hydrophobic moieties; the textile sample with the nanoparticle coating was immersed in a chlorodimethyl-1*H*,1*H*,2*H*,2*H*-perfluorodecylsilane solution. The additional step resulted in higher CA (160°) and smaller RA (5°) compared to the previously reported results [81] for the sample with $r = 0.9$. More importantly, analysis of the evolution of the CA and RA on prolonged contact with water indicated high long-term chemical stability of the designed coatings in an aqueous medium. It is noteworthy that prior to the above described research [81, 82], Ivanova and Zaretskaya had reported the production of superhydrophobic cotton (CA > 150°) using a commercial fluoroalkylsiloxane as a hydrophobic agent [83]. In this early work of 2010 [83], nanoparticles were not used to induce roughness, but it was reported that the achieved superhydrophobicity originated from nanosized aggregates (50–200 nm) which were formed by the hydrophobic agent molecules.

Ag nanoparticles were attached on cotton textiles by Shateri-Khalilabad and Yazdanshenas through a chemical process [84]. Treated cotton was subjected to hydrophobization using octyltriethoxysilane (OTES). Particle aggregates and smaller particulates with average sizes of about 500 nm and 100 nm, respectively, were formed on the surface of the Cot-Ag-OTES fibers, inducing superhydrophobicity and water repellency as evidenced by the high CA (156°) and low WSA (8°). Untreated cotton (Cot), cotton treated only with Ag nanoparticles (Cot-Ag), and cotton treated only with OTES (Cot-OTES) were included in the study for comparative purposes. Water drops were absorbed by the Cot and Cot-Ag fibers. The surface of the Cot-OTES sample was hydrophobic with CA = 136° and WSA = 31°. Significant antibacterial effects against *S. aureus* and *E. coli* bacteria were induced by the Ag nanoparticles as revealed by the photographs in Fig. 5. Cotton samples were placed on bacteria-inoculated agar plates and were observed for antibacterial activity. Bacterial growth was observed for the Cot and Cot-OTES samples. Distinct zones of inhibition were observed around the Cot-Ag and the Cot-Ag-OTES samples revealing the antibacterial activity of Ag. Finally, it was reported that excellent UV-blocking property of the multifunctional Cot-Ag-OTES fabric was achieved and good durability of the finishing during laundering was demonstrated [84].

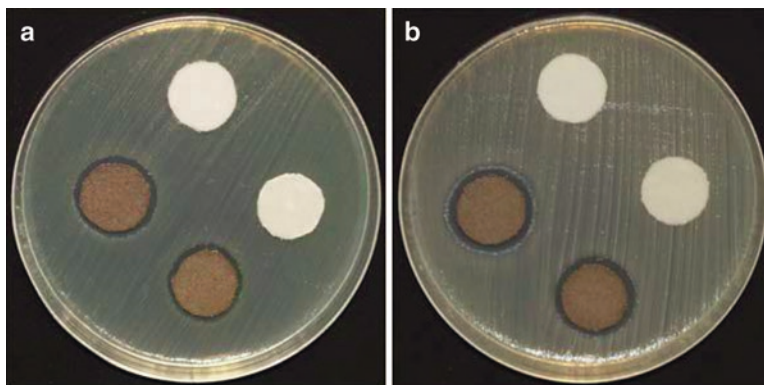


Fig. 5 Antibacterial activities of the fabrics placed on the agar plate inoculated with (a) *E. coli* and (b) *S. aureus*: (top) the untreated cotton, (right) the Cot-OTES, (left) the Cot-Ag, and (bottom) the Cot-Ag-OTES (Reprinted with permission from [84], Copyright Taylor & Francis Ltd, <http://www.tandfonline.com>)

Cotton/polyester and wool samples were coated by Attia et al. [85] using SiO_2 and TiO_2 nanoparticles with a commercial binder (MTP acrylate). Superhydrophobicity ($\text{CA} > 150^\circ$) was reported for textiles treated with TiO_2 by adjusting the mass ratio of the nanoparticles. The ultraviolet protection factor of coated fabrics was significantly enhanced, more than sixfold greater compared to untreated samples. The coatings offered protection against *S. aureus* bacteria and improved the mechanical properties. The significant role of ultrasonication during the preparation of the dispersion was revealed [85].

In a recent article published by Aslanidou and Karapanagiotis [86], the composite coating previously produced [78] was enriched with an antimicrobial agent which is provided in Table 3. The coating offered extreme wetting (superhydrophobicity and superoleophobicity) and good antimicrobial properties to the treated silk. It was shown that the resistance of treated silk against microorganism attack was raised by the antimicrobial agent and was highly promoted by the superhydrophobic character of the coating. Other important properties which were achieved were as follows: the multifunctional coating induced a moderate reduction in vapor permeability of the treated silk, and it showed very good durability against abrasion and had a minor visual effect on the aesthetic appearance of silk [86].

Khan et al. used two formulations, consisting of ZnO and TiO_2 nanoparticles, to coat cotton [87]. Samples were also treated with an organic-inorganic binder and a fluorocarbon-based repellent finish. With both formulations, superhydrophobicity was achieved. The protection of the coatings in the UV radiation was evaluated, and it was concluded that TiO_2 offered better shielding than ZnO . The treated fabrics showed excellent antibacterial activity against *E. coli* and *S. aureus* which were durable up to 20 washing cycles.

Shaban et al. used zinc acetate dihydrate as precursor and monoethanolamine as a stabilizer in a sol-gel method to produce ZnO nanoparticles which were loaded on

cotton fabrics by spin coating [88]. Magnesium acetate tetrahydrate was used as the dopant. The effects of the precursor concentration, precursor solution pH, number of coating runs, and Mg doping percent on the morphology and wettability of treated cotton were investigated in detail. Selection of the optimum concentrations and parameters was crucial to achieve superhydrophobicity, which was evidenced by a large CA (154°) of water drops. The extreme wettability had excellent abrasion resistance and environmental durability under UV illumination as well as in an outdoor environment. Also, functionalized fabrics showed antimicrobial activity against microorganisms such as *S. typhimurium*, *E. coli*, *B. subtilis*, and especially *K. pneumoniae*.

Subramani et al. used exclusively herbal nanomaterials to treat cotton. In particular, they prepared natural nanoparticles from *Aloe vera* plant leaves which were mixed with a chitosan suspension [89]. The mixture was deposited on cotton, and an *A. vera* nanopowders-chitosan composite was formed on the cotton surface which obtained superhydrophobicity ($CA > 150^\circ$); antimicrobial properties against, for instance, *S. aureus* and *E. coli*; and UV protection properties. The performance of treated cotton was affected by washing cycles (Test No. 1 of IS: 687-1979), but overall the washing durability was acceptable.

Bu et al. treated viscose samples using tannic acid to grow Ag nanoparticles onto the textile surface which were then coated by a hydrophobic agent [90], as described in Table 3. The treated textile obtained superhydrophobic properties with CA and SA of water drops of $\sim 155^\circ$ and $\sim 3^\circ$, respectively, which induced self-cleaning abilities. Moreover, treated viscose obtained durable antibacterial properties against *S. aureus* and *E. coli* bacteria. Both superhydrophobic and antibacterial properties were maintained after 50 washing cycles. Treatment had only a slight effect on the air permeability of viscose but a considerable effect on the color of the textile.

Likewise, the goal of Riaz et al. was to develop superhydrophobic and antibacterial cotton fabric with washing durability and without impairing hand feel [91]. For this reason, SiO_2 nanoparticles were functionalized with silane coupling agents (Table 3) which increased their affinity for cotton. By adjusting the relative concentrations of the coupling agents, enhanced hydrophobicity was achieved with CA of drops of 148° , while antibacterial properties (against *S. aureus* and *E. coli* bacteria) were induced and maintained after 20 industrial washing cycles. The fabric's comfort properties, bending rigidity, and tensile strength were improved by the treatment. In another report [92], Riaz et al. functionalized TiO_2 nanoparticles using two agents which are provided in Table 3. The modified nanoparticles were attached onto cotton [92]. The effects of the relative compositions of the modifiers on the wetting properties were investigated. The highest achieved CA of water drops was 151° which was reduced to 131° after 20 industrial laundering cycles. Other properties which were imbued to the cotton by the coating were photocatalytic dye degradation, ultraviolet protection, and antibacterial activity (examined against *S. aureus* and *E. coli* bacteria).

5 Superhydrophobic Textiles for Water-Oil Separation

Water cleaning and harvesting are essential to address increasing demands for clean water and for environmental purposes. The use of textile membranes with extreme wetting properties can become a cost-effective strategy for water-oil separation, as demonstrated in various reports which are summarized in Table 4 and discussed below.

In 2013, two similar processes were suggested by Zhang et al. [93] and Qing et al. [94] to fabricate superhydrophobic membranes made of treated cotton for water-oil separation. Zinc oxide (ZnO) nanoparticles were synthesized and were hydrophobicized, by hydrothermal reaction processes using stearic acid [93] and dodecafluoroheptyl-propyl-trimethoxysilane [94]. The sizes of the nanoparticles were reported as follows: average width and length were approximately 60 and 120 nm according to Zhang et al. [93], whereas in the study reported by Qing et al., the length of the nanoparticles ranged within 50–200 nm [94]. The modified nanoparticles were added in polystyrene solutions, and the dispersions were deposited onto cotton textiles. By adjusting the concentrations of the components appropriately, high values for CA were achieved, corresponding to 155° [93] and 158° [94], induced by nanoscale granules [93] and dual type roughness [94] which were created on the surface of the treated cotton. Zhang et al. reported that superhydrophobicity was maintained after extensive immersion of treated textiles in corrosive liquids and oil and repeatedly wetting-drying-wetting cycles by oil [93]. In both studies it was demonstrated that the superhydrophobic cotton displayed excellent properties in water-oil separation [93, 94].

A versatile method was developed by Sasmal et al. [95] which was used to impart superhydrophobicity to various materials including cotton wool and other textiles. The fabrication of materials with extreme wetting properties was based on the chemical reduction of copper acetate by hydrazine hydrate. The produced Cu nanoparticles were deposited onto various surfaces, which were immersed into a reaction vial. Interestingly, the sizes of the Cu nanoparticles deposited on various substrates were different. Cu nanoparticles on cotton wool ranged within 50–300 nm. The variation of the CA with the volume of the water drop, which ranged within 5–20 μL , was briefly investigated. Coated surfaces obtained superhydrophobic (CA > 160°), roll-off, and self-cleaning properties. The antimicrobial activity of the Cu films was tested against both Gram-negative and Gram-positive bacteria using glass surfaces, whereas coated cotton wool appeared to be effective for water-kerosene separation.

Polyester was treated by Li et al. [96] to produce textile membranes which could remove insoluble oils and soluble dyes from water. Polydopamine and Ag nanoparticles were first deposited on polyester. A top superamphiphilic layer and a bottom superhydrophobic/superoleophilic layer were formed by immobilizing Ag_3PO_4 nanoparticles and using dodecyl mercaptan, respectively. Water with soluble organic dyes could only selectively wet the top layer which could decompose the organic molecules due to its visible-light photocatalytic activity. The water-insoluble oils

Table 4 Nanoparticles and other materials which were used to coat various textiles to obtain extreme wetting properties and to be used for water-oil separation (WOS). Superhydrophobicity (SH), superoleophobicity (SO), and antimicrobial/bacterial activity (AM) are indicated in separate columns. Other properties which were evaluated according to relative tests are indicated as follows: *DUR* durability, *TRA* transparency, *UVS* UV shielding, *APE* air permeability

Particle used (size)	Other materials for particle modification and/or post-treatment	Treated textile	SH	SO	AM	WOS	Other	Ref
ZnO (60 nm in width and 120 nm in length)	Stearic acid	Cotton	✓			✓	DUR	[93]
ZnO (50–200 nm in length)	Dodecafluoroheptyl-propyl-trimethoxysilane	Cotton	✓			✓		[94]
Cu (50–300 nm)	–	Cotton wool	✓		✓	✓		[95]
Ag based	Polydopamine, dodecyl mercaptan	Polyester	✓			✓	DUR, UVS, photocatalytic dye degradation	[96]
Fe ₃ O ₄ /polydopamine/Ag	1H, 1H, 2H, 2H-perfluorodecanethiol	– ^a	✓ ^b		✓	✓	Liquid marble	[97]
SiO ₂ (15–100 nm), TiO ₂ (25–300 nm)	Vinyltriethoxysilane	Cotton and other textiles	✓			✓	DUR	[98]
Cu	Dodecyl mercaptan	Cotton	✓			✓	DUR	[99]
Fe ₃ O ₄ (20 nm)	1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane, PDMS	Polyester	✓			✓	DUR, droplet transportation	[100]
ZnO nanoplates	Octadecylamine	Fabric (80% polyester and 20% cotton)	✓			✓	DUR	[101]
ZnO (15 nm)	Polyvinylsilsesquioxane	Cotton	✓		✓	✓	DUR, UVS, mechanical properties were improved	[102]
Fe ₃ O ₄ and TiO ₂	Dodecylamine	Cotton	✓ ^c			✓	DUR, UVS	[103]

^aThe nanoparticle powder was not deposited on textiles and was used directly for AM and WOS tests

^bEnhanced hydrophobicity was achieved

^cSwitchable wettability

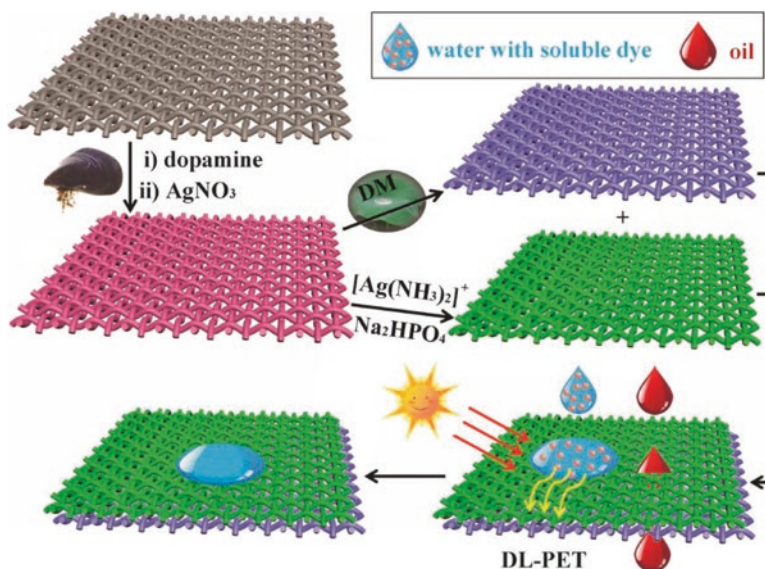


Fig. 6 Polyester is first treated with polydopamine and Ag nanoparticles which were produced from an AgNO_3 solution. A top superamphiphilic layer and a bottom superhydrophobic/superoleophilic layer were formed by immobilizing Ag_3PO_4 nanoparticles and using dodecyl mercaptan (DM), respectively (Reprinted with permission from [96], Copyright American Chemical Society)

could penetrate both layers. These properties of the fabricated membranes are demonstrated in Fig. 6. Treated textiles were characterized by extremely low WSA ($<4^\circ$). Mechanical stability was demonstrated by abrasion and laundering durability tests. Moreover, treated textiles were stable against UV irradiation and resistant to various organic solvents and oils (chemical stability).

Wang et al. fabricated core-shell structured nanoparticles composed of Fe_3O_4 (core) and subsequent layers of polydopamine (PDA) and Ag nanoparticles [97]. After surface modification with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, the spherical and hybrid nanoparticles became highly hydrophobic and were used to form “liquid marble” drops. The latter exhibited non-sticking and rolling-off behavior on various surfaces, including glass, paper, plastic, textile, and ceramic. Furthermore, the structured nanoparticles had other interesting properties. For example, they were used for water-oil separation and had both a magnetic property endowed by Fe_3O_4 and an antibacterial property endowed by Ag.

Wu et al. produced several coatings by mixing vinyltriethoxysilane with various SiO_2 and TiO_2 nanoparticles [98] with size ranges as described in Table 4. The coatings were deposited on various substrates including cotton and two other textile materials. The obtained superhydrophobic surfaces exhibited CA $> 150^\circ$ and SA $< 5^\circ$. Superhydrophobicity on the cotton surface was maintained after several types of tests, including finger wiping, brushing, knife scratching, and sandpaper-induced abrasion. Therefore, the coatings exhibited good mechanical stability and,

moreover, long-term durability. Finally, coated cotton and other materials were successfully used as filter elements for water-oil separation [98].

Wang and Wang produced superhydrophobic-superoleophilic cotton fabrics designed for water-oil separation [99]. Cu nanoparticles were deposited on cotton by immersing the fabric in copper chloride and sodium borohydride solutions. The last step was modification of the Cu coated fabric using dodecyl mercaptan. CA of around 155° was measured for water drops on the surface of modified cotton. The as-prepared fabrics exhibited high efficiency ($>94.5\%$) for the separation of water-oil mixtures. Oils included in the study were n-hexane, toluene, chloroform, gasoline, and diesel. Moreover, the chemical and mechanical stability of the fabrics were excellent; after 400 cycles of abrasion, the highly hydrophobic character of the fabric was maintained, as CA was 145° .

Su et al. reported a magnetic field manipulation strategy to fabricate superhydrophobic polyester with lotus leaf-like and rose petal-like wettabilities on the two sides of the textile [100]. Fe_3O_4 nanoparticles were first coated with 1H,1H,2H,2H-perfluorooctyltriethoxysilane and were then added to a PDMS solution with its curing agent (Sylgard 184). The textile was immersed in the mixture and was subsequently dried and cured at 80°C in the presence of a magnet. Nanoparticles migrated along the magnetic field, resulting in the formation of discrepant hierarchical structures on the two sides of the textile. The surface facing the magnet obtained water-repellent properties with low SA ($\approx 8^\circ$), whereas the pinned state was observed on the other surface of the textile as water droplets firmly adhered even at vertical and inverted angles. Both textile surfaces corresponded to CA $>150^\circ$. The surface morphology and wetting mode were adjustable by varying the ratios of the nanoparticles and PDMS. The as-fabricated superhydrophobic textile showed excellent chemical stability which was evaluated using baths of different solvents and acidic/alkaline solutions. Moreover, the fabricated textile was successfully applied in droplet transportation and water-oil separation.

Lyotropic zirconium phosphate (ZrP) nanoplates were produced and deposited in situ on a commercially available fabric (80% polyester and 20% cotton) by Zeng et al. [101]. In a second step, octadecylamine, acting as both a healing and hydrophobic agent, was introduced into the layered architecture of ZrP. The fabricated membranes presented superhydrophobicity, as the CA of water drops was around 154° . Moreover, high CAs ($>140^\circ$) were measured under a wide range of salinity. The efficacy of the membranes for water-oil separation was investigated using dodecane. Other properties which were imbued to the cotton by the coating were photocatalytic dye degradation, which was mixed with aqueous phases and under extreme pH values. A remarkable separation efficiency of 99.9% was reported which remained steady even after 25 separation cycles [101]. Other organic materials (e.g., toluene, diesel, etc.) were also separated from water by the membrane. The self-healing capability of the membrane was very interesting. After treatment with air plasma, the membrane became hydrophilic because of the formation of polar functional groups, and therefore the water-oil separation efficiency was dramatically reduced. Hydrophobicity and separation efficiency were restored after exposing the air-plasma-oxidized membrane to the air for 48 h. CA was measured over

different etching-healing cycles, and it was shown that it dropped to a stable value of around 135° .

Mai et al. produced multifunctional cotton fabrics by combining the advantages of polyvinylsilsesquioxane and ZnO nanoparticles [102]. The effects of the add-on (ZnO) percent on the following investigated properties were revealed. Superhydrophobicity was achieved with CA of water drops on treated cotton up to 160° , which remained practically unaffected by repeated washing cycles (40 washing times). The treated fabrics appeared to be successful in oil (chloroform)-water separation. Moreover, the composite coating induced UV-blocking and antibacterial properties, according to results which were obtained using *E. coli* and *S. aureus* bacteria. The durability of the functionalized cotton fabrics was satisfactory after several washing cycles. Most notably, the mechanical properties of cotton fabrics were significantly improved by the composite coatings, without compromising their thermal stability, as compared to pristine cotton fabric.

Yan et al. produced a magnetic textile which had a switchable and pH-controllable wettability for applications in water-oil separation and oil-spill treatment [103]. For this purpose, Fe_3O_4 nanoparticles were synthesized using iron chlorides [104], and modified TiO_2 nanoparticles were produced using tetrabutyl orthotitanate and dodecylamine [103]. The as-prepared materials were used to coat cotton samples. The textile showed its superhydrophobicity and superoleophilicity for neutral water ($\text{pH} = 7$). When the textile was wetted with acidic water ($\text{pH} = 2$), it became superhydrophilic and superoleophobic, thus demonstrating the pH-switchable wettability of treated cotton. Superoleophobicity was demonstrated using a large variety of organic solvents and oils. Treated cotton which possessed excellent water-oil separation efficiency ($> 99\%$) showed good durability, recyclability, and stability under UV illumination and high temperature. Finally, the treated textile could be attracted by a magnet bar, indicating that it can be recovered and removed by magnets [103].

6 Conclusions

Nanoparticles opened new avenues for the production of multifunctional textiles. The deposition of nanoparticles onto textiles is an effective route to control the surface morphology and chemistry, therefore promoting repellency of liquids by the treated textile. If the particles are functionalized, then extreme wetting properties, such as superhydrophobicity (Table 1) and superoleophobicity (Table 2), might be achieved by a one-step treatment process (i.e., particle deposition). However, in most of the suggested methods, nanoparticles are combined with finishing, low surface energy agents, to promote the extreme wetting properties and to enhance the binding of the deposited coating on the textile. Liquid repellency is usually accompanied by antimicrobial/bacterial activity (Table 3). The latter can be further promoted if the chemical composition of the selected nanoparticles (e.g., ZnO, Ag, Cu) inherently offers resistance against microorganism attacks. The aforementioned achievements can be extremely useful for the textile industry, particularly when the

useful dewetting and antimicrobial properties show good physical, chemical, and mechanical durability, resistance to the deteriorative effects of the UV light, and cause no discomfort effects when the treated textiles are in touch with the human body. Membrane technology can also benefit from these innovative textiles (Table 4). For example, superhydrophobic and superoleophilic textiles are low-cost materials, which are effective in water cleaning and harvesting. The efficient management and the increase of the available reserves of clean water are top priorities for the next several decades, according to the UNESCO guidelines.

Acknowledgments The authors thank Ms. Lamprini Malletzidou (Aristotle University of Thessaloniki) for useful discussions.

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Self-Recovery Superhydrophobic Surfaces



Wendong Liu, Michael Kappl, and Hans-Jürgen Butt

1 Introduction

Superhydrophobic surfaces are extremely water-repellent. Their receding contact angle (CA) with water is above 150° , which implies that the sliding angle of a water droplet is typically below 10° . Superhydrophobicity is attributed to the combination of micro-/nano-hierarchical rough structures and low surface energy material. The synergetic action of this combination enables water droplets deposited on the surface to establish Cassie-Baxter contact with an air layer formed underneath the droplet. This in turn allows the droplet to maintain its spherical morphology while preventing the liquid wetting the rough structures [1]. As a result, the ability to retain or recover the Cassie-Baxter contact with an air layer is an essential factor when creating superhydrophobicity durability. On account of the low adhesion and extremely small contact area between the water droplet and the solid surface, superhydrophobic surfaces are potentially promising in applications such as self-cleaning [2], oil/water separation [3, 4], antifouling [5], anticorrosion [6, 7], and others [8–12]. Various methods have already been developed to fabricate superhydrophobic surfaces [13–15]. However, due to their poor durability, practical applications are still hindered [16, 17]. The superhydrophobicity of a topological surface can be significantly degraded in two ways: (1) loss of surface structure caused by impact or abrasion, resulting in the increase of the interfacial area between the water droplet and the surface, and (2) loss of low surface energy caused by contamination or damage to the hydrophobic coverage [18]. As a result, the task of creating superhydrophobic surfaces with enhanced durability for practical use has become a challenge.

Different approaches have been attempted to prevent degradation: (1) using harder materials to fabricate hierarchical topological structures to reduce mechanical

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M. Hosseini, I. Karapanagiotis (eds.), *Materials with Extreme Wetting Properties*, https://doi.org/10.1007/978-3-030-59565-4_2

abrasion, (2) introducing inert hydrophobic materials to retard the increase of surface energy and maintain hydrophobicity, and (3) preparing bulk superhydrophobic surfaces (without microstructures or nanostructures) to strengthen durability [19]. These methods have already had the effect of prolonging the lifetime of superhydrophobic surfaces. However, for most of the potential applications under consideration, durability is still limited. The process of enhancing the durability of superhydrophobic surfaces in a simple and universal manner is now an important challenge.

In contrast to artificial materials, plant leaves, the wings of insects, or bird feathers can effectively maintain superhydrophobicity during their lifetime by continuously restoring the epicuticle wax layer or natural renewal of the surface structure after being damaged [18, 20]. Inspired by the self-recovery ability of plants and animals, self-recovery artificial superhydrophobic surfaces have been developed in the last few years. The aim is to enhance durability and to prolong the lifetime when used in practical outdoor applications without the surface needing an external supply of low surface energy components. The mechanism of such improvement is mainly based on the storage of low surface energy components inside the rough structure or/and regeneration of microstructures or nanostructures. When surface wettability is degraded, the preserved hydrophobic materials can be released or moved to the surface to reduce surface energy. This results in the recovery of intrinsic hydrophobicity, as the regenerated microstructure/nanostructure can recover the surface topography after damage to the roughness.

In this chapter, it begins by providing an overview of the progress of fabricating self-recovery superhydrophobic surfaces based on different recovery approaches. It then continues by introducing certain applications of superhydrophobic surfaces processing enhanced durability. Finally, an outlook is offered on the development of fabrication techniques of robust superhydrophobic surfaces which could take place in future research.

2 Techniques to Achieve the Self-Recovery of Superhydrophobicity

A self-recovery surface is a surface which after being damaged can spontaneously restore its own wettability without additional deposition or external modification of hydrophobic components. The self-recovery process of superhydrophobic surfaces is mainly based on the regeneration of the surface chemistry and the restoration of topological structures.

Depending on the process, self-recovery superhydrophobic surfaces can be classified into three categories: migration of low surface energy materials to the surface, restoration of rough topography, and the combination of both. Depending on the damage, one of the three processes is required.

2.1 Migration of Low Surface Energy Materials to the Surface

Migration of low surface energy materials to the surface is the most widely used technique to recover superhydrophobic surfaces when they have been chemically damaged. Additional low surface energy materials are preserved in the rough structures of the surface to mimic the self-regeneration phenomenon of the hydrophobic epicuticle wax layer that can be found in natural plant leaves. As shown in Fig. 1, when the surface chemistry layer with low surface energy decomposes or is degraded, the preserved low surface energy materials are either released spontaneously, or under external stimuli (such as temperature, humidity, ultraviolet light, etc.). The released materials diffuse to the damaged area to reduce the surface energy, resulting in self-recovery of the superhydrophobicity. This directed diffusion is spontaneous as the damaged area possesses high surface energy and the material released reduces the surface energy.

Zhou et al. prepared robust, self-recovery superamphiphobic fabrics by means of a two-step dip-coating of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS), and modified silica nanoparticles [21]. After coating textiles, the modified fabrics showed a static contact angle of 172°, 165°, and 160° to water, soybean oil, and hexadecane, respectively. The coated fabric exhibited remarkable durability to hot water, strong acid and alkali solutions, washing, and abrasion. The self-recovery ability of the coated fabric was further demonstrated by plasma etching in order to introduce hydrophilic groups onto the surface. After 5 min of plasma etching, the upper layer of the surface was enriched with hydroxyl groups, and the coated fabric became both hydrophilic and oleophilic with a contact angle of 0° to water, soybean oil, and hexadecane. However, after annealing the plasma-etched fabric at 135 °C for 5 min, the surface recovered its superamphiphobicity with a contact angle of 171°, 165°, and 160° to water, soybean oil, and hexadecane, respectively. This method of self-recovery behavior is repeatable. After 100 cycles of the etching and heating, the coated fabric maintained its superamphiphobicity, which indicated its excellent ability for self-recovery. The self-recovery mechanism is based on the migration of the low surface energy materials (PVDF-HFP and FAS) embedded in the coating. Plasma etching damaged the surface and introduced polar groups to the surface, and this resulted in hydrophilicity and lipophilicity due to the increased surface energy. During heat

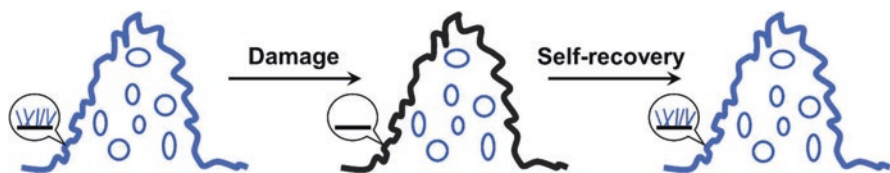


Fig. 1 Principle of self-recovery superhydrophobic surfaces based on migration of low surface energy materials. Blue represents the low surface energy materials; black represents the basic structural materials

treatment conducted at a temperature above the glass transition temperature of PVDF-HFP (-40°C), the fluorinated alkyl chains (PVDF-HFP and FAS) migrated to the surface and replaced the hydrophilic polar groups. As a result, the surface free energy decreased, and the superamphiphobicity recovered. The PVDF-HFP in the coating acted not only as a low surface energy material but also as a binding agent to fix the silica nanoparticles and improve the durability of the coated fabric. A standard machine laundry test demonstrated that the coated fabric maintained its superamphiphobicity after 600 cycles of washing, suggesting that the surface property of the coated fabric can maintain up to 11.5 years of uses when washed once a week. Abrasion durability was investigated using the Martindale method. After 8000 cycles of abrasion with a load pressure of 12 kPa, the coated fabric still demonstrated a sliding angle lower than 10° for all the liquids. After 25,000 abrasion cycles, the coated fabric still retained its superhydrophobicity, although it lost its oleophobicity.

Li et al. fabricated self-recovery superhydrophobic surfaces by spraying polyelectrolyte complexes of poly(allylamine hydrochloride)-sulfonated poly(ether ether ketone) (PAH-SPEEK), poly(acrylic acid) (PAA), and the healing agent of perfluorooctanesulfonic acid lithium salt (PFOS-Li) on a substrate [22]. Alternating spraying of PAA and PAH-SPEEK formed porous and rough (PAA/PAH-SPEEK)*80 structures on the substrate. After spraying PFOS on the (PAA/PAH-SPEEK)*80 structure, the surface energy was further reduced and formed a superhydrophobic surface PFOS-(PAA/PAH-SPEEK)*80. During the spray coating process, a large amount of PFOS was preserved in the (PAA/PAH-SPEEK)*80 structure due to the electrostatic interaction between the sulfonate group and the protonated amine groups of the PAH, serving as a healing agent. The self-recovery ability was characterized by decomposing the top PFOS layer with O_2 plasma to mimic chemical damage of the surface. The surface became superhydrophilic with a water CA of 0° after 1 min of O_2 plasma treatment, indicating that the PFOS layer was etched off and formed oxygen-containing hydrophilic groups on the (PAA/PAH-SPEEK)*80 surface. The combination of the rough structure and the increased surface energy endowed the plasma-treated surface with superhydrophilicity. After exposing the plasma-treated surface in an ambient environment of 40% relative humidity for 4 h, the original superhydrophobicity was restored. The preserved PFOS within the (PAA/PAH-SPEEK)*80 structure was expelled and spontaneously migrated to the surface to reduce the surface energy. Meanwhile, the polar hydrophilic groups produced by O_2 plasma etching were buried inside the hydrophilic polyelectrolyte coating. In this manner, superhydrophobicity was self-recovered. Due to the electrostatic interaction between the PAA and PAH-SPEEK layers, the PFOS-(PAA/PAH-SPEEK)*80 surface possessed satisfactory mechanical stability to guarantee long-term self-recovery. After repeating the etching recovery processes for several cycles, the PFOS-(PAA/PAH-SPEEK)*80 surface was still able to maintain its superhydrophobicity with only an insignificant change in the water contact angle while maintaining small sliding angles. Taking advantage of this method of fabrication by full spraying, a superhydrophobic surface could be achieved 25 times faster than traditional dipping layer-by-layer assembly. In addition, the superhydrophobic coating

could regain its ability to recovery by simply respraying low surface energy POTS (1H,1H,2H,2H-perfluorooctyltriethoxysilane) when the preserved healing agents are consumed after multiple healing processes.

In another approach, self-recovery superhydrophobic surfaces were fabricated by preserving the low surface energy component either in a porous structure on a substrate or in capsules embedded in the superhydrophobic layer [23–28]. Wang et al. fabricated a self-recovery superamphiphobic surface based on an anodized aluminum oxide (AAO) substrate [29]. The AAO surface possesses hierarchical structures with innumerable nanopores orthogonally aligned in the microstructures. The nanopores served as reservoirs for low surface energy materials. After perfluorooctyl acid (PFA) was loaded into the nanopores and modified on the surface, a superamphiphobic surface was obtained. After the surface was decomposed by O_2 plasma, the difference in surface energy between the damaged surface and the PFA-loaded nanopores drove the PFA migrating to the damaged surface to spontaneously minimize the surface energy. The recovered surface once again possessed superhydrophobicity and superoleophobicity (hexadecane contact angle was larger than 150°). The self-recovery process could be repeated for at least six cycles, and additionally, it could be accelerated at a higher temperature, which enhanced the mobility and migration of PFA.

Similarly, Chen et al. prepared a self-recovery superhydrophobic surface based on UV-responsive microcapsules [30]. UV-responsive microcapsules were synthesized by Pickering emulsion polymerization of styrene using TiO_2 and SiO_2 nanoparticles as the Pickering agents. Dodecafluoroheptyl-propyl-trimethoxysilane (FAS-12) was preserved in the microcapsules during the synthesis process. Superhydrophobic surfaces were made by coating a mixture of the microcapsules, heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane (FAS-17)-modified SiO_2 , and polysiloxane latex on a target substrate. When the surface was physically damaged or contaminated by oil, its surface wettability could be recovered by UV irradiation. Under UV irradiation, the entrapped FAS-12 in the microcapsules was released due to the photocatalyzed degradation of polystyrene. As observed previously, the released FAS-12 diffused to the damaged area and reduced the surface energy. As a result, the surface regained its liquid repellency. The obtained superhydrophobic surface retained its superhydrophobicity in an outdoor environment for more than 2160 h. The damage-recovery process could be repeated for at least ten cycles without a loss in the surface wettability, demonstrating finely enhanced durability, which has clear potential for outdoor applications.

The self-recovery superhydrophobic surfaces mentioned above are all based on fluorine compounds. Nevertheless, fluorine materials can be easily degraded and released into the environment and are harmful to humans and wildlife. Given this, considerable effort has been made to fabricate self-recovery superhydrophobic surfaces based on fluorine-free materials [31–34]. Such environmentally friendly fluorine-free surfaces are more beneficial and suitable for practical use, thus increasing the application range of superhydrophobic surfaces. By using polystyrene/ SiO_2 core/shell nanoparticles as a rough skeleton followed by spraying them with polydimethylsiloxane (PDMS) as a hydrophobic interconnection, Xue et al. were

able to prepare durable and self-recovery superhydrophobic surfaces [35]. When the surface wettability was damaged by O_2 plasma, the PDMS embedded in the rough structures migrated to the hydrophilic region to minimize surface energy and recover superhydrophobicity. The self-recovery process proceeded spontaneously over 12 h at room temperature. It could be repeated many times, endowing the surface with prolonged durability. Self-recovery could also be sped up by heating or applying tetrahydrofuran. Tetrahydrofuran dissolves in the matrix and enhances the mobility of PDMS chains inside the coating.

Similarly, Liu et al. spray-coated substrates with an all-in-one suspension, which contained aluminum phosphate, TiO_2 nanoparticles, and octadecyltrichlorosilane (OTS) [36]. The coating proved to be superhydrophobic due to the combination of highly textured surface structures formed by TiO_2 nanoparticles and the low surface energy of OTS. OTS, which acts as surface modification and recovery material in the coating, provided low surface energy for the textured structure and recovered low surface wettability after damage. When the surface was decomposed by hot water, O_2 plasma, or amphiphiles, the embedded OTS was released from TiO_2 structures and moved to the damaged surface to recover superhydrophobicity. Such a surface should not, however, be exposed to continuous UV light as TiO_2 is a photocatalyst which decomposes the OTS under UV light.

Recently, Zeng et al. also fabricated a self-recovery superhydrophobic surface without using fluorine compounds [37]. By using an interfacial crystal growing process, zirconium phosphate (ZrP) nanoplates were grown on textiles in situ. After infiltration with octadecylamine (ODA), a superhydrophobic surface was obtained. ZrP nanoplates provide the structure necessary for liquid repellency and also serve as chemistry barriers, while the ODA provides low surface energy. After undergoing a plasma etching process, the damaged liquid repellency could be recovered by exposing the surface to air for 48 h at room temperature. The superhydrophobicity was restored in a shorter time by heating the damaged surface to 65 °C to enhance the thermal migration of ODA to the decomposed area and reduce surface energy.

These fluorine-free methods have expanded the range of use in which self-recovery superhydrophobic surfaces can be applied, such as water treatment, fuel purification, and cleanup of oil spills.

Some of the self-recovery processes rely on external stimuli to induce the migration of low surface energy materials, such as temperature, humidity, or light, which limit the range of practical application. In other cases, the self-recovery process could also be conducted in an ambient environment but required additional time. Given this, ongoing efforts are aimed at both accelerating the self-recovery of superhydrophobic surfaces and inducing self-recovery under more practical conditions.

2.2 Restoration of Surface Topography

Reconstruction of surface roughness or structure is another aspect of recovering the superhydrophobicity (Fig. 2). Recovery is required after physical damage to the surface's topography, such as abrasion/scratching or crushing. One challenge of recovering the surface topology of superhydrophobic surfaces concerns their intrinsic hierarchical structure. Topology on different length scales has to be recovered. Considerable effort has been made to fabricate self-recovering topography in superhydrophobic surfaces [38–42]. What follows here is an overview of how such superhydrophobic surfaces may recover their surface topography. Even though the restoration of topography here is not as perfect as natural living things able to grow rough structures by themselves, the restoration of the surface roughness is still beneficial to surface wettability recovery.

One method is to restore the surface roughness by rearranging of the components in the coating. Puretskiy et al. obtained a self-recovery superhydrophobic surface based on highly fluorinated crystalline fusible wax with incorporated colloidal particles (Fig. 3a) [43]. With the help of the high crystallization tendency of the wax, a rough fractal structure can form spontaneously on the coated surface (Fig. 3b). When the top layer of the coating was scratched with a razor blade, the surface became smooth and lost its superhydrophobicity (Fig. 3c, e). The surface wettability recovered after the damaged coating was melted at 60 °C for 30 sec (Fig. 3e). Self-recovery is attributed to the migration of colloidal nanoparticles that had become embedded in the coating during the melting process. The melting of wax allowed the nanoparticles to become mobile. Phase segregation then drove the nanoparticles toward the surface to form a similar structure present before damage (Fig. 3d). Using this method, superhydrophobicity could be regained even after the repetition of multiple structure damage-recovery cycles (Fig. 3e).

Similarly, researchers have utilized polymers for structural restoration based on the rearrangement aggregation. Bai et al. prepared a self-recovery superhydrophobic surface by spraying a mixture of polymethyl methacrylate (PMMA), zinc oxide (ZnO), and stearic acid (STA) onto a surface [44]. The introduction of ZnO into the mixture and the spraying process resulted in a coating with a rough structure. Meanwhile, the long hydrophobic alkyl chains of STA and ZnO provide low surface energy, resulting in superhydrophobicity with a water CA of up to 158° (Fig. 4a). After strong and repeated droplet impact, the topography changed and became



Fig. 2 Principle of self-recovery superhydrophobic surfaces based on restoration of surface topography

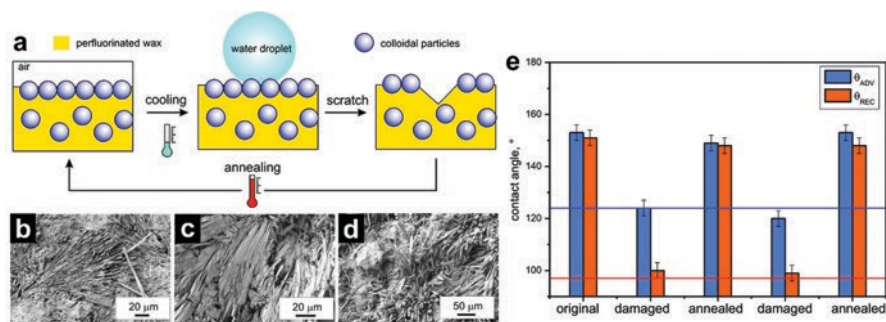


Fig. 3 (a) Schematic of materials with self-recovery superhydrophobicity. (b–d) Morphology (CryoSEM images) of perfluorinated wax-particle blends as prepared (b), scratched (c), and annealed (d) after scratching. (e) Advancing (blue) and receding (red) water contact angles on the surface of perfluorinated wax with incorporated particles after different stages of treatment. (Reproduced with permission from reference [43] Copyright 2012, American Chemical Society)

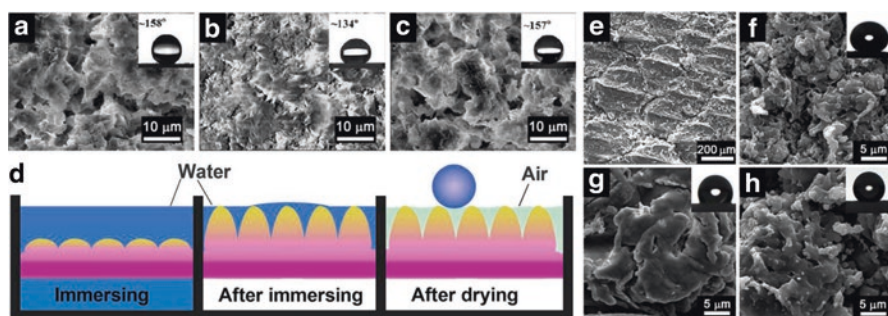


Fig. 4 SEM images of a superhydrophobic coating prepared from a mixture of PMMA, ZnO, and STA (a–c). The superhydrophobic coating before (a) and after (b) damage by droplet impacting and after recovery of topography by immersion in water and drying at 80 °C (c). The inserts show the CA images corresponding to each morphology. (d) Schematic of the self-recovering mechanism of superhydrophobic coating. (Reproduced with permission from reference [44] Copyright 2016, Elsevier). SEM images of sharkskin-templated PDMS films (e–h). (e) PDMS film with grooved structure. (f–h) Topographic structure of enlarged PDMS film: original (f), mechanically damaged (g), and self-recovered (h) inserts – water CA photographs of the biomimetic PDMS films in each state. Reproduced with permission from reference [48] Copyright 2016, Elsevier)

smooth. Superhydrophobicity was subsequently lost, and the water CA decreased to 134° (Fig. 4b). The original structure and wettability could be restored by immersing the damaged surface in deionized water for 30 min and then by drying at 80 °C (Fig. 4c). Superhydrophobicity was restored after the damage and could be recovered repeatedly. The mechanism of structure restoration, in this case, was attributed to the swelling behavior of PMMA in water [45–47]. As shown in Fig. 4d, once the destroyed surface is soaked in water, water will penetrate into the damaged structure and induce the swelling of PMMA, which will restore the topographic structures compressed during the impacting process. After the drying process, the water in the

recovered structure evaporated leaving the holes with hydrophobic air again, thus restoring superhydrophobicity. This particular recovery process is simple and environmentally friendly, fulfilling outdoor application requirements.

Recently, Liu et al. fabricated a self-recovery superhydrophobic surface by replicating the surface of a shark's skin in a PDMS surface. Replication was followed by grafting poly(2-perfluorooctylethyl methacrylate) (PFMA) using surface-initiated atom transfer radical polymerization (SI-ATRP) (Fig. 4e) [48]. After immersing the surface in ether ethanol or DMF, the PFMA brushes assembled into irregular structures (Fig. 4f). A combination of microscale grooves with a size of ca. 80 μm and irregular structures on a 0.5–5 μm length scale resulted in the formation of a superhydrophobic surface. Contact angles with 10 μL water were reported to be 158°. With the help of these grooved structures, the prepared surface demonstrated wear resistance. The surface was able to retain its superhydrophobicity after ten times abrasion with sandpaper (1 $\times$ 1 cm^2 , 200#) loaded with a 500 g weight. Each time, the sample was moved 10 cm over the sandpaper. The self-recovery ability was investigated by using the finger wiping test. After the surface was wiped, it became flat with less irregular structures compared to those of the original surface. This flattening was due to the aggregation and collapse of PFMA chains caused by abrasion (Fig. 4g). The damaged surface structure could be restored after immersing the damaged surface in DMF for 1 h. Since DMF is a good solvent for PFMA, the polymer brush in the damaged area became mobile and reassembled into an irregular structure and thus was able to restore the surface topography and wettability (Fig. 4h). The damage and self-recovery process could be repeated for at least eight cycles.

However, when surfaces are severely scratched and many cuts extend over 10 μm in width and depth, the component rearrangement strategy described above is often unsuccessful. Given this, the film needs to be thicker, and restoration needs to include healing of the bulk of the film, even in the area underneath the direct surface region. One such example is reported by Wu et al., who fabricated a conductive superhydrophobic film. Wu's group prepared surfaces by depositing a layer of Ag nanoparticles and Ag nanowires (AgNPs-AgNWs) on a film of polycaprolactone (PCL)/poly(vinyl alcohol) (PVA), followed by hydrophobization with 1H,1H,2H,2H-perfluorodecanethiol (PFDT). The synergism of low surface energy of PFDT and the hierarchically rough structure of AgNPs-AgNWs resulted in a superhydrophobic film with a water CA of about 158° and sliding angle of 3° (volume of droplet, $V_{\text{drop}} = 4 \mu\text{L}$). By applying voltage or near-infrared light, the loss of wettability of such a surface could be recovered even after being severely scratched [49]. When an electric current or NIR light is applied, it leads to an increase in temperature and thermal healing of the PCL/PVA film. Hundreds of micrometer wide cuts could be restored rapidly and repeatedly, or at least the width of the cuts could be greatly narrowed. They cut the PFDT/AgNPs-AgNWs/(PCL/PVA)*7 film with a knife, the cut having a width of 136 μm which penetrated down into the underlying substrate. The damaged region became sticky so that a water drop adhered to the surface, even when it was turned upside down. Such a change in wettability is caused by the exposure of hydrophilic (PCL/PVA)*7 to the air. Superhydrophobicity could be recovered

by applying 4 V voltage (0.32 W/cm^2) to the destroyed film for 1 min. The cut became narrow and superhydrophobicity was recovered. Water CA hysteresis and the water sliding angle were reduced to 2° and 3° ($V_{\text{drop}} = 4 \mu\text{L}$). The bottom of the cut was recovered by the hierarchical structure of AgNPs-AgNWs. However, when a cut was made across the entire length of the prepared film perpendicular to the current direction, voltage application was ineffective as the top layer was no longer conductive. In this case, near-infrared (NIR) light was used to induce the recovery process based on the photothermal effect of AgNPs-AgNWs. When a cut was made with a width of $72 \mu\text{m}$, which was across the entire length of PFDT/AgNPs-AgNWs/(PCL/PVA)*7 film, the damaged surface lost its superhydrophobicity. However, after being irradiated by 812 nm NIR light ($\approx 1.4 \text{ W/cm}^2$) for 1 min, the separated film reconnected with hierarchically structured AgNPs-AgNWs, and superhydrophobicity was restored. The restoration of physical damage, in this case, was driven by the flow of the thermally healable (PCL/PVA)*7 layer beneath the AgNPs-AgNWs texture. When voltage or NIR light is applied to the scratched surface, the AgNPs-AgNWs can act as an electrothermal or photothermal heater, heating up the (PCL/PVA)*7 to its melting temperature. Then the molten film will flow to the damaged region driven by capillary pressure to reduce surface energy. Due to the strong adhesion between the PFDT/AgNPs-AgNWs layer and the (PCL/PVA)*7 film, the flow of the (PCL/PVA)*7 film pulls the separated PFDT/AgNPs-AgNWs layers toward each other, thus recovering liquid repellency.

Similarly, Li et al. prepared a self-recovery superhydrophobic surface by using a two-step spray coating [50]. A layer of epoxy resin (EP)/PCL was first sprayed onto a substrate. Afterward, a mixture of fluorinated SiO_2 (F- SiO_2), Fe_3O_4 , EP, and PCL was sprayed on top. After the solvent evaporated, the particles in the top layer provide the structural roughness necessary for superhydrophobicity. In combination with the low surface energy of fluoroalkyl silane grafted onto the SiO_2 nanoparticles, the obtained surface exhibited superhydrophobicity with a water CA of 158° . Here, the pure EP/PCL layer acted as healing material, while the Fe_3O_4 nanoparticles efficiently absorbed light and acted as a photothermal heater. The scratched surface could recover its original morphology and superhydrophobicity rapidly after exposing the surface to NIR light ($\approx 1.2 \text{ W/cm}^2$) for 1 min. Fe_3O_4 nanoparticles converted the IR light to thermal energy and heated the EP/PCL film beneath. When the temperature reached the melting point of the film, the polymers flowed to the damaged region, meanwhile pulling the separated surfaces toward each other to restore the surface roughness and wettability. The damage-recovery process could be repeated at least ten times without losing any superhydrophobicity. This method enhances the durability in practical applications such as decoration, construction, electronics, and wearable devices. In general, the restoration of surface topography achieved through the use of self-healing materials radically improves the performance of superhydrophobic surfaces exposed to harsh environments.

Another technique for topography restoration is based on shape memory polymers (SMP). SMP are stimuli-responsive materials which possess the ability to recover their original morphology after being temporarily deformed when exposed

to an external stimulus. Using this kind of material for superhydrophobic surface fabrication can completely restore the damaged structure [51–53].

Using epoxy SMP as building materials, Chen et al. prepared a self-recovery superhydrophobic surface based on micropillar arrays with a high aspect ratio (height/diameter) [54]. They prepared micropillar arrays in a square lattice arrangement, each micropillar having an aspect ratio of three. The large spacing between pillars provided high air/liquid area fraction, which resulted in a superhydrophobic surface with the water CA reaching 155° . When the vertical micropillars were deformed by an external force, water drops changed to the Wenzel state, and superhydrophobicity was lost. After annealing the deformed surface at 80°C (above the T_g of the SMP of $\sim 60^\circ\text{C}$) for about 50 sec, the deformed micropillar structure was restored to the original vertical morphology with a square lattice arrangement. As a result, superhydrophobicity recovered as well.

Since high aspect ratio pillars are typically not mechanically stable and unfavorable for dynamic control, Lv et al. designed a superhydrophobic surface based on epoxy SMP micropillar array with an aspect ratio of 1 (Fig. 5a, d) [55]. Water drops formed a contact angle of 151° on these surfaces (Fig. 5d, inset). After the surface was deformed by heating and mechanically pressing with a clean glass slide at a given pressure, the water CA decreased to 110° (Fig. 5b, e). Superhydrophobicity could be restored by annealing the deformed surface at 120°C for around 45 sec. The original micropillar structure recovered, and the water CA returned to 151° (Fig. 5c, f). Due to the relatively low aspect ratio of the micropillar arrays, this superhydrophobic surface was more durable, and superhydrophobicity could be recovered for 50 cycles of repeated deformation and recovery (Fig. 5g).

Wang et al. reported the first superamphiphobic SMP surface. This surface not only was able to repel water but also showed high contact angles with oils [56]. Using thiol-ene-/acrylate-based thermoresponsive SMP as a building material, mushroom-like structures with reentrant features were obtained through applying a combination of photolithography and reactive ion etching. After modifying the obtained structure with low surface energy heptadecafluoro-1,1,2,2-tetrahydrodecyl

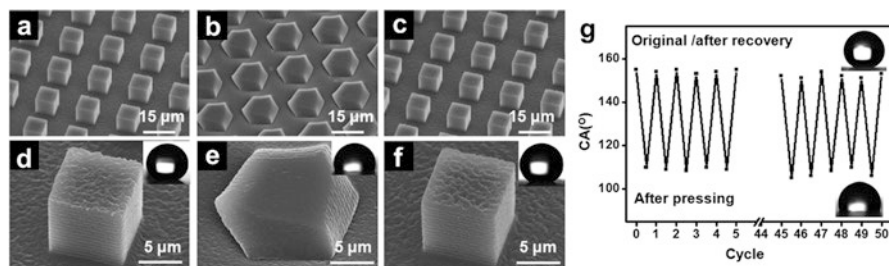


Fig. 5 (a–f) SEM images of SMP micropillar-based superhydrophobic surface viewed at a tilt angle of 40° : (a, d) The original achieved structure, (b, e) deformed pillar structure, (c, f) morphology recovery of deformed pillars under 120°C . Insets show the photographs of water droplets in different states. (g) Change in water CA of the pressed and self-recovered surface. (Reproduced with permission from reference [55] Copyright 2016, American Chemical Society)

trichlorosilane, superamphiphobicity was obtained. The SMP surface showed a similar pattern of morphology recovery as the abovementioned epoxy SMP surface. The mushroom-like structure could be reversibly switched between the original morphology and the deformed shape through pressing-recovery processes. The surface could be restored so that both water and *n*-hexadecane assume the original low adhesive Cassie-Baxter state. In the deformed state, hexadecane wets the substrate and assumes a Wenzel state. In contrast, the water was in the Cassie-Baxter state even on the deformed surfaces. On the deformed surface, the loss of the reentrant structure had no significant influence on the water wetting state. However, *n*-hexadecane absorbed into the structure and finally changed the oil into the Wenzel state [51]. Wang et al. anticipate applications in rewritable liquid patterns, liquid-liquid separation membranes, and biosensors.

Besides using stimuli-responsive SMP as building materials, Das et al. developed a robust self-recovery bulk superhydrophobic surface [57]. The superhydrophobic surface was achieved by a 1,4-conjugate addition reaction between aliphatic primary amine groups and aliphatic acrylate groups. The aliphatic primary amine groups were provided by using branched poly(ethylenimine) (PEI) and amino graphene oxide (AGO); the aliphatic acrylate groups were provided by using dipentaerythritol penta-acrylate (5AcI). The combination of random aggregation of granular polymer domains with AGO sheets allowed a surface with a porous structure to form. After modifying the residual acrylates groups in the coating with decylamine molecules, the surface became superhydrophobic with an advancing water CA of 162° and CA hysteresis of 3°. By applying a 188 kPa pressure on the coating over an area of 0.5 cm² for 10 sec, this porous structure was deformed, resulting in a loss of superhydrophobicity. The original nonadhesive superhydrophobic surface became highly adhesive with a CA hysteresis of 50°. However, the deformed structure could be recovered by exposing it to an ambient environment for 1 day after releasing the pressure. Such spontaneous recovery behavior could be repeated for 40 damage-recovery cycles while maintaining the surface topography and wettability. Recovery could be sped up by increasing the amount of AGO in the coating. When the AGO concentration reached 30.8 µg/mL in the coating solution, the complete recovery of the coating was concluded within 30 min under ambient conditions. The fast recovery from the state of adhesive wetting to nonadhesive repellency makes it possible to develop rewritable aqueous patterns on an extremely water-repellent polymeric coating.

2.3 Combination of Low Surface Energy Material Migration and Rough Topography Restoration

In an ideal situation, these recovery methods are combined to repair both physical and chemical damages (Fig. 6) [58–61].



Fig. 6 Principle of self-recovery superhydrophobic surfaces based on the combination of low surface energy material migration and rough topography restoration. Blue represents the low surface energy materials; black represents the basic structural materials

Wang et al. developed a superamphiphobic surface by coating a fabric substrate with fluoroalkyl surface-modified silica nanoparticles (FS-NP). This first step was followed by an additional coating of a mixture of fluorinated decylpolyhedral oligomeric silsesquioxane (FD-POSS) and tridecafluorooctyl triethoxysilane (FAS) [62]. A surface created by this process showed excellent liquid repellency. 10 μL water, hexadecane, and anhydrate ethanol droplets deposited on the surface formed CAs of 171° , 157° , and 151° , respectively. After treating the surface with air plasma to introduce polar groups onto the surface, the surface became hydrophilic, and its surface energy increased. The superamphiphobic surface became amphiphilic, with contact angles of 0° for both water and oil. The degraded surface could be recovered after annealing at 140°C for 5 min. High temperature enhanced the mobility of preserved FAS, which migrate to the polar area to minimize surface energy. The SiO_2 nanoparticles protected the FD-POSS/FAS directly underneath the nanoparticles, so that superamphiphobicity could be maintained even after 100 cycles of plasma etching and heating. In addition, the surface wettability could be degraded by abrasion with 1200# sandpaper. After annealing at 140°C for 30 min, the FD-POSS and SiO_2 nanoparticles were able to reconstruct the surface roughness. This morphological rearrangement led to the structure necessary for superamphiphobicity recovery. Wang et al. report that superamphiphobicity could still be retained after 2000 cycles of abrasion and recovery.

Qin et al. prepared a fast self-recovery superhydrophobic surface by integrating the hierarchical structure of Super P (a conductive carbon black) and TiO_2 nanoparticles onto a PDMS-GA (gallic acid) network cross-linked by dynamic pyrogallol-Fe coordination, followed by a modification of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS-17) [63]. The loss of superhydrophobicity caused by plasma etching or physical scratching could be speedily recovered by applying a current of 10 V, resulting in an increase in the temperature of the coating, and weakening the coordination of pyrogallollic moiety and Fe^{3+} between PDMS-GA chains in the network. Weakening the coordination had two effects: Firstly, it allowed the preserved FAS-17 in the hierarchical texture to minimize the surface energy by migrating to the surface. Secondly, part of the PDMS-GA chains were released from the cross-linked network. They flowed to the physically damaged gap and healed the bottom layer. The recovery of the PDMS-GA network drove the separated structural surface areas toward each other to restore the surface

topography. This closing of gaps resulted in the recovery of surface wettability even after physical scratching.

By using epoxy-based SMP, Lv et al. also obtained a superhydrophobic surface that could recover from both surface structure deformation and surface chemistry decomposition [64]. The recovery process was initiated by heating. Chemical damage was reversed by migrating polymer chains to polarized areas to reduce the surface energy. Meanwhile, the deformed hierarchical structure could also be restored due to the thermal-responsive SMP. It could be transformed from its temporary shape back to its permanent structure after heating. The combination of being able to reverse both chemical and physical damages could further enhance durability while meeting the requirements posed by different internal and external conditions, resulting in a wider range of usage for superhydrophobic surfaces.

3 Application of Self-Recovery Superhydrophobic Surfaces

Being able to make more durable self-recovery super liquid-repellent surfaces offers a more relevant range of application. In this section, an overview of potential applications of self-recovery superhydrophobic surfaces is provided.

3.1 Prevention of Corrosion

By directly modifying a surface to become superhydrophobic and thus water-repellent, contact between water and the substrate can be prevented, therefore reducing possible corrosion of the substrate. Ezazi et al. fabricated a self-recovery superamphiphobic surface aimed at corrosion protection [65]. In their work, a copper mesh was spray-coated with a cross-linked mixture of epoxidized soybean oil, perfluorinated epoxy, citric acid, and silica nanoparticles. The coating was superamphiphobic due to the low surface energy of the perfluorinated epoxy and the hierarchical structure formed by silica nanoparticles. A 3 μL *n*-dodecane drop formed a CA of 151° and slid off the surface at an angle $<10^\circ$. These surfaces showed good corrosion protection. The corrosion rate of the coated copper mesh was reduced to about 20% of the conventional superhydrophobic corrosion protection coating when immersed in corrosion agent (3.5 wt% NaCl aqueous solution). The diffusion of the corrosion agent into the coating was greatly reduced with complete saturation after 108 h. In contrast, when using commercial paint, it took only 0.3 h. Importantly, once the surface was physically damaged, the loss of wettability and anticorrosion was spontaneously recovered by annealing the surface at 60°C for 1 min, resulting in efficient, long-term anticorrosion performance.

When a corrosion inhibitor was integrated inside the self-recovery superhydrophobic coating, improved anticorrosion behavior could be achieved. Qian et al. developed a self-recovery superhydrophobic surface, which was fabricated on a

steel substrate based on the replication of a lotus-like structure using epoxy-based SMP. They added the corrosion inhibitor benzotriazole (BTA) [53]. Thanks to the shape memory property of SMP, a physical scratch could be restored after a short period of heating. At the same time, heating prolonged the anticorrosion ability. The combination of having an SMP plus a corrosion inhibitor reduced the corrosion rate to about 10% compared to the SMP coated steel substrate without BTA preservation.

Ding et al. prepared a superhydrophobic coating based on mechanized silica nanoparticles for reliable protection of magnesium alloys [66]. The anticorrosion coating was obtained by coating a mixing mechanized silica nanoparticles (MSNPs) and self-assembled nanophase silica particles, followed by a modification of 1H,1H,2H,2H-perfluorodecyl triethoxysilane (PFDS). With the help of the finely ordered mesopores that MSNPs possessed, a corrosion inhibitor (2-hydroxy-4-methoxy-acetophenone, HAMP) was successfully encapsulated in the MSNPs and preserved in the coating. Here, nanoparticles provided the structural necessity, while PFDS provided the coating with low surface energy. The HAMP preserved in the MSNPs was released under alkali or Mg^{2+} stimuli produced by the corroding micro-regions of magnesium alloy. The combination of corrosion inhibition properties of the released HAMP and the restorable liquid repellency due to the self-recovery ability of the coating led to long-term anticorrosion behavior.

3.2 Oil/Water Separation

Self-recovery superhydrophobic surfaces with (super) oleophilicity could be used for oil/water separation in environmental protection and resource preservation since oil can easily penetrate the surface while the water stays. Li et al. grafted MnO_2 nanoparticles on cotton fabrics using an in situ growth method, followed by a modification of stearic acid (STA) [67]. With the help of a hierarchical structure formed by MnO_2 and low surface energy provided by STA, the fabric obtained was superhydrophobic. The preserved STA in MnO_2 structures provided the coated fabric with the ability to recover after chemical decomposition. When using the coated fabric to separate a mixture of 1,2-dichloroethane and distilled water ($V_{oil}:V_{water} = 1:1$), the oil could infiltrate the fabric quickly, while water could only be retained on the top. The efficiency of oil/water separation was greater than 90% even after many separation cycles. Once the surface wettability was damaged, it could be recovered by heating the fabric at 130 °C for 10 min. After treatment, the oil/water separation efficiency was also recovered. Liu et al. also reported the use of fabrics coated superhydrophobically for oil/water separation [68]. Instead of using a hybrid of inorganic nanoparticles and organic materials, the fabric was coated with perfluorodecyl acrylate. It had a water CA of 152 ° and a water sliding angle of 7 ° ($V_{drop} = 5 \mu L$). The wettability loss caused by abrasion could be recovered by annealing the surface at 110 °C for 5 min. The coated fabric could be used for the separation of various oil/water mixtures, such as chloroform, toluene, peanut oil, and

silicone oil. All of these oil/water mixtures could be effectively separated with the separation efficiency being higher than 96%.

Besides coating fabrics, the electron-spinning of polymers with low surface energy is another strategy to prepare superhydrophobic membranes for oil/water separation. Fang et al. fabricated a superhydrophobic membrane by electro-spinning *N*-perfluorooctyl-substituted polyurethane (PU-C₈F₁₇) [69]. Several organic liquids with a surface tension lower than 30 mN/m, including *n*-hexane, petroleum ether, bromoethane, ether, and toluene, mixed with water ($V_{oil}:V_{water} = 1:1$), could be successfully separated through such a superhydrophobic membrane. Since the fibers are so thin, electro-spun membranes can be highly porous, leading to high flux. Oils showed a large flux permeating through the membrane with the average values of 2580, 2962, 3165, 4253, and 2483 L/m² per hour, respectively. The separation was conducted under ambient conditions without adding external pressure. The superhydrophobic membrane also demonstrated high separation efficiency for the above-mentioned oil/water mixtures with values of 99.2, 99.4, 99.5, 99.7, and 99.2%, respectively. The described superhydrophobic membrane showed self-recovery abilities. Once damaged by abrasion or plasma etching, the surface wettability could be recovered by annealing the membrane at 50 °C. It also retained its ability to separate oil from water. After 20 cycles of plasma etching and heating, the separation efficiency of oils was still above 98%. This kind of superhydrophobic membrane could also be used for water-in-oil emulsion treatment with a separation efficiency of 99.3%. After 20 cycles of plasma etching and heating, the efficiency was slightly reduced to 98.1%. Such high separation efficiency and durability makes the superhydrophobic membrane an ideal candidate for practical applications in the field of oil/water separation.

3.3 Drag Reduction

Drag reduction at low flow speed is one potential application for the use of superhydrophobic surfaces. In particular, when it comes to thin channels or capillaries, the energy required to push through liquid is high. In order to save energy, it is desirable to reduce drag. When liquid flows over a superhydrophobic surface, an air layer between the liquid and solid surface is retained. A free liquid surface cannot sustain shear stress. As a result, the usual no-slip boundary condition at the solid-liquid interface is replaced, which reduces drag [70–74]. Slip can be quantified by slip length (Fig. 7). The slip length b is related to the flow velocity at the interface by u_0 :

$$u_0 = b \left| \frac{\partial u}{\partial y} \right|$$

If b is a finite value, a slip speed must exist at the boundary. On superhydrophobic surfaces, an air layer is formed between the liquid and solid phase, as long as it is in

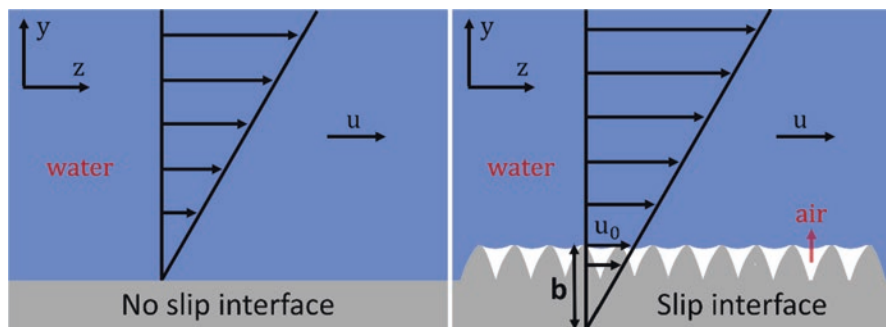


Fig. 7 Schematic diagram of the slip boundary

the Cassie-Baxter state. By replacing the solid-liquid interface to the liquid-gas interface, the liquid can move freely at the contact interface. Effective slip can be generated during this process and reduce the flow resistance, suggesting that superhydrophobic surfaces possess a drag reduction effect [74, 75]. However, this principle breaks down as soon as the surface is destroyed by contamination or mechanical damage, and this is difficult to avoid. Thus, self-recovery superhydrophobic surfaces are the better choice for a long-term drag reduction.

Liu et al. prepared a self-recovery superhydrophobic surface for drag reduction based on hot-pressing fluorinated silica particles (F-SiO₂) on a resin matrix [76]. A processable epoxy pre-polymer was prepared by thiol-ene click reaction of a soft monomer trimethylolpropane tris(3-mercaptopropionate) (TMPMP) and glycidyl methacrylate (GMA). The pre-polymer was further mixed with the curing agent, 4-aminophenyl disulfide (APDS), which contains disulfide bonds, to form a self-healing resin matrix. After hot-pressing the self-healing resin matrix and F-SiO₂, a self-recovery superhydrophobic surface was obtained. A water droplet on the surface showed a CA of 164 ° with a sliding angle of 2 ° ($V_{\text{drop}} = 8 \mu\text{L}$), indicating the excellent superhydrophobicity. The drag reduction property was investigated by testing friction torque on the rheometer. The drag reduction rates were calculated as:

$$DR = 1 - \frac{M_{sa}}{M_{sm}}$$

where M_{sa} and M_{sm} represent the torque of the superhydrophobic surface and smooth surface, respectively. According to the friction torque difference between superhydrophobic and flat surfaces obtained under different rotation speeds, the maximum drag reduction rate of the superhydrophobic surface reached 28%, suggesting significant drag reduction. Due to the self-recovery ability of the surface, even after 50 and 100 abrasion recovery cycles, no significant changes in drag reduction rates were observed. By replicating a shark skin structure with PDMS and further modified with PFMA brushes, Liu et al. also developed a self-recovery superhydrophobic surface with a drag reduction effect [48]. The maximum drag reduction rate was

22%, which was better than that of bare PDMS films with a shark skin topography (drag reduction rate of 5.4%). The obtained superhydrophobic surfaces showed durable superhydrophobicity and reduced hydrodynamic drag.

3.4 Anti-icing

Another potential application of a self-recovery superhydrophobic surface is in the field of anti-icing. Due to the low adhesion and extremely small contact area between water droplets and superhydrophobic surfaces, superhydrophobic surfaces are considered good candidates for use in anti-icing processes. As conventional superhydrophobic surfaces are often fragile and deteriorate during repeated icing-melting cycles, self-recovery superhydrophobic surfaces are one way of making more durable anti-icing surfaces. The self-recovery superhydrophobic surface developed by Qin et al. showed excellent anti-icing properties [63]. Compared to the pristine PDMS-GA film, the TiO_2 particle coated PDMS-GA film which they prepared demonstrated a much longer delay time in the formation of ice. Furthermore, ice adhesion to the superhydrophobic surface was much weaker than on the pristine counterpart. Such anti-icing properties rely on the trapped air in the hierarchical structures. The air pocket greatly reduces the contact area between the water droplet and solid surface and slows down heat transfer at the interface. Thus, ice formed can be easily removed from the superhydrophobic surface. This particular surface developed by Qin et al. was also able to self-recover after sustaining both physical and chemical damages. The wettability could be recovered in addition to delayed icing and low adhesion to ice.

Li et al. developed an anti-icing self-recovery superhydrophobic surface by spraying a solution of PU and hexadecyl polysiloxane modified SiO_2 ($\text{SiO}_2@$ HD-POS) [77]. The obtained surface was superhydrophobic with a water CA of 164° and a sliding angle of 4° ($V_{\text{drop}} = 10 \mu\text{L}$). Anti-icing behavior was investigated by applying static and dynamic experiments in outdoor environments (-15°C , relative humidity = 54%). The authors found that the freezing of water drops on the surface they fabricated was delayed. A $60 \mu\text{L}$ of water droplet began to freeze, taking on a hazy appearance at 34 min and was completely frozen after 41 min. In comparison, the water droplet began to freeze after 5 min 28 sec on a bare glass slide and was completely frozen after 9 min 58 sec. Thus, the surface fabricated in this study was able to delay icing by about 30 min even under extremely freezing weather conditions. The prepared surface showed durable anti-icing properties with the superhydrophobicity maintained after 60 cycles of icing-melting, showing a longer lifetime than other reported anti-icing coatings [78, 79].

In addition to the applications mentioned above, self-recovery superhydrophobic surfaces are said to have potential applications in solar steam generation [80], water-energy harvesting [81], superior microwave absorption [82], (anti-)condensation [83, 84], and other fields [42, 85, 86].

4 Conclusion

In the last decade, significant progress has been made toward fabricating super liquid-repellent surfaces which can recover their wetting properties after chemical or physical damage. Recovery is spontaneous at room temperature or in many cases after exposure to an external stimulus. The ability to self-recover brings superhydrophobic surfaces closer to being applied in fields such as reducing corrosion, separating oil from water, drag reduction, and anti-icing. Significantly improved durability allows superhydrophobic surfaces to fulfill harsh requirements and expand their use in outdoor applications.

5 Future Outlook

In future work, despite remarkable development achieved in self-recovery superhydrophobic surfaces, limitations and challenges are still eagerly required to be solved for practical applications: (1) Developing simple, fast, low-energy consumption and large-scaled fabrication process is highly welcomed to overcome the complicated condition in conventional methods. Alternative fluorine-free materials with low surface energy are more desirable in terms of nontoxic, eco-friendly, and economical to human beings, wildlife, and environment. In addition, it is of great significance to develop robust superhydrophobic surfaces on diverse substrates, especially on smooth substrates which would be damaged in larger scale with simple scratch. (2) Surfaces with ultrafast self-recovery duration (completely recovered in few seconds or minutes) is vital for many practical applications, e.g., anticorrosion. More importantly, design of stimuli-free self-recovery process is highly desirable and essential for practical utility. (3) Characterization standards need to be established to compare the productions. It is eagerly required especially in specific field, e.g., self-cleaning coatings for the automotive industry, textiles, or architectural structures.

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Structured Surfaces with Engineered Wettability: Fundamentals, Industrial Applications, and Challenges for Commercialization



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1 Introduction

Many industrial applications of conventional and advanced technologies demand materials and devices with certain surface properties to fulfill specific goals. As a fundamental property that describes how a liquid contacts a solid surface, wettability greatly affects the physicochemical interactions between the two. Quantified by the contact angle (CA) of water on them or water contact angle (WCA), solid materials are hydrophilic or hydrophobic, exhibiting WCA up to 120° [1, 2] on their smooth surface. Since wettability is governed by the morphology as well as chemical composition of the surface, the solid surfaces can be roughened to expand their wettability range to superhydrophilic (SHPi) ($\text{WCA} < 10^\circ$) or superhydrophobic (SHPo) ($\text{WCA} > 150^\circ$) regimes [3–5]. This approach to extend the water wettability is, in principle, valid for other liquids as well, leading to superoleophobic, superlyophobic, etc. and even superomniphobic. The timely advances in nanotechnology

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and surface engineering have led to many artificial surfaces with special wettability and provided new functional materials and devices for various industrial sectors.

In this review, first the fundamentals of engineered wettability for its classification, control, and fabrication will be summarized. Subsequently, several important surfaces with engineered wettability and their applications along with their current or future markets will be overviewed, focusing on the mainstream examples of technological development and competition. Finally, the main challenges to commercialize the wettability-control technologies will be discussed.

2 Fundamentals

2.1 Wettability Classification and Terminologies

When a liquid drop is placed on a solid surface in a vapor (or gas), it spreads toward a low energy state of the solid-liquid-vapor system, forming a three-phase contact line. Wettability, i.e., the ability of a liquid to keep contact with a solid surface, is normally quantified by the solid-liquid CA shown in Fig. 1a. Assuming water for the liquid, a solid surface may be classified as being hydrophilic ($CA < 90^\circ$) or hydrophobic ($CA > 90^\circ$) with additional classification of being SHPi ($CA < 10^\circ$) or SHPo ($CA > 150^\circ$) to address the unusual wettability of structured surfaces. Incidentally, the definitions of the new terminologies are still evolving, as one can see from the requirement of roll-off (or tilt, sliding) angle or CA hysteresis (CAH) smaller than 5° or 10° being added to the initial requirement of $CA > 150^\circ$ for a surface to be SHPo.

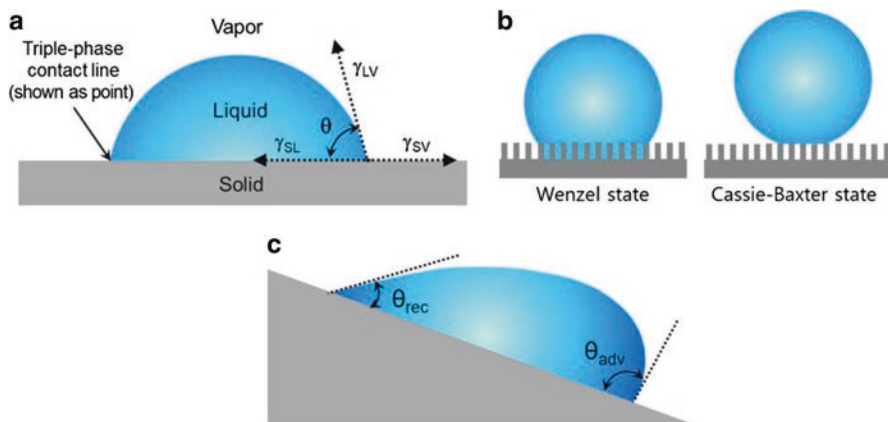


Fig. 1 Schematics of a liquid droplet showing: (a) contact angle (CA) on a smooth and flat solid surface; (b) two wetting states on a rough solid surface, Wenzel state (left) and Cassie-Baxter state (right); (c) advancing contact angle (θ_{adv}) and receding contact angle (θ_{rec}) on a tilted solid surface

If the liquid is not water, the prefix “hydro-” (meaning water) in the classification terms would change to something else, such as “oleo-” (meaning oil) to say a surface is superoleophobic or super-nonwettable to oil (i.e., with CA > 150°). Because the surface energy of oils ($\gamma = 25\text{--}32 \text{ mJ/m}^2$) [6] is much lower than that of water ($\gamma = 73 \text{ mJ/m}^2$), a superoleophobic surface [7] is naturally SHPo as well. An extreme case would be the surfaces that are super-nonwettable to all liquids [8], i.e., super-omniphobic (“omni” meaning all) surface, which is naturally superoleophobic and SHPo as well. However, there are exceptional and peculiar wettability properties, such as the surfaces that are superoleophobic and SHPi (i.e., opposite to the natural state of being superoleophilic and SHPo) [9]. Since these newly discovered or designed properties continue challenging the existing definitions of terminologies to evolve, herein the authors will refrain from delving into the relatively new terminologies.

2.2 Rough Surfaces and Moving Liquid

The wetting behavior of a liquid on a smooth surface can be described by Young’s equation [10], which balances the interfacial tensions between solid-liquid (γ_{sl}), solid-vapor (γ_{sv}), and liquid-vapor (γ_{lv}) in equilibrium to provide the equilibrium CA (θ_o), as follows:

$$\cos\theta_o = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \quad (1)$$

The wetting behavior of a liquid on a rough (e.g., textured) surface can be described similarly by adding the roughness value and depending on whether the liquid fills or sits on the roughness: Wenzel regime [11] and Cassie-Baxter regime [12], respectively (Fig. 1b). If a droplet is in the Wenzel state, the effective equilibrium CA (θ^*) on rough surface is determined by the roughness factor (r) as well as the equilibrium CA on smooth surface (θ_o), as the following equation [11]:

$$\cos\theta^* = r \cos\theta_o \quad (2)$$

The roughness factor (r) is defined as the ratio of the actual solid surface area to the projected (i.e., looking from top) area. Equation 2 implies the roughness would amplify the inherent wettability; in other words, a wettable surface would become more wettable and a nonwettable surface more nonwettable when roughened. If a droplet is in the Cassie-Baxter state, where the contact surfaces are heterogeneous, i.e., solid-liquid and vapor-liquid, the effective equilibrium CA (θ^*) on rough surface is determined by the solid fraction (ϕ_{sl}) and the vapor fraction (ϕ_{vl}) as well as the equilibrium CA on smooth surface (θ_o), as the following equation [12]:

$$\cos \theta^* = \phi_{sl} \cos \theta_o - \phi_{vl} \quad (3)$$

where ϕ_{sl} and ϕ_{vl} are the ratios of the solid-liquid and vapor-liquid surface areas to the total surface area, respectively. Equation 3 implies the solid fraction (ϕ_{sl}) would amplify the inherent wettability and the vapor fraction (ϕ_{vl}) would amplify the inherent non-wettability. Note Equation 3 reduces to Equation 2 if $\phi_{vl} = 0$, because it also means $\phi_{sl} = r$. In other words, the Wenzel state is a special condition of the Cassie-Baxter state. If the solid-liquid and vapor-liquid interfaces are both flat as shown in Fig. 1b, the above equation reduces to a more commonly used form, as follows:

$$\cos \theta^* = \phi_{sl} (\cos \theta_o + 1) - 1 \quad (4)$$

Since Cassie-Baxter state is usually metastable and can be transformed into the stable Wenzel state, there is also a transitional state between the two states [13].

As another important parameter to describe the liquid wetting behavior, CAH can be intuitively understood by a droplet resting on a tilted surface [14, 15]. Because gravity pulls on the droplet to move it downward while CAH tries to keep it in place, the droplet deforms to an asymmetric shape with the advancing contact angle (θ_{adv}) at the leading end and the receding contact angle (θ_{rec}) at the following end, as illustrated in Fig. 1c. The CAH is the difference between them and usually measured by the tilt angle for convenience. The tilt angle, also called sliding angle or roll-off angle, is the angle above which the droplet moves down the inclined substrate. Note, however, unlike CAH, which is determined solely by the wettability, the tilt angle is not fundamental because it is affected by the volume of the droplet as well.

2.3 Wettability Expansion and Control

In general, the wettability of a solid surface can be controlled by the surface chemistry and surface roughness. To obtain a SHPi surface, a high-energy material such as TiO_2 and SiO_2 can simply be roughened [16] because they are intrinsically hydrophilic ($\theta_o < 90^\circ$). To obtain a SHPo surface, usually a material is roughened and coated with a low-energy material, such as fluoropolymer, which is intrinsically hydrophobic ($\theta_o > 90^\circ$). However, it is difficult to obtain a superoleophobic surface because oils would intrinsically wet ($\theta_o < 90^\circ$) all materials including fluoropolymer. Because no known solid surface is intrinsically nonwettable ($\theta_o > 90^\circ$) to the common low-energy liquids (e.g., $\gamma < 30 \text{ mJ/m}^2$), surface roughness with a reentrant profile (e.g., T-shaped [7], inverse trapezoidal-shaped [17], mushroom-like [8]) has been developed to induce Cassie-Baxter state and an apparent nonwettability. Once induced nonwettable ($\theta^* > 90^\circ$), super-nonwettability ($\theta^* > 150^\circ$) may be obtained by reducing the solid fraction (ϕ_{sl}).

The surface wettability can be dynamically tuned or switched by reversible changes in the surface chemistry and/or the surface morphology in response to corresponding external stimuli, including light, electrical potential, temperature, pH, stress, solvent, and ion [18, 19]. The stimuli-responsive surfaces have been developed commonly by using active functional polymers, which can translate a molecular change in charge or dipole or conformation into a change in a macroscopic function such as polarity and roughness [19]. As a special case, a light-responsive surface could be fabricated by using photosensitive materials of oxides (e.g., TiO_2 , SnO_2 , ZnO , WO_3 , V_2O_5 , and Ga_2O_3) as well as polymers with photochromic functional groups (e.g., azobenzene, spiropyran, and diarylethene) [18]. The inorganic materials have the advantages of lower toxicity and greater mechanical/chemical/thermal stability but also the drawbacks of slow response and common use of ultraviolet (UV) light irradiation. The organic materials have more advantages with respect to chemical modification and reaction diversity under UV or visible light, in spite of the shortcomings of smaller wettability change and weak mechanical/thermal/radiation stability.

2.4 Fabrication Methods for Wettability Engineering

Various fabrication methods have been used to obtain super-wetting and super-nonwetting surfaces. They are, in general, composed of two main procedures – modifying surface chemistry and structuring surface morphology. According to the processing order, they can be classified into three types: pre-roughness post-chemistry, pre-chemistry post-roughness, and one-step roughness/chemistry [20]. For example, super-nonwetting surfaces are usually produced as follows. In the first type, substrate surface was etched (with or without lithography) or coated (with particles or fibers) to form rough structures and then chemically modified with silane- or fluorine-containing polymers. In the second type, particles or fibers were first chemically modified and then spray-coated on substrate to generate rough surface. In the third type, chemically modifying layers with rough structures were in situ synthesized or polymerized onto substrate surface via vapor phase polymerization, electrodeposition, co-condensation, etc.

In terms of how to generate the surface roughness, the fabrication methods can be also categorized into another three types: top-down, bottom-up, and combination approaches [21]. For top-down approach, rough surface structures were produced by etching (with or without lithography) or templating. For bottom-up, coating or self-assembly was commonly used. For the combination, surfaces with hierarchical roughness were obtained in two steps of top-down fabrication for microstructures and bottom-up fabrication for nanostructures.

3 Applications

3.1 Self-Cleaning

Self-cleaning surfaces and coatings are used mainly for glasses in building, cars, and solar panels but also for paints and textiles. The self-cleaning coatings have been developed through two categories of SHPo and SHPi films [22]. A self-cleaning SHPo surface cleans itself by letting a water droplet roll over the rough surface in Cassie-Baxter state. Since most particles (dirt) are hydrophilic, the rolling water droplet picks up and carries the particles with it, as illustrated in Fig. 2a. In comparison, a self-cleaning SHPi surface can also clean itself by letting water sheet over the rough surface in Wenzel state. If the roughness scale is smaller than the particle scale, the adhesion between the particles and solid surface is relatively small so that the sheeting water picks up and carries the particles with it, as illustrated in Fig. 2b.

The most common type of SHPo coating is created by using hydrophobic fumed silica (SiO_2) particles, whose surface has been modification with silicone oil or functional silanes such as dichlorodimethylsilane (DDS), hexamethyldisilazane (HMDS), polydimethylsiloxane (PDMS), or octametylcyclotetrasiloxane (D4) [23]. By a facile technique of dip or spray coating, it was easily coated as a SHPo film with rough porous surface originated from the aggregated nanoparticles (NPs). Self-cleaning of this type of SHPo surfaces was demonstrated on various practical substrates, such as window glass, building wall, solar cell panel, motorcycle body, clothing fabrics, cotton shoes, wood, marble, etc. [24]. The sprayable SHPo coatings based on the hydrophobic fumed silica have been commercialized as multiple products (e.g., AEROSIL®, CAB-O-SIL®, HDK®, NeverWet®, Ultra-Ever Dry®) due to cost-effective production capability as well as the additional performance benefits such as optical transparency, scratch/abrasion resistance, corrosion resistance, and reduced moisture adsorption.

Self-cleaning SHPi coatings are mostly based on titania (TiO_2) with both photo-induced hydrophilic conversion and photocatalytic properties [16, 22]. Rough titania surfaces can turn from hydrophilic to SHPi under UV radiation, which changes the valence of Ti^{4+} to Ti^{3+} with the release of O_2 , followed by water occupation of the oxygen vacancies [25]. The UV radiation also generates electron-hole pairs on the TiO_2 surface to react with water and oxygen into reactive oxygen species (such as

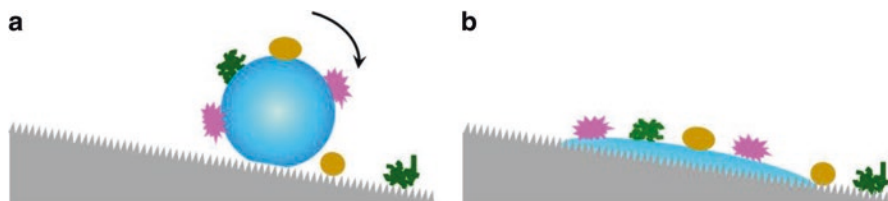


Fig. 2 Schematic illustration of self-cleaning processes on (a) SHPo and (b) SHPi surfaces

OH and O_2^-), which can decompose organic pollutants into harmless CO_2 and H_2O [26, 27]. Stronger photocatalytic and SHPi properties can be obtained by using anatase with an open crystal structure (vs. densely packed rutile phase) and increasing NP concentration due to the larger specific surface area [16, 22]. Although ZnO and SnO_2 also have both photoinduced hydrophilicity and photocatalysis [26], TiO_2 is much more preferred for commercial products (e.g., Pilkington Activ™, Sun Clean Glass®, NEAT®, HYDROTECT®, Bios Self-Cleaning®, SGG BIOCLEAR®) because of non-toxicity, high chemical/thermal stability, and low cost.

For self-cleaning applications, TiO_2 -based SHPi coatings are more extensively utilized than SiO_2 -based SHPo ones because the former can also have antifogging, antireflective, deodorizing, and antibacterial properties [16, 26]. Furthermore, their self-cleaning activity can be further improved through chemical modifications. TiO_2 -coated surfaces typically lose the SHPi property within minutes to hours in dark without UV radiation (only 3–5% of sunlight) [16], limiting their practical applications. This critical drawback could be overcome by metal ion doping (Cu, Fe, Co, Sn, or V), noble metal loading (Ag, Au, or Pt), non-metal doping (N, S, or C), or hybrid nanocomposite (apatite/ TiO_2 , Fe_3O_4/TiO_2 , carbon nanotube (CNT)/ TiO_2 , or Cu/ TiO_2/C) [27]. The high bandgap of TiO_2 (~3.2 eV) can be narrowed to absorb visible light by introducing additional energy levels within the band gap and heterojunction coupling. The modified TiO_2 NPs showed photocatalytic antibacterial activity in response to visible light illumination.

3.2 Antifouling

Fouling is the accumulation of undesirable materials on a solid surface, causing functional degradation by physical and/or chemical interactions between them. In a marine environment, foulants are microorganisms (bacteria, diatoms, etc.) and macroorganisms (macroalgae, mussels, barnacles, etc.) [28]. The biofouling roughens the surface and increases the drag of a ship moving through water, consequently raising fuel consumption and greenhouse gas emission. Antifouling coatings are estimated to save the shipping industry \$60 billion in fuel consumption and reduce 384 and 3.6 million tons in CO_2 and SO_x emissions, respectively [29]. For marine application with the biggest portion of antifouling coating market, the most well-known is the self-polishing copolymer (SPC) containing dicopper oxide (Cu_2O) as the main biocide along with booster biocides [28]. As the international regulations on marine environment are tightened, fouling release coating (FRC) has been focused on as a new eco-friendly technology that is copper-free, biocide-free, and metal-free. Two main approaches of FRC are the detachment of settled biofoulants on hydrophobic surface by hydrodynamic stress during ship navigation (Fig. 3a) and the prevention of biofouling attachment on hydrophilic surface by keeping it hydrated (Fig. 3b) [30]. The first approach uses polymer materials with low surface

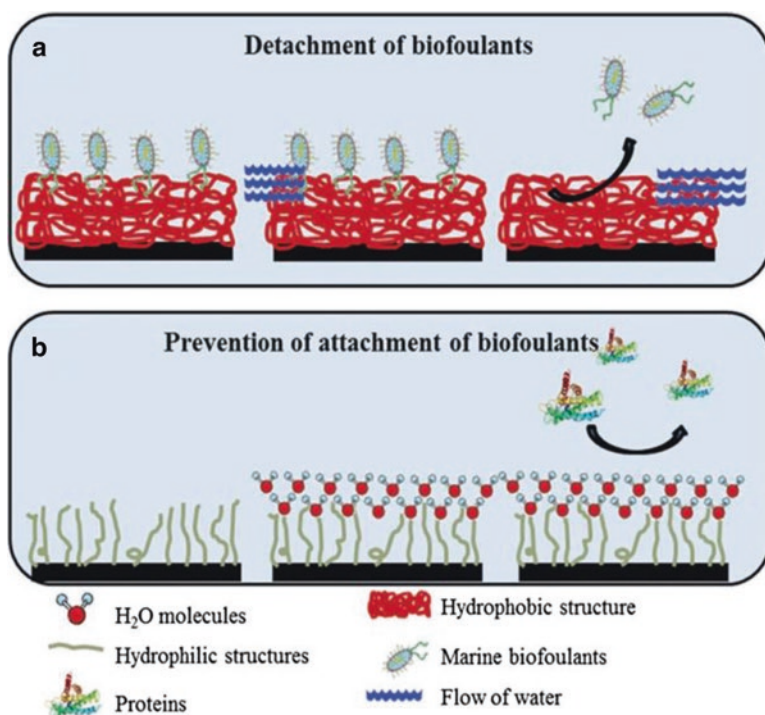


Fig. 3 Schematic illustration of fouling release coating approaches for marine application: (a) hydrophobic coating to detach settled biofoulants by hydrodynamical stress during ship navigation; (b) hydrophilic hydrating coating to prevent attachment of biofoulants. (Reproduced from reference [30])

energy and low elastic modulus such as polysiloxanes and fluoropolymer. With $\sim 23 \text{ mJ/m}^2$ of surface energy and 2 MPa of elastic modulus [31], PDMS is most widely used for commercial products including Hempasil® 77500, Intersleek® 700, SigmaGlide® 990, and Surface Coat (Duplex Fouling Release System) [28]. The second approach uses polymers with much higher surface energy to retain a permanent hydration layer which prevents the adhesion of proteins, the triggering process of biofouling attachment, by providing very low interfacial energy between water and a surface. The most commonly used is poly(ethylene glycol) (PEG), which has a high surface energy ($>43 \text{ mJ/m}^2$) and low water interfacial energy ($<5 \text{ mJ/m}^2$) [30]. The first approach (i.e., hydrophobic FRC) is commercially more successful than the second approach (i.e., hydrophilic non-stick FRC) because of the higher performance proven except under no or slow water flow. The drawbacks of PDMS, i.e., poor adhesion and mechanical durability, could be improved by incorporating inorganic filler (SiO_2 , CaCO_3 , TiO_2 , Fe_2O_3 , or carbon black) and polymer segments (epoxy or polyurethane (PU)) [30, 32].

Biomedical application is an emerging area of antifouling coatings for future markets. The surface fouling of biomedical devices by protein and microbial attach-

ment is responsible for a significant portion of healthcare-acquired infections (HAIs) [33], which result in 1.7 million infections and 99,000 associated deaths each year [34]. Two strategies are used to prevent the device-associated HAIs: one is an antimicrobial material to kill microorganisms or inhibit their growth through biocide release or contact kill, and the other is an antifouling coating to prevent protein and bacterial adhesion [33]. For the biomedical antifouling, hydrophilic PEG-based coatings have been more widely investigated than SHPo coatings, which easily become SHPi under usage in practice.

Like biomedical applications, consumer electronics including displays and touch panels is a niche market for antifouling coatings. High anti-fingerprint (AF) performance has been demonstrated by various oleophobic surfaces with hierarchical or reentrant structures, but the complex surface structures are inconvenient for low-cost manufacturing in industrial scale [35]. AF coating can be more efficiently accomplished by a facile method using transparent polymers with low surface energy and strong mechanical durability on glass such as perfluoropolyether (PFPE) [36].

3.3 *Anticorrosion*

Corrosion is a natural slow process that destructs materials (usually metals) by converting them into a more chemically stable form (such as oxide, hydroxide, or sulfide) through a chemical and/or electrochemical reaction with their environment, resulting in functional damage on bridges, cars, water heaters, and countless other products. The global cost of corrosion was estimated to reach 2.5 trillion USD, which was equivalent to 3.4% of the global gross domestic product (GDP) in 2013, and 25–30% of the cost could be saved by employing optimum corrosion management practices [37]. Metal corrosion proceeds via two different processes, the movement of metal ions into solution on active areas (anodes) and passage of electrons from a metal to an acceptor (such as oxygen, hydrogen ions, or another oxidizing agent) on less active areas (cathodes) [38].

In accordance with the protective mechanism, anticorrosion coatings are generally classified into three types: sacrificial, barrier, and inhibitive coatings [39]. Sacrificial coatings use an electrochemically more active metal pigment (most commonly 92–95 wt% zinc), which corrodes preferentially to protect the surface from corroding by cathodic protection (or galvanic effect). Barrier coatings consist of polymer binder (e.g., epoxy, urethane, acrylic, alkyd) and inert inorganic pigment (e.g., TiO_2 , micaceous iron oxide of Fe_2O_3 , glass flakes) at a lower volume concentration, resulting in dense and cohesive coatings that impede the transfer of aggressive species (liquids, gases and ions) into the coating-substrate interface. When inhibitive coatings are permeated by moisture, the inhibitive pigments of slightly water-soluble inorganic salts (e.g., phosphates, chromates, molybdates, silicates) are partly dissolved and carried into the coating-substrate interface, forming a passivation layer by the reaction of dissolved ions with substrate. Barrier coatings are

most widely used because they can be used for immersed environments (underwater or buried in soil) as well as for marine and industrial atmospheres. Furthermore, they can be applied for primer, intermediate coat, and topcoat of multilayered systems, while the others can be only for the primer on substrate. With increasing environmental regulations against volatile organic compounds (VOCs) emissions [40], waterborne acrylic and inorganic powder coatings are currently focused on as eco-friendly anticorrosion technologies. Inorganic powder coating is more beneficial due to superior durability, scratch resistance, gloss retention, and resistance to chalking.

Superhydrophobic coatings have been developed for a new high-performance anticorrosion technology, because the air trapped in the surface roughness under water can effectively isolate the substrate from aqueous corrosive media (Fig. 4a) and the water forms droplets (rather than an electrolyte film) in humid air, suppressing the electrochemical reaction (Fig. 4b) [41]. Inorganic NP-based coatings are especially promising for an environmentally friendly and mechanically durable anticorrosion. Common examples are silane-modified oxide NPs and polymer/inorganic NP composites. The former imparted superhydrophobicity on metal surfaces by combining low surface energy of silane or fluorosilane with surface roughness of oxide NPs such as silica (SiO_2) [42] and zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$) [43]. The latter was composed of polymer bases and embedded inorganic NPs such as polytetrafluoroethylene (PTFE)/ SiO_2 [44], PU/ Al_2O_3 [45], and epoxy/graphene [46]. The latter is more advantageous for high mechanical durability because the polymer base can improve the cross-linking of NPs and the adhesion with substrate.

To compete with the conventional anticorrosion coatings, SHPo coating should have high mechanical durability for long-lasting performance as well as high corrosion resistance. Some methods have been researched to improve the durability of SHPo coating such as self-healing ability after mechanical damage, mechanically robust surface with hierarchical structures, and multiple hybrid coatings consisted of inhibitor-doped primer and SHPo topcoat [47]. Meanwhile, conventional barrier coatings have been modified with siloxane having strong Si-O bonds or polyaniline (PANI) as a conductive filler, resulting in increased resistance against mechanical wear, weathering, or delamination [48]. It is still unclear whether SHPo anticorrosion coatings can have a better mechanical durability than conventional anticorrosion coatings. The authors are not aware of any published research work on this issue to date. Moreover, it is not clear if the SHPo property can be maintained under service because SHPo surfaces easily become SHPi in practice.

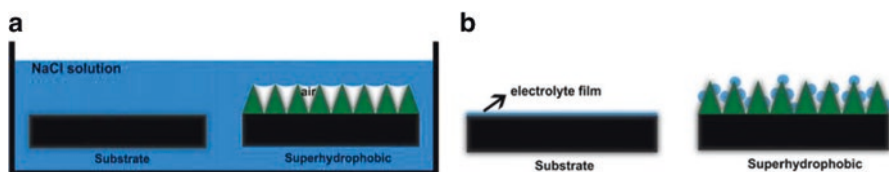


Fig. 4 Schematic models to explain corrosion resistance on SHPo surfaces in (a) corrosive solution and (b) humid air. (Reproduced from reference [41] with permission from Elsevier)

3.4 Oil-Water Separation

Many industries (mining, petrochemical, metal/steel, textile, food, etc.) produce massive amount of oily wastewater every day, and frequent oil spill accidents cause serious environmental pollution. To address these issues, a variety of oil-water separation methods have been used, such as gravity or centrifugal settling, bioremediation, electrochemical, coagulation, and air floatation [49]. A simple and cost-effective method is filtration and absorption technology using meshes/membranes and 3D porous materials (sponges, foams, textiles, or aerogels) [50]. Meshes or membranes are used to separate immiscible or emulsified oil-water mixtures, while 3D porous materials are used to quickly absorb oil in lakes, rivers, or oceans without any specialized equipment for emergency response of oil spillage. Special wetting materials have been researched to develop advanced filters and absorbents with high separation efficiency and high flux rate or absorption capacity.

Two types of meshes/membranes with specific wettability are applied for filtration: one that blocks water and passes oil through because it is both SHPo and superoleophilic (Fig. 5a) and another that passes water through and blocks oil because it is both SHPi and superoleophobic (Fig. 5b) [51]. The first type is not suited for gravity-driven separation of light oils from immiscible mixtures of oil and water because water will sink below the light oil to form a thick underlayer preventing the oil from continuing to pass through the mesh [52]. Moreover, the viscous oils easily adhere to the mesh and impede its flow, significantly decreasing the flux rate of oils. The second type can overcome this deficiency and provide advantages for some applications such as fuel purification, oil fence for an oil spill accident, and separation of high viscosity oils [49]. Hydrophilic materials with micro/nano-hierarchical surface structures can show superhydrophilicity and underwater superoleophobicity in oil-water mixtures because water molecules are trapped in the rough surface structures to repel oil droplets from adhering onto the water-solid composite surface. Typical water-passing meshes have been fabricated by coating metal meshes with nanostructured materials such as hydrophilic oxides ($\text{Cu}(\text{OH})_2$, CuO , TiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, or graphene oxide) [50], hydrophilic hydrogel

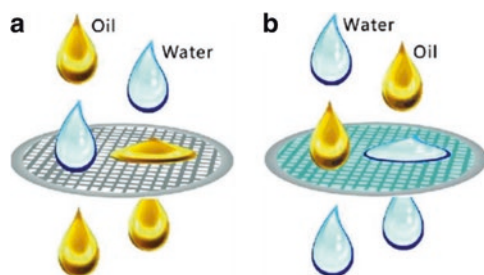


Fig. 5 Schematic illustration of oil-water filtration mesh: (a) oil-pass-type mesh that is both SHPo and superoleophilic and (b) water-pass-type mesh that is both SHPi and superoleophobic. (Reproduced from reference [51] with permission from PCCP Owner Societies)

(polyacrylamide (PAM) [53] or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [54]), and hydrophilic-oleophobic synthetic or blended polymers (poly(diallyldimethylammonium chloride)-perfluorooctanoate (PDDA-PFO) [55] or fluorodecyl polyhedral oligomeric silsesquioxane (F-POSS)/cross-linked poly(ethylene glycol) diacrylate (x-PEGDA) [49]).

Membranes with small pores ($<1\ \mu\text{m}$) are more suitable than meshes to separate oil-water emulsions (e.g., 1 wt% oil-in-water or 1 wt% water-in-oil) [50], where oil or water droplets are much smaller than those in immiscible oil-water mixtures. Polymer membranes are much more widely used than ceramic ones due to low cost, superior chemical/mechanical stability, and highly integrated operation [56]. An oil-passing poly(vinylidene fluoride) (PVDF) membrane that is both SHPo and superoleophilic could separate both nano-sized surfactant-free and surfactant-stabilized water-in-oil emulsions with high separation efficiency ($>99.95\ \text{wt}\%$) and flux rate (several times higher than those of commercial filtration membranes) [57]. In comparison, water-passing membranes that are both SHPi and underwater superoleophobic can have much better antifouling property and resulting recyclability due to the ultralow oil adhesion. Water-passing PVDF membranes have been fabricated by surface grafting with a zwitterionic polyelectrolyte brush (poly(3-(N-2-methacryloxyethyl-N,N-dimethyl) ammonatopropanesultone (PMAAPS) [58] and PEGDA [59].

The conventional absorbents are commonly used to remove oil spill from water, including inorganic minerals (zeolite, silica aerogel, expanded vermiculite, clay, activated carbon), synthetic porous polymers (nonwoven polypropylene (PP), melamine (MA), PU foam), and natural fibers (cotton, wool, milkweed, etc.) [49]. Their separation efficiency and oil absorption capacity could be improved by hydrophobic surface modifications, as in the examples of fluoro- or alkyl-modified silica aerogel [49], CNT/nanofiber coated vermiculite [49], organically modified clays (with inorganic cations replaced with organic cations) [49], dodecanoic acid-copper particle coated PU foam [60], and polymerized octadecylsiloxane (PODS)-coated MA sponge [61]. As another approach to obtain advanced absorbents, novel synthetic porous materials have been developed, including inorganics (CNT sponge [62], twisted carbon fiber aerogel [63], graphene-CNT aerogel [64], silicon sponge [65]), organics (nanoporous poly(divinylbenzene) (PDVB) [66], methyltriethoxysilane (MTES)-dimethyldiethoxysilane (DMDES) aerogel [67], supermacroporous polystyrene (PS) monolith [68]), and organic-inorganic hybrid or composite (fluorinated metal-organic framework (MOF) [69], PVDF/camphor soot NP composite [70]).

In addition to good performance, environmental friendliness is another important factor in developing advanced materials for oil-water separation, especially in the case of absorbents with a shorter service life than filters. Nanocellulose (NC)-based oil absorbents have been fabricated, such as TiO_2 -coated NC aerogels [71] and octyltrichlorosilane (OTCS)-modified NC aerogels [72], because NC is a low-cost, renewable, and biodegradable material [49]. Reusable oil absorbents have also been fabricated with magnetic-controllable special wetting materials, which consist of magnetic materials (Fe , Fe_2O_3 , Fe_3O_4) and hydrophobic/oleophilic materials (carbon

materials, organoclays, polymers) [49, 50]. These particles could float on contaminated water to absorb spilled oil and could be collected after oil absorption by applying an external magnetic field. The absorbed oil could be readily removed from the particle surfaces by a simple ultrasonic treatment and the particles still retained their highly hydrophobic/oleophilic characteristics.

3.5 *Droplet Handling for Biomedical Analyses*

Molecular diagnostics is one of the most important tools to analyze pathogen biomarkers due to its high sensitivity and specificity. Biological fluids (blood, serum, plasma) are the main sources of biomarkers but contain an extremely small number of biomarkers in the early stage of many diseases. For successful diagnosis of a small volume biofluid (10^1 – 10^3 nl), a novel handling technique without a sample holder has the advantages of eliminating the wall adsorption and avoiding the contamination induced by the sample-wall interaction [73]. Ultrasonic levitation is currently used for contactless analyses of liquid droplets [74, 75] but has the limitations of complex experimental setup, bulky transducer, and high cost. Superhydrophobic surfaces have emerged as a simple low-cost method of contactless liquid handling due to their ability to minimize the liquid-surface contact area and resultant sample contamination [73].

Liquid holders with SHPo (i.e., nearly contactless) surface were fabricated with an array of micro/nano-sized Si pillars, whose top surfaces were modified by silanization to impart superhydrophobicity [76] or by Ag nanoparticle incorporation and subsequent hydrophobic polymer coating to attain surface-enhanced Raman scattering (SERS) effects as well as hydrophobicity [77]. Liquid sample droplets on the surfaces exhibited the Cassie-Baxter state, greatly reducing the effective contact area and contamination. Furthermore, the droplet could be effectively evaporated to reduce its volume while maintaining the quasi-spherical shape, concentrating the biomarker by 10^2 – 10^3 [73]. The droplet position could be controlled by introducing a hydrophilic region within the SHPo surface to improve the sample stability during experimental setup such as X-ray beam alignment (Fig. 6a) [76]. These contactless droplet handling techniques have been applied to many diagnostic tools such as SERS, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), and X-ray phase contrast imaging (XPCI).

High-throughput screening (HTS) is a primary experimentation method used in biomedical research, especially for drug discovery. A microplate with an array of wells is still commonly used as liquid sample carrier for automated HTS systems in industries despite its drawbacks of high consumption of valuable samples or expensive reagents. Droplet microarray on patterned SHPi/SHPo surfaces can be a new miniaturized platform for HTS of biomedical samples such as blood, cell, protein, and biomaterial [73, 78]. Grid-like arrays of SHPi spots confined by thin SHPo barriers have been produced on different substrates by a variety of fabrication methods. For an example, an SHPi, biocompatible and transparent nanoporous film of

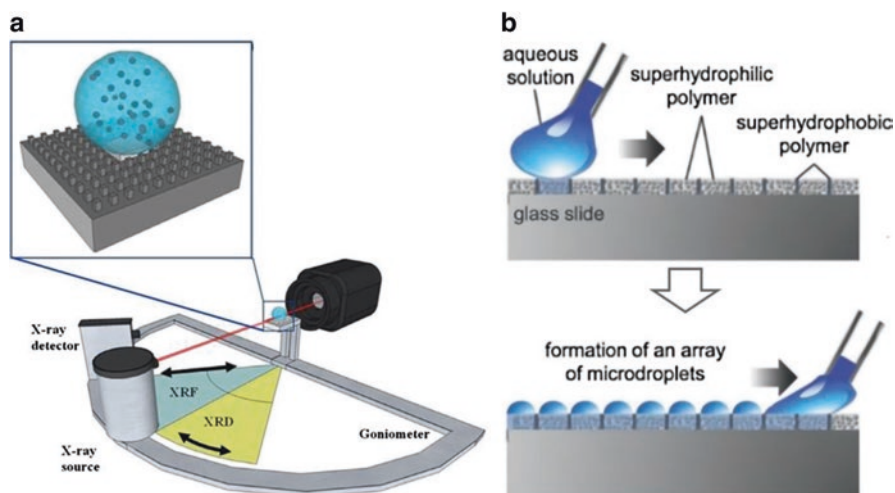


Fig. 6 Schematics of patterned (super)hydrophilic/SHPo surfaces used for (a) combined measurements of X-ray fluorescence (XRF), phase contrast imaging (XPCI), and diffraction (XRD). (Reproduced from reference [76] with permission from Elsevier). (b) Single-step spontaneous formation of a high-density array of completely separated microdroplets. (Reproduced from reference [79] with permission from The Royal Society of Chemistry)

poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) (HEMA-EDMA) was coated on a glass plate, and a SHPo barrier pattern was formed by photografting of 2,2,3,3,3-pentafluoropropyl methacrylate (PFPPMA) brushes (Fig. 6b) [79]. Another example is when a smooth surface of PS substrate was roughened by phase separation methodology to make it SHPo, and SHPi areas were patterned by exposing UV/ozone irradiation [80]. Dense arrays of micro/nanoliter droplets [80, 81] have demonstrated appropriate performances for diverse biomedical screening systems of biomaterial-body fluid interaction and cell-cell/cell-protein/cell-biomaterial interactions [78]. Bioactivity of different inorganic NPs could be reliably tested under exactly same conditions by dispensing and drying NP suspensions onto SHPi regions and then immersing the entire chip in simulated body fluid [82]. Multiplexing test of protein-cell interaction could be performed for various independent combinations with different compositions and total concentrations of a binary protein system by sequential processes of first dispensing protein solution, allowing reaction for protein adsorption and washing chip and then dispensing culture medium, reaction for protein-cell interaction, and washing chip [80].

3.6 Drug Delivery System

A drug delivery system (DDS) is a formulation or a device that transports therapeutic substances into the body, and conventional DDSs have evolved into smart DDSs to enhance the therapeutic efficiency of drugs. Smart DDSs should release drug at specific target site in a controlled manner for a necessary period to reduce drug concentration fluctuation, dosage frequency, drug toxicities, and side effects [83]. One of key elements for smart DDSs is controlled release technology by which drug can be released at a constant rate for a prolonged time. In many cases, the release of therapeutic agent relies on interfacial properties between the DDS and the biological environment through which the mass transport occurs. Thus, wetting properties of DDS surfaces have a great influence on drug releasing behavior.

Three-dimensional (3D) SHPo mesh can be used as a novel matrix of prolonged and local DDS for long-term treatment of pain and chronic diseases [84]. Biocompatible poly(ϵ -caprolactone) (PCL) microfibers were electrospun to form a porous bulk mesh, whose hydrophobicity was increased by doping of poly(glycerol monostearate-co- ϵ -caprolactone) (PGC-C18). When the 3D SHPo mesh was exposed to the aqueous release medium, water penetrated into it in a timely manner to displace its entrapped air (Fig. 7). The air acted as a removable barrier component within the 3D SHPo mesh, effectively slowing drug release that can occur only at the mesh-water interfaces. The releasing rate could be tuned by the design parameters (mesh thickness, fiber size, hydrophobic doping amount) for structural geometry and surface roughness of the mesh [83, 84]. Electrospun polymer fibers were very suitable to fabricate 3D SHPo mesh-based DDSs due to their high drug loading (up to 60%), high encapsulation efficiency (up to 100%), polymer diversity to physicochemically distinct agents, process simplicity, and cost-effectiveness [85].

Stimuli-responsive release has been widely used to achieve controlled-release, and a DDS surface could be switched from SHPo to SHPi [86]. A light-triggered DDS was fabricated with mesoporous silica nanoparticles (MSNs), whose surface was made SHPo with single molecule layer of octadecyltrichlorosilane (OTS) and

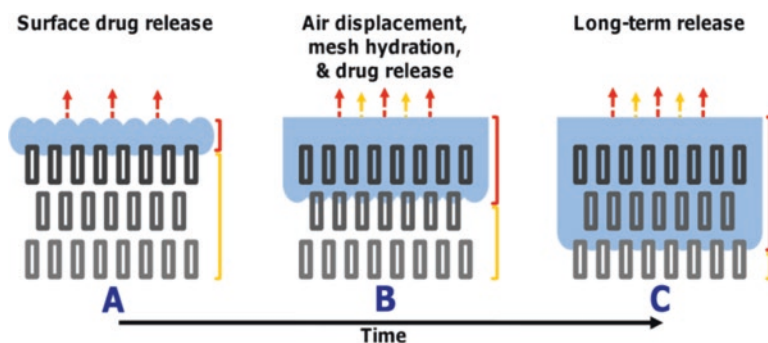


Fig. 7 Schematic explaining the time-controlled drug release of 3D superhydrophobic mesh. (Reproduced from reference [84] with permission from the American Chemical Society)

switched to be SHPi by decomposing the OTS with UV irradiation [87]. The change of MSNs surface from SHPo (closed) to SHPi (open) state was followed by drug release from MSNs' pores. An ultrasonic-controlled DDS was developed with a dense vertical array of titanium oxide nanotubes (TNTs), whose surface was converted to be SHPo by a fluorination with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) [88]. Ultrasonication could remove the air layer trapped on the surface of SHPo TNTs array, leading to the release of loaded drug. Ultrasound may be a better trigger than light due to the ability to focus precisely into the target region deep under the skin.

Superhydrophobic surfaces can be applied to a fabrication tool for DDSs as well as to DDSs themselves. They were used as an innovative platform for more efficient and cost-effective processes to produce various particles of spherical shape, which is the most commonly employed geometry for particle-based DDSs [78]. Aqueous solutions containing polymeric precursor and bioactive agent were dispensed onto SHPo surfaces by a micropipette, and the liquid droplets were hardened to form spherical particles through chemical cross-linking or solvent evaporation. High encapsulation efficiency (up to 100%) could be accomplished due to the negligibly small droplet-surface contact area and the absence of a surrounding liquid medium, to which the encapsulated molecules may be easily diffused and lost.

3.7 *Microfluidics*

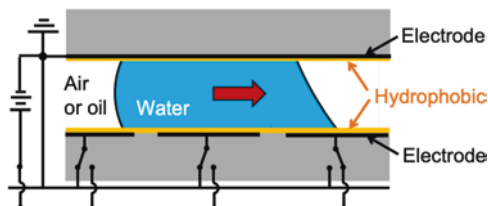
Microfluidics is a core building block for many biochemical applications, especially for point-of-care testing (POCT). Microfluidic devices generally consist of structural components for the manipulation (e.g., moving, stopping, mixing, separating, filtering) of liquid sample and/or reagents in microchannel networks. They are divided into many different types according to liquid form, liquid driving force, and fabrication materials/methods, but regardless of the type, control of surface wettability can play an important role in enhancing their functional performances.

A microchannel with SHPo walls can reduce pressure drop of the liquid flowing in it, resulting in smaller pump, less power consumption, and low cost. The air trapped inside the structures on a submerged SHPo surface allows liquid flow with an effective slip, whose amount is generally determined by the surface structures, resulting in a reduction of drag. The drag reduction effect becomes larger as the channel becomes smaller, favoring microchannels over regular-size channels. However, since SHPo surfaces capable of inducing a larger slip are in general more vulnerable to losing its trapped gas [89], the SHPo walls of microchannel should be designed accordingly, considering the trade-off between drag reduction and robustness in a wide range of flow rate [1]. Capillary-induced microfluidic devices have

the advantages of low resource settings, no power consumption, and low cost, compared with active types of pressure-driven, electrokinetic and centrifugal devices. Hydrophilic microchannels are used for capillary pumping (i.e., wicking), and (super)hydrophobic patches incorporated in the hydrophilic microchannel act as a passive valve [1]. Performance (i.e., opening pressure) of the hydrophobic valve was mainly determined by geometric design (height, width) and fine-tuned by the surface nanostructures (spacing, height) [90]. Open microfluidic devices have been explored for low-cost POCT devices by using cheap substrate materials (polymer, paper, textile) due to their advantages of simple and low-cost fabrication as well as easy introduction of liquid sample and reagent. The wettability contrast of (super) hydrophilic/SHPo patterned surface could induce a surface tension-driven force controlling the liquid flows in open microfluidics [91]. The SHPi paths of liquid flow could be patterned on SHPo substrates as the following examples. Superhydrophobic surface was formed on PS substrate by phase separation technique, and then SHPi paths were created by a UV/ozone or plasma exposure through a photomask [92]. Superhydrophobic paper was obtained by surface precipitation of polyhydroxybutyrate (PHB), and hydrophilic channels were patterned by argon plasma treatment [93].

Unlike continuous flow microfluidics, digital microfluidics is based on the manipulation of individual droplets on a surface for the advantages of less reagent consumption, fast response rate, and parallel processing capability. Only by using gravity force, basic manipulations of droplets (e.g., moving, stopping, mixing) could be accomplished on SHPo anodized aluminum oxide (AAO) surface with hydrophilic polydopamine micropatterns (channels, patch) [94]. For accurate and complex manipulations, droplets have been actuated by different methods of electrical field, optical force, surface acoustic wave (SAW), and thermocapillary and magnetic field [95]. The most well-known actuation technique is electrowetting-on-dielectric (EWOD), where a droplet is placed on a hydrophobic dielectric surface between two imbedded electrodes and actuated by the voltage applied between them [96], as drawn in Fig. 8. Efforts have been made to operate EWOD on SHPo surfaces, anticipating such combination would enhance the EWOD effect and expand microfluidic functionalities [97].

Fig. 8 Droplet actuation by electrowetting-on-dielectric (EWOD), illustrated with the common device configuration of two parallel plates



4 Challenges

4.1 Mechanical Durability

Mechanical durability is one of the critical challenges for many practical applications (self-cleaning, anti-fouling, anticorrosion, oil-water separation, etc.) of most structured surfaces. More vulnerable are SHPo surfaces because they usually employ a soft polymer material and protruding (i.e., pillar-like) structures, compared with SHPi ones which usually employ a hard material and depressed (i.e., hole-like) structures. The primary durability performance of SHPo coating is in general determined by adherence to substrate, resistance to abrasive force, and dynamic impact and stability in dynamic liquid bath condition [98]. Some strategies have been developed to improve the mechanical stability of SHPo surface for a long life time [99, 100].

A simple and straightforward method is to directly generate surface topography from hydrophobic bulk material with mechanical durability. But it is very difficult to find non-polymer hydrophobic material because most ceramics and metals are hydrophilic. An alternative approach is to use organic-inorganic composite materials composed of hydrophobic polymers and mechanically durable ceramics or metals. A SHPo composite film was fabricated by blending fluoro-methacrylic latex with montmorillonite clay NPs, whose surface was modified by anaerobic acrylic adhesive and demonstrated to remain SHPo after dynamic impacts [101]. A cross-linked PDMS matrix containing hydrophobic silica NPs, whose surface was modified by fluorinated alkyl silane (FAS), showed remarkable mechanical durability against repeated machine washes, severe abrasions and boiling water, as well as excellent corrosion resistance to strong acid or base [102].

Dual-scale surface roughness is a common method to preserve the Cassie-Baxter state even after some surface features are mechanically worn out [99]. The hierarchical-structured surfaces with dual-scale roughness consisted of microscale topography for mechanical robustness and superimposed nanoscale roughness for SHPo property. A hierarchical SHPo Si surface was produced by two-step etching processes to form micro-sized pyramids and nanostructures on their surfaces, followed by perfluorooctyl trichlorosilane (PFOS) treatment for surface fluorination [103]. Compared with Si surface with only the nanostructures, it exhibited less degradation of CA and CAH properties after abrasion test. Interestingly, while poly(ethylene terephthalate) (PET) fabric coated with polymethylsilsesquioxane (PMSQ) nanofilaments retained a low water sliding angle after abrasion test, a glass slide coated with the same PMSQ lost its SHPo property [104].

Self-healing material is an emerging strategy to attain mechanical durability by making an autonomously repairable SHPo surface [99]. A layered porous flexible polymer film containing a large amount of absorbed FAS hydrophobic surfactant could restore superhydrophobicity after mechanical or chemical damage, such as a surface scratch or decomposition of fluoroalkyl chains [105]. The self-healing mechanism was explained by the migration of absorbed healing agent onto the

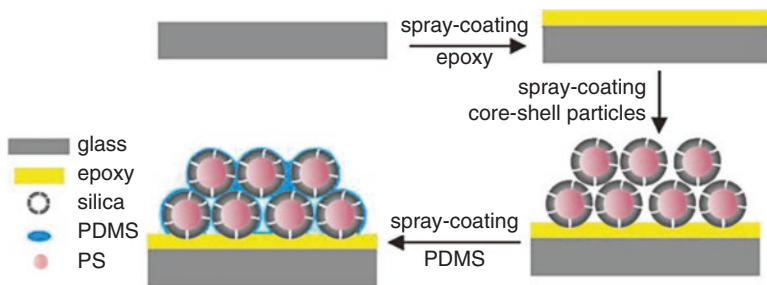


Fig. 9 Schematic explanation of how a SHPo surface with self-healing hierarchical-structured composite is fabricated. (Reproduced from reference [108] with permission the Royal Society of Chemistry)

surface in the presence of humidity to minimize its surface energy. An anticorrosion coating based on both a benzotriazole (BTA) corrosion inhibitor and an epoxy-based shape memory polymer (SMP) could rapidly heal the damage of surface morphology (crushed areas or scratches) through a mild heat treatment at 60 °C for 20 min or in sunlight for 1 h [106].

The combination of the individual methods described above is another strategy to develop a mechanically durable SHPo surface. An epoxy/CNT composite hierarchical structure was produced by spray-coating of epoxy/CNT/acetone mixture on a micropatterned epoxy surface and by thermal annealing for strong bonding between CNT and substrate [107]. It showed no significant deterioration in CA and CAH properties after long-term exposure to water or exposure to high water pressure, but the similar hierarchical structures using lotus wax instead of CNT lost superhydrophobicity. A self-healing hierarchical-structured composite was fabricated by sequential spray coatings of epoxy resin base, PS/SiO₂ core/shell NPs, and PDMS hydrophobic interconnection as shown in Fig. 9 [108]. It could maintain SHPo properties (CA > 150 ° and CAH < 10 °) after several sand impacts and automatically restored the SHPo properties after air plasma damage by releasing hydrophobic PS through thermal curing at room temperature for 12 h or at 150 °C for 1 h.

4.2 Scalable Manufacturing

Although various methods have been successfully demonstrated to fabricate structured surfaces in small quantities for characterization and evaluation purposes, scalable manufacturing is still a key barrier for commercialization of the R&D results. It requires the fabrication at industrially relevant scale and low cost, with sufficient production yield and reproducibility while also within environmental, health, and safety guidelines [109]. For low-cost large-area processing, solution-based coating (sol-gel, electrospinning, electrochemical deposition, etc.) is more preferable than vapor deposition, and nanoimprint or self-assembly lithography is better than

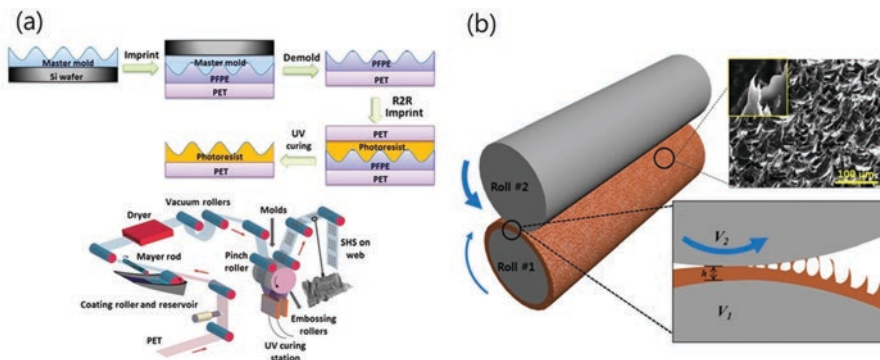


Fig. 10 (a) Schematics of R2R nanoimprinting processes to fabricate a large-area SHPo antibacterial film. (Reproduced from reference [110] with permission from the American Chemical Society). (b) A double-roll based coating process to fabricate a shark-skin-like patterned film. (Reproduced from reference [111])

conventional photo or electron-beam lithography. For scalable industrial production, it is suitable to employ processes such as continuous roll-to-roll (R2R), self-assembly, and one-step spray coating. Based on R2R nanoimprinting, a large-area SHPo antibacterial film could be continuously manufactured by using a hierarchical-structured mold of poly(2-hydroxyethyl methacrylate) (PHEMA) and a flexible PET substrate coated with UV-curable photoresist containing ultralow surface energy monomer of 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA), as shown in Fig. 10a [110]. Without any patterned mold, a double-roll based process could coat SHPo film with shark-skin-like roughness on the roll at the lower rotating speed (#1 Roll at V_1) by using a high viscosity paste comprised of multiwalled CNTs dispersed in PDMS matrix, as shown in Fig. 10b [111].

To manufacture transparent self-cleaning SHPo surfaces, the bottom-up method based on self-assembly of colloidal silica NPs could be more advantageous than the top-down one using plasma etching or soft lithography (nanoimprint lithography, replication) [112]. The former is more suitable for low-cost mass production of various rough substrates, while the latter provides a well-defined size and shape of surface structures. In the former case, the size and surface chemistry of NPs should be finely controlled to balance the forces in colloidal systems, which determine the film morphology and uniformity after dip, spin, or spray coating. A stable SHPo surface with hierarchical arrays could be fabricated by two-step self-assembly of colloidal silica NPs and surface functionalization with fluorosilane. Non-close-packed (NCP) colloidal multilayers were first spin-coated, and then uniform NPs were assembled on the NCP microspheres by second spin coating [113].

Spray-coating is a facile and cheap method, which can be easily applied to any substrate and used even for consumer applied coating. A transparent superoleophobic surface was spray-coated in one step with a solution of stringed amphiphilic silica NPs in amphiphilic sol [114]. The stringed NPs formed a fractal-like nanoporous network, while the sol acted as surface modifier and binder to enhance the

coating durability against heating (up to 400 °C), water jetting, and sand abrasion. Spray-coating of durable SHPo composite films usually requires harsh or volatile organic solvents for solution processing of polymers and dispersing hydrophobic NPs. The replacement of harmful organic solvents with water can enhance the scalability of spray-coating without the increased cost in chemical handling and environmental safety concerns. An environment-friendly method of spray-coating was developed with a water-based solution, which was comprised of exfoliated graphite nanoplatelets (xGnPs), polyolefin (PE) dispersion, and ammonium hydroxide [115]. In this method, hydrophobic components (xGnPs) could be stabilized in water by utilizing chemicals containing acid functional groups (acrylic acid), which can become ionized in aqueous environments under proper pH control ($\text{pH} > 7$). The PE dispersion contained polyethylene-acrylic acid copolymer (~40%) and ammonium hydroxide (used as a pH adjuster). After spray-coating and drying at 80 °C for 1 h, the xGnPs became water insoluble to promote liquid repellency.

4.3 Multifunctionality

Multifunctionality is another important requirement for increasing product value and expanding applications of structured surfaces with engineered wettability. Self-cleaning coatings for optical applications would require high transparency for visible light and self-cleaning ability for long service life. However, it may be difficult to combine a specific wettability designed for a specific application with other desired functions. For example, surface roughness is beneficial to enhance or reduce wettability but will likely increase light scattering. Thus, to fabricate desired wetting surfaces that satisfy multiple functionalities, materials, structures, and processes should be designed by simultaneously considering their effects on different functionalities. Antireflective self-cleaning coatings could be generally fabricated by using sub-100 nm surface roughness as well as a transparent material (ceramics or polymers) [116, 117]. Many research works have been conducted to develop multifunctional coatings and textiles based on specifically prescribed wettability. An antireflective, self-cleaning, and antifogging film was deposited on glass substrate by sol-gel coating of oxide double layers for application of photovoltaic cells [118]. The bottom layer of a hybrid methyl-functionalized nanoporous SiO_2 exhibited high transparency (antireflective), high water repellency, and high mechanical stability. The top layer of an ultrathin nanoporous TiO_2 imparted high water wettability (for antifogging) and photocatalysis (for self-cleaning) on the surface. The thicknesses and refractive indices of two layers were controlled to adjust the antireflectivity in the visible wavelength range. A free-standing transparent stretchable and SHPo composite film was fabricated by two-step spraying of resin and SHPo silica NP paint, followed by subsequent demolding of the resin composite paint [119]. It could sustain the SHPo property after straining (up to 100%), immersing in various corrosive liquids, pollution by sludge water, sandpaper abrasion, and

heat treatment (at 150 °C for 24 h) due to its multifunctional properties of anticorrosion, self-cleaning, and mechanical/thermal stability.

A self-cleaning, antibacterial, and UV protective textile was fabricated from a polyester/wool fabric by enzymatic pretreatment to hydrolyze the fabric surface and was followed by dip coating with TiO₂ NPs and cross-linking agent of butanetetracarboxylic acid (BTCA) [120]. The self-cleaning and antibacterial properties were verified by color removal from the stained fabric and by inhibited growth of gram-negative bacteria (*E. coli*). A flame-retardant, self-healing, and waterproof film was dip-coated on cotton fabric with a trilayer of branched poly(ethylenimine) (bPEI), ammonium polyphosphate (APP), and F-POSS [121]. When directly exposed to flame, the trilayer coating generated a porous surface layer of char (residual black carbon material) to give a self-extinguishing property. It could repeatedly restore its SHPo property after O₂ plasma etching by just keeping in a slightly humid environment (with a relative humidity of 35%) for 1 h. Furthermore, it could endure more than 1000 cycles of abrasion with metal under a pressure of 44.8 kPa without losing the flame retardancy and self-healing SHPo properties.

In order to achieve multifunctionality, surfaces are commonly designed with sophisticated structures and chemical heterogeneity, but it is difficult to secure their mechanical durability and develop scale-up fabrication for industrial production. Therefore, it is important to obtain a proper combination of design simplicity and multifunctional performances for successful commercialization.

5 Conclusions

The research activities on structured surfaces of controlled wettability have been increasing rapidly, and researchers have made great progress so far in applied technology as well as basic science. Nowadays, SHPi or SHPo surface can be obtained on any substrate (metal, ceramic, polymer, or textile) by nanotechnology-based surface modification or coating, and SHPi or SHPo regions can be placed on a given substrate in a desired pattern. In addition, major application areas of certain wettable surfaces have been explored, including self-cleaning, antifouling, anticorrosion, and oil-water separation. In another application field, biomedical devices have also been explored, such as contactless liquid handling platform for biomedical analyses, controlled-release drug delivery system, and simple low-cost microfluidics for POCT.

Meanwhile, significant commercialization has been achieved mainly in self-cleaning and antifouling fields, although there still are common challenges for practical applications, such as mechanical durability, scalable manufacturing, and multifunctionality. In general, the first two are essential to secure long-term performance and cost competitiveness for commercial products, and the last one is optional to promote the product value. It is highly recommended to review the existing research outcomes in order to advance the technologies of wettability engineering for successful commercialization in the future. For this purpose, it is helpful to

understand which technologies are promising for each application and to analyze their relative competitiveness against existing products. For self-cleaning applications, TiO_2 -based SHPi coatings are more extensively used than SiO_2 -based SHPo ones due to their multifunctionality such as deodorizing and antibacterial performances. For marine application, PDMS-based SHPo antifouling coatings are accepted more than PEG-based SHPi ones due to their higher performance in the normal conditions of water flows. However, for biomedical application, the PEG-based SHPi surface seems to be better due to the higher resistance to irreversible, nonspecific absorption of proteins. Among many SHPo anticorrosion coatings, the best one appears to be based on polymer/inorganic NP composite (such as PTFE/ SiO_2 and PU/ Al_2O_3) due to the relatively high mechanical durability and environmental friendliness. However, to date there has not been research work that demonstrates its superiority over existing products.

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Superhydrophobic Polymer/Nanoparticle Hybrids



Saravanan Nagappan and Chang-Sik Ha

1 Introduction

Superhydrophobic surface is one the most interesting topics in this recent days due to excellent water-repellent and self-cleaning behavior of the surface [1, 2]. The so-called “lotus leaf” effect possessing superhydrophobic and self-cleaning properties is mainly due to the presence of micro-nano hierarchical structure and low surface energy of the surface. Similarly, various kinds of natural surfaces such as rose petal, rice leaf, canna leaf, taro leaf, cicada wings, butterfly wings, water strider, gecko feet, Namib Desert beetle, fish scale, and mosquito eyes can also express an excellent water-repellent behavior due to the reduction of water adhesion on the surface [3]. Superhydrophobic surfaces have received considerable attentions due to the fact that they can be adopted for various applications such as oil-water absorption and separation, anti-icing, anticorrosion, anti-fouling, anti-bacterial, metal and dye adsorption, biomedical applications, sensors, transparent substrate, and etc. (Fig. 1) [4]. The nonstick and easier self-cleaning nature of the superhydrophobic surface may lead to attract far more interests in wider applications [5].

An ideal superhydrophobic surface can show high contact angle (CA), stable Cassie wetting state, and lower contact angle hysteresis (CAH). The surface wettability of a substrate can be measured from their water contact angle [6]. In general, superhydrophobic surface can show the water contact angle of 150° and above [7]. Various fabrication routes such as top-down, bottom-up and combination of both top-down and bottom-up approaches are used for the development of superhydrophobic coatings [2, 8]. The superhydrophobic surface property depends upon several factors such as effect of surface roughness, surface energy, micro-nano architecture, water droplet adhesion, choice of substrate, and pre-treatment.

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M. Hosseini, I. Karapanagiotis (eds.), *Materials with Extreme Wetting Properties*, https://doi.org/10.1007/978-3-030-59565-4_4

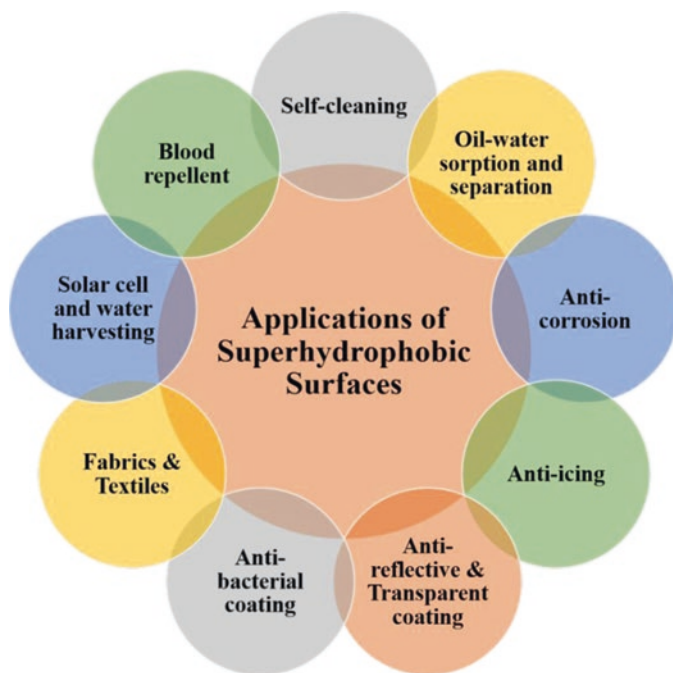


Fig. 1 Various applications of superhydrophobic surfaces

Similarly, numerous natural and synthetic polymers and metal nanoparticles have been used so far for the development of superhydrophobic surfaces due to easier formation of hierarchical structure by using the materials. The combination of polymer and metal nanoparticles such as organic and inorganic hybrid materials can have a huge impact in the development of superhydrophobic materials due to the formation of micro-nano hierarchical surface and the presence of low surface energy material [9, 10]. Several review articles and research papers were deeply studied on various polymers and metal nanoparticles for the development of superhydrophobic coatings and surfaces in diverse applications [9, 11–13]. The combination of polymer and nanoparticles may provide superhydrophobic property easily due to the surface bonding of nanoparticles with the substrate as well as with polymer. The introduction of nanoparticles with various kinds of polymers can create more micro-nano hierarchical surface morphology required for developing superhydrophobic surface, because the nanoparticles strongly interact with the polymers as well as aggregate together with the hydrophobic and low surface energy material that may reduce the water adhesion on their surface and enhance nonstick and self-cleaning behavior. Currently, numerous methods and approaches have been used to synthesize novel materials and various fabrication techniques for water-repellent coating. On the other hand, a simple fabrication method with durable and robust surface properties is highly required to be used for industrial application as well as for the commodity usage.

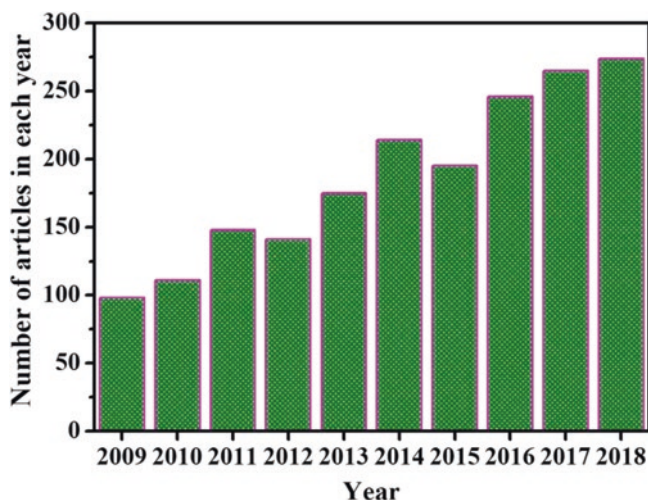


Fig. 2 Number of papers published under the topic of superhydrophobic polymers from 2009 to 2018. (Source: Web of Science)

In this chapter, we briefly overview the role of natural polymers and biopolymers, synthetic, and conducting polymers as well as various metal nanoparticles to prepare organic-inorganic hybrid materials used for superhydrophobic coatings. The number of papers published under the topic of superhydrophobic polymer for the last 10 years was shown in Fig. 2. The continuous increase of the number of papers clearly highlights the importance of various polymers for the fabrication of superhydrophobic surface. Moreover, various monomers and polymers were considered for the development of stable superhydrophobic surface on various substrates. The addition of nanoparticles with the polymers may also enhance the stability as well as their applicability for practical end uses, because various nanoparticles have their own special characteristics for a particular application. Thus, the polymer/nanoparticle composite-based coating materials have attracted much attention in endowing superhydrophobic surface property on various substrates as well as for various applications.

2 Superhydrophobic Surface Based on Polymers

Thermoplastic and thermoset polymers both have considerable attention in various applications [14]. Thermoplastic polymers have the ability to remold to a desired shape and also possess highly flexible and soft nature, whereas thermoset polymers cannot be processed again due to the formation of cross-linking network structure [15]. The use of both types of polymers was considered largely to develop superhydrophobic surface. On the other hand, thermoplastic polymers are used widely for

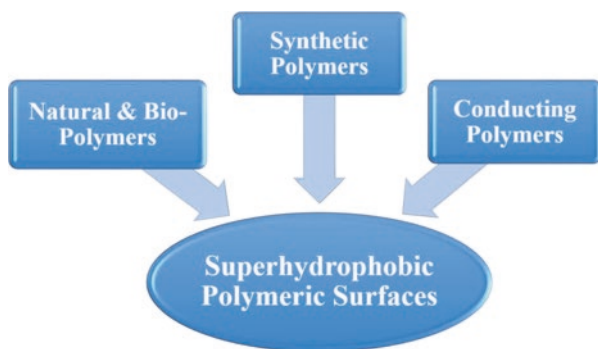


Fig. 3 Various polymers used for the development of superhydrophobic surfaces

superhydrophobic coating as compared to thermoset polymers. Several natural, bio-, synthetic, and conducting polymers were already used to produce the superhydrophobic surface on various substrates as well as for the applications (Fig. 3). Hence, we first focus on the role of polymers for the development and fabrication of superhydrophobic coating.

2.1 *Natural Polymers and Biopolymers*

Natural polymers and biopolymers are obtained mostly from the sources of natural raw materials which can have both hydrophilic and hydrophobic properties. Natural polymers and biopolymers are focused generally for the fabrication of superhydrophobic surfaces because of their biodegradable and biocompatible nature. The use of natural polymers and biopolymers is also easily compatible with various metal sources. Wen et al. briefly reviewed the biomimetic surfaces and various polymers used for the fabrication of superhydrophobic surfaces and their vast applications in various fields [4]. Sasaki et al. used a natural cotton fabric for the fabrication of superhydrophobic surface by spray coating of ethyl- α -cyanoacrylate and hydrophobized SiO_2 nanoparticles [16]. The materials have biocompatible nature by spray coating on the substrate, whereas the surface property of the coated material depends on the distance between the substrate being coated by the material as well as the distance between the spray gun and substrate (Fig. 4). A porous natural sponge obtained from *Luffa cylindrica* showed superhydrophobic surface property by modifying the sponge with hydrophobic modifier such as aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) or trisilanolphenyl POSS solution [17]. The fabricated superhydrophobic porous sponge showed excellent oil adsorption with 8 to 12 times of its weight for various kinds of oils. Razavi et al. realized a highly stable superhydrophobic surface on a copper substrate by pre-treating the substrate surface followed by liquid phase deposition of naturally derived hydrophobic agents such as cinnamic acid or myristic acid in ethanol solution [18]. The authors found

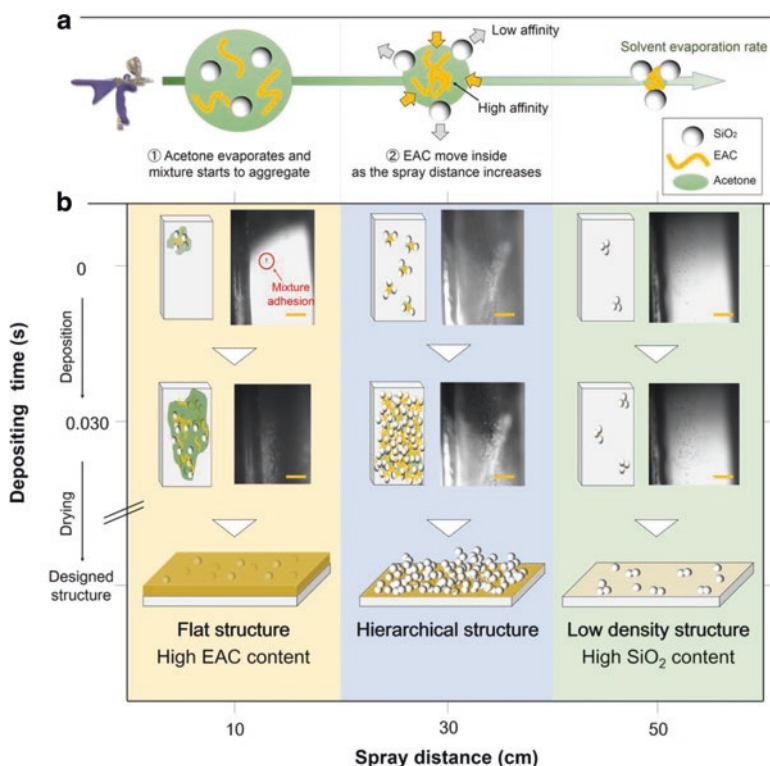


Fig. 4 Illustration of the behavior of the sprayed mixture with increasing spray distance: (a) sprayed mixture in flight and (b) illustration and images of the mixture after reaching surfaces at different distances. Scale bars are 1 mm. (Reproduced with permission from reference [16], Copyright 2015 American Chemical Society)

that the use of naturally derived cinnamic acid (154°) or myristic acid (165°) can lead to form a highly superhydrophobic surface with low contact angle hysteresis ($<15^\circ$) on the copper substrate as compared to previously reported acid derivatives used before for the development of superhydrophobic surfaces.

A sustainable and biodegradable superhydrophobic polymeric foam was developed by using poly(lactic acid) (PLA) and dioxane followed by sublimation of dioxane crystals, which exhibited porous micro-nano structures with skin peeling (Fig. 5) [19]. The developed biopolymer derived superhydrophobic foam can be used for the continuous sorption (12–31 times its own weight) and separation (over 98% for 10 cycles) of various oils from the oil-water mixtures based on the density and viscosity of oils [19]. Alves et al. studied the cell adhesion behavior on the superhydrophobic poly(L-lactic acid) (PLLA) membrane film modified with simulated body fluid (SBF) solution [20]. The superhydrophobic PLLA membrane film showed very low cell adhesion behavior as compared to the pristine PLLA membrane.

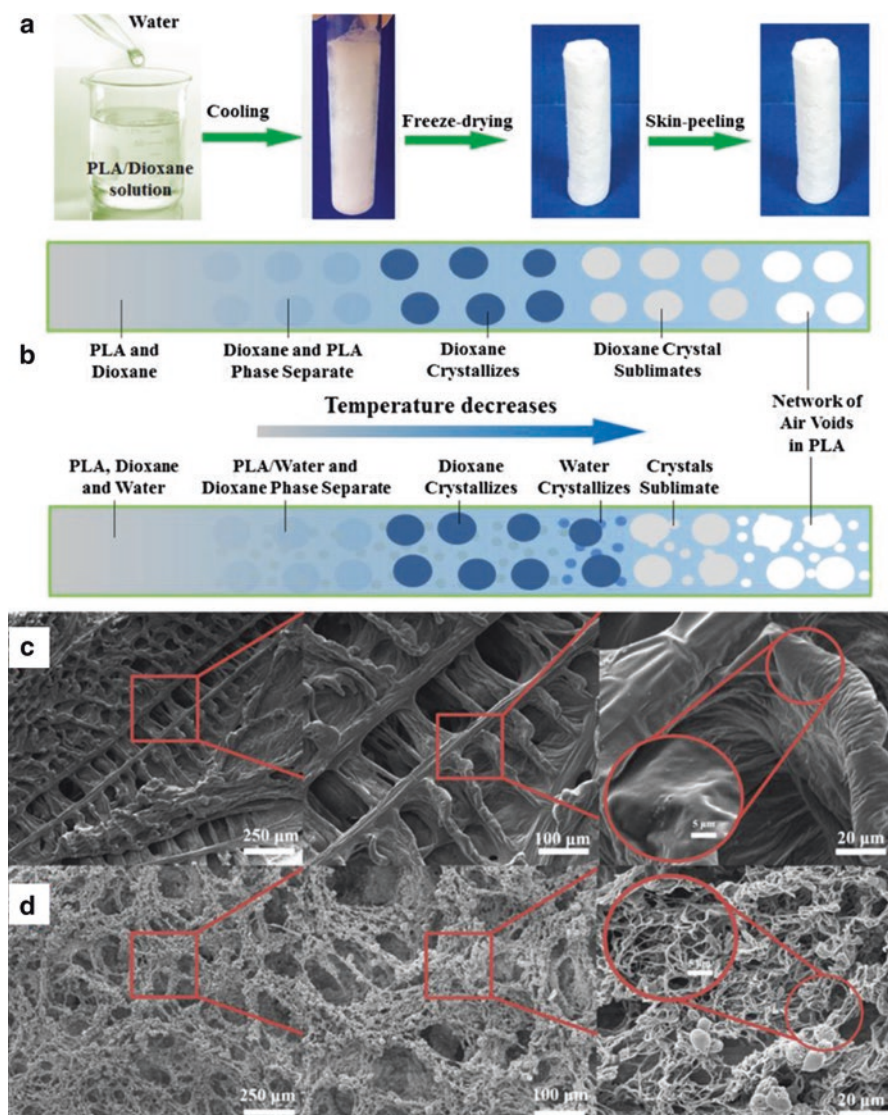


Fig. 5 (a) Fabrication process of PLA foam. (b) Schematic of the phase inversion process. (c, d) SEM images of the cross section for PLA foam (c) without (F0) and (d) with 4 mL of water (F4). (Reproduced with permission from reference [19], Copyright 2019 American Chemical Society)

Xie et al. developed novel magnetic-sensitive nanoparticles to have superhydrophobic property via self-assembly of a biopolymer obtained from big fat-based polyol and polymethylene polyphenylene isocyanate [21]. The developed superhydrophobic material showed excellent magnetic-sensitive behavior as well as slow and sustainable release (more than 100 days) of fertilizer. Electro-spraying blends

of two biocompatible polymers such as polycaprolactone (PCL, $M_w = 45 \text{ kgmol}^{-1}$) and poly(glycerol monostearate carbonate-co-caprolactone) (PGC-C18, $M_w = 30 \text{ kgmol}^{-1}$) showed the superhydrophobic (150°) surface property with controlled drug delivery nature [22]. Biocompatible spherical particles synthesized on a transparent superamphiphobic surface using poly(D,L-lactide-co-glycolide)/ciprofloxacin suspensions in dioxane (PLGA) also displayed controlled drug release as well as excellent antibacterial property to various microorganisms [23].

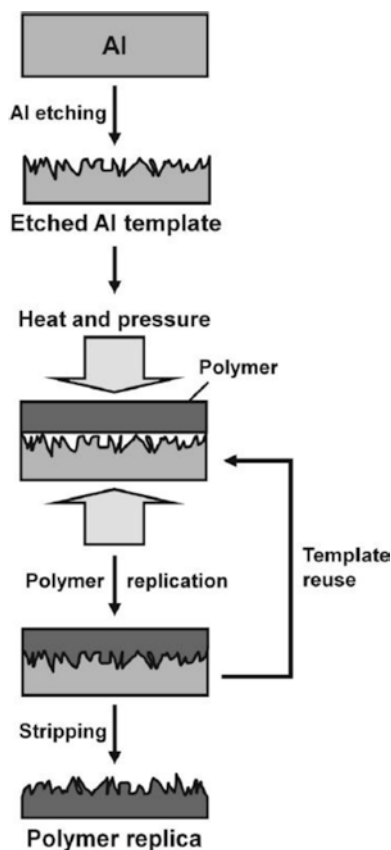
Non-fluorinated natural polymers and biopolymers are widely focused for the development of superhydrophobic surfaces because of their excellent biocompatible as well as biodegradable nature. The drawbacks of fluorinated polymers are the high cost of the material and low biocompatibility as compared to other non-fluorinated polymers for superhydrophobic surfaces. At the same time, fluorinated polymers have been also focused widely for the superhydrophobic coatings due to their excellent thermal and chemical stability under severe environmental conditions as well as their low surface energy nature, which is important for the development of the durable superhydrophobic surface for various applications.

Khanjani et al. used fluorinated cellulose nanocrystals (FCNCs) for the preparation of superhydrophobic paper. A commercial filter paper (Staples A4 80 gsm multipurpose paper) is used as a substrate which is treated by FCNCs obtained by the modification of CNCs with 2H,2H,3H,3H-perfluorononanoyl chloride [24]. The FCNCs were spin-coated on the substrate at 4000 rpm for 1 min followed by subsequent drying at 80°C and repeating the spin-coating for 10 mins. A biocompatible xerogel coating was developed by hydrolysis and condensation of colloidal silica obtained from the mixture of (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (17FTMS) and tetraethyl orthosilicate (TEOS) and methyltrimethoxysilane (MTMOS). The prepared colloidal suspension was spread-cast on an ozone/ultraviolet (UV)-treated glass substrate and dried for overnight. The fabricated opaque xerogel coating exhibited excellent antibacterial property as well as low bacterial adhesion on the superhydrophobic surface as compared to other substrates studied for the comparative experiment.

2.2 Synthetic Polymers

Synthetic and engineering polymers are used generally for the development of superhydrophobic surfaces because of the formation of durable and stable surface under severe environmental changes. Moreover, synthetic polymers have the ability to be molded for the required shape as well as can change the configuration and flexible and bendable nature under external stimuli. Lee et al. fabricated a biomimetic superhydrophobic surface on various thermoplastic polymer substrates by a polymer replication method [25]. A superhydrophobic surface was obtained by first etching an aluminum sheet in Beck's dislocation etchant which is a mixture of hydrochloric acid (HCl, 37 wt.%), hydrofluoric acid (HF, 50 wt.%), and distilled

Fig. 6 Schematic illustration of the fabrication of polymer replicas having various surface structures from etched Al templates with micrometer-sized irregular steps and nanometer-sized hierarchical structures by using the heat- and pressure-driven polymer replication method. (Reproduced with permission from reference [25], Copyright 2010 American Chemical Society)



water at (28.1:2.2:69.7). The polymer substrates such as high-density polyethylene (HDPE), poly(ϵ -caprolactone) (PCL), polypropylene (PP), and polystyrene (PS) were kept on the patterned Al template, and a hierarchical structure was developed by using heat and pressure on a hot plate for 10 mins (Fig. 6). The polymer replicas were obtained by stripping the substrate from the template. The obtained hierarchical surface showed stable superhydrophobic property. A free-standing superhydrophobic flexible film on the low-density polyethylene (LDPE) film can also be developed by a lamination templating method [26]. Nylon mesh is used as a template for LDPE, and stainless steel mesh is used as a support to sandwich the LDPE and nylon mesh. After a subsequent heat and pressure treatment, the laminate stack is cooled and peeled off the mesh template to produce superhydrophobic free-standing polymer film (Fig. 7). The authors also checked by varying the mesh types, heating, pressure, and time of lamination, suggesting that at most of the cases, they can obtain the free-standing superhydrophobic films due to the formation of array of neat and textured surface on the LDPE film.

Mondal et al. fabricated a superhydrophobic surface by deposition of a layer of hydrophobically modified silica nanoparticles covered by laminating an ultrahigh

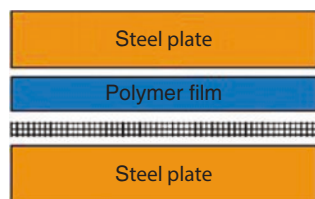
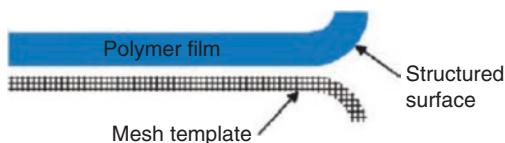
Step 1. Laminate assembly under heat and pressure**Step 2. Cool and peel off mesh**

Fig. 7 Schematic illustration of the lamination peeling process. (Reproduced with permission from reference [26], Copyright 2011 American Chemical Society)

molecular weight polyethylene (UHMPE) at 177 °C under 70 MPa for 45–60 min [27]. On the other hand, Zhang et al. developed a mechanically stable superhydrophobic film by hot-press laminating and peeling technique using blend of PP and UHMPE as well as HDPE [28]. First, they prepared both films separately by hot-pressing the polymer granules at 200 °C for 2 min under the pressure of 3 MPa. The PP/UHMWPE film was placed over the HDPE film, and similar hot-press lamination and peeling process was carried out to develop a superhydrophobic surface on the HDPE film. An injection molding technique was used to replicate the textured surface on the PP surface [29, 30]. The texture pattern surface was developed by micro-working robot which is transferred first on the stainless steel surface followed by patterning on the PP surface [30]. The fabricated PP surface showed various micro-nano textured surface morphology based on the conditions used to provide superhydrophobic property on the surface (Fig. 8).

More recently, Kim et al. developed a flexible and translucent superhydrophobic tube by replication and detachment process using polydimethylsiloxane (PDMS) as a main source of pre-polymer used to produce the tube [31]. The tube was developed on the Al surface which is pre-treated by etching, desmutting, and alkalinizing to produce hierarchical structure followed by modification of the surface by self-assembly with hydrophobic agent such as heptadecafluoro-1,1,2,2-tetra-hydrodecyl-trichlorosilane (HDFS). The hydrophobic treatment helps to reduce adhesion force between the mold and PDMS, so that the tube can be easily released from the mold and maintain the hierarchical surface morphology with low surface energy materials on the surface. The tube can show excellent superhydrophobic property and also maintain the optical and mechanical stability. The superhydrophobic tube can show the wider applicability in the liquid transportation as well as excellent blood-repellent nature as compared with a normal tube. The optical and microscopic images clearly illustrate the blood-repellent property of the superhydrophobic tube as compared to the normal tube (Fig. 9). These results suggest the superhydrophobic tube can be used in wide variety of applications. A superhydrophobic polyimide (PI) mat was developed by first synthesizing fluorinated polyimide (FPI) using 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (6FBAPP) with 4,4-oxydiphthalic anhydride (ODPA) followed by electrospinning the FPI with

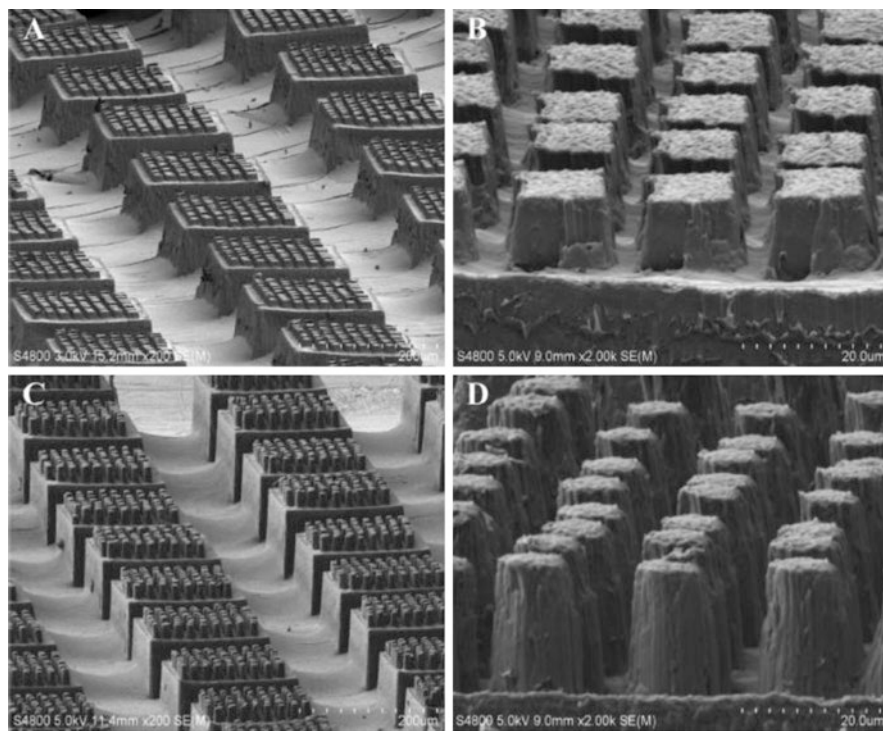


Fig. 8 Scanning electron microscopy (SEM) images of hierarchical micro-microstructures on a PP surface: (a) hierarchical micro-microstructure (square-square), (b) a close-up, (c) hierarchical micro-microstructure (square-barrel), and (d) a close-up. (Reproduced with permission from reference [29], Copyright 2012 American Chemical Society)

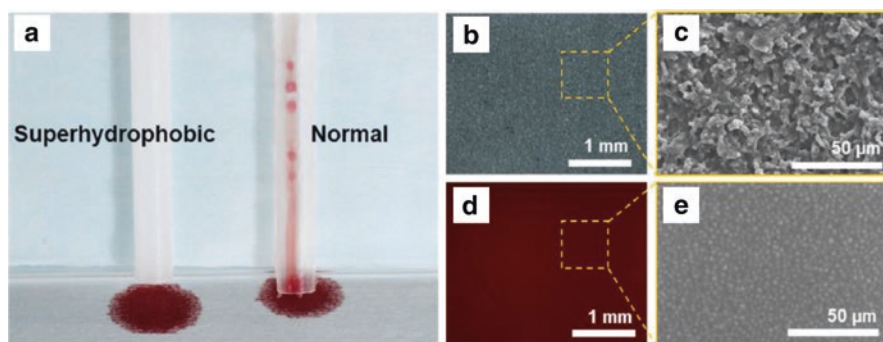


Fig. 9 Blood-repellent property of the superhydrophobic tube. (a) Photograph of the superhydrophobic tube and a normal tube when 200 μL of sheep blood was transferred through the tubes. The tubes with 80 mm length were inclined at 45° . Zoom microscope and SEM images, respectively, of the area where blood rolled over the inner surface of the (b, c) superhydrophobic tube and the (d, e) normal tube. (Reproduced with permission from reference [31], Copyright 2019 Elsevier B.V)

different ratios of dimethylacetamide (DMAc) and tetrahydrofuran (THF) to achieve better superhydrophobic surface [32].

2.3 *Conducting Polymers*

Conducting polymer is one of the interesting polymers with comprehensive π -electron delocalization in their chemical backbones which make the polymer as good electrical conductors [33]. Conducting polymers are used widely in various applications because they express both the electronic properties of semiconductors and good usability like conventional polymers [34, 35]. Electrochemical and chemical oxidation/reduction methods are used most widely for the introduction of charge carriers or to dope the conjugated polymer to be conductive. The partial oxidation by electron acceptors or partial reduction by electron donors of a polymer can introduce the charge carriers which create defects in the polymer backbone and make them conductive [33]. The fabrication of superhydrophobic surface by the use of conducting polymers can show wider usage of the surface property on various applications especially in the electronic devices as well as for the anticorrosion applications [33]. Electrochemical polymerization of a monomer or electrodeposition of a conducting material on a substrate is used generally to fabricate a superhydrophobic surface. Electrochemical polymerization was performed in a three-electrode setup using platinum disk, gold plate, or carbon cloth or other conductive substrates that can be used as a working electrode, whereas platinum wire, glassy carbon, or carbon rod is used as a counter electrode, and secondary calomel electrode (SCE) or Ag/AgCl is used as a reference electrode. Cyclic voltammetry (CV) is performed for analyzing the oxidation and reduction behavior of the conducting polymers.

Recently, the conducting superhydrophobic thin film prepared by spray coating the mixture of carbon nanotubes (CNT) mixed with Triton-X-100, silica nanoparticles (7 nm), zirco-aluminate coupling agent, and PDMS [36]. The fabricated substrate showed excellent electrical heating behavior as well as deicing nature. Darmanin et al. fabricated a superhydrophobic surface by electrochemical and polymerization technique and studied the effect of hydrocarbon versus fluorocarbon on the surface fabrication [37]. Some of the hydrocarbon and fluorocarbon used for this study expressed excellent superhydrophobic property based on their chemical compositions. In a similar fashion, Zenerino et al. synthesized new semi-fluorinated (C_4F_9 , C_6F_{13}) 3,4-ethylenedioxy pyrrole derivatives and performed electrochemical polymerization on a platinum plate to develop a highly stable superhydrophobic and oleophobic property on the surface [38]. The Guittard group also performed similar electrochemical polymerizations with various kinds of monomers and studied the effect of superhydrophobic and oleophobic behaviors [39].

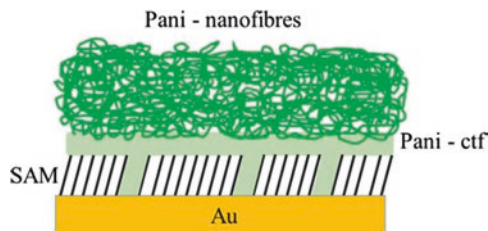


Fig. 10 Schematic illustration of the deposition of polyaniline on dodecanethiol SAM-modified gold electrodes showing the initial deposition of the polymer within defects in the SAM, followed by the formation of a compact thin film (ctf) of thickness 1 μm and, lastly, the transition to a spaghetti-like morphology of polymer nanofibers. (Reproduced with permission from [40], Copyright 2015 American Chemical Society)

Jabarullah et al. fabricated superhydrophobic gold electrode for surge protection devices by first self-assembly of 1-dodecanethiol (0.01 M, DDT) on an electrode by self-assembled monolayer (SAM) followed by electrochemical deposition of the mixture of polyaniline (0.5 M, Pani) and methanesulfonic acid (2 M) in deionized water [40]. The electrochemical deposited polyaniline, which was doped with methanesulfonic acid, showed a nanofiber spaghetti-like morphology with a high surface area to volume ratio (Fig. 10). The fabricated substrate showed superhydrophobic property with the contact angle of 152° and enhanced current-limiting properties. The authors also suggested the best surface property can be achieved by increasing the immersion time to greater than 24 to 72 h for SAM of DDT, so that the electrochemical doping of polyaniline-methanesulfonic acid occurred uniformly on the surface of the gold electrode, showing superhydrophobic property and enhanced current-limiting behavior. Likewise, the authors also suggested that the presence of SAM on the gold electrode would initially limit the electrochemical deposition of polyaniline-methanesulfonic acid for 20–30 s due to the diffusion of oxidized monomers which form a dense layer on the electrode surface and solution interface and block the current flow, whereas increasing the deposition time leads to uniformly deposit the polyaniline-methanesulfonic acid on the pinholes of SAM and express the superhydrophobic surface on the substrate.

Ren et al. carried out an electropolymerization on a carbon cloth surface by polymerizing the pyrrole monomer with anionic surfactant dioctylsulfosuccinate (AOT) at constant current density (5 mA cm^{-2}) for 10 mins [41]. The fabricated substrate illustrated excellent superhydrophobic property and reversible organic contaminant adsorption behaviors. The polypyrrole (PPy), doped with anionic surfactant AOT carbon cloth, showed excellent adsorption behavior to various organic contaminants with adsorption capacity of 570 mg pollutant/g polymer. Moreover, the fabricated substrate maintained excellent stability for continuous adsorption and desorption recycling test.

3 Superhydrophobic Surface Based on Organic-Inorganic Hybrid Materials with Metal Nanoparticles

Organic and inorganic materials or a combination of organic-inorganic hybrid materials is used commonly for the fabrication of superhydrophobic surface, because organic-inorganic hybrid material can have low surface energy as well as micro-nano hierarchical surface morphology by self-assembly on a substrate [7]. Various organic and inorganic precursors were used widely for the superhydrophobic coating. In this chapter, we review organic-inorganic hybrids with nanoparticles showing hierarchical surface morphology on a substrate which is responsible to fabricate superhydrophobic surface. We will broadly overview various fabrication techniques used in the development of superhydrophobic surface by just focusing the role of various organic-inorganic precursors as well as inorganic materials. Especially, we will focus the role of silica or siloxane, iron, titanium, zinc, copper, and other inorganic-based materials for superhydrophobic surface fabrications (Fig. 11).

3.1 Silica Nanoparticles and Functional Siloxane-Based Nanoparticles

Silica- and siloxane-based organic-inorganic hybrids are used widely in the development of superhydrophobic coating because of their low toxicity as well as huge availability of silica-based sources from the earth crust (59%). Moreover, silica-based



Fig. 11 Various organic-inorganic nanoparticles for the development of superhydrophobic surfaces

materials are easily attached with various substrates by either hydrogen bonding or weak van der Waals force of attraction or strong covalent bonding with various functional groups. Hydrophobic modification of silica nanoparticles or hydrophobic silane precursors or functional siloxanes is the main source for the development of superhydrophobic surface. Ixzh et al. fabricated a transparent superhydrophobic surface on various substrates by placing various precursors such as decane, TEOS, and perfluorodecalin or perfluorohexane inside microwave, and plasma polymerization occurred at argon atmosphere [42]. The use of hydrocarbon and fluorocarbon with hydrophilic silane precursor made the surface superhydrophobic and ultraviolet (UV)-stable. Yilgor et al. studied the effect of hydrophobic silica nanoparticle (H2S) dispersion with various polymers such as polydimethylsiloxane-urea copolymer (TPSU), a polyether-based polyurethane urea (TPU), poly(methyl methacrylate) (PMMA), PS, polycarbonate (PC), and a cross-linked epoxy resin used for the fabrication of superhydrophobic surface by spin-coating technique [12].

Nagappan et al. developed a highly transparent and stable hydrophobic and oleophobic surface on a glass substrate by synthesizing polymethylhydrosiloxane (PMHS)-based organic-inorganic hybrid materials by surface grafting the PMHS with 2,2,3,4,4,4-hexafluorobutylmethacrylate (HFBMA) via hydrosilylation reaction followed by reacting with TEOS [44]. The fabricated transparent substrate also showed excellent anti-stain property. Likewise, they also developed a highly transparent hydrophobic surface for anti-stain coating using polyvinyl chloride (PVC)-functional silane-based organic-inorganic hybrid metallopolymer [45]. The PVC metallopolymer (without functional silane treatment) obtained in their work also suggested that almost nearly superhydrophobic surface could be obtained by coating the solution on a glass substrate. A lotus leaf powder (LLP)-based organic-inorganic hybrid material was developed by mixing the lotus leaf powder, polymethylhydroxysiloxane (PMHOS), and phenyl-substituted silica ormosils (PSiOr) [43]. The prepared suspension showed excellent and stable superhydrophobic property on various substrates and almost maintained the superhydrophobic stability over 6000 s and up to 500 °C (Fig. 12). The fabricated superhydrophobic substrate showed nonstick and self-cleaning property. Moreover, loading the hybrid material on a melamine-formaldehyde sponge followed by surface treatment with PDMS also maintained the superhydrophobic property on the substrate and also expressed an excellent sorption of various oils and organic solvents from oil-water and solvent-water mixtures. Similarly, superhydrophobic hybrid materials and suspensions were also developed by using other leaf powder instead of LLP and are used for various kinds of applications [46, 47]. They also synthesized PMHOS superhydrophobic powder and used it for the adsorption of methylene blue dye [48]. Furthermore, in situ addition of graphene oxide during the hydroxylation of PMHS also provided superhydrophobic surface property with excellent anti-icing performance [49].

Li et al. prepared a superhydrophobic melamine-formaldehyde sponge (SMF) in two steps, by first synthesizing superhydrophobic silica nanoparticles by sol-gel method using TEOS, decyltrimethoxysilane (DTMS), and 3-methacryloxypropyltri methoxysilane (KH-570), followed by free radical polymerization of water-based

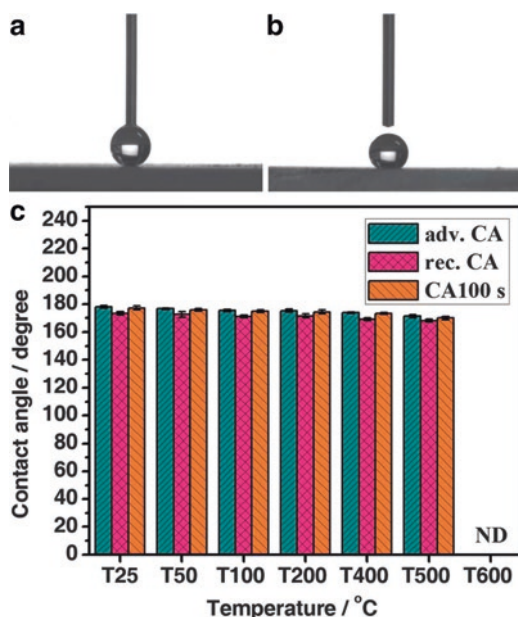


Fig. 12 (a and b) The highly stable superhydrophobic surface maintained superhydrophobic properties up to 500 °C for 5 h and more than 6000 s upon contact with water. (c) Dynamic contact angle (DCA) of the cast lotus leaf powder-polymethylhydroxysiloxane-phenyl-substituted silica ormosils (LLPPSiOr) hybrid substrate cured at various temperatures for 5 h by slow heating (1 h to the desired temperature) and cooling to room temperature. Notes: *adv. CA* advancing contact angle, *rec. CA* receding contact angle, *T* temperature, *s* seconds, *ND* not detected. (Reproduced with permission from [43], Copyright 2013 Royal Society of Chemistry)

acrylic copolymer to produce an emulsion which was loaded on the MF sponge by immersion (Fig. 13) [50]. The fabricated sponge showed stable superhydrophobic property with the contact angle of $153 \pm 1.6^\circ$ and also showed excellent absorption and separation behavior to various oils and organic solvents, as well as oils from oil-water emulsion. The fabrication method is much simple and cost-effective as well as environmentally friendly for oil and organic solvent sorption and separation applications.

3.2 Iron- or Magnetic-Based Nanoparticles

Recently considerable attentions have been focusing on the use of iron-based nanoparticles or magnetic materials for the development of superhydrophobic surfaces. Nagappan and Ha briefly reviewed the importance of superhydrophobic surface property based on magnetic materials and their fabrication methods as well as various applications (Fig. 14) [51]. Zheng et al. synthesized a micellar catalyst in biphasic water-in-oil or oil-in-water type pickering emulsion using the framework

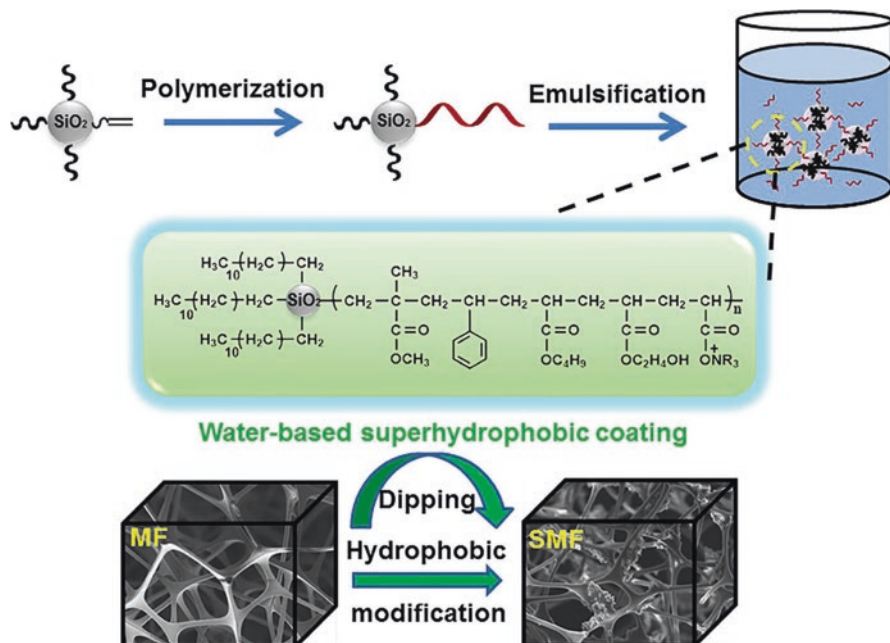


Fig. 13 Schematic illustration of the synthesis process of superhydrophobic melamine-formaldehyde sponges (SMF). (Reproduced with permission from [50], 2019 Elsevier B.V)

of magnetic superhydrophobic polymer nanosphere [52]. The catalyst was developed by modifying the Fe_3O_4 magnetic nanoparticles by cross-linking with hydrophobic PS to form a core-shell-type nanosphere, which was grafted further using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). The synthesized magnetic-responsive catalyst showed excellent catalytic behavior for the Montanari oxidation of alcohols as well as good recycling ability due to easy separation of the nanosphere with external magnet and without loss of catalyst.

Superhydrophobic magnetic-responsive nanoparticles or surfaces have been developed largely for various applications, at the same time, which are used widely in oil-water sorption and separation application because of the continuous need of new methods and technologies to capture oils from water. Recently, considerable attentions were paid to produce various methods and approaches to develop novel superhydrophobic surfaces for oil-spill capture and separation [53–56]. Dutra et al. synthesized novel magnetic-responsive superhydrophobic nanoparticles by hydrophobic modification of the magnetic nanoparticles with 2,3-dihydroxypropyl stearate (2,3-DHPS) and used them for the capture of oils from the water surface [57]. On the other hand, a novel magnetic superhydrophobic sponge was fabricated by using commercial polyurethane sponge, which was modified by straw soot followed by loading magnetic nanoparticles and hydrophobic blocking using PDMS [58]. The fabricated sponge showed stable superhydrophobic as well as magnetic-responsive nature and is used for the sorption of large scale of oil from water. Su

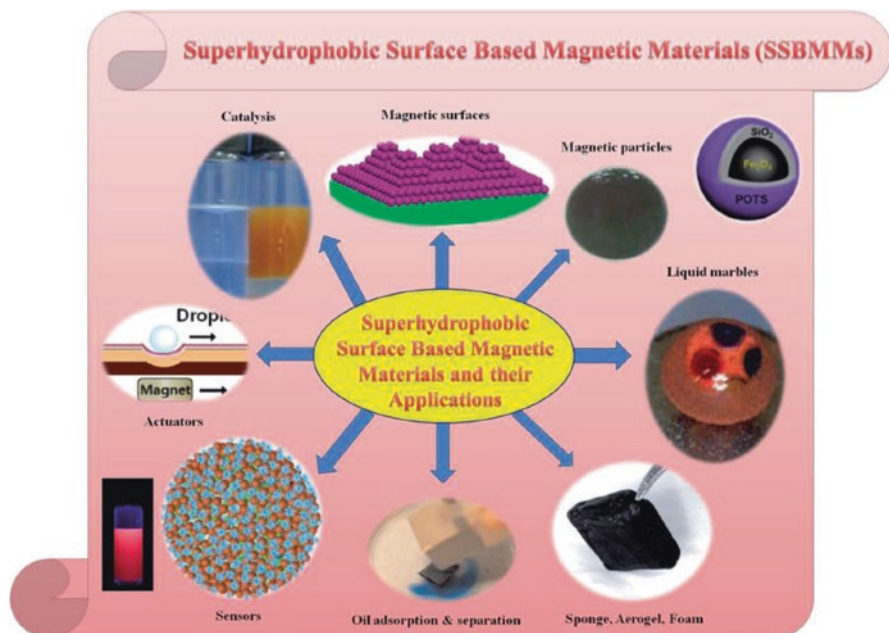


Fig. 14 Various ways of preparing superhydrophobic surface-based magnetic materials (SSBMMs) and their potential applications. (Reproduced with permission from [51], Copyright 2015 Royal Society of Chemistry)

et al. fabricated a dual functional superhydrophobic textile for oil-water separation by first preparing a hydrophobically modified magnetic nanoparticles using 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES) and Fe_3O_4 followed by addition of PDMS and two-component cross-linkable resin (Sylgard 184) to make hydrophobic suspension [59]. A piece of pre-cleaned textile was immersed into the hydrophobic suspension and cured at 80 °C for 20 mins in the presence of magnet. The fabricated textile showed excellent superhydrophobic property and was used for the continuous separation of various oils from water.

Tian et al. designed a method to develop porous magnetic chitosan (PMCS) particles with superhydrophobic property for the adsorption of Cu(II) ions in water (Fig. 15) [60]. First, they developed a porous fluorinated polyimide matrix (PFPI) by electrospinning technique using fluorinated polyimide (FPI). The porous structure was developed on nanofibers by removing the tetrahydrofuran (THF) solvent in a vacuum oven at 100 °C for 24 h. The developed porous FPI (PFPI) showed hydrophobic to superhydrophobic property based on the concentration of FPI. They also prepared a magnetic chitosan suspension (MCS) by dissolving chitosan in acetic acid (HOAc) under mechanical stirring for 1 h and Fe_3O_4 nanoparticles suspension in deionized water separately and mixed together with sodium sulfate under mechanical stirring for 1 h. The obtained MCS was spray coated on the developed PFPI mat and dried in vacuum oven at 140 °C for 10 min. The PMCS was obtained

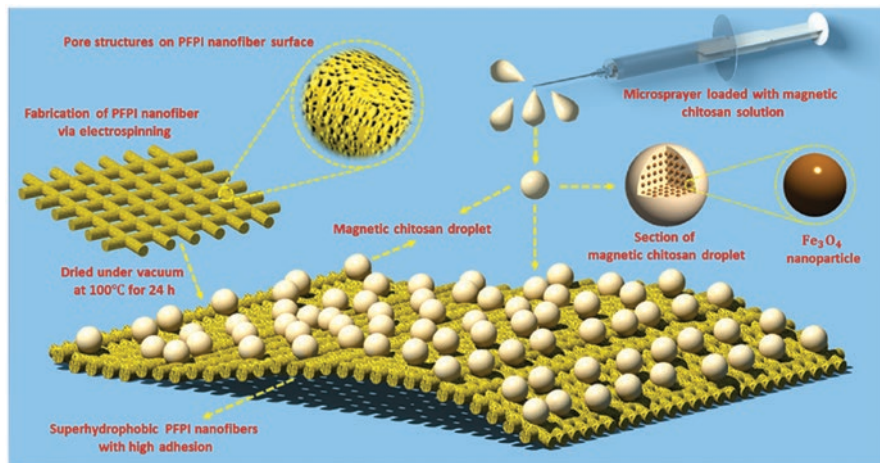


Fig. 15 Diagram illustrating the fabrication of high-adhesive superhydrophobic PFPI fiber mat and PMCS particles. (Reproduced with permission from reference [60], Copyright 2018 American Chemical Society)

by dissolving the MCS coated PFPI mat in THF followed by washing with deionized water and ethanol and dried to remove all the solvents. The PMCS particles showed excellent Cu(II) adsorption in aqueous solution with the maximum adsorption capacity of 188.68 mg g^{-1} .

3.3 Titanium-Based Nanoparticles

Titanium is one of the most important inorganic materials used for various fields due to the high corrosion resistance and high tensile strength-to-density ratio, as well as photocatalytic behavior. Similarly, titanium dioxide (TiO_2) nanoparticles are considered in various applications because of their excellent photocatalytic property as well as hydrophilic nature [61]. Thus, it is performed largely in self-cleaning coating application because it can easily degrade or clean dirt particles on their surface without any additional force. Titanium-based nanoparticles have been also used extensively in various applications as well as in the preparation and fabrication of superhydrophobic coating [62–64]. The nonstick behavior of superhydrophobic surface could enhance the self-cleaning property further by the introduction of titanium-based nanoparticles [65–67]. Several review articles discussed briefly on the use of titanium-based nanoparticles for the development of superhydrophobic surfaces as well as switchable superhydrophobic surfaces for various applications [68–70].

Gao et al. fabricated a superhydrophobic wood surface using TiO_2 nanoparticles and (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (FAS-17) (Fig. 16) [71].

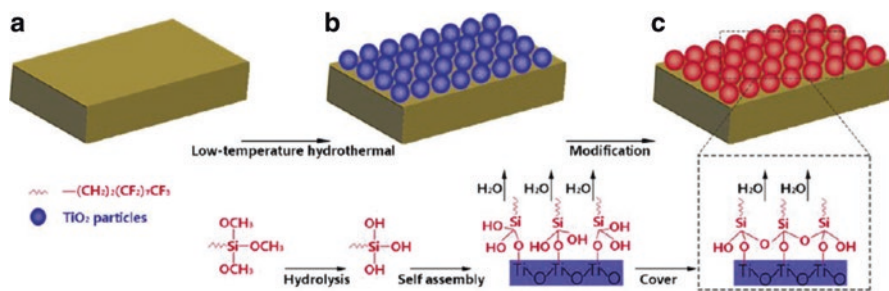


Fig. 16 Schematic illustration of the synthetic process of the superhydrophobic wood treated by TiO_2 and FAS-17. (Reproduced with permission from reference [71], 2014 Elsevier B.V)

The wood surface was pre-treated by ultra-sonication in deionized water followed by drying in oven at 105°C for 48 h. TiO_2 film was produced on the treated wood surface by low-temperature hydrothermal method at 90°C for 5 h followed by washing and drying at 60°C for 24 h in nitrogen atmosphere. Furthermore, the TiO_2 film deposited wood surface was modified further by preparing FAS solution in methanol and deionized water which was transferred to the Teflon container followed by immersing the TiO_2 film deposited wood surface and kept at 80°C for 5 h followed by similar washing and drying process. The as-fabricated wood surface showed excellent superhydrophobic surface property as well as resistance to strong acid as well as humidity and stable at higher temperature. Li et al. also developed a durable superhydrophobic self-cleaning wood surface by the similar concept and with slight modifications as the work by Gao et al. [72]. They used bamboo timber and carried out the TiO_2 deposition at the similar temperature conditions followed by modification of the surface with FAS-17 in a container placed in an oven at 130°C for 3 h. The fabricated substrate also showed excellent chemical stability against strong acids, good mechanical stability, longtime usability, and self-cleaning property. Rezaei et al. developed a PS-POSS- TiO_2 nanocomposite on a glass substrate and compared the role of TiO_2 in the nanocomposite for development of superhydrophobic surface [73]. They found that the prepared glass substrate showed superhydrophilic surface property without the addition of TiO_2 . On the other hand, the introduction of TiO_2 with PS-POSS may lead to produce superhydrophobic surface. The fabricated surface maintained the superhydrophobic stability for several falling test cycles.

3.4 Copper-Based Nanoparticles

Copper is also one of the widely available inorganic materials like silica-based materials from the earth which is used in various kinds of applications especially in the electronic field due to excellent electrical conductivity of copper. The use of copper-based materials was focused largely for the fabrication of superhydrophobic

surface [74–76]. Copper mesh was used widely for the fabrication of superhydrophobic surface as well as for the oil-water separation application [77–79]. Various surface pre-treatments of copper substrate as well as hydrophobic modifications were carried out to form hierarchical surface morphology with low surface energy materials coating on the surface in order to obtain the superhydrophobic property. Crick et al. used aerosol-assisted chemical vapor deposition (AACVD) for the fabrication of superhydrophobic surface on copper mesh. Sylgard 184 silicone elastomer, a kind of PDMS-based polymer, was converted to aerosol and deposited on the copper mesh by AACVD under nitrogen atmosphere for 30–40 min [77]. The authors discussed the CA of the uncoated copper mesh vary based on the mesh pore dimensions. The hydrophobic CA of the substrates become superhydrophobic by AACVD deposition of the Sylgard 184 silicone elastomer. The fabricated substrate was used for the separation of various types of oils and organic solvents from water.

Zhang et al. also fabricated superhydrophobic surface on a copper substrate by first cleaning the substrate in acetone, deionized water, and absolute ethanol, respectively, followed by hydrophobic modification and anodization of the substrate using myristic acid in ethanol and HCl. The copper substrate was used as an anode, aluminum plate used as a cathode [78]. The prepared myristic acid solution was used as an electrolyte, and anodization process and hydrophobic treatment were performed with DC power supply for 15 min under 10 V. The anodized sample was cleaned in ethanol and dried in a vacuum oven at 60 °C for 20 min. The fabricated superhydrophobic mesh substrate showed excellent usage in oil-water separation according to the schematic representation (Fig. 17). The superhydrophobic mesh showed over 93% of separation efficiency (E) to all the oils used in the separation study and also maintained the E over 87% after ten consecutive uses. In another method, the copper mesh was pre-cleaned in the above method and chemically etched using 35% ferric chloride (FeCl_3) followed by oxidation with 30% hydrogen peroxide (H_2O_2). The oxidized copper mesh was treated with stearic acid in ethanol-water solution for 30 h at 60 °C. The fabricated copper mesh also exhibits superhy-

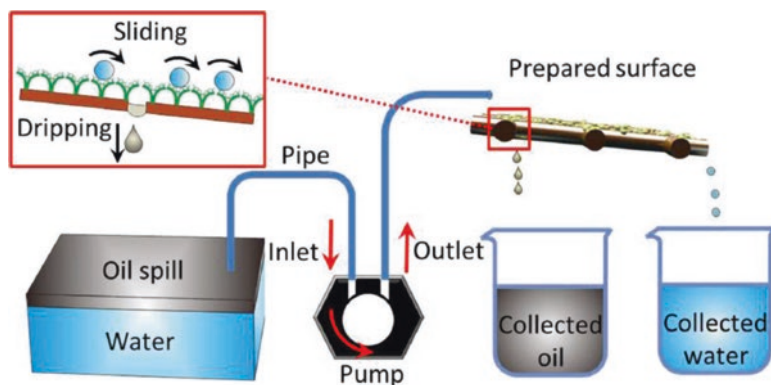


Fig. 17 The schematic diagram for describing the water-oil separation mechanism on the prepared surface. (Reproduced with permission from reference [78], 2018 Elsevier B.V)

drophobic surface property and excellent oil-water separation (E, >97%). The authors also compared the E values with stearic acid modified copper mesh substrates with various hydrophobic modified copper mesh substrates and expressed that stearic acid-treated superhydrophobic copper mesh showed higher E value than other hydrophobic modifications. Su et al. used a steel mesh substrate for the fabrication of superhydrophobic surface by polishing the substrate using sand paper followed by washing in acetone, deionized water, and ethanol, respectively [80]. The substrate was further kept in copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) solution and washed and dried at ambient condition. The copper-deposited mesh was further immersed in the solution prepared by mixing vinyl-terminated polydimethylsiloxane (VPDMS), trimethylolpropane triacrylate (TMPTA), and 2-hydroxy-2-methylpropiophenone (Darocur 1173) in hexane for 60 s and UV cured for 120 s and dried at 80 °C for 4 h. The fabricated superhydrophobic steel substrate also illustrated excellent separation behavior of oil from water. Jain et al. fabricated a durable self-cleaning superhydrophobic copper substrate by electrodeposition of copper ion on the copper substrate followed by immersing in stearic acid solution, which showed stable superhydrophobic property.

3.5 Other Metal-Based Nanoparticles

Various nanoparticles are contributing for the development of superhydrophobic surface. Apart from the aforementioned silica, siloxane, iron, titanium, and copper, various other metal nanoparticles were also studied in various applications. Especially, zinc, aluminum, silver, gold, zirconium, cobalt, calcium, magnesium, tungsten, boron, etc. were used already to fabricate superhydrophobic surface for different applications [81–86]. Zinc, silver, and gold nanoparticles in the superhydrophobic coating can make the surface to be applied for various biological and electrical applications. Aluminum nanoparticles as well as superhydrophobic aluminum substrate can be used in anti-icing coating as well as in other applications. Similarly, other nanoparticles can be used in various applications based on the requirement of end-use properties.

4 Conclusions

Superhydrophobic surface is recommended highly on various substrates because of the ease of usage in various applications. The nonstick ability without adherence of water droplet as well as repelling of water droplet on a substrate can show excellent self-cleaning property to the substrate. These properties are highly needed for various coating applications because of the extension of product life as well as their durability. Polymers are used widely for the development of superhydrophobic coating materials because of their excellent properties such as low surface energy,

hydrophobic and hydrophilic character, durability for environmental conditions, flexibility, etc. Similarly, nanoparticles also showed much attention in superhydrophobic coatings due to their easy formation of micro-nano hierarchical structure, hydrophobic modification on the surface by self-assembly, enhancing the surface roughness, catalytic, and other properties for particular applications. The polymer/nanoparticle hybrids would be more advantageous for the superhydrophobic coatings because of the advantages of both properties of polymers and nanoparticles in a single body. Moreover, durable and robust surface properties can be obtained by using the polymer/nanoparticle composite coating on a wide variety of substrates. Recently, stimuli-responsive as well as self-healing superhydrophobic surface properties are attracted widely for various applications. The durability of the surface property can be also enhanced by using the polymer/nanoparticle hybrids. We briefly discussed some of the important polymers and nanoparticles used for developing the superhydrophobic surface on various substrates. Continuous research efforts have been undergone on the development of superhydrophobic surface for various applications. On the other hand, the durability and robustness of the superhydrophobic surface need to be studied for our daily used products, and continuous studies need to be performed deeper to make robust superhydrophobic surface on any substrate. We hope that polymer/nanoparticle hybrids can meet the required property by selecting proper materials.

Acknowledgments We would like to thank our project supporter “National Research Foundation of Korea” (NRF) Grant funded by the Ministry of Science and ICT, Korea (NRF2017R1A2B3012961), and Brain Korea 21 Plus Program (21A2013800002) for writing this chapter.

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Nanoengineered Surfaces as a Tool Against Bacterial Biofilm Formation



Alan dos Santos da Silva and João Henrique Zimnoch dos Santos

1 Introduction

Persistent bacterial infections are an extreme problem for humanity, causing countless deaths and demanding investment in social and medical improvement. It is estimated that 80% of persistent bacterial infections are correlated with biofilms [1]. In short, biofilms can be understood as microbial cell multi-structured organizations attached to a living or inert surface surrounded by an extracellular matrix [2]. This type of organization is considered an adaptation mechanism that is adopted by many microorganisms as a way to promote, among other things, protection against the exterior environment [2, 3]. Due to their resistance and ability to attach to surfaces with different properties, biofilms have been revealed as a substantial problem in many areas, including the clinical environment [2–6], where biofilms can be found on innumerable medical devices and have, consequently, been recognized as a key factor in many cases of hospital infections [2–6]. The relevance and impact of this theme have been reflected in the dramatic increase in the number of publications about biofilms during the last 10 years, as depicted in Fig. 1. According to the Scopus database, approximately 30% of these publications are in the field of medicine.

Unfortunately, the deep complexity and organization of biofilm structures provide a high resistance profile, including resistance to conventional antibiotic treatments, even those successfully applied against planktonic cells (microbial cells not attached) [3, 7–10]. Thus, due to the extreme impact of biofilm-related infections on human health, many groups have investigated alternatives to inhibit/eradicate this kind of structure. However, before proposing potential approaches to solve this problem, understanding some aspects related to the biofilm structure and its organization is required.

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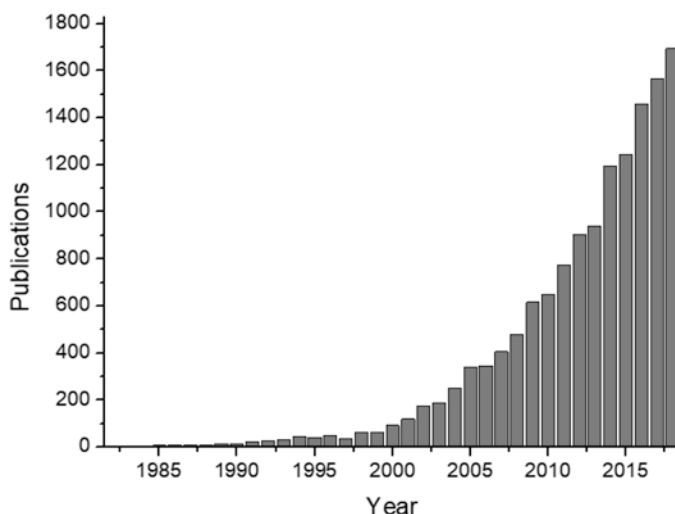


Fig. 1 Number of publications related to bacterial biofilm and infection from 1982 to 2018, according to the database Scopus. The search was performed using the keywords “bacterial,” “bio-film,” and “infection”

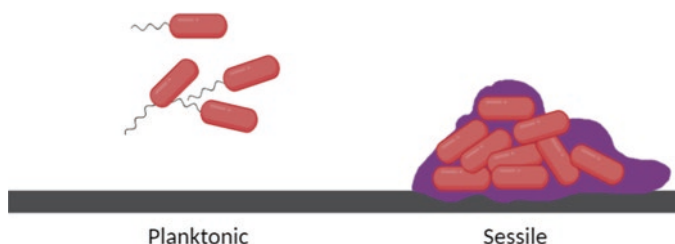


Fig. 2 Types of bacterial cell organization

1.1 Biofilms: Structure and Organization

Bacteria can be found in two different forms, i.e., planktonic state (not attached) and sessile state (attached to a surface) [4], as shown in Fig. 2. Both states are very important in biofilm formation and are part of different steps in this process.

Biofilm formation includes several stages, such as adhesion, microcolony/macrocology formation and dispersion, in a cyclic way (Fig. 3) [4, 11].

In the adhesion stage, cells attach to abiotic surfaces generally by unspecific interactions, while living cells are involved in specific interactions [11]. The unspecific interactions can be understood as physical forces, such as van der Waals, Lewis acid and base, or electrostatic forces, whereas the specific interactions are ruled by protein-based interactions, such as adhesion [4, 11, 12]. Furthermore, there are many mechanisms ruled by bacterial appendages, such as pili, flagella, and

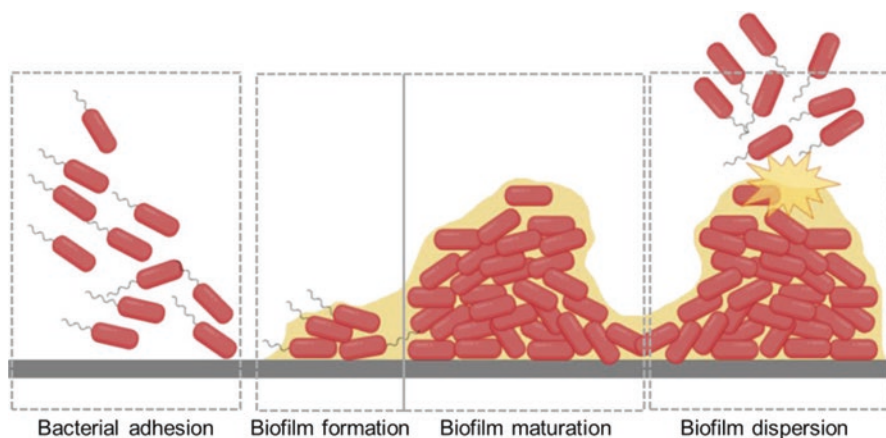


Fig. 3 Illustration of some steps involved in biofilm formation

nanofibers [1, 3, 4, 11], where those structures are used to bond the cell to a surface. After cells adhere, microcolony formation occurs due to intracellular aggregation [3, 4, 11, 13]. Once stable, the cells start growing and maturing by intercellular interactions in a polymicrobial cooperative environment [4, 7]. In this stage, autoinducer signals are produced, resulting in the expression of a complex and bacteria-dependent mixture named extracellular polymeric substances (EPS), constituted by polysaccharides, fatty acids, proteins, and nucleic acids, which enclose more cells, providing more stabilization for the biofilm network and, consequently, more protection against antibacterial agents and the external environment [4, 7, 14]. Then, in the dispersion stage, some sessile bacterial cells are scattered from the biofilm structure to the external environment, returning to the planktonic form [8].

Biofilms show extremely complex structures, making it very difficult to develop new strategies to eradicate them, mainly in the cases of living surfaces or medical devices that are difficult to remove, i.e., pacemakers, cardiac implants, prostheses, etc. [9]. Thus, based on the impact of medical devices as a path for bacterial infections and the decrease in the difficulty of handling synthetic materials due to manipulating them in a more aggressive environment with higher pressures and temperatures and physical and chemical treatments when compared to living systems, the next sections of this chapter will focus on approaches based on nanoengineered abiotic surfaces with the aim of hindering or preventing biofilm-associated bacterial infections.

2 Nanoengineered Surfaces

Considering the extreme difficulty associated with bacterial biofilm eradication, the development of approaches based on inhibition of biofilm formation is impactful and relevant. Considering the adhesion stage as the target of these approaches, the contact area is a key factor, and based on that, the production of new materials with minimal bacteria-substrate contact area has attracted attention. Among these materials, superhydrophobic materials have become attractive due to their microdomains and nanodomains achieved through nanoengineering processes.

Superhydrophobic materials are characterized by static contact angle values higher than 150° , as illustrated in Fig. 4.

Nanoengineering is based on the production of artifacts on the nanoscale through structural modification of the material surface. This type of approach has attracted attention as an interesting alternative to material treatment with biocides or antibiotic coatings due to increasing bacterial antibiotic resistance in addition to the dissemination of relevant antibiotic resistance genes [15–19].

Natural superhydrophobic surfaces presenting hierarchical patterns on the microscale and nanoscale have been able to prevent microbial contamination, even in an environment with several potential contaminants [20]. In nature, there are several examples of hierarchical surfaces that have superhydrophobic behaviors, such as self-cleaning and water repulsion. The capability of a water strider to walk on water (Fig. 5) and the most famous example in nature the high water repellency of the lotus flower leaf (*Nelumbo* sp.) (Fig. 6) can be attributed to hierarchical microstructures and nanostructures [21, 22].

The substantial impact and importance of natural hierarchical structures as a strategy for antibacterial adhesion was verified through a study carried out by Ivanova et al. [23]. The study investigated the adhesion of Gram-negative bacteria *Pseudomonas aeruginosa* on insect wings using a species of cicada (*Psaltoda claripennis*) as a model due to its superhydrophobic characteristics. During the investigations, it was discovered that the bacterial cells were not repelled; instead, they were killed by the nanopillars present on the surface [23]. Membrane rupture properties were assigned to the cicada nanopillars [20] (Fig. 7)

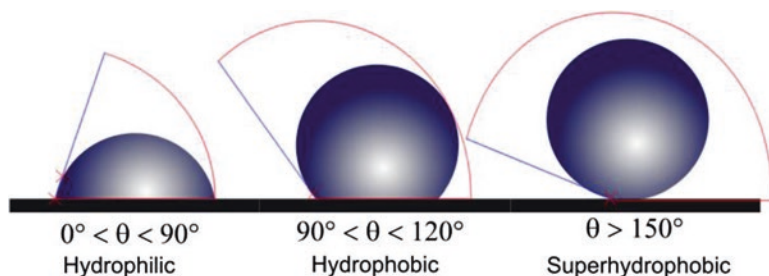


Fig. 4 Classification of hydrophilic, hydrophobic, and superhydrophobic materials according to the static contact angle

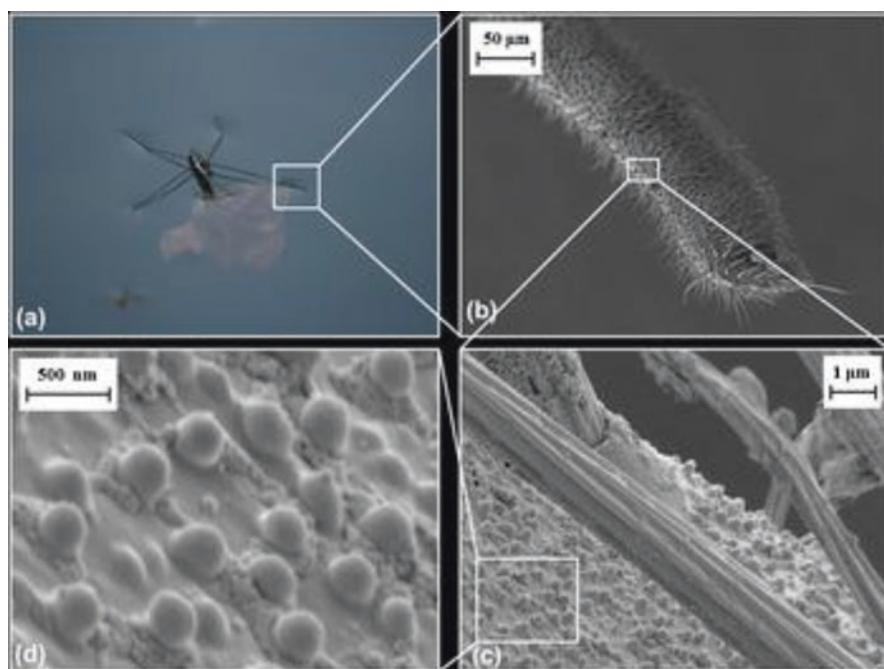


Fig. 5 Two-level hierarchical structure of a water strider's leg, which exhibits microstructures with fine nanoscale grooves under FESEM: (a) a *G. remigis* insect floating in a pond; (b) a water strider's front leg, which is covered by numerous oriented needle-shaped microsetae; (c) the nano-grooves of a microseta, which is composed of several papillae (d). (Reproduced with permission from Ref. [21])

The understanding of natural superhydrophobic surfaces with self-cleaning, anti-fouling, and antibiofouling properties has provided excellent clues about the properties needed to achieve synthetic materials with antibacterial functionality and, consequently, for the development of new materials that mimic those surfaces.

There are a wide variety of techniques employed to produce microstructured and nanostructured surfaces according to the surface and coating composition, type of structure, size, orientation, etc. Among these techniques, anodization, photolithography, plasma treatment, etc. are frequently used.

Anodization is based on the electrochemical oxidation of a specific metal (and its alloys) that forms the anode [24–26] to provide a protective oxide layer on the substrate. The first report about this process is attributed to Buff, H., in 1857 [24, 27, 28], who discovered the very thin aluminum oxide layer that formed during anodic oxidation. Currently, this type of process has been applied to different metals, such as titanium [29–32], magnesium [33–35], and aluminum [36, 37]. In the case of aluminum, the aluminum oxide layer has the characteristics of high hardness, is a relatively inert insulating material, and can absorb dyes to form colored films [25], and these properties have made it the most common material applied in anodization processes. Different surface properties [24, 36, 38] can be achieved by fine-tuning

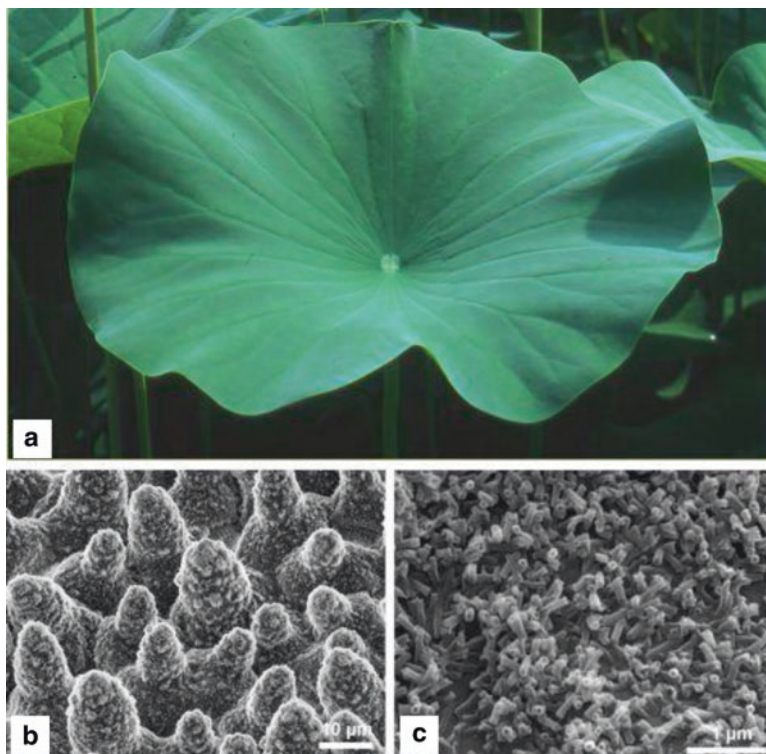


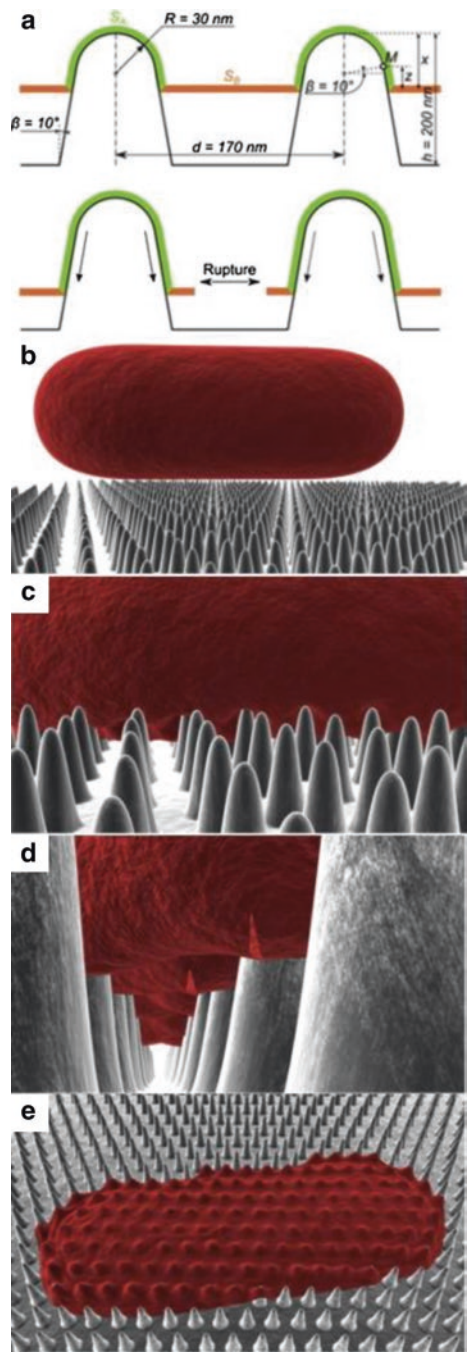
Fig. 6 (a) Lotus leaves, which exhibit extraordinary water repellency on their upper side. (b) Scanning electron microscopy (SEM) image of the upper leaf side prepared by “glycerol substitution” shows the hierarchical surface structure consisting of papillae, wax clusters, and wax tubules. (c) Wax tubules on the upper leaf side. (Adapted from Ref. [22])

several parameters during synthesis, such as temperature, voltage, stirring, and electrolyte solution [24, 39, 40]. Due to these properties, anodization has been applied to surface nanoengineering. Hizal F. et al. [41] investigated the applicability of nanoengineered aluminum surfaces on *Staphylococcus aureus* and *Escherichia coli*. A representative scheme of the steps involved in the anodization processes is shown in Fig. 8.

In this work, the authors investigated the influence of the physical and chemical characteristics of a surface on bacterial adhesion. Therefore, hydrophilic surfaces with flat, nanoporous, and nanopillar profiles were synthesized, and the bacterial surface adhesion forces were determined using atomic force microscopy [42–44] (Fig. 9).

For the bacterial adhesion force determination, the surface texture seems to have a direct influence on adhesion, achieving *S. aureus* and *E. coli* adhesion reductions of approximately 88% and 92%, respectively, on the nanopillared surface compared to the flat surface. This texture effect increased when the nanopillars were coated with Teflon to obtain superhydrophobic surfaces (static contact angle of 162°),

Fig. 7 Biophysical model of the interactions between cicada (*P. claripennis*) wing nanopillars and bacterial cells. **(a)** Schematic of a bacterial outer layer adsorbing onto cicada wing nanopillars. The adsorbed layer can be divided into two regions: region A (in contact with the pillars) and region B (suspended between the pillars). Because region A adsorbs and the surface area of the region (SA) increases, region B is stretched and eventually ruptures **(b–e)**. (Reproduced with permission from Ref. [20])



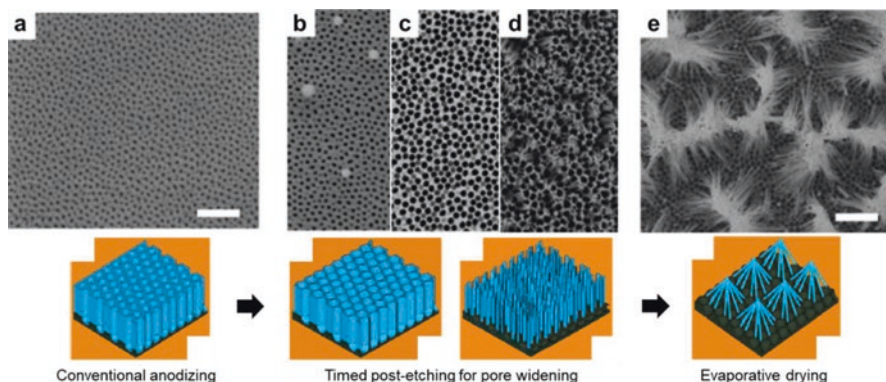


Fig. 8 Schematic of the fabrication process to transform nanoporous structures of anodic aluminum oxide (AAO) into nanopillar structures: (a) initial nanoporous AAO pattern; (b–c) nanoporous AAO pattern with enlarged pore size by a pore-widening (postetching) process; (d) nanopillar AAO pattern with further etching, resulting in the formation of disconnected individual pillar nanostructures; (e) nanopillar AAO pattern with evaporative drying, resulting in the aggregation of the individual pillar structures and hence the formation of the clustered pillar (or conical) structures due to capillary force. (Adapted with permission from Ref. [41])

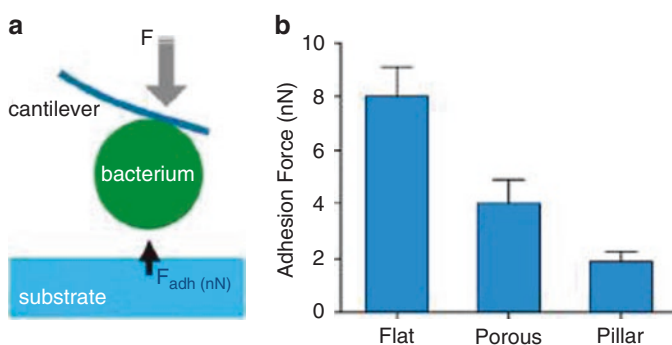


Fig. 9 Bacterial adhesion forces. (a) Scheme of single-bacterial contact probe atomic force microscopy with an immobilized bacterium attached on a tipless cantilever applied to measure bacterial adhesion forces. (b) *S. aureus* adhesion forces on hydrophilic flat, nanoporous, and nanopillared AAO surfaces. (Reproduced with permission from Ref. [41])

providing 98% and 99% *S. aureus* and *E. coli* inhibition, respectively, compared to the hydrophilic flat surface. Figure 10 shows the impact of hydrophilic/hydrophobic behavior on nanopillared surfaces for *S. aureus* and *E. coli* adhesion.

Figure 10 shows the high efficiency of a nanopillared aluminum oxide surface against bacterial adhesion, revealing it as a powerful tool to reduce biofilm-associated bacterial infections. However, this approach is limited to only specific metals. As a way to expand the application possibilities, photolithography has been successfully used to avoid bacterial adhesion through nanostructured surfaces.

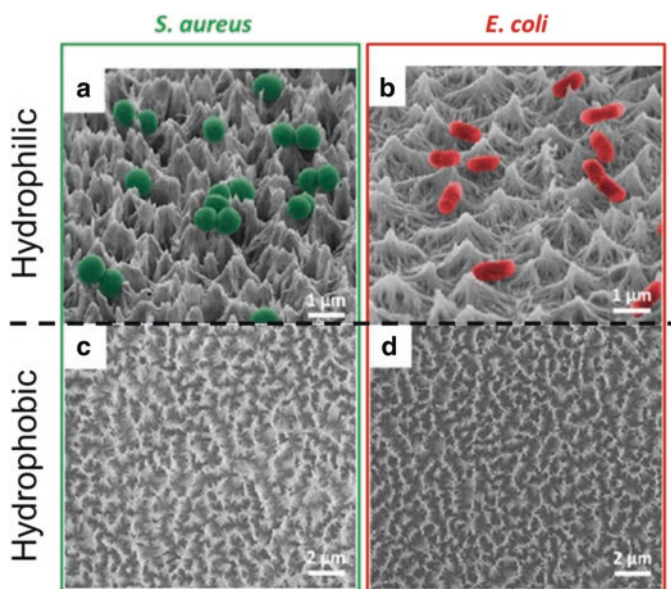


Fig. 10 FE-SEM images: **a–b**, representing bacterial adhesion on hydrophilic nanopillared surfaces; **c–d**, representing the bacterial adhesion on hydrophobic nanopillared surfaces. *S. aureus* and *E. coli* are represented by artificially added green and red colors, respectively. (Adapted with permission from Ref. [41])

Conventional photolithography can be used to produce micropatterns through a desired mold (photomask) and UV-curable polymers previously deposited on a substrate [45]. Unfortunately, conventional photolithography is size limited to approximately 1 micron [46]. This limitation has been overcome with the development of lithography using electron beam and focused ion beam techniques, called nanolithography [46–49]. However, the high complexity of these alternatives, which involve very complex instruments, could be an obstacle to using them. Thus, an interesting alternative could be to combine the strengths of different approaches, for example, using anodization to produce a nanometric mold for conventional lithography.

Wu et al. [50] proposed the use of aluminum anodization to produce a nanoporous template, which was used as the mold (or photomask) to achieve nanostructured polymeric surfaces by lithography. They applied a solution of a photosensitive polymer to cover the nanoporous template, and then the polymer solution was light activated by ultraviolet radiation to achieve a solid and nanoporous polymeric substrate. This study revealed the impact of the nanostructure organization, achieving surfaces with a bactericidal efficiency of 98–100% under optimum conditions, with a nanopillar density of approximately 40 units per μm^2 . Through a combination of techniques, several polymeric molds were synthesized to investigate the importance of surface features, such as nanopillar height, center-to-center distance, uniformity, etc., in bactericidal effects.

This kind of approach has a substantial impact on the development of superhydrophobic surfaces due to the ability to make nanopatterned structures with extreme organization control [51, 52]. However, due to the specificity and cost of the equipment used in these techniques, some chemical approaches have been employed as alternatives to build new materials with microdomains and nanodomains. There are various types of chemical approaches, including deep-coating or spray-coating processes to functionalize surfaces. Tingting Ren et al. [53] investigated the application of nanoparticles spray-coated on a glass substrate. In this work, spray-coated systems with hydrophobic SiO_2 nanoparticles 45 nm in diameter (labeled as F- SiO_2 , where “F” denotes fluorinated groups) and a mix of the same SiO_2 nanoparticles plus CuO nanoparticles 3–5 nm in diameter (noted as F- SiO_2 &CuO) were employed against bacterial adhesion. According to the results of bacterial adhesion (Fig. 11), both systems showed an anti-adhesion efficiency of 99.9% and only 78.5% for the glass treated with CuO nanoparticles, revealing a nanostructure dependence. Furthermore, this work revealed the possibility of building hybrid systems with synergic properties against bacterial infections, for example, the material F- SiO_2 &CuO, which shows superhydrophobicity (static contact angle of 163°) and high bacterial anti-adhesion (Fig. 11) properties from silica, and a high bactericidal effect correlated with the CuO nanoparticles (Fig. 12).

3 Conclusions

The development of the science of microbial biofilms has been extremely helpful for better comprehension of the structure, organization, and function of biofilms, which are commonly involved in infection mechanisms and drug resistance profiles, among other relevant aspects related to microorganisms. A better understanding of this complex type of system allows researchers to develop more efficient approaches to prevent biofilm formation, as a strategy to inhibit bacterial infections but also as a powerful tool to be applied against problems correlated to bacterial contamination in the food industry, water treatment plants, pharmaceutical industry, and so on. Figure 13 depicts an illustration of techniques that produce nanopatterned materials and their influence against bacterial adhesion.

As already shown in this chapter, simple comprehension of the steps in biofilm formation enables the elaboration of strategies to avoid biofilm formation. Considering the first step of biofilm formation, i.e., the adhesion stage, as the focus of antibiofilm approaches, the contact surface area of bacteria seems to play a key role in bacterial attachment on the surface. On the other hand, it is not about simply producing surfaces with low contact area but also with some degree of organization, i.e., an adequate density of microstructures and nanostructures per area, etc.; in other words, nanoengineering-based approaches are necessary. Therefore, there are innumerable techniques and combinations that can be applied with this goal, according to the material, expertise and available infrastructure, final application, and so on. Each of these approaches has its own limitations and potential, making it pos-

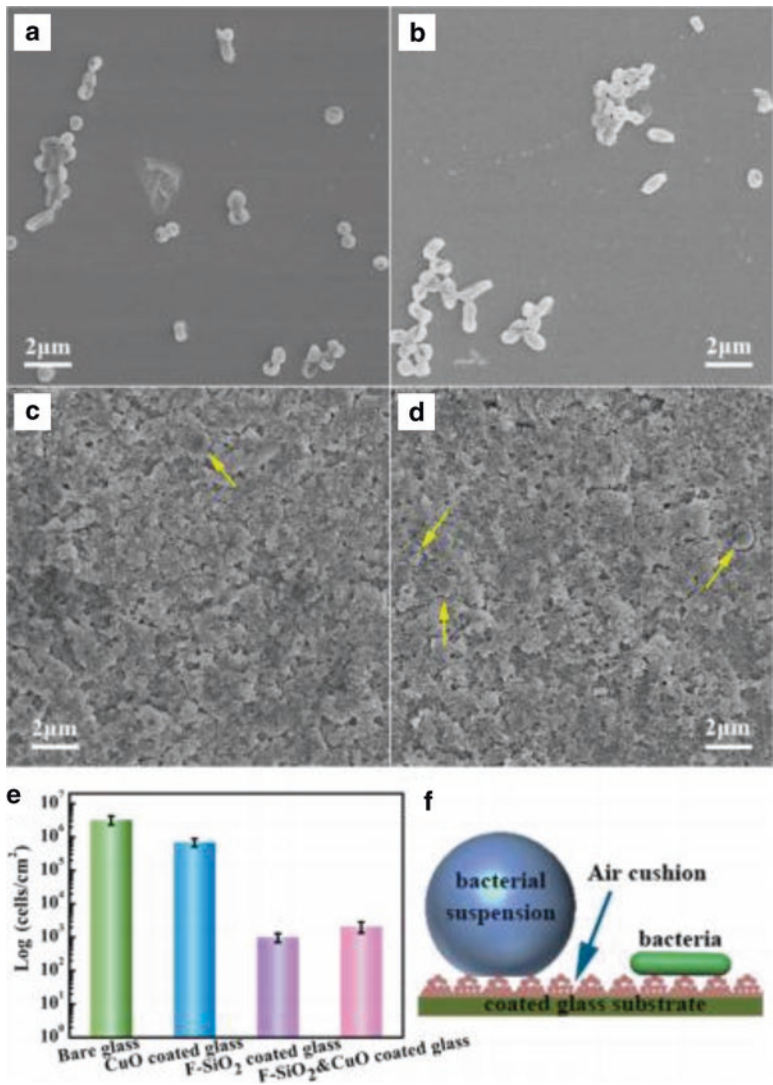


Fig. 11 SEM images of *E. coli* attachment on bare glass (a), CuO-coated glass (b), F-SiO₂-coated glass (c), and F-SiO₂&CuO-coated glass (d) at identical magnification (*E. coli* are indicated by yellow arrows on the F-SiO₂-coated glass and FSiO₂&CuO-coated glass). (e) Bacterial attachment density on each specimen. (f) Illustration of bacterial adhesion on superhydrophobic surfaces. (Reproduced with permission from the Ref. [52])

sible to achieve countless structures, forms, functions, etc., but clues can always be obtained by observing nature. With all these possibilities and their potential, a great challenge is to apply these approaches to biocompatible materials, allowing the development of implantable devices with antibacterial properties.

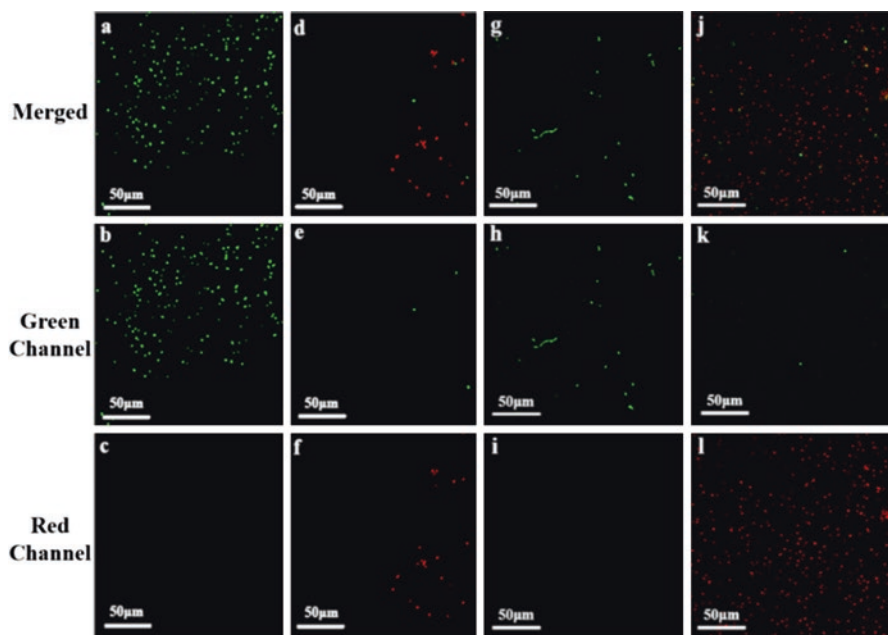


Fig. 12 Confocal laser scanning microscopy (CLSM) images of bare glass (**a–c**), F-SiO₂&CuO-coated glass (**d–f**), F-SiO₂-coated glass (**g–i**), and CuO-coated glass (**j–l**) in the presence of live/dead two-color fluorescence staining after exposure to an *E. coli* suspension for 24 h. Green and red refer to live and dead bacterial cells, respectively. (Reproduced with permission from the Ref. [52])

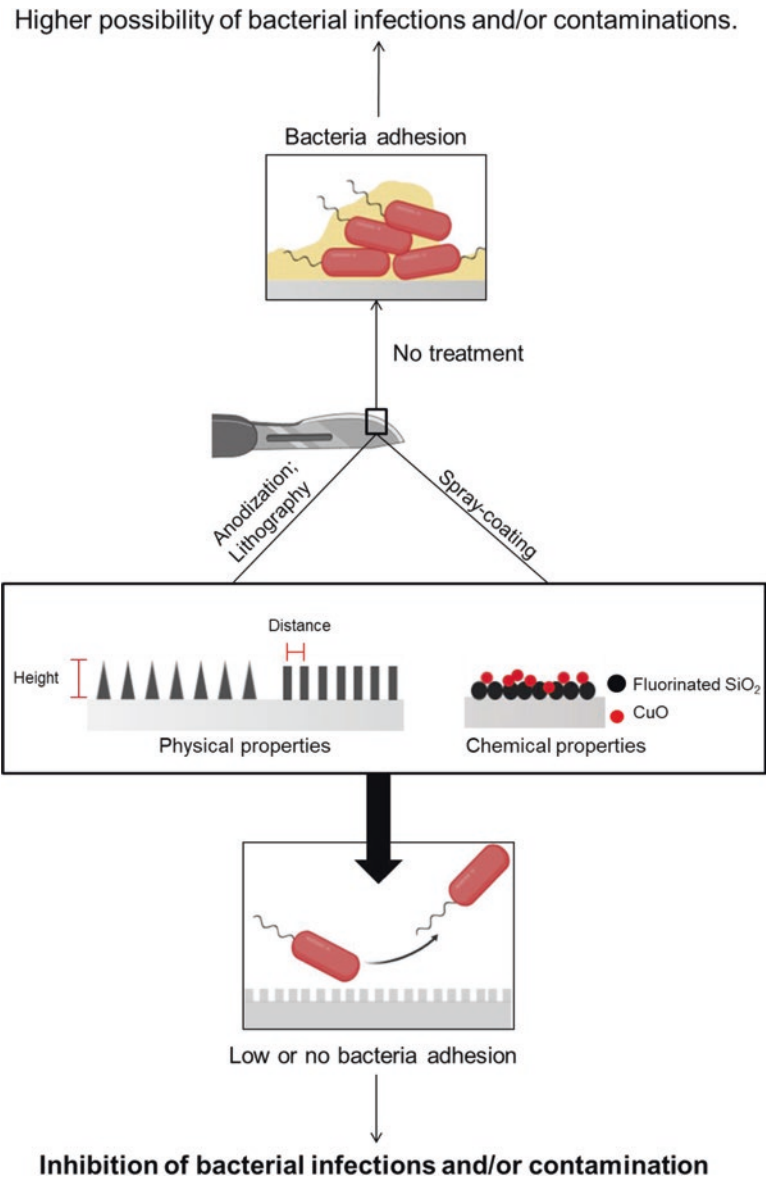


Fig. 13 Illustration of the potential against bacterial adhesion shown by treated surfaces through some examples of methods

Acknowledgments This work was partially financed by FAPERGS (Project # 19/2551-0001869-0).

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Non-fluorinated Superhydrophobic Surfaces: A New Scenario for Sustainable Applications



Oriol Rius-Ayra and Nuria Llorca-Isern

1 Introduction

Superhydrophobic surfaces have been studied recently due to their anti-wetting properties. Generally, a superhydrophobic surface is defined as having a static water contact angle (WCA) $> 150^\circ$ [1]. Meanwhile, if the sliding angle (SA) and the contact angle hysteresis (CAH) are lower than 10° , the surface presents self-cleaning properties because of high droplet mobility [2]. These surface characteristics allow different and innovative strategies to be applied to these materials as a solution for environmental issues such as oil/water separation [3, 4], corrosion barriers [5–7], or icephobic materials [8, 9].

Non-fluorinated superhydrophobic surfaces (nFSHS) have attracted attention during the last decade due to their sustainability and benign properties. The number of publications that combines the concept superhydrophobic and non-fluorinated surface has experienced a moderate increase since 2008, while the number of citations for non-fluorinated surfaces alone has shown a considerable increase. Despite the overall number of publications remaining low, this recent trend reflects the increasing interest of the scientific community in nFSHS, which opens new possibilities in superhydrophobic surfaces that use these characteristic compounds (Fig. 1).

In this chapter, different strategies shall be considered for producing nFSHS. On the one hand, the development of these systems can be carried out considering environmental and sustainable concepts such as environmentally friendly reactants or methods. On the other hand, it is important to consider the durability of nFSHS in front of abrasion as well as their environmental applications such as oil/water separation and corrosion prevention.

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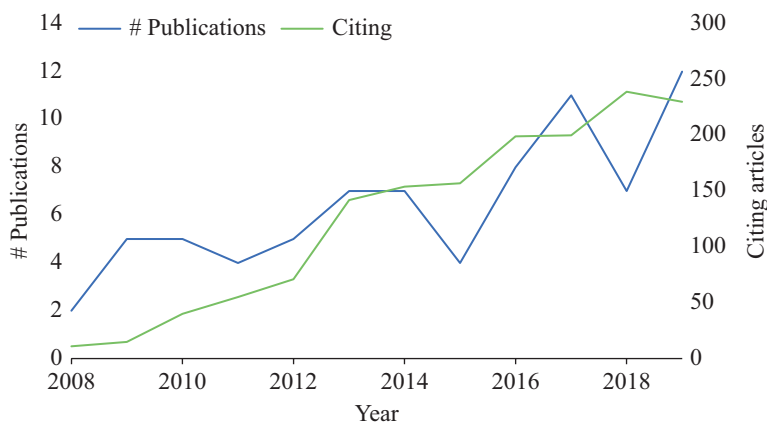


Fig. 1 The number of publications as well as cited articles has increased during the last decade and opens a new scope in superhydrophobicity (data has been collected from Web of Science – Clarivate Analytics)

Table 1 List of surface tension (γ) values of different compounds at liquid state

Compound	CAS	γ (mN/m) at T (°C)	Reference
H ₂ O	7732-18-5	72.5 (20 °C)	[19]
Oleic acid	112-80-1	29.6 (70 °C)	[20]
Myristic acid	544-63-8	27.9 (70 °C)	[20]
Lauric acid	143-07-7	25 (70 °C)	[20]
PTFE	9002-84-0	20.0 (20 °C)	[19]
PDMS	9016-00-6	19.8 (20 °C)	[19]

The theoretical aspects of superhydrophobic surfaces are well-known and described in literature [1]. Superhydrophobic surfaces are built up in two different levels that combine a microstructure with a nanostructure; this system combination is known as a hierarchical structure. Therefore, these features are responsible for increasing the roughness of the surface until a WCA $\geq 150^\circ$ is achieved. In addition to their surface morphology, surface tension (γ) plays a key role on modifying its wettability properties with several compounds being used for this purpose: polydimethylsiloxane (PDMS) [10, 11], fatty acids like stearic acid [12, 13] or lauric acid [14, 15], and polystyrene (PS) [16]. Taking into account the variety of surface energy modifiers, they can be summarized by their alkyl chain (decreasing surface energy) as follows: $\text{CH}_2 > \text{CH}_3 > \text{CF}_2 > \text{CF}_2\text{H} > \text{CF}_3$ [17, 18], where CH_2 is the highest value of surface tension while in case of CF_3 it is the lowest one (Table 1). Here, the present challenge is to prepare naturally derived new materials that paradoxically have the highest values of surface tension but also possess WCA $\geq 150^\circ$ and behave as superhydrophobic surfaces.

Despite factors like hierarchical structure or the surface tension of superhydrophobic surfaces, a key point of these particular materials is their sustainability.

Indeed, non-fluorinated compounds, like fatty acids that are naturally derived modifiers or PDMS as a biodegradable silicone, play an important role because of their non-toxicity. Therefore, these compounds can be used in outdoor applications and especially those that are environmentally applied, which opens a new field of promising surface applications.

2 Robust Superhydrophobic Surfaces

Superhydrophobic surfaces can be applied in several environments, but it still remains a challenge to obtain superhydrophobic materials that are highly durable and also scalable, which is the main challenge for these types of surfaces. Despite the great variety of methods that have been used for the last several years, it is important to consider how the durability of superhydrophobic surfaces can be measured when they sustain mechanical damage. In fact, there are numerous publications that propose methods for evaluating their robustness [21–23]. For instance, a solid impact test was carried out to study the durability of a superhydrophobic (168°) silica coating prepared by the electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT) and modified by chemical vapor deposition (CVD) of tetraethoxysilane (TEOS); after the test, the surface showed a WCA = 153° which revealed a high durability of the superhydrophobic surface [24]. The robustness of a polyester fabric modified with silica NP and tridecafluorooctyl triethoxysilane (FAS) with a WCA = 171° was determined by performing a blade scratch test; after the test fabric surface exhibited a WCA = 150° [25]. Rotary slurry was used to test the durability of amorphous perfluoropolymer CYTOP fluoropolymer prepared by hot embossing (WCA = 160°). After 4 h of abrasive testing, the surface was slightly damaged and retained its superhydrophobic properties [26]. With the aim to simulate damage caused by rain, a water jet impact test was performed on a polyurethane/fluoroacrylic/organoclay superhydrophobic nanocomposite coating, where the surface exhibited a WCA = 154° before the water jet impact test and 148° after it [27]. All of these tests can be used when considering not only the robustness but the end use of the materials, such as in outdoor uses under rain or in dusty conditions [23].

2.1 Durability Tests

Among the large variety of abrasive tests, it is important to take into account that a consensus exists concerning the use of the abrasive paper test as a potential procedure to evaluate the robustness and consequently the durability of superhydrophobic surfaces against mechanical damage [28–30]. However, despite this fact, there is not any kind of standard concerning how to carry out the test due to the large variety of existing superhydrophobic surfaces. A frequently used test for durability

measurements is the abrasive paper test (APT) – the superhydrophobic surface is placed in contact with the sandpaper with a normal load on it. After that, the surfaces are rubbed across the sandpaper at a constant distance, and the process is repeated for several cycles or when loss of superhydrophobic properties is detected (Fig. 2). Finally, parameters like static contact angle, sliding angle, or contact angle hysteresis are measured in order to establish the durability of superhydrophobic surfaces. It is important to stress that as a non-standardized procedure, different grain size grinding papers (e.g., P240 to P1200), different loads on the surface, or long rubbing distances can be used. Therefore, it is urgent to establish some kind of standardized method to determine the durability aspects of superhydrophobic surfaces.

As described before, superhydrophobic surfaces are severely damaged after abrasive tests which increases water droplet adhesion to the surface, and consequently the WCA dramatically decreases indicating loss of superhydrophobicity. Indeed, this change of wettability behavior is explained by considering two different wetting states: Wenzel [31] and Cassie-Baxter [32]. The difference between both states is well-known and will not be discussed in this chapter, but in summary, the former is defined as a homogenous regime where only two phases (solid-water) are present, while the latter is known as heterogeneous, in which there are three different phases (solid-water-air). In addition, several air pockets can be identified that promote superhydrophobicity. The issue that causes a decrease in WCA and the loss of superhydrophobic properties is that wear will introduce pinning sites at the superhydrophobic surface [33], and therefore the surface will change from a Cassie-Baxter state to the Wenzel, where water droplets will adhere onto the surface, thus avoiding superhydrophobicity.

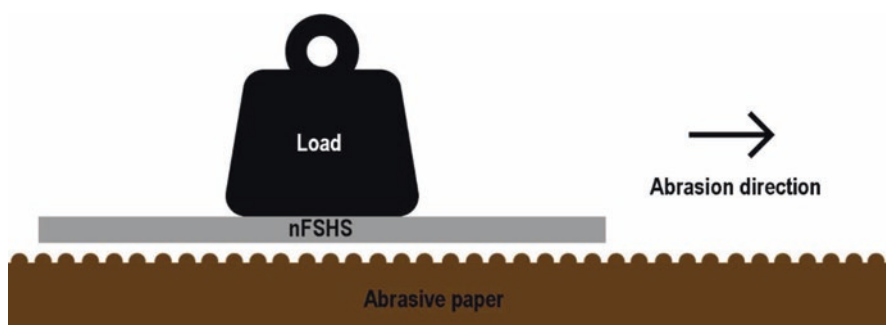


Fig. 2 Schematic illustration of abrasive paper test when a constant load is applied. After that, the sample is moved across the surface for several cycles until loss of superhydrophobic properties

2.2 Reinforcement of Superhydrophobic Surfaces with Ceramic Particles

As mentioned above, durability studies of coatings have demanded considerable effort for the last several years [34–36]. However, nature provides examples of how living organisms are able to resist wear from the environment. Illustrative examples are rice leaves (*Oryza Sativa* L.) that are superhydrophobic and durable [37, 38]. In fact, they are composed of biosilica particles at the epidermal region, which enhances durability of leaves against natural wear such as that caused by rain droplets that can be heavy in some rice production regions, or by dust [39, 40]. Bioinspired by rice leaves, the use of ceramic particles is attracting attention due to the inherent mechanical properties of these materials, especially its high hardness. Different procedures will now be discussed on how to achieve superhydrophobic and durable surfaces using ceramic particles like WC/WS₂, SiO₂, or α -Al₂O₃.

The first methodology is based on the electroplating of Ni reinforced with tungsten ceramic particles by Watt's bath (NiSO₄·6H₂O, NiCl₂·6H₂O, and H₃BO₃) modified with CTAB (hexadecyl trimethyl ammonium bromide) onto mild steel (AISI 1020) [41]. The composite coating was modified with stearic acid (C₁₈H₃₆O₂) in order to confer superhydrophobic properties (WCA = 170° and SA = 0°). In order to improve mechanical properties, WS₂ NP (200 nm) and WC NP (400 nm) were used in Watt's bath. The authors analyzed that different proportions of ceramic NP (WC:WS₂), ranging from ratios 0:5 to 10:20, led to the formation of clusters when only one kind of ceramic NP was used. When both carbide and sulfide were used, the obtained coating was homogeneous, and there were no clusters throughout the surface. The interesting point is how the ceramic particles enhanced the durability of the as-prepared superhydrophobic coating. As described in Sect. 2.1, the abrasive paper test is an important tool used to study durability in superhydrophobic coatings. In this study aluminum oxide abrasive paper (360 grit) was used. WCA were measured after every cycle through a 14 m wearing distance (Fig. 3).

Taking into account WCA measurements and the worn distance, it can be determined that the abrasion presented in three different stages: the first one ranges from the initial step without abrasion until the 2 m distance of abrasion test. Here, the WCA measurements slightly decreased from 166° to 160° because the surface suffered minor damage caused by the Al₂O₃ abrasive paper. Afterward, the WCA remained around 156° and 153° for the next 8 m distance of the abrasive test. In the second stage, the behavior is quite interesting since WS₂ NPs are self-lubricating; as such this stage was long-lasting because the ceramic particles underwent an exfoliation process. Finally, the third stage ranges from 10 m distance to the loss of superhydrophobic characteristics (WCA = 128°); at this stage the self-lubricating properties fail. This change in wettability properties is explained by the roughness of the coating. Indeed, the roughness plays a key role in superhydrophobic properties, as when it decreases and the coating surfaces become smoother, the superhydrophobicity and WCA decrease as well (Fig. 4) [41]. At this point, the surface

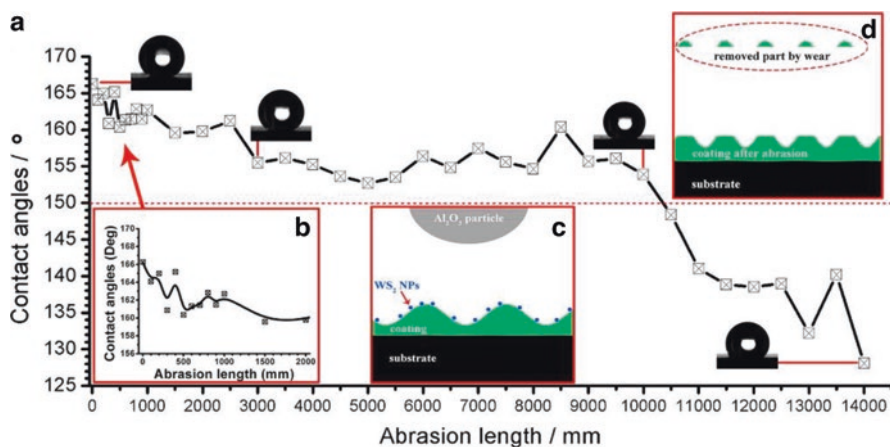


Fig. 3 Abrasive test: (a) measurements of WCA after every abrasion cycle carried out with sand-paper (P360); (b) magnification of WCA before 2000 mm of abrasion; (c–d) schematic illustration of coating removal. (Reprinted with permission from Ref. [41], copyright Elsevier)

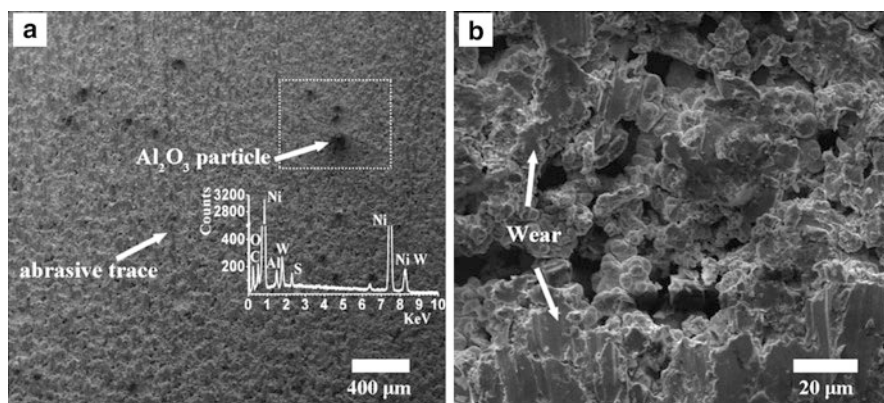


Fig. 4 Morphology of the superhydrophobic surface: (a) after abrasion test and corresponding EDS and (b) its magnification. (Reprinted with permission from Ref. [41], copyright Elsevier)

showed wear damage, and some alumina particles from the abrasive paper were found.

Another ceramic commonly used for wear resistance is silicon oxide. Silicon oxide nanoparticles (SiO₂ NPs) are used for enhancing robustness of superhydrophobic surfaces. In one method, tetraethyl ortosilicate (TEOS) was used as a precursor of SiO₂ NPs modified with hexamethyl disilazane (HMDS) in order to obtain HMDS-SiO₂. Then, dip-coating method was used, and superhydrophobic SiO₂-based nanoparticles with hydroxyl acrylic resin (HAR) and hydrophobic commercial SiO₂ NPs were formed [42]. The as-prepared superhydrophobic coating presented a rough and porous surface showing WCA = 164° and SA = 2°. Mechanical

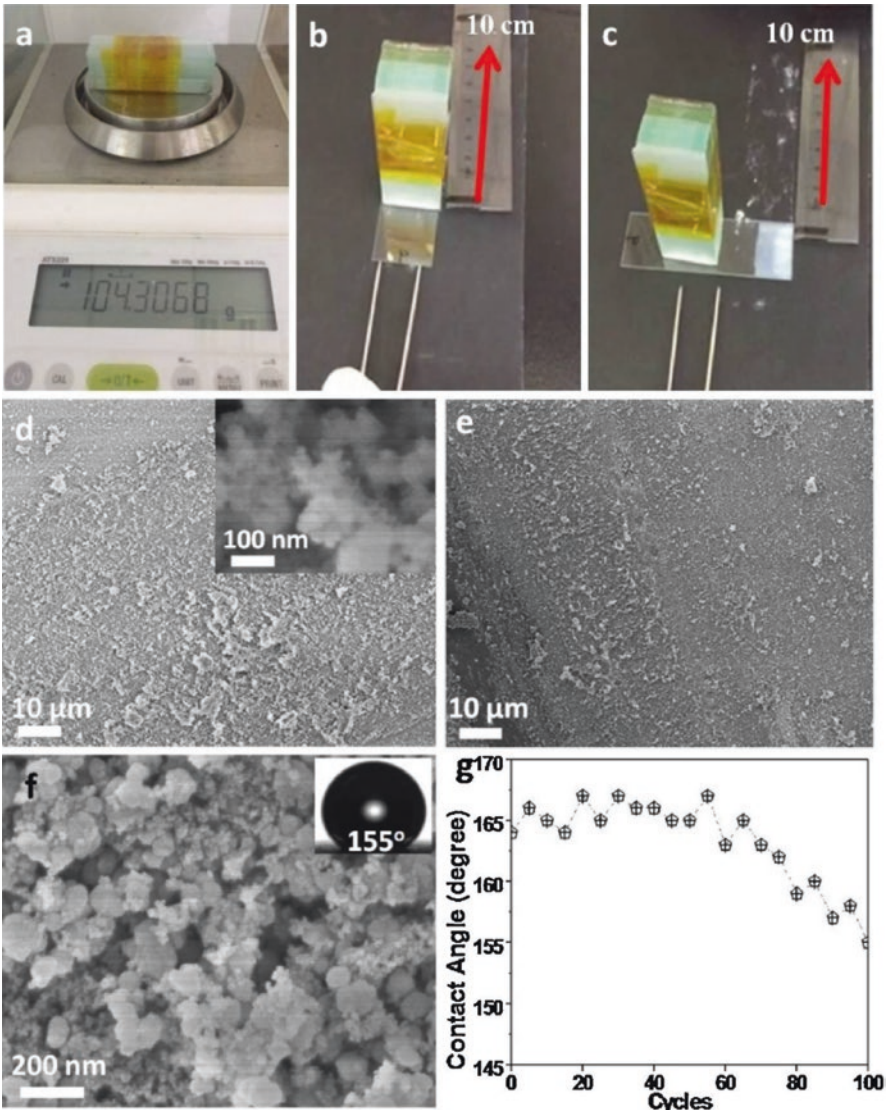


Fig. 5 Sandpaper abrasive test. (a–c) Procedure test with a constant load of 100 g; surface morphology after (d) 50 cycles and (e) 100 cycles; (f) magnification of micrograph from 100 cycles and its corresponding image of WCA = 155°. WCA after each abrasion cycle that reveals water repellence after 100 cycles. (Reprinted with permission from Ref [42], copyright Elsevier)

durability testing was carried out by abrasive sandpaper (P800) and a constant load of 100 g (Fig. 5a–c). Afterward, the samples were moved across 10 cm through the abrasive paper. After 100 cycles the superhydrophobic coating retained its wettable properties, exhibiting WCA = 152° [42].

The coating labelled as HAR-HMDS-SiO₂-ComSiO₂ was not severely affected by the abrading test (Fig. 5d–g). The authors explained the durability of the composite coating first by the use of commercial SiO₂ NPs that improved adherence of the coating mixed with HAR at different substrates such as aluminum or glass. Secondly, the fact that SiO₂ NPs were modified with HMDS improved the mechanical properties caused by the strong bonding between modified NPs and the acrylic HAR matrix. In addition, small quantities of hydrophobic commercial NPs were deposited on the prepared SiO₂ NPs, so a hierarchical structure was built. It can be concluded that with these combined effects, the robustness was enhanced by the presence of strong chemical binding between the particles and the chemical compounds used to form the coating.

Finally, the third ceramic material to consider is aluminum oxide and in particular its hardest phase known as corundum (α -Al₂O₃). An example of this is the electrodeposition (EDP) of ZnCl₂, combined with lauric acid as the surface tension modifier and α -Al₂O₃ with a particle size of 0.3 μ m, onto an aluminum substrate [43]. After 20 min of EDP, the substrate is completely covered with a flower-like structure, which is formed by zinc laurate and α -Al₂O₃ particles. Alumina particles are also deposited onto the surface due to electrophoretic interactions, because under a constant electric field the surface of particles is charged and move toward the cathode where electrodeposition takes place and the superhydrophobic coating is formed. In this case, zinc laurate is responsible for the surface tension decrease, while the combination of flower-like structures on the as-prepared coating along with the alumina particles leads to the needed hierarchical structure. Both features generate a Cassie-Baxter state that yields superhydrophobic properties (WCA = 170° and SA = 1°). The authors studied the coating durability with several methods like high impact test and the rotary slurry test, where alumina particles of 140 μ m were used. Additionally, an abrasive paper test was also carried out with SiC sandpaper (P1200) along 1 m distance; after 10 cycles with applied constant loads of 15 and 30 g, the coatings were evaluated. Field-emission scanning electron microscopy allows for the determination of the damage suffered by the coating after the abrasion test (Fig. 6). As can be seen, when a load of 15 g (Fig. 6 top) was applied to the surface, it becomes slightly rough, and there are alumina particles from the superhydrophobic coating. Additionally, the EDS spectrum allows for the identification of Zn and Al peaks that are characteristic of the as-prepared coating, where Al is assigned to the presence of α -Al₂O₃. For 30 g of applied load (Fig. 6 bottom), the surface was smoother than the 15 g load which indicates that a higher load modified the coating surface.

The experimental procedure is clearly distinct because roughness (RMS) was measured before and after the abrasive test, so there is a quantitative measurement that explains the change in wettability properties. At the beginning of the test, the sandpaper showed a white fine powder due to the loss of alumina particles from the upper part of the coating. Despite WCA as well as SA slightly decreasing after every abrasive cycle, the coating was still superhydrophobic after 1 m of test. Before

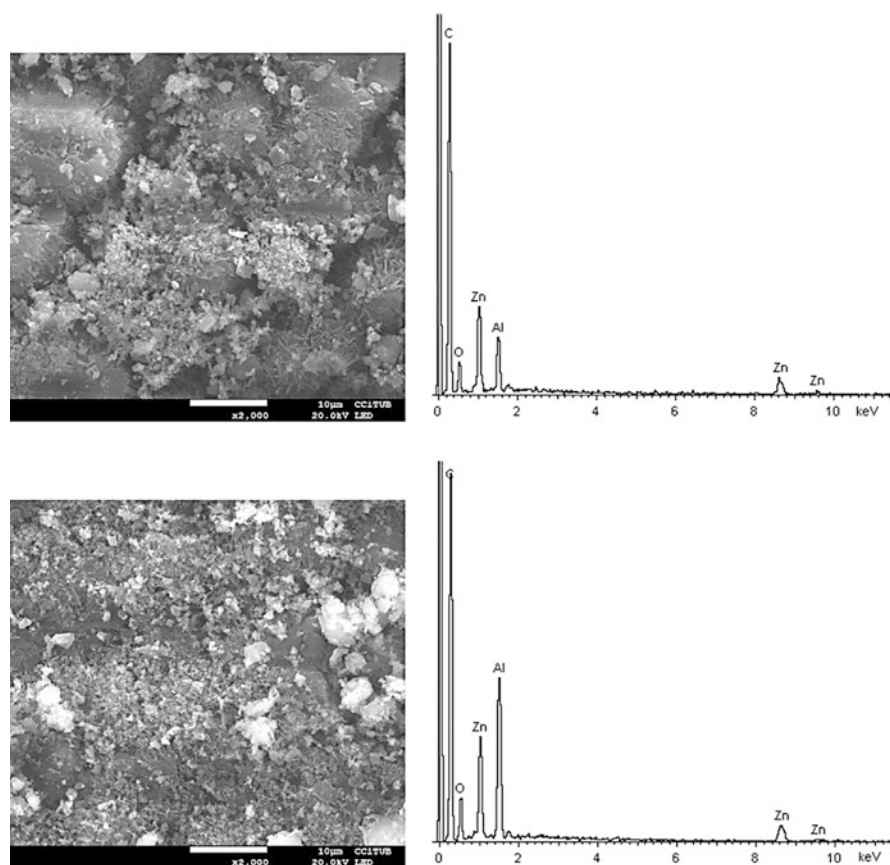


Fig. 6 FE-SEM micrographs of the superhydrophobic coating reinforced with α - Al_2O_3 after sandpaper abrasive test with a constant load of 15 g (upper) and 30 g (bottom). (Reprinted with permission from Ref. [43], copyright Elsevier)

the sandpaper test, the superhydrophobic coating had a value of $\text{RMS} = 3.86 \mu\text{m}$ which indicated a high roughness of the surface. That, combined with low surface tension, conferred its characteristic wettable properties. After the test, the roughness measurements were as follows: RMS (15 g) = $1.22 \mu\text{m}$ and RMS (30 g) = $1.19 \mu\text{m}$. The roughness was slightly similar despite the increase of load. These results revealed that abrasive test smooths the surface of the superhydrophobic coating and consequently the roughness and WCA/SA decreased as well. Despite this decrease of wettability properties, the values of WCA are still higher than 150° , and the SA are smaller than 10° which denotes a great resistance against abrasive test. Improvement of durability of the as-prepared superhydrophobic coating and keeping its self-cleaning properties were achieved.

3 Oil/Water Separation

Nowadays, there is a wide variety of applications for superhydrophobic surfaces. Indeed, a superhydrophobic surface can be described by considering the different phases that are present in the system, which are the water droplet, the gaseous phase (i.e., air), and the solid phase (i.e., superhydrophobic surface). When these surfaces are immersed under water and an organic solvent such as oil is present, the three-phase system switches to a solid-water-oil system, and the latter is adsorbed through the completely superhydrophobic surface. The capacity of surfaces to switch their wettability properties is known as superwettability. In the previous case, the surface changes from a superhydrophobic state to a superoleophilic one [44, 45]. This particular behavior allows oil/water (o/w) mixture separation whether the oil is stabilized (emulsions) or not [46, 47]. It is important to consider that stabilized emulsions increase the difficulty of o/w separation due to interactions of the emulsifier with the superhydrophobic surface.

Several solutions are found to separate oil from water with varying effectiveness. Materials such as sponges are used in order to remove organic solvents such as oils or emulsions. In this case a non-fluorinated sponge was used as a superhydrophobic material able to separate oil from water [48]. The authors used a sustainable method to synthesize a superhydrophobic sponge made of melamine. A water-based acrylic copolymer combined with superhydrophobic coating based on silica (WPAC) was synthesized in the surface of functionalized superhydrophobic SiO₂ NPs. After immersing the melamine-formaldehyde (MF) sponge into the WPAC solution and being subsequently heat-treated, a superhydrophobic melamine-formaldehyde (SMF) sponge was formed. The as-prepared sponge revealed excellent oil sorption and was able to separate different oils. The wettability properties of the as-prepared sponge were measured in order to determine its superhydrophobic and superoleophilic characteristics; WCA = $153.5 \pm 1.6^\circ$, while the contact angle of organic solvent or oil was 0° . Initially, two different oils were used to study the oil absorption of sponges, xylene and chloroform. Despite their differing densities, the sponge was able to quickly absorb xylene as well as chloroform. The authors also determined the absorption capacity of different oil/organic solvents such as ethanol, n-hexane, gasoline, and pump oil. They found that the capacity was affected by the density and viscosity of the solvents, and the time for absorption increased because of the low diffusion speed of the more viscous solvents. The sorption capacity was measured considering the weight of the sponge before and after the oil removal (g/g) which amounted to capacities ranging from 78–172 (g/g). An interesting point of these superhydrophobic-superoleophilic surfaces is the recyclability of the surface itself. The reusability of the as-prepared sponge was evaluated by the immersing-squeezing-heating methods [48]. After the organic solvent was absorbed by the sponge and weighed immediately, it was then squeezed and dried at 120°C for 10 min in order to evaporate the solvent. For xylene, the process was repeated for 30 cycles without loss of absorption properties, despite the WCA being affected and decreased to 147.6° . Finally, as described previously, the system is able to

separate oil/water emulsions prepared by different oils (toluene, chloroform, or gasoline) and using as emulsifier Span 80 (a non-ionic surfactant of sorbitan oleate). In order to determine the removal of surfactant-stabilized w/o emulsions, a device driven by gravity was used (a top funnel and a bottom conical flask) where the emulsion was poured into the funnel and the sponge kept water droplets on the top while the organic solvents were collected in the conical flask [48]. It was observed that the milky emulsion changed abruptly after the filtration and turned to a transparent phase of pure oil (Fig. 7). This can be contrasted with optical microscopy images where before the separation process (feed) there were water-in-oil droplets present while after the filtration there was a continuous phase without presence of droplets.

It is well-known that several materials and substrates are used in order to generate superhydrophobic surfaces; among them, glass fibers can be modified to confer superhydrophobicity and to allow oil/water separation [49]. In one study, these glass fibers (GF) were initially cleaned with acetone and ethanol and dried. Then, the GF were modified under reflux in toluene (24 h) with trimethoxymethylsilane (SPho-GFMM). Finally, they were washed several times and dried at 100 °C for 1 h. This procedure was repeated with two more surface tension modifiers like triethoxyvinylsilane (SPho-GFEV) and 3-chloropropyltrimethoxysilane (SPho-GFCP). The main difference between modifiers is their nature ($-\text{CH}_3$, $-\text{CH}_2-$, and $-\text{CH}=\text{CH}_2$) and therefore their surface tensions which are 38.28 mN/m (SPho-GFCP), 34.72 mN/m (SPho-GFEV), and, the lowest value, 24.51 mN/m (SPho-GFMM). The latter was the only modifier that led to a superhydrophobic surface with a WCA = 152° and an oil contact angle (OCA) of 0°. In order to determine the capability of oil/water separation of glass fibers, a laboratory-made filtration apparatus was used (Fig. 8) with three different types of oil/organic solvents which were hexane, soy oil, and olive oil [49].

Oil/water mixtures (1:1 v/v) were poured into the separation apparatus where the two phases were separated by the modified glass fiber and driven by gravity. The separation efficiency was above 98% for the various kinds of organic solvents. The authors concluded that this result was dependent on the viscosity of the used oil. In fact, the separation rate decreased, while viscosity increased; thus water could not pass through the glass fiber membrane.



Fig. 7 Destabilization of an oil-in-water emulsion before (left) and after the oil is completely separated from water phase (right). Optical microscopy images allow comparing both vials during the separation process. (Reprinted with permission from Ref. [48], copyright Elsevier)

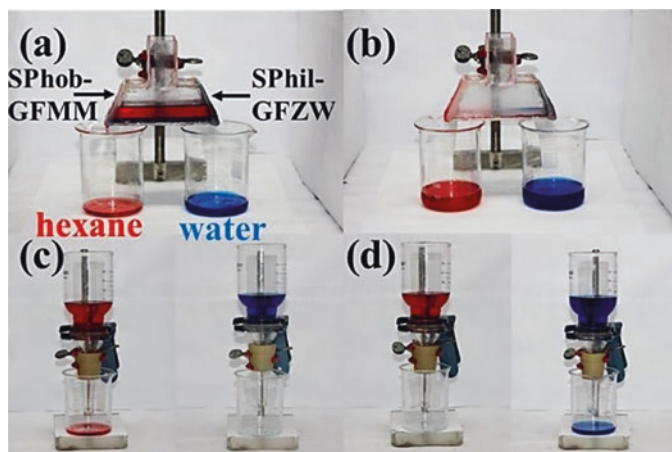


Fig. 8 Oil/water separation process of glass fiber (SPho-GFMM) where the water phase is retained in the separation apparatus while hexane is separated and recollected. (Reprinted with permission from Ref. [49], copyright Elsevier)

The above examples are representative of different strategies for oil/water separation: sponges, particles, or fibers when their surface is modified to yield superhydrophobic properties. This modification can also improve their efficiency of other important properties, in particular their superoleophilicity.

4 Corrosion Prevention

In the wide possible applications of superhydrophobic surfaces, it is important to consider that these surfaces or coatings can behave as a corrosion barrier to prevent degradation of metals such as aluminum, magnesium, or other alloys by environmental corrosion.

As defined previously, superhydrophobic surfaces are water repelling because of the presence of a thin air layer at the interface of the solid-liquid systems in the pockets of the hierarchical structure (Cassie-Baxter wetting regime). Due to these air pockets, superhydrophobic surfaces behave as a corrosion barrier in metals or can be used in ceramics, like concrete, in order to prevent the corrosion of metallic parts [50].

Portland cement with sand, water, and a commercial water-based stone protector containing silane and siloxane were mixed to form a uniform paste. The paste was used to coat a concrete block, and the outer surface was covered with a nylon mesh of varying pore sizes ranging from 20 to 1150 μm . After removing nylon mesh from the concrete coating, the surface was covered with square structures, with their size corresponding to the mesh pore size. The obtained structure of the coating was rough and combined a microstructure (from the nylon mesh) with nanometer

particles [50]. Superhydrophobic characteristics ($\text{WCA} > 150^\circ$) were revealed in those samples covered with nylon mesh with a pore size from 37 to 700 μm . For example, a mesh size of 300 μm leads to $\text{WCA} = 160 \pm 1^\circ$ and a sliding angle of $5 \pm 0.5^\circ$. If the mesh was too small or too large, the coating was only hydrophobic.

In order to study the anti-corrosion properties of the as-prepared coating, a reinforced rebar in concrete was taken as the control sample (O-concrete), while another was coated with the superhydrophobic coating (S-concrete) [50].

Initially, the samples were soaked in a NaCl solution (3.5 wt. %) for 24 h at room temperature. Then both samples were electrochemically corroded by applying 26 V for 20 min in seawater (Fig. 9a). This experimental setup allowed comparison of the metallic rebar in both conditions, where the coated concrete solution was kept unaltered after the corrosion process (Fig. 9b top). When this test was carried out to the uncoated material, the aqueous solution became turbid which indicated corrosion (Fig. 9b bottom). After breaking the concrete samples, it was seen that the O-concrete sample was severely corroded after the electrochemical corrosion process while the S-concrete did not present microscopically visual evidence of corrosion (Fig. 9c). Anti-corrosion behavior was also studied by using different techniques such as potentiodynamic polarization curves or electrochemical impedance spectra (EIS), both in a 3.5 wt. % NaCl aqueous solution. EIS revealed that the S-concrete coating was highly protective because its impedance value was ten times higher than O-concrete (Fig. 9d). Additionally, polarization curves were compared between

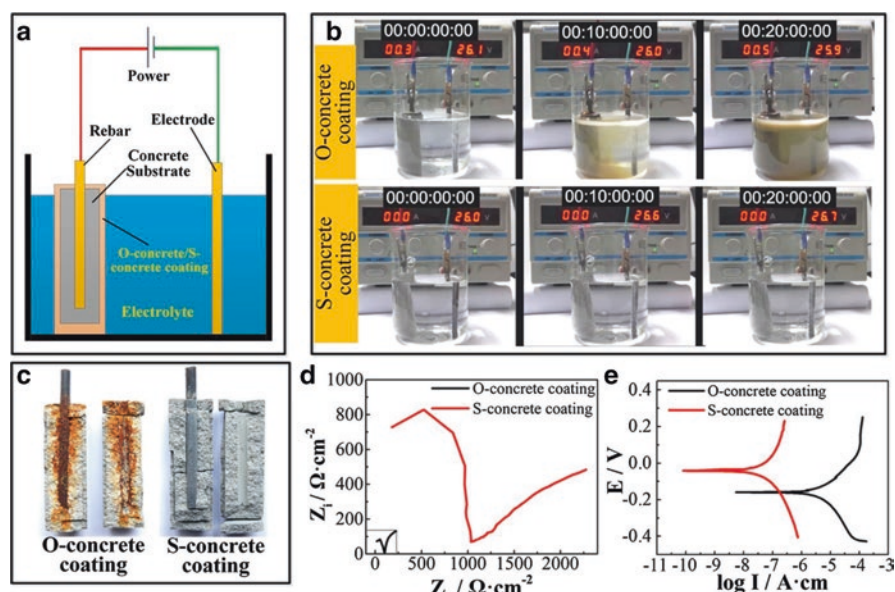


Fig. 9 Images of electrochemical corrosion procedure: (a) schematic image of the used devise; (b) electrochemical corrosion tests of both samples; (c) images of rebar in uncoated concrete sample (left) and superhydrophobic sample (right); (d) EIS of rebar samples; (e) polarization curves of both samples. (Reprinted with permission from Ref. [50], copyright Elsevier)

both samples, and as depicted in Fig. 9e, the coated samples were more protective than the uncoated one because the curves were displaced to more positive potential, with a difference between samples of 0.12 V and lower values of intensity.

In order to protect the aluminum surface, the electrodeposition of manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) combined with hexadecenoic acid in absolute ethanol was carried out where aluminum sheets acted as the cathode and platinum was used as the anode [51]. A voltage of 30 V was applied for 2 min at room temperature in order to obtain a superhydrophobic coating onto the cathode that presented a $\text{WCA} = 166 \pm 3^\circ$ (before electrodeposition aluminum substrate exhibits $\text{WCA} = 48.5 \pm 2^\circ$). Spectroscopic techniques revealed that the chemical composition of the as-prepared superhydrophobic coatings was manganese palmitate ($\text{Mn}(\text{CH}_3(\text{CH}_2)_{12}\text{COO}^-)_2$), which was responsible for the decrease in surface tension. The surface morphology was made up of many clusters of papillae-like structures, much like those observed in lotus leaves. These features led to a hierarchical structure that increased roughness ($R_a = 493$ nm) compared to bare aluminum substrate ($R_a = 2$ nm). With the EIS technique and using Nyquist and Bode plots, the authors studied the corrosion resistance in a 3.5 wt. % NaCl aqueous solution.

The Nyquist plot (Fig. 10a, b) of both samples presented fitting curves with only one single capacitive impedance loop. The difference between both samples came from the diameter of their loops; it can be seen that the one that corresponds to the superhydrophobic coating was much larger than the Al substrate. Therefore, the superhydrophobic coating protected the aluminum substrate against corrosion. Considering the Bode plots (Fig. 10c), the results indicated that the $|Z|$ modulus of superhydrophobic coating was three times higher than the uncoated aluminum substrate, which suggested better corrosion prevention. Additionally, if the phase angle vs. $\log F$ is studied, it can be seen that there are two different time constants in the frequency range of the superhydrophobic surface. This particular behavior was assigned to the different electrochemical behavior of the as-prepared coating that includes the metal/film process at the interface in low frequencies and the electrode process in high frequencies [51].

Hence, there are several observations that indicate corrosion protection – in particular superhydrophobic coatings suit well with novel applications of these surfaces.

5 Challenges

This chapter began by looking at the trends arising from the analysis of the state of the art of non-fluorinated superhydrophobic surfaces (nFSHS). Next, the durability of superhydrophobic surfaces was considered to be a key point that usually limits their possible applications in the outdoors or in industry. Nowadays, research efforts are focused on improving the mechanical properties of these surfaces by means of incorporating ceramic particles. Therefore, in the wide variety of procedures enhancing durability, it is a significant challenge to explore the use of ceramic particles and to study how they influence superhydrophobic surfaces durability together

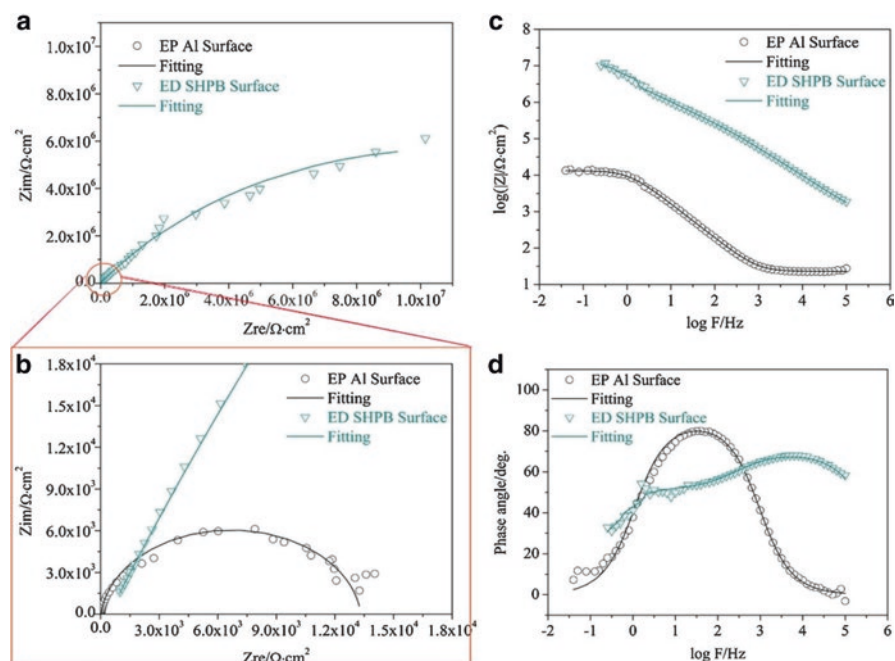


Fig. 10 Electrochemical impedance spectra (EIS) of coated and non-coated samples. (a) Nyquist plot of both samples and (b) its magnification at low values of $|Z|$; (c) Bode plot of both surface where $\log |Z|$ in superhydrophobic sample is three times higher than the uncoated one and (d) Bode plot of phase angle of both samples. (Reprinted with permission from Ref. [51], copyright Elsevier)

with the selection of the most suitable ceramics. The different tests carried out to evaluate quantitatively this durability were also discussed. Despite the abrasive grinding paper test being the most commonly used procedure for the evaluation of the durability of superhydrophobic surfaces, there are many other possible tests or even variables to modify (such as abrasive particles' nature (Al_2O_3 or SiC), number of cycles and distance of each cycle, or the constant load applied among others) if the intent is to describe a more standard methodology. Distinctly, a constant load should be taken in consideration because it is the variable that will determine the mechanical robustness of the superhydrophobic surfaces and consequently their durability and possible applications. As mentioned previously, the abrasive grinding paper test causes a decrease in the roughness of surfaces. After the test, the surfaces become smoother, decreasing the WCA as well as the SA. Once the relevant issues of this type of testing is observed, it is necessary to perform a standard testing procedure in order to provide equivalent and significant criteria for a behavior comparison of superhydrophobic surfaces in terms of durability and to correlate it to the possible applications of these surfaces.

Secondly, it is shown that superhydrophobic surfaces switch their wettability properties when immersed under water to superoleophilic surfaces. This behavior

opens up a new variety of applications like oil/water separation. Despite the increasing attention of this topic in a considerable number of studies, only oils with a well-known chemical composition or high purity were used. However, in environmental disasters such as oil spills, the chemical components are usually extremely complex, and their composition is not easily determined. Therefore, it is necessary to improve the ability of non-fluorinated superhydrophobic surfaces to efficiently separate extremely complex oil/water mixtures. In addition, due to this intricate system, it is of significant interest to study and to determine how the non-fluorinated compounds, such as fatty acids, interact with pure oil and mixtures in order to avoid its dissolution in the organic solvents or to lose its superhydrophobic/superoleophilic character. Considering the capability of oil/water mixtures, it is important to stress that until now most of these surfaces, and in particular non-fluorinated ones, are able to separate immiscible or extremely low miscible organic solvents in water. However, it remains a challenge to completely separate miscible organic solvents like ethanol or acetone. Because of that, interface interactions between non-fluorinated surfaces-oil-water should be an important area of investigation to improve the separation of these solvents. It is worth noting that the ability of oil/water separation is a potential application in water purifications industries and would help to open a new approach in oil removal using sustainable reactants.

At last, it was also shown that nFSHS are able to prevent corrosion in 3.5% wt. NaCl aqueous solutions, although the protection of the surfaces takes place by using a coating on metallic substrates. Indeed, it is important to explore superhydrophobic properties of metallic substrates without coatings, only directly modifying metallic surfaces as a corrosion barrier. Although standard saline solutions are used mainly in corrosion tests, it would be very interesting to explore their protection capacity in more severe or corrosive environments such as in acid and alkaline media or by using oxidative compounds such as CuCl_2 . Finally, characterization techniques such as EIS or polarization curves which provide quantitative information about the corrosion behavior of the as-prepared surfaces illustrate an extremely important method of corrosion characterization.

6 Conclusions

To conclude, non-fluorinated superhydrophobic surfaces (nFSHS) are revealed as potential materials for technological and industrial uses due to the nature of the surface tension modifiers used (PDMS or fatty acids with C-H bonds) and also to their environmentally benign properties. Indeed, their applications appear to not cause damage to the environment. They will also enable innovative applications like oil/water separation or corrosion prevention in natural environments. Durability of superhydrophobic surfaces, and in particular nFSHS, usually has been a critical determining factor that limited their outdoor or industrial applications due to the lack of robustness. Reinforcement of the organic component by the use of ceramic particles (SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, or WC) has been proved to increase the durability of

nFSHS in extreme abrasion conditions such as in case of abrasive testing. The excellent results obtained from durability tests of these surfaces are due to the combination of ceramic particles that have been treated with surface tension modifiers. Despite the surfaces losing reinforcement particles and WCA slightly decreasing after every cycle, the ceramic particles are responsible for retaining superhydrophobicity without pinning sites through the whole surfaces.

Non-fluorinated superhydrophobic surfaces have proved to be excellent oil removal from water mixtures that have high efficiency without loss of their properties. This behavior is explained by the nature of the modifiers themselves, as they are composed of long hydrocarbon chains that act as hydrophobic/oleophilic systems which lead to a better interaction with the organic solvents than with water. This ability to switch from a superhydrophobic state to a superoleophilic one opens up a new variety of processes for wastewater treatments of organic solvents and oil spills as well. Despite that, it is necessary to keep improving the recyclability of these surfaces in order to be applied industrially. Concerning their corrosion behavior, it was found that nFSHS are able to prevent oxidation of metallic surfaces in sodium chloride environments or under constant voltage. In fact, the thin air layer that formed between the water and the solid is responsible for the improvement of the corrosion properties. The reason leans on its Cassie-Baxter wetting state. Furthermore, it also avoids pitting oxidation via chlorine ions on the metallic surface. Summarizing, non-fluorinated superhydrophobic surfaces will contribute to a new generation of high-performance functionalized coatings with sustainable synthesis and treatment strategies.

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Hydrophobized Granular Materials for Ground Infrastructure



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1 Introduction

Functionalizing granular materials to render them hydrophobic allows their use in infrastructure to delay or restrict water infiltration and thus prevent infrastructure failure and long-term degradation. The use of hydrophobic granular materials such as sand offers the following benefits over existing techniques such as geosynthetics and clays: (1) a wide range of coatings, including organic coatings, can be used to induce hydrophobicity and (2) the level of hydrophobicity can be tailored to suit various applications (from impermeable to semipermeable conditions). Hydrophobic granular materials contribute to this strategy as shallow covers or barriers: for slopes, to reduce pore water pressure built-up in natural or infrastructure slopes and other sloping grounds; for clay deposits, to reduce the risk of volumetric changes and desiccation cracks; for landfills and porous pavements, as a layered hydrophilic/hydrophobic system, to drain or store water; for water harvesting, to collect rainfall in arid regions; in flood defenses, to form a temporary barrier to flooding water; and for foundations, to minimize concrete degradation by aggressive pore water.

Hydrophobized granular materials have unique challenges that diverge from other hydrophobic materials within the context of materials for infrastructure. (1)

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Porosity creates difficulties on assessing hydrophobicity due to gravity and air-water meniscus pinning. (2) The physical properties of the coatings need to be considered for the mechanical behavior – with different types of hydrophobic compounds providing the same level of hydrophobicity but different physical properties (coating thickness). (3) Being irregular the particles' surfaces (i.e., with a shape that deviates from a sphere) creates an uneven distribution of coatings. (4) The exact lifespan needs to be established, including its degradation mechanisms and methods to recover hydrophobicity. For instance, unlike solid surfaces hydrophobicity cannot be recovered by reapplying hydrophobic compounds. (5) Being hydrophobized granular materials which initially dry, their response in an unconfined environment will be influenced by particle detachment (critical for slopes).

The overarching aim of this paper is to provide an introduction and review of recent research on hydrophobized granular materials for infrastructure. The specific objectives are (1) to provide a theoretical background and methods, as relevant to granular materials, (2) to review the physical and chemical properties of hydrophobic coatings and the hydraulic and mechanical properties of hydrophobized coated particles, and (3) to address some constraints of these new materials (durability) and potential applications in infrastructure (slopes).

2 Background

2.1 *Hydrophobicity and Wetting Models*

To account for the effect of surface roughness present in granular materials, which deviates them from ideal ones, a modification of Young's equation [1] by a material-independent parameter, r , according to Eq. (1) was proposed by Wenzel [2] to obtain Wenzel's contact angle (CA_W). r is referred to as the roughness ratio and defined as the ratio between the true and apparent surface area of a granular material. The interfacial forces of the solid-liquid, solid-gas, and liquid-gas phases along the horizontal contact line are represented, respectively, by γ_{sl} , γ_{sg} , and γ_{lg} . Because r always exceeds unity, for a granular material with Young's contact angle (CA_Y) less than 90° , the Wenzel model predicts a decrease in hydrophobicity, whereas for a granular material with CA_Y greater than 90° , an increase in hydrophobicity is expected. The Wenzel model assumes a complete wetting regime where the interactions between the solid and liquid are strong (Fig. 1(a)).

$$\gamma_{lg} \cos CA_W = r(\gamma_{sg} - \gamma_{sl}) \quad (1)$$

In cases where a complete wetting regime is absent, i.e., a gas phase (air) is present between the solid and the liquid (Fig. 1(b)), the Wenzel model is not applicable. To account for such chemical heterogeneity, the Cassie-Baxter equation [3] is used. Equation (2) shows the Cassie-Baxter equation adapted to two-phase porous media

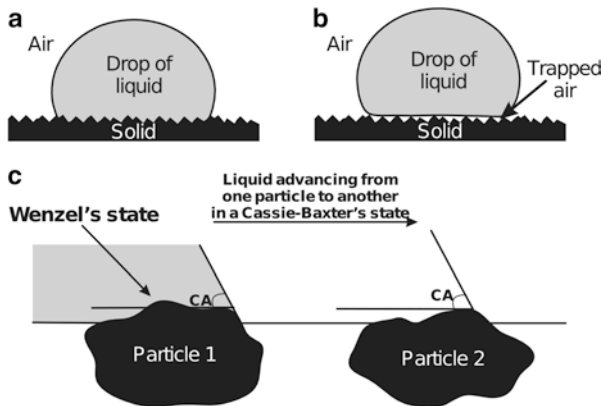


Fig. 1 Schematic representation of a drop of water (a) in the Wenzel state and (b) Cassie-Baxter state and (c) bridging from one particle to another according to the model proposed by Bachmann and McHale [5]

such as granular materials with f_1 and f_2 being the fractional areas of the solid in contact with the liquid and air, respectively. The sum of f_1 and f_2 is equal to 1 and CA_{CB} is the Cassie-Baxter contact angle.

$$\cos CA_{CB} = f_1 \cos CA_Y - f_2 \quad (2)$$

Theoretical evaluations of the hydrophobicity of granular materials which consider both the effects of surface roughness and air have been investigated by McHale et al. [4] and Bachmann and McHale [5]. The latter postulated a combination of the Wenzel and Cassie-Baxter models to obtain CA_{BM} on granular materials such as soil. This combination consists of the topmost surfaces of the particles being in the Wenzel state, i.e., completely immersed in the liquid, followed by a Cassie-Baxter state as bridging of the liquid in between the two particles occurs with air entrapped (Fig. 1(c)). This model, mathematically represented by Eq. (3), considers the packing of granular materials by means of a spacing parameter, ϵ , and has been shown to concur with experimentally obtained data on both spherical glass spheres and sands.

$$\cos CA_{BM} = \frac{\pi(1 + \cos CA_Y)}{\sqrt{3}(1 + \epsilon)^2} \cos CA_Y - \left(1 - \frac{\pi \sin CA_Y^2}{2\sqrt{3}(1 + \epsilon)^2}\right) \quad (3)$$

2.2 Hydrophobic Coatings for Granular Materials

Hydrophobicity in granular materials can be induced by chemicals such as organo-silanes. The chemical modification of granular materials using organo-silanes such as dimethyldichlorosilane (DMDCS), trimethylchlorosilane, n-octyltriethoxysilane,

and trimethylhydroxysilane has been successfully achieved on granular materials such as soils [6–10]. Because of the strong covalent bonds formed between the organo-silane molecules and the silica-rich granular materials, the hydrophobic coatings induced by organo-silanes provide a long-lasting effect. Although the lifespan of granular materials coated with organo-silanes remains largely unknown, some studies [9, 11] estimate the hydrophobicity of soils to be at least 30 years, while organo-silanes used for the protection of reinforced concrete structures have been reported to have a lifespan of at least 20 years [12].

Fatty acids, such as tung oil, generate hydrophobic coatings on soil mineral surfaces and induce soil hydrophobicity [13]. These coatings are classified as condensed, expanded, and vapor based on the orientation and package density of fatty acids. Fatty acids with straight and long hydrocarbon chains (e.g., stearic acids) are closely packed and orientated towards the mineral surface and consequently form condensed coatings in a crystalline state [14]. The condensed coatings have a strong resistance to displacement or infiltration by water. Therefore, soils with such coatings usually have stable hydrophobicity (i.e., persistent hydrophobicity). Expanded coatings occupy a larger area on particle surfaces and are formed by those fatty acids with bent or short hydrocarbon chains which result in lower packing density. Expanded coatings can cause a less stable soil hydrophobicity (i.e., shorter WDPT). Vapor coatings refer to the unstable monolayers in which fatty acids are separate and can move freely on particle surfaces. These coatings can be dispersed or dissolved when contacted with water.

A cost-effective fatty acid is tung oil which contains alpha-eleostearic acids with bent hydrocarbon chains [15]. When exposed to the atmosphere, alpha-eleostearic acids can oxidize and form semi-solid hydrophobic coatings. Therefore, tung oil has been used as a waterproof coating material in historical wooden structures [16]. Of interest to granular materials, tung oil has been proved to induce soil hydrophobicity successfully by covering the expanded coatings on particle surfaces [17]. At elevated temperature (150–250 °C), alpha-eleostearic acids undergo oxidative polymerization and turn expanded coatings into a crystalline state (i.e., condensed coatings), which contribute to a more stable soil hydrophobicity.

Techniques to control and optimize the hydrophobicity of coated granular materials include physical ones such as the use of their particle size, particle shape, and surface roughness. These inherent characteristics of granular materials are known to influence their hydrophobicity [2, 18–20]. Bachmann et al. [18] demonstrated that soils with finer particle sizes were more hydrophobic than their coarser counterparts, and other studies [19, 20] investigating the effect of particle shape showed that for a given chemistry, particles with shapes deviating from that of a sphere were more hydrophobic. The surface roughness of granular materials can be broadly separated into two scales, namely, the surface roughness of (a) individual particles and (b) a series of particles [19, 21]. For a given chemistry, the magnitude of the surface roughness of a series of particles measured using a confocal laser scanning microscope was shown to exhibit a negative correlation with hydrophobicity [19].

Figure 2(a) illustrates the concentration curves of two sands (fine and coarse) and silica powder after being chemically modified by DMDCS. The difference in

hydrophobicity between the two sands at their critical concentrations, quantified by the contact angle (CA), is ascribed to their particle sizes, whereas the relatively higher CA achieved by the silica powder is due to both the effects of particle size and particle shape. The effect of particle shape for a given particle size of two granular materials (near-spherical glass beads and a quartzitic sand) is shown in Fig. 2(b) via the concentration curves. The comparatively larger CA achieved by the quartzitic sand is due to pinning effects caused by the sharper edges of the sand.

2.3 Switchable Wettability

Hydrophobized granular material can be switched to a hydrophilic state. One general way of switching the wettability is to alter the interfacial tension. Techniques to alter surface energies that have been commonly reported include the use of bacteria, surfactants, and electrowetting [22–24]. For hydrophobized granular materials, surfactants might be the simplest method to trigger infiltration into the material by reducing liquid surface tension and solid-liquid interfacial energy [25, 26]. By mixing surfactants with water, the surface tension of the surfactant-water solution decreases significantly and the CA on hydrophobized granular materials changes. Surfactants have been widely used in varied fields such as oil recovery and agriculture. Electrowetting is another popular method for changing surface wettability in solid non-porous surfaces [24]. It can change the wettability of a solid surface without altering its material properties. By applying an external electric field, the interfacial energy of a water droplet and the solid surface is changed. Thus, the three-phase contact angle is reduced. The relationship between contact angle and voltage applied is given by Young-Lippmann equation (Eq. 4) [24, 27]:

$$\cos\theta(V) = \cos\theta(0) + \frac{\epsilon_0\epsilon_l V^2}{2\gamma_{LG}d} \quad (4)$$

where $\theta(V)/\theta(0)$ is the contact angle at V /zero voltage, ϵ_0 is the permittivity of vacuum, ϵ_l is the relative permittivity of the dielectric layer, V is the applied voltage, d is the dielectric thickness, and γ_{LG} is the interfacial energy between liquid and gas. However, starting from the nineteenth century when Lippmann first observed capillary depression of mercury in contact with electrolyte solution under voltage, the research on electrowetting mainly focused on liquid-flatten solid surfaces or two immiscible fluids. Limited research has been done on granular materials. Research conducted in [28] on parylene C (a poly(p-xylylene) polymer which is dielectric and with low permeability to moisture)-coated porous brass plate has validated the feasibility of manipulating wettability of granular materials.

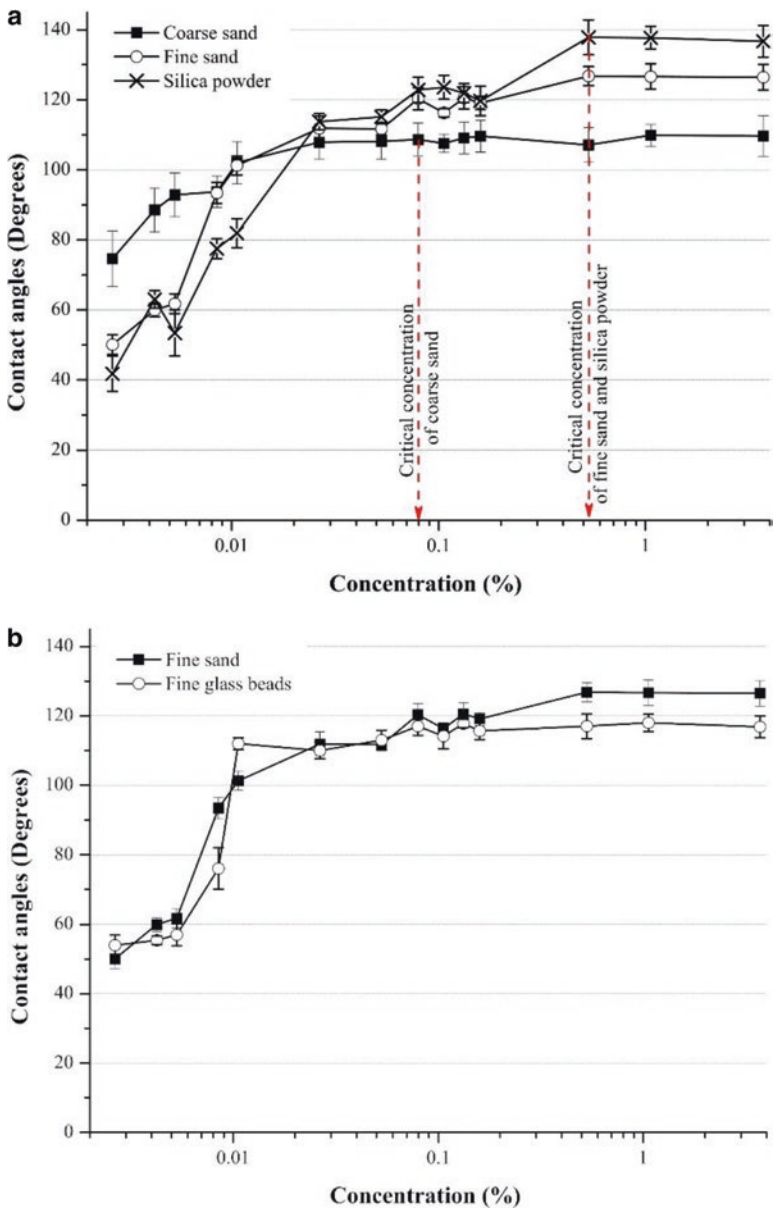


Fig. 2 Concentration curves showing the effect of (a) particle size and (b) particle shape on hydrophobicity for Fujian sand

3 Methods

3.1 Sample Preparation

Organo-silanes

DMDCS in its liquid form has been widely used for chemically inducing hydrophobicity in granular materials such as soil [5, 6, 19, 28–32]. Its reaction with the surface of soil particles results in the deposition of polydimethylsiloxane coatings (PDMS) with hydrophobic properties. One of the main reasons for the use of this organo-silane in liquid form is its reproducibility as opposed to deposition in the vapor phase [33]. The sample preparation for hydrophobizing granular materials with DMDCS includes determining its critical concentration – the smallest concentration of DMDCS needed for a granular material to reach maximum hydrophobicity. By administering different volumes of DMDCS by means of micro-pipettes to a fixed mass of air-dried granular materials in a glass beaker, concentration is defined according to Eq. (5) as a mass ratio of DMDCS added to the granular materials, expressed as a percentage. This is followed by constant and gentle stirring by hand for a couple of minutes in a fume cupboard. To ensure that the reaction is complete, the samples are left exposed to ambient conditions for 24 hours before any subsequent tests.

$$\text{Concentration} = \frac{\text{Mass of DMDCS}}{\text{Mass of granular materials}} \times 100 \quad (5)$$

Figure 2(a) illustrates the concentration curves of two sands (fine and coarse) and silica powder after being chemically modified by DMDCS. The difference in hydrophobicity between the two sands at their critical concentrations, quantified by CA, is ascribed to their particle sizes, whereas the relatively higher CA achieved by the silica powder is due to both the effects of particle size and particle shape. The effect of particle shape for a given particle size of two granular materials (near-spherical glass beads and a quartzitic sand) is shown in Fig. 2(b) via the concentration curves. The comparatively larger CA achieved by the quartzitic sand is due to pinning effects caused by the sharper edges of the sand.

Tung Oil and Other Fatty Acids

Tung oil is amber-colored and transparent, with a density of 0.94 g/cm³. Samples are prepared by mixing air-dried granular materials with tung oil. To ensure tung oil has been oxidized completely and formed hydrophobic coatings, samples are exposed to ambient conditions for 1 week. Elevated temperature results in the oxidative polymerization of fatty acids and contributes to a more stable soil hydrophobicity [17]. An oven or furnace with air inlets can be used to provide a high-temperature

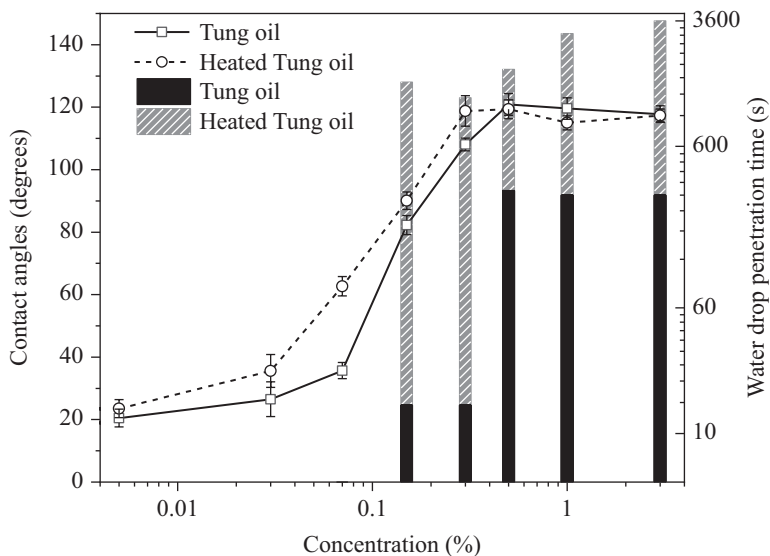


Fig. 3 Concentration curves for tung oil and heated tung oil on Fujian sand

condition with free availability of oxygen. The temperature and heating duration is in the range 150–250 °C and 1–3 hours, respectively, depending on the particle size and tung oil concentration. The thickness of samples should be lower than 10 mm to avoid temperature gradients [34]. Hydrophobicity increases with the concentration of tung oil and heating. Figure 3 illustrates the effect of tung oil concentration and high temperature on hydrophobicity in a natural quartzitic sand (Fujian sand) whose initial contact angle is 21.2° and particle size is 63–425 μm . For tung oil, contact angles rise to 120.9° at the critical concentration of 0.50%, with prolonged WDPTs from 0 s to ~300 s. The heated sample shows higher contact angles and longer WDPTs.

3.2 Contact Angles in Granular Materials

A plethora of methods for assessing the wettability of granular materials has been introduced in the past decades. Sessile drop method (SDM) offers a straightforward way to measure the CA directly at the three-phase contact point. However, as mentioned in literature [35], drops should be placed on homogeneous and plain surfaces to ensure the precision of measurements, which could be challenging for granular materials such as soil. The method of applying pressure on granular samples to replicate flat surfaces was used in some studies but mainly for relatively compressible materials like peat and clay [36, 37]. Using double-sided adhesive tapes in SDM, as proposed by Bachmann et al. [38], allows measurements on

incompressible granular surface which originally exhibits irregularly rough surfaces (e.g., sandy soil). By attaching a double-sided adhesive tape to a smooth glass slide, solid particles are then sprinkled and fixed on the slide forming a monolayer structure. Sieved particles (to the same size) are used to limit the heterogeneity, with the main purpose of using the double-side tape to restrict any motion of the particles. A drop of deionized water is next dispensed on the particles. The commonly used volume of the drops is 10 μl , but volumes ranging from 0.5 to 20 μl have also been reported. Images or videos of the droplet motion should then be recorded. Further analysis can be done in image processing software to deduce the apparent CA.

Water entry pressure (WEP), or water entry value, has been recognized as an increasingly important parameter to assess hydrophobicity of granular materials. It is also known as breakthrough pressure of water because of its definition as the critical pressure at which water starts to infiltrate or breaks through into the pores [39]. The WEP of a granular material demonstrates its ability to retard or impede infiltration of water [40]. For hydrophobic granular material, its WEP has a positive value. While for hydrophilic material, the WEP is negative due to suction (or capillary pressure).

The measurement of WEP is often found in studies of soil, and two methods have been suggested. The water-ponding method (Fig. 4(a)), which is simple and effective, is the most widely used method for measuring the WEP of hydrophobic soil, as well as the tension-pressure infiltrometer (TPI). By applying an increasing water head on top of a soil column within a transparent tube, the WEP can be recorded once the water breaks into the soil pores. The onset of infiltration can be recognized by observation of a sudden drop of water head or pressure at the soil-water interface, or by sensors mounted in soil structure [41, 42]. Variations of the setup allow the application of WEP methods in different test conditions [40, 43]. The TPI method to measure WEP was introduced by Wang et al. (2000) [44]. The TPI setup (Fig. 4(b)) is suitable for measuring WEP for both hydrophilic and hydrophobic soil as the tension infiltrometer can supply pressures less than or equal to zero [44]. By adjusting the depth of a bubble tube in the bubble tower, different suctions or positive water heads will be imposed on the soil surface. Hence, the WEP of the soil can be determined by recording the suction or water head at the infiltration onset [40, 43].

3.3 Other Methods to Quantify Wettability

Conventionally used in physical chemistry to assess hydrophobicity, the use of the Wilhelmy plate method (WPM) to measure contact angles of granular materials was initiated by Bachmann et al. [45]. The WPM allows the measurement of CAs within the range of 0° to 180° . The steps in measuring CA with the WPM involve immersing a one-layer sample of granular materials into a liquid and retracting it in the opposite direction. As these are carried out, the changes in mass are recorded. The CAs obtained as the sample is immersed and retracted are, respectively, called the advancing and receding CA.

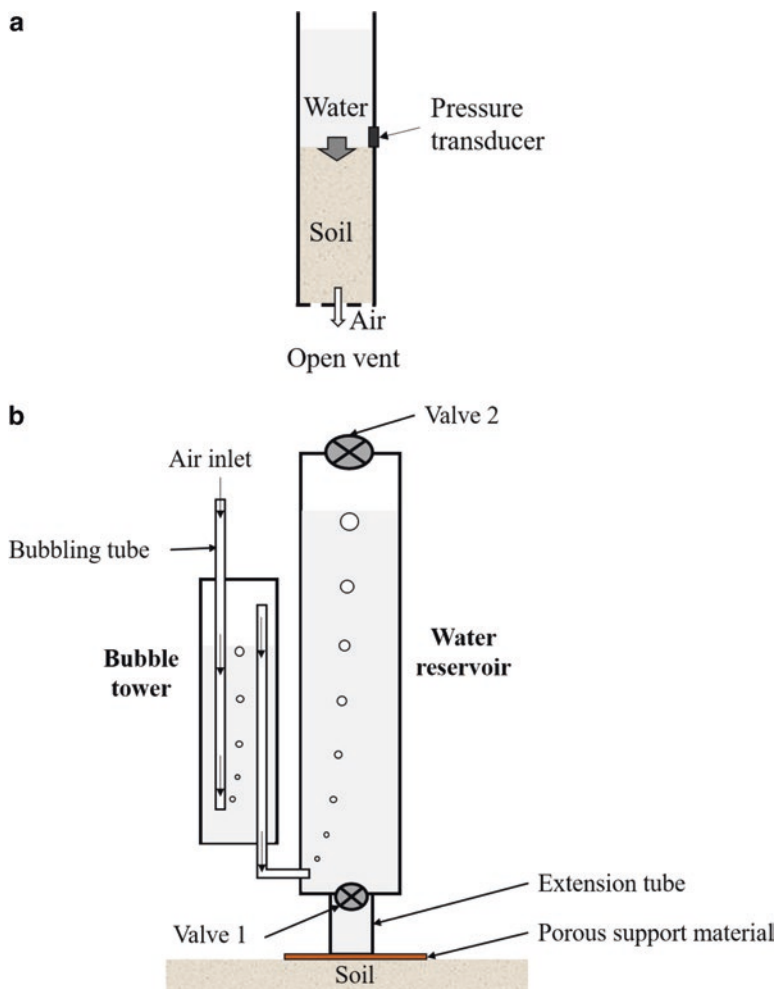


Fig. 4 Setups for water entry pressure measurement: (a) water-ponding method; (b) tension-pressure infiltrometer

As opposed to the SDM and WPM, the capillary rise method (CRM) allows the measurement of CAs by making use of a bulk sample in the form of a column. The principle of the CRM is based on the Washburn equation [46] with vertical capillaries, mathematically expressed according to Eq. (6) where h is the height to which the liquid front rises, γ_{lg} is the surface tension of the liquid, η is the viscosity of the liquid, and r_c is the effective radius of the capillary. The CRM is initially carried out using a liquid such as hexane, which, hypothetically, completely wets the sample to obtain r_c and then repeated with water. Although being a sensitive method for measuring CAs, the main limitation of the CRM is its inability to generate values of CAs larger than 90° .

$$h^2 = \left(\frac{\gamma_{lg} \cos CA}{2\eta} \right) r_c t \quad (6)$$

The water drop penetration time (WDPT) test is a relatively inexpensive test which involves the addition of water drops on layers of granular solids and measuring the time required for them to infiltrate [47]. Therefore, the granular material is initially assumed to be hydrophobic, and the WDPT test measures the time it takes for the granular material to change from a state of non-wetting to wetting. The procedure for the test involves adding a 10 g mass of granular materials to a 50 mm diameter dish with drops of water (50–80 μ l) dispensed by means of a micro-pipette from a height of at most 5 mm to prevent any cratering effect. The samples are then categorized according to different wettability classes ranging from hydrophilic to extremely hydrophobic [48, 49]. A limitation of the test as mentioned by King [50] is that the test is only sensitive within a small range.

3.4 Coating Properties

Surface Roughness

Optical interferometers can be used to measure the surface roughness of natural sand particles [51–53]. Therefore, it has the potential to detect the presence of the coatings including their characteristics such as thickness and their distribution (patchy versus continuous). Compared to the other techniques for surface roughness measurement, it has a relatively larger size of field of view and faster testing speed. Its working principle is shown in Fig. 5. A light beam emitted from the white light source is divided by a beam splitter into two half beams, which will be reflected by a reference mirror and the rough surface of tested sand particle, respectively. The interference induced by these two reflected beams generates the three-dimensional image of the tested rough surface by a couple-charged device camera. The lateral resolution is 0.184 μ m, and the vertical resolution could be as high as 10 nm. The maximum size of field of view is 107 $\times$ 140 μ m² (Fogale-Nanotech, Nimes, France).

To exemplify its use in hydrophobized granular materials, particles should be oven-dried and cleaned prior to surface roughness measurement. Particles are placed on the metallic plate and moved to the position below the optical axis of the microscope manually. A table stabilizer is placed under the microscope to minimize the influence of vibration. The three-dimensional image of the surface is obtained and recorded by the FOGALE Pilot 3D software. The shape motif method built in the FOGALE Viewer 3D software is used to separate the whole surface into shape and roughness as shown in Fig. 6. After flattening, the surface roughness could be quantified by flattened root-mean-square roughness RMS_f , which is defined by Eq. (7) as follows:

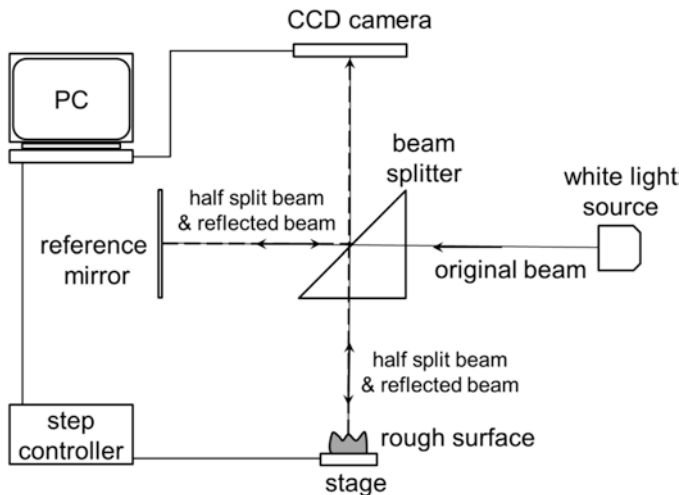


Fig. 5 Working principle of the optical interferometer on a particle surface

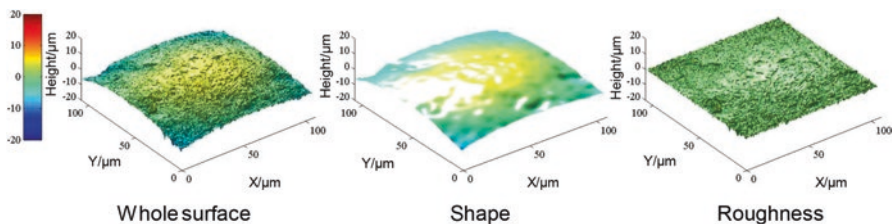


Fig. 6 Shape motif method separating surface into shape and roughness

$$RMS_f = \sqrt{\frac{1}{MN} \sum_{i=1}^M \sum_{j=1}^N (h^2(i,j))} \quad (7)$$

where M , N are the numbers of points along the X , Y directions; $h(i,j)$ is the height of discrete point to the mean plane.

Due to the relatively low reflectivity of the coatings (DMDCS or tung oil), the amount of the invalid pixels (green dots) within the maximum size of field of view ($140 \times 107 \mu\text{m}^2$) is rather high. Therefore, the size of field of view is usually reduced to minimize the percentage of the invalid pixels in order to ensure the reliability of the experimental results. The coatings on the surfaces of the particles are usually uneven. Therefore, a number of particles should be tested to obtain a statistically representative result [54–58].

As the surface topography often follows a random process [59], its characterization by using power spectral density (PSD) method has been proved to be useful [60–64]. Person [65] calculated the PSD when all the depressions in a rough surface are filled with water. This resembles hydrophobized granular materials, such as

those being presented in this chapter, which makes the PSD method a potential candidate to characterize the surface of coated particles as suggested by [65, 66]:

$$\text{PSD}(q_x, q_y) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} A(x, y) e^{-i(xq_x + yq_y)} dx dy \quad (8)$$

where $A(x, y)$ is the auto-correlation function of surface heights $h(x, y)$ and q is the spatial frequency or wavevector (in μm^{-1}). A routine angular averaging can then be performed where the surface is assumed to be isotropic so that the $\text{PSD}(q_x, q_y)$ reduces to $\text{PSD}(q)$ and is independent of x or y direction. When particles are treated with DMDCS, the downshifting of the PSD (representing the surface of treated particles) accompanied with a smaller S_q value (Fig. 8) reflects the smoother surfaces for treated particles as observed in Fig. 7, which shows the usefulness of using PSD to characterize surfaces of treated particles.

Physical and Chemical Properties

Coating stiffness is an important factor of granular materials as it could affect the contacts between particles and hence influence the macro properties [70, 71]. However, the measurement of coating stiffness is challenging due to the nano- to microscale of the coatings [72]. Normal methods like direct tensile test [73] are therefore not applicable. Nanoindentation, with a resolution smaller than 0.1 nm, is

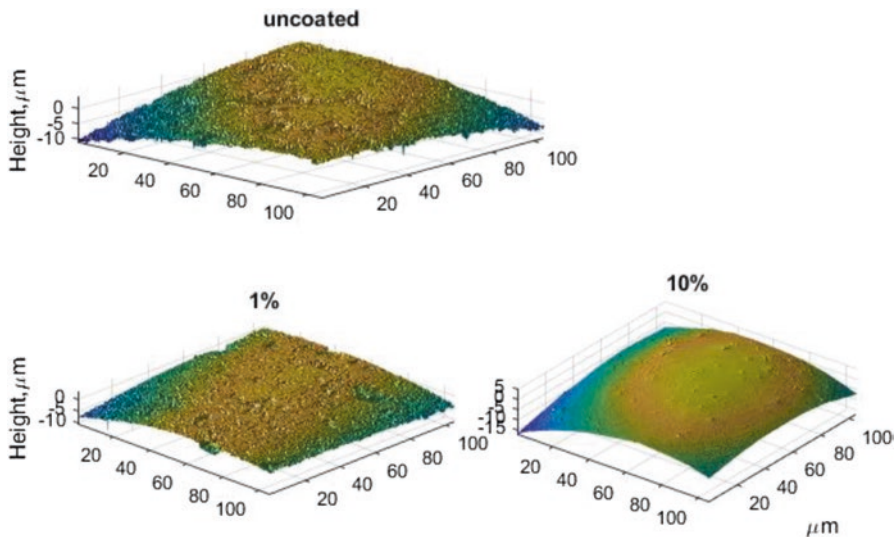


Fig. 7 Typical surface topography of randomly selected sand particles of size 1.18–2 mm which are untreated and treated with 1% and 10% concentration (mass ratio) of DMDCS. Tested particles are Fujian standard sand samples which are relatively spherical quartzitic particles

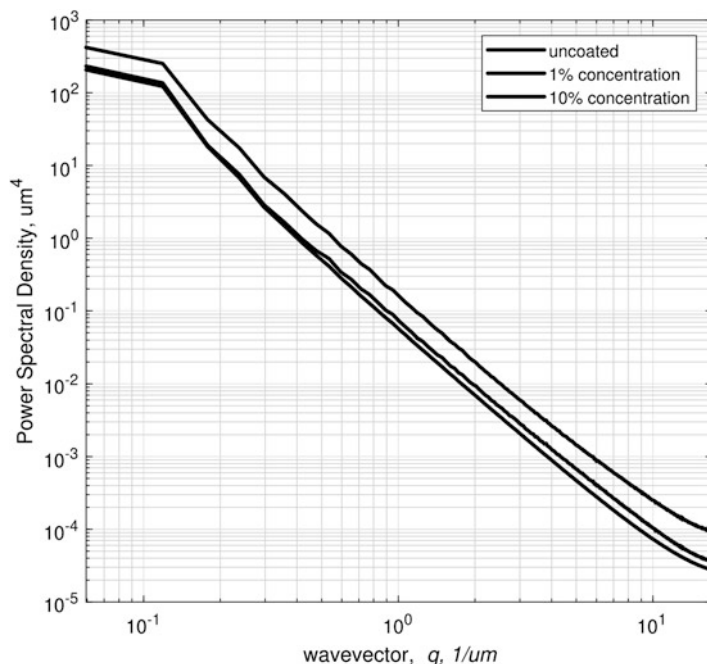


Fig. 8 Power spectral density of sand coated at different concentrations (uncoated, 1% and 10%) of DMDCS. The PSD for each concentration is averaged over each surface measurement

a more suitable technique [74]. However, for hydrophobized granular materials, one difficulty that might be encountered when testing coating stiffness is the sample preparation. Hydrophobized particles may exhibit irregular shapes and are hard to be fixed on the loading stand. To fix the particles on the substrate, relatively nondeformable glue like epoxy resin should be used. The glue should be coated on the microscope slide beforehand, and to obtain better uniformity, a spin coater can be used. A particle is then put on top with a relatively flatten part towards up. After fully curing of the glue (24 h for epoxy resin), samples can finally be fixed on the loading test stand for nanoindentation tests [75].

Chemical characterization of PDMS or tung oil-coated particles has been conducted by thermogravimetry (TG) and Fourier transform infrared spectroscopy (FTIR). TG measures the mass of a sample with elevated temperature and is performed with a thermogravimetric analyzer (TGA). From the temperature-weight curve, extrapolated onset temperature can be obtained, which denotes the temperature where the weight loss begins. TG analysis can be carried out to investigate the change of chemical compositions such as fatty acids or PDMS in hydrophobized granular materials. For instance, it has been observed that the onset temperature of PDMS decreased from 250 °C to 150–200 °C due to oxidation after a 2-month nitric acid aging [67]. The onset temperature of fresh tung oil was ~180 °C, while it increased to ~300 °C due to the oxidative polymerization [68]. Fourier transform infrared spectroscopy (FTIR) can obtain the infrared spectrum of absorption or

emission of samples, which displaces the existances of chemical compositions. Fatty acids have absorption peaks at 2933 and 2853 cm^{-1} which denote the existence of C-H and 1745 cm^{-1} which indicates C=O [68]. For PDMS, peaks at 1100 and 1020 cm^{-1} represent Si-O-Si stretching which are characteristic of its polymeric networks [69].

4 Properties of Hydrophobized Granular Materials

4.1 Mechanical

The presence of hydrophobic coating may significantly change the shear strength. Byun et al. [76] and Lee et al. [77] studied a coated sand (treated by n-octyltriethoxysilane) through shear box tests and showed a reduction of shear strength compared to that of natural sand. Kim et al. [78] indicated that the friction angle of coated sand treated by n-octyltriethoxysilane significantly decreases compared to that of natural sand. Kim et al. [78] proposed that the presence of the coatings serves as a lubricant and leads to the reduction of the friction angle. Through triaxial tests, Liu et al. [72] investigated the effects of PDMS coatings on a natural sand. This previous study also showed that the shear strength of coated sands is reduced compared to that of natural sand. In addition, the extent of the reduction of the shear strength is highly dependent on the coating thickness. A typical result is illustrated in Fig. 9. On the contrary, Bardet et al. [79] argued that the shear strength of wax-coated sand is less sensitive to the variation of water content with the friction angle unaffected. In general, these previous studies showed that the shear strength of hydrophobic coated sands is strongly associated with the properties of coatings.

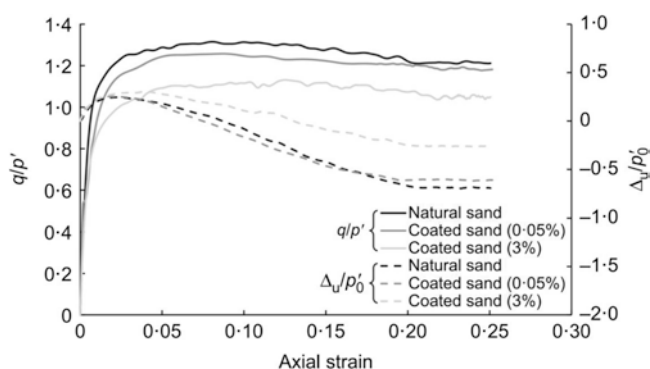


Fig. 9 Shearing behavior of uncoated and coated Fujian sand particles ($p_0' = 200\text{ kPa}$, $e \approx 0.711$)

4.2 Hydraulic

Czachor et al. [80] obtained the soil water retention curves (SWRC) for sands prepared at different wettability levels (mostly sub-critical range $< 90^\circ$) and up to suctions of 4 kPa by the hanging column method. The results revealed differences between the drying and wetting paths. Liu et al. [81] obtained the SWRC at low suctions with the hanging column method and the pressure plate up to the air-entry value (15 bars = 1500 kPa) from coarse materials to a silty soil. The drying SWRCs revealed several domains with the hydrophilic and hydrophobic paths overlapping for specific ranges of the soil water content. Davis et al. [82] used the vapor equilibrium technique to measure total suctions up to 20 MPa in hydrophilic and artificially induced hydrophobic silty loam samples equilibrated to different relative humidities generated by salt solutions. The results revealed hysteresis in the water content-suction relation for the hydrophilic samples, but to a lesser extent for the hydrophobic samples. From these studies, uncertainty remains in the water retention behavior of soils with subcritical hydrophobicity. Recently, Lourenço et al. [83] revealed a lower water retention and greater CAs for the subcritical hydrophobic samples, following both drying and wetting paths. Hysteresis was present in the relation between the contact angles and suction for the subcritical hydrophobic samples.

As for permeability, a limited number of studies have been reported on the relationship between permeability and hydrophobicity. Findings include a positive correlation of hydrophobicity and permeability reported by Mehrab et al. and Bardet et al. [72, 73]. In both studies, hydrophobized sands were prepared by thoroughly mixing melt wax with preheated sand, and falling head method was used to measure permeability. It was shown in [85] that 6% of wax by mass ratio caused an around 50% increase in permeability. Results in [84] indicated an almost triple increase of permeability with wax content increased to 6%. Mechanisms to explain the enhanced permeability due to hydrophobicity have been discussed as follows: (1) friction is lowered by wax coating offering a slippery surface for water to flow; (2) wax coating increases particle roundness by filling the angular troughs and resulting in a lower energy loss; and (3) aggregation of small particles due to wax roughens coarser particles and generates larger pores. However, the opposite correlation between permeability and hydrophobicity has been found by Hardie et al. [86]. In their study, an ethanol solution was used in permeability tests to overcome the effect of hydrophobicity on a natural soil. Intrinsic permeability was calculated from the unsaturated permeability as the dynamic viscosities of the two fluids are different. Higher intrinsic permeability was obtained from using the ethanol solution which suggests that hydrophobicity reduced intrinsic permeability. However, although different permeability trends were reported, the results in [84, 85] and [86] are not comparable due to differences in the materials, coatings, and methods: (1) The properties of natural hydrophobic soils and manufactured hydrophobized soils can diverge, namely, the coating thickness and its distribution, including the magnitude and persistency of hydrophobicity. (2) The strategy to assess the effect of hydrophobicity was different. For the studies on wax-coated sand, permeability of

hydrophobized sand was compared with permeability of untreated sand, while in [86] an ethanol solution was used to overcome the effect of hydrophobicity. (3) Methods of permeability measurement were different. The falling head method was used in [84, 85]. While in [86], the intrinsic permeability is calculated from unsaturated hydraulic conductivity which was measured using tension infiltrometers.

4.3 *Hydrophobicity Stability and Durability*

The lifespan of hydrophobicity in soils is variable, with previous studies reporting a range from a few months to decades. For example, Cerdà and Doerr [34] reported a lifespan of 5 years in a wildfire-induced hydrophobic soil, with the hydrophobic loss of soils related to the vegetation recovery. Salem et al. [54] claimed that hydrophobicity in soils can last beyond 30 years in agricultural land. Keesstra et al. [55] monitored a natural hydrophobic soil in Israel for 1 year, with hydrophobicity diminishing after 3 months owing to an increasing water content induced by rainfall, and then recovering with the evaporation of water. This suggests that soil could switch from hydrophobic to hydrophilic temporally, and vice versa, by the change of environmental factors. This temporal variation refers to the stability of soil hydrophobicity. The stability depends on (1) the soil organic matter and (2) the forming process of soil hydrophobicity (e.g., wildfire, biological activities, or the leachate of wax from vegetation). By testing a forest soil in Portugal, Doerr and Thomas [56] showed that the soil hydrophobicity has a temporal variation due to the change of soil water content and the new input of hydrophobic substances.

Compared to natural hydrophobic soils which contain various hydrophobic mixtures, in hydrophobized granular materials, the compounds are polymeric substances with a defined chemical structure. At the same time, hydrophobized granular materials have a simple coating particle structure that polymeric coatings cover on the mineral surfaces. Therefore, they can be treated as polymeric materials.

The durability of polymers used in construction materials is influenced by the intrinsic chemical properties and environmental factors such as water, sunlight, temperature, and biological activities [87]. The degradation is majorly related to two types of chemical changes, oxidation or hydrolysis, depending on the polymer type. For instance, hydrolysis contributes to the deterioration of polyesters, aramids, and polyamides during the application, while for polyolefins, it is majorly driven by oxidation [88]. Application environments can accelerate the hydrolysis or oxidation and consequently affect the durability of polymeric materials. For example, in soil environments, water and biological activities can cause the degradation of polymers, and therefore polymers which are buried in the soil can undergo a more aggressive degradation than polymers applied in building structures.

For hydrophobic granular materials, the durability refers to the long-term decline in hydrophobicity. PDMS has been reported as a durable hydrophobic material. By performing a 168-day outdoor weathering, Xu et al. [89] reported that PDMS coatings remained hydrophobic with $CA > 100^\circ$. The same finding has also been

observed by others, but for a shorter monitoring range (e.g., 28 days [90]; 9 days in Trantidou et al. [91]). Although little is known about the hydrophobicity variation of tung oil under long-term weathering, it has been reported that tung oil coatings can be degraded by microorganisms in soils [15, 92], which could further reduce its hydrophobicity.

5 Applications of Hydrophobized Granular Materials

Despite the adverse effects of hydrophobic soils in the natural environment, their ability to impede water infiltration has suggested their potential use as infiltration barriers in the built environment. A variety of applications of hydrophobized granular materials can be found in the literature. Meyers and Frasier [93] used hydrophobized granular materials for water harvesting purposes; hydrophobized granular materials were used, in combination with soil stabilizers, to seal the soil surface and construct efficient and low-cost harvesting catchments. To protect the pavement from freezing and thawing, DeBano [94] proposed the installation of a hydrophobized granular material layer immediately below the pavement. Although the soil strength may not be improved, water infiltration was prevented and the dry condition of soil was maintained, and thus the excess pore water pressure induced by traffic loads can be avoided. Similarly, hydrophobized granular materials were also utilized on sports fields and horseracing tracks to maintain consistent properties under unfavorable weather conditions [84]. As the mechanical and hydraulic properties of sandy materials in these applications are moisture content-dependent, their performance may deteriorate under rainstorm. By coating the materials with a thin layer of wax to render them hydrophobic, Bardet et al. [84] concluded that hydrophobized granular materials could avoid degradation of material properties under rainfall. Recent research showed that hydrophobized granular materials may also be employed in landfill covers to improve their long-term performance. Dell'Avanzi et al. [95] explored the potential use of hydrophobized granular materials in landfill cover system, by conducting physical model tests with hydrophobized granular materials. Subedi et al. [96] then proposed a hydrophobized landfill cover system which outperformed the conventional ones, including completely prevented water infiltration and avoided formation of cracks after dry-wetting cycles in traditional sealing materials.

Rainfall-induced slope failures are reported to take place during intense or prolonged rainstorm [97], and its initiation mechanism has been investigated in detail [98, 99]. Given the hydrophilic nature of slope soils, penetration of rainwater through the slope and formation of a saturated zone above the impermeable layer are allowed. Subsequently, rapid rise in excess pore water pressure and decrease in effective stress and soil strength are anticipated, leading to slope failure on the slip

surface. Therefore, the combination of intense rainfall and hydrophilic soils is considered to be necessary to trigger this type of slope failure. As infiltration of rainwater plays a critical role in the development of slope failure, applying hydrophobized granular materials as infiltration barriers on slopes has practical advantages. One of the major advantages of hydrophobized granular materials is that the level of hydrophobicity can be manipulated to cope with various applications, from hydrophilic to slightly hydrophobic, to extremely hydrophobic. This feature implies that hydrophobized granular materials with controlled magnitude of hydrophobicity may be utilized in fill slopes or natural slopes, where the infiltration into slope is suppressed to lower the risk of rainfall-related slope failure.

Recently, the hydrological response of model slopes with hydrophobized granular materials under artificial rainfall has been investigated, providing an insight into the application of hydrophobized granular materials in slope engineering. Lourenço et al. [100] conducted a series of flume tests to model the response of slopes, which were constructed with hydrophobized sand of various hydrophobicity levels. With the increase of hydrophobicity level, the infiltration pattern was observed to transform from a parallel wetting front to preferential flow and surface runoff, and the infiltration rate decreased gradually until water penetration was fully prevented. The results revealed that soil hydrophobicity had substantial impacts on the responses of slopes. Moreover, the hydrological response of model slopes of a different material, hydrophobized decomposed granite, was quantitatively explored [101]. With the increased hydrophobicity, the decreased wetting front movement, shortened time to surface ponding, and decreased water storage were reported. In particular, this study highlighted the interplay between soil hydrophobicity, relative compaction, and rainfall intensity and confirmed that the isolated influence of soil hydrophobicity was profound while the effects of other factors were relatively limited.

Besides hydrological behavior, erosional behavior of hydrophobized granular materials is also crucial to the stability of slopes. As an important component of land degradation, soil erosion was observed to increase significantly on naturally occurring hydrophobic soils [102], due to enhanced rain splash detachment of soil [103] and increased soil erodibility [104]. Nevertheless, little exists on the erosional response of hydrophobized granular materials, which is believed to differ from natural hydrophobic soils, given their thin (up to 10 μm), soft, and smooth coatings [72]. Lourenço et al. [100] observed the failure modes of model slopes of hydrophobized sand and documented that infiltration-initiated retrogressive slides were the failure mode of hydrophilic sand whereas surface runoff-caused erosion dominated the failure of hydrophobic sand. In addition, Zheng et al. [105] carried out flume tests on hydrophobized granular materials with varying magnitude of hydrophobicity. The results revealed that increased hydrophobicity did not necessarily lead to increased soil erosion yield, and its impact was dependent on material grain size, with the erosion loss increasing for coarse-grained material, but decreasing for fine-grained material.

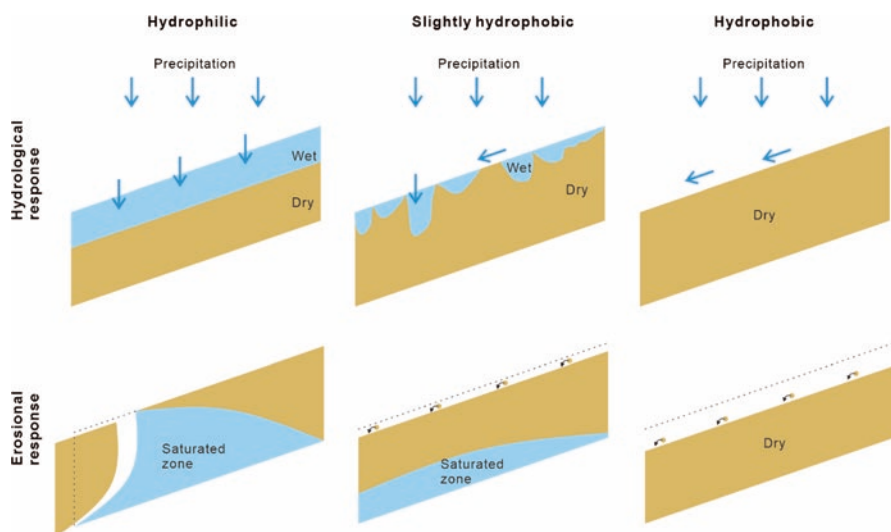


Fig. 10 Comparison of hydrological and erosional responses between hydrophilic and hydrophobic slopes

As summarized in Fig. 10, the transition of hydrological response (from parallel wetting front for hydrophilic material to preferential flow and surface runoff for hydrophobized material) and erosional response (from sliding failure for hydrophilic material to erosion for hydrophobized material) implies that a hydrological optimum condition could be achieved by adjusting hydrophobicity level, and infiltration can be reduced without amplifying erosion and therefore contribute to the slope stability.

In order to facilitate the utilization of hydrophobized granular materials in the built environment, a preliminary protocol for their field use is proposed as below:

1. Raw material selection. As the erosional effect of hydrophobicity depends on material grain size, it is crucial to make sure that appropriate granular materials can be selected so that erosion is not promoted by induced hydrophobicity.
2. Level of hydrophobicity. The hydrophobicity level of granular materials is dependent on their application. For cover systems, extremely hydrophobic materials should be adopted, whereas for slope stabilization purpose, slightly hydrophobic materials are recommended.
3. Material treatment. The amount of hydrophobizing agent required is dependent on the material used, and therefore laboratory testing should be conducted to determine the agent concentration at first; then the material is expected to be treated in a factory to avoid possible environmental issues from by-products.
4. Material placement. Once the treatment is complete, the material is transported to the site and then compacted to reach the required level of relative compaction.

6 Conclusions

This chapter has introduced hydrophobicity in granular materials and their implementation in ground infrastructure. The specific challenges associated with the different methods of synthesizing granular materials to achieve the desired level of hydrophobicity, their eventual characterizations, as well as their engineering properties have been detailed. With the primary objective to exploit an already abundant natural resource, the hydrophobization of soils allows for a more sustainable approach to be used in ground infrastructure. Up-to-date research from the particle to field scales have demonstrated the peculiarity of hydrophobic granular materials as opposed to other materials. While the physicochemical techniques used to induce, enhance, and switch hydrophobicity of granular materials have been amply investigated, future works examining their durability, their upscaling for field use, and their numerical modelling remain important aspects to be looked into.

Acknowledgments This work was supported by the General Research Fund (Grants 17221016, 17203417) from the Research Grants Council of Hong Kong Special Administrative Region, China.

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Superhydrophobic Metal Surface



Debasis Nanda, Apurba Sinhamahapatra, and Aditya Kumar

1 Introduction

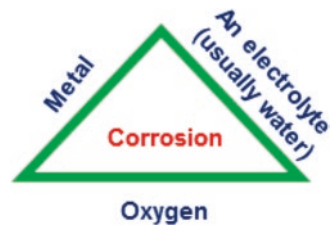
Metals are substances that have properties such as being shiny and malleable and conduct electricity [1–3]. Metals that are frequently used are iron, copper, aluminum, and some of their alloys such as brass and steel. Metals have applications in various fields such as in automobiles, construction, reactors, catalysts, medical purposes, etc. [4–8]. The long-time use of metals comes with problems such as corrosion, fouling, etc. [9–11]. Besides these, other important issues like accumulation of ice on the metal surface in cold conditions can be often observed in cold weather [12]. Ice on metal surfaces causes severe headaches to several technologies. For example, ice buildup can add extra weight to airplane wings, turbine blades, telecommunications and electrical equipment, which in turn can lower performance efficiency and compromise safety. Further removal of ice buildup may need extra efforts and cost.

Corrosion on metal surfaces creates problems such as failure in bridges, houses, aircraft, automobiles, etc. The annual loss of revenue is estimated to be \$2.4 trillion [13]. A schematic diagram illustrates the different components that are responsible for corrosion (Fig. 1). It is observed that the main components of corrosion depend on the surface (metal that gets corroded), an electrolyte (mainly aqueous), and oxygen. In order to prevent corrosion, it is highly essential to remove any one of these components. Different traditional methods have been studied for the prevention of corrosion for metals such as protective coating methods, barrier coatings, galvanizations, preparation of alloys, and cathodic protection [14]. However, there are many

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Fig. 1 Schematic diagram of different components that are responsible for corrosion



disadvantages associated with these abovementioned protection techniques like high cost of production, regular removal of aqueous solution and reapplying of aqueous paint avoiding cracks and scratches that can increase the corrosion rate when creating alloys [14, 15], as well as the environmental and carcinogenic issues associated with chromium(VI) electrodeposition [16].

Icing is another problem that occurs on the surface of metals due to the freezing of water droplets. It reduces the efficiency of equipment and also affects the transmission of electricity.

2 Superhydrophobic Surfaces

Water is a factor for corrosion that changes the surface of the metal to metal oxides. Similarly, the formation of the ice on the metal surface takes place by the solidification of deposited water with a decrease in temperature and adhesion of ice on the surface. So, to overcome these problems, it is essential to remove water from the surface.

Before going to a detailed study, an overview of the phenomenon of the formation of water droplets on a surface will be provided. Water droplets resting on the surface of metals form a certain angle which depends on two forces, adhesion and cohesive forces. The higher the adhesion force between the metal surface and water droplet compared to the cohesive force, the lower will be the contact angle and vice versa, as shown in Fig. 2. The water's contact angle on a surface is measured by Young's equation which is given by:

$$\gamma(sv) - \gamma(sl) - \gamma(lv) \cos \theta = 0 \quad (1)$$

where (sv) is the solid-vapor interface, (sl) stands for solid-liquid interface, $\gamma(lv)$ represents liquid vapor interface, and θ is the water contact angle on the surface.

Based on the contact angle formed by the water droplet, metal surfaces are mainly categorized as superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic, as shown in Fig. 3. Superhydrophobic surfaces are those surfaces that can repel water from its surface. In these surfaces, a water droplet forms a spherical structure with minimum surface contact and a water contact angle $>150^\circ$. The synthesis of artificial superhydrophobic surfaces was inspired by nature. Different surfaces such as lotus leaf, rose leaf, legs of spiders, and butterfly wings [17] show

Fig. 2 Schematic diagram of the behavior of water droplet on the metal surface. (a) High adhesive force and (b) high cohesive force

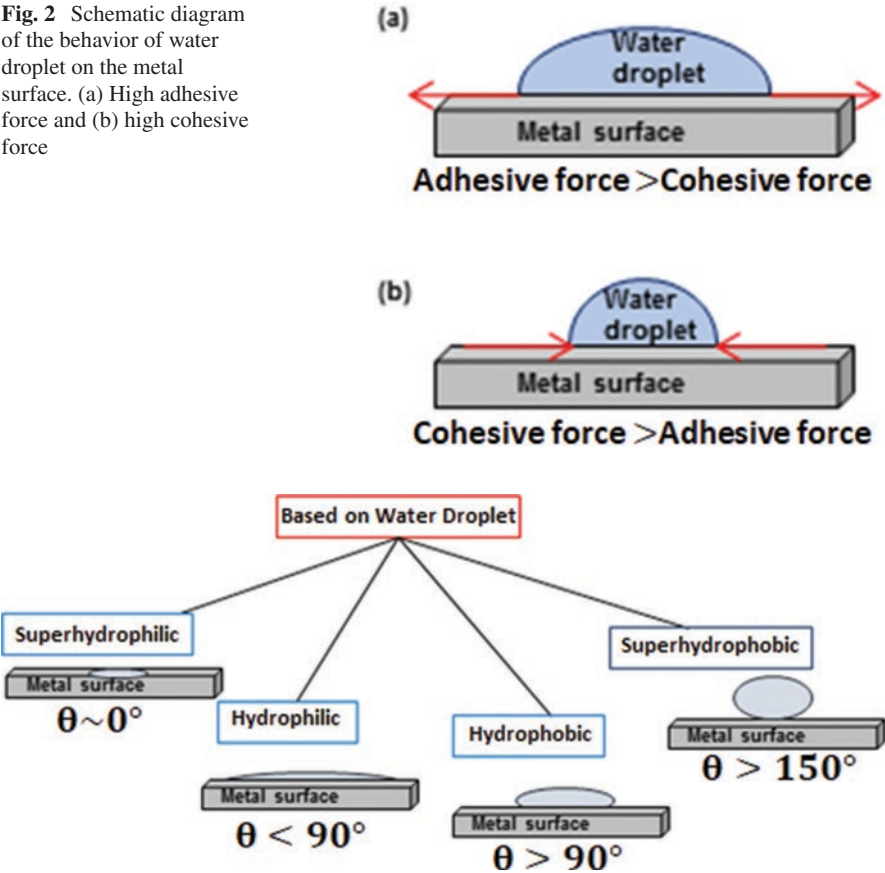


Fig. 3 Schematic diagram representing different types of surfaces based on the contact angle of water

non-wetting properties and low adhesive characteristics that inspired the creation of a superhydrophobic surface.

Superhydrophobic surfaces are formed by making the desired surface rough followed by the application of a material with low surface energy (Fig. 4). The combination of these two factors makes the surface superhydrophobic. Two different models proposed for superhydrophobic surfaces are the Wenzel state and the Cassie-Baxter state [18, 19]. Substances with low surface energy that are reported for the synthesis of artificial superhydrophobic surfaces are polymers, silanes, fatty acids, waxes, etc.

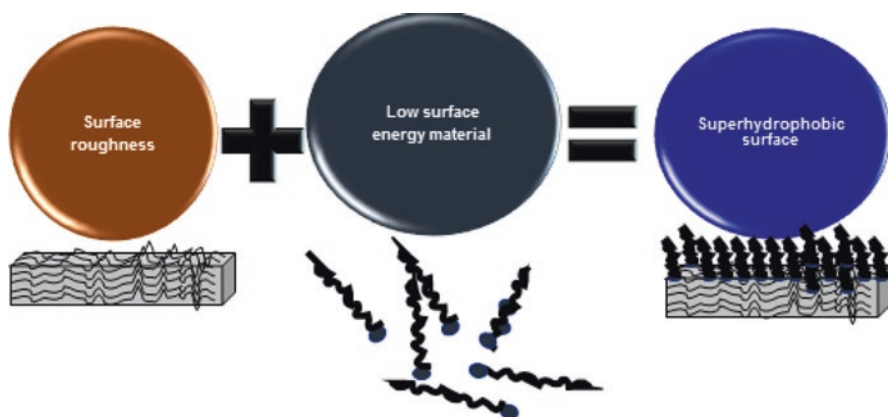


Fig. 4 Schematic diagram of different factors that govern the development of a superhydrophobic surface

3 Different Synthesis Techniques

In the last few decades, research has been performed to make a superhydrophobic metal surface for corrosion resistances taking inspiration from nature. Many methods are reported for the synthesis of artificial coatings on metal surfaces to make the surface anticorrosive. Besides their anti-corrosive properties, these coatings also provide other advantages by lowering the adhesive force of the surfaces for which these metal surfaces can further expand their applications in anti-icing, anti-fogging, reducing drag coefficient, oil-water separation, etc. This section will review different techniques that are followed in developing a superhydrophobic coating on metal surfaces with anti-corrosive properties. Different synthesis methods are summarized below.

3.1 Dip-Coating

The dip-coating method is the simplest and most frequently used. Synthesis of a coating is carried out by a dip-coating instrument, where the metal surface is dipped and removed from the coating solution at a constant rate. The metal surface is made to be immersed in the solution for a few seconds before removing the sample as represented in Fig. 5. After coating, the surface is then dried to achieve superhydrophobicity. Qing et al. (2016) [20] dip-coated copper surfaces with solution of (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane-modified TiO_2 nanoparticles and γ -aminopropyltriethoxysilane (KH-550), polyvinylidene fluoride (PVDF), and sodium dodecylbenzene sulfonate (SDBS). The contact angle exhibited was 162.3° with anti-corrosive and UV-based reversible properties. Mo et al. (2015) [21] dip-coated the surface of steel with a composite of stearic acid-modified TiO_2

Fig. 5 Schematic diagram of the dip-coating technique

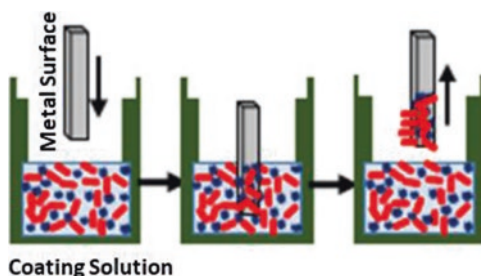
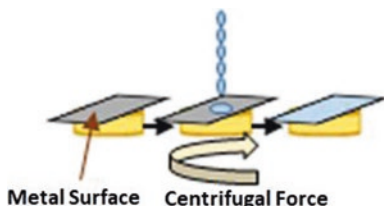


Fig. 6 Schematic diagram of carrying out spin coating on a surface



nanoparticles, fluoro-methylhydro-silicone oil, and 3-(methylacryloxy)propyltrimethoxysilane. The developed coating had a water contact angle of 151° with good anti-corrosive properties.

Yang et al. (2017) [22] synthesized different samples by dip-coating an epoxy layer along with fluorographite and graphene oxide, respectively, onto a copper surface. The coated surface showed a contact angle of 154° with excellent mechanical, chemical stability, and self-cleaning properties. Luo et al. (2018) [23] dip-coated copper mesh using a solution of SiO_2 nanoparticles, PDMS, PVDF, and 3-aminopropyltriethoxysilane (KH-550). The prepared mesh showed a contact angle of 160° with excellent mechanical strength and could be used for oil-water and self-cleaning applications. A superhydrophobic copper surface was developed using the dip-coating technique by Rao et al. (2011) [24]. The copper surface was treated with solution of methyltriethoxysilane, methanol, and water. From the solution, silica spheres are deposited to form a coating, and the contact angle was found to be 155° with excellent stability to different pH and anti-corrosive properties.

3.2 Spin Coating

Spin coating is carried out via centrifugal force using a spin coater. In this method, the metal surface is placed over a platform with vacuum in order to keep the metal surface in place. The coating solution is added from the top, while the metal surface rotated as shown in Fig. 6. The coating takes place by the movement of solution in outward direction due to centrifugal force. Pawar et al. (2017) [25] developed an anti-corrosive coating by spin coating the surface of mild steel using a solution containing methyltrichlorosilane-modified SiO_2 nanoparticles and achieved a contact angle of 158° . Liu et al. (2014) [26] synthesized a non-wetting, mechanically

stable, anti-corrosive coating on an aluminum alloy by the spin coating technique. The surface of the metal was coated with hydrazine monohydrate-modified graphene oxide which increased the contact angle to 153.7° .

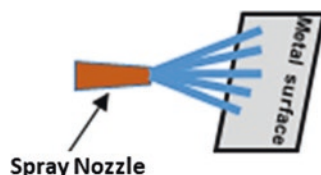
Yu et al. (2013) [27] carried out electroless deposition and spin coating techniques on carbon steel to make an anti-corrosive coating. The surface was first deposited with Ni-P, followed by spin coating with layers of TiO_2/ZnO , and CTAB along with TiO_2/ZnO , and then immersed in octadecyltrimethoxysilane to increase the contact angle to 160° . Long et al. (2017) [28] developed a thermal healing superhydrophobic coating on an aluminum surface. The surface was first etched with HCl for roughness and then spin-coated by PDMS to increase the contact angle to 158° . The prepared sample showed excellent mechanical and chemical stability. Weng et al. (2012) [29] developed a fluorinated polyacrylate silica composite coating by spin coating on cold-rolled steel. The coated surface showed a suitable anti-corrosive property to seawater and exhibited a contact angle of 153.2° . Liu et al. (2016) [30] prepared superhydrophobic aluminum surfaces that exhibited anti-icing property. The surface of aluminum was first spin-coated with a solution of SiO_2 and polystyrene. Then the coated surface energy was reduced by 1H,1H,2H,2H-perfluorooctyltriethoxysilane vapors that increased the contact angle to 163° .

3.3 Spray Coating

In this method, the coating solution is sprayed on the surface of the metal through a nozzle. The solution is released through the nozzle at high pressure, which gets deposited on the metal surface as represented in Fig. 7. After the coating, the sample is kept for drying to remove excess solvent. Pan et al. (2016) [31] created a superhydrophobic steel surface by spray coating. The surface exhibited anti-icing and anti-corrosive properties. The surface was spray-coated with a sol-gel of 1H,1H,2H,2H-perfluoroalkyltriethoxysilane-modified silica nanoparticles and poly(methyl methacrylate) which increased the contact angle to 158° . Nine et al. (2015) [32] developed a superhydrophobic coating on different surfaces, including a copper plate spray-coated with a solution of graphene oxide, diatomaceous earth (DE), and polydimethylsiloxane (PDMS). The contact angle increased to $170^\circ \pm 2^\circ$ with the addition of TiO_2 . The superhydrophobic surfaces showed excellent self-cleaning, acid, and scratch resistance along with anti-corrosive properties.

Zhang et al. (2018) [33] spray-coated, dip-coated, and painted on different surfaces like glass and steel mesh, yielding excellent mechanical strength. The

Fig. 7 Schematic diagram of the spray coating technique



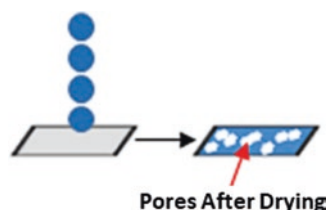
superhydrophobic steel mesh was used for oil-water separation as it showed a contact angle of 154.8° for water and 0° for oil. Wang et al. (2017) [34] developed a superhydrophobic surface on an aluminum surface with wear resistance, low drag coefficient, and anti-corrosive properties. The surface was spray-coated with a two-step method. First, the surface was spray-coated with hydrocarbon resins to increase adhesive power followed by spray coating with dichlorodimethylsilane-modified SiO_2 nanoparticles, which increased the contact angle to $153^\circ \pm 5^\circ$. Hu et al. (2017) [35] developed a superhydrophobic chemically stable nickel surface for oil-water separation. In this process, nickel foam was etched using sonication and hydrochloric acid to create roughness. The roughened foam was spray-coated using a solution containing fluorinated ethylene propylene, polyvinylidene fluoride, ultrafine polyurethane, and hydrophobic silica nanoparticles that resulted in a contact angle of 157° .

3.4 Phase Separation

Phase separation-based coating for the synthesis of superhydrophobic coating is represented in Fig. 8. In this method, the coating solution is made of two different immiscible solvents of varying evaporation rates. When the solution is made to spread on the metal surface, due to the difference in the evaporation rate of both the liquids, the surface forms pores on the surface which acts as roughness along with low surface energy materials, changing the surface of the metal to superhydrophobic.

Baktash et al. (2017) [36] prepared a sol-gel of [tetraethyl orthosilicate](#) and methyltrimethoxysilane in alkaline conditions to produce silica nanoparticles. These nanoparticles were then coated on copper wire followed by immersion in methanol to achieve superhydrophobicity. The prepared surface was used for solid-phase microextraction of chlorobenzene. Jicheng et al. (2016) [37] synthesized a superhydrophobic coating with a 155° contact angle on a magnesium alloy by the phase separation method. PVC was coated onto an anodized magnesium surface with ethanol as the non-solvent. The surface provided resistance to acid and alkaline solutions along with anti-corrosive properties. Zhang et al. (2008) [38] synthesized a superhydrophobic coating with a contact angle of 160° on an aluminum surface. The surface was dipped in a solution containing polycarbonate and its solvents and non-solvents. The developed surface also showed excellent mechanical and chemical stability.

Fig. 8 Schematic diagram of the superhydrophobic coating phase separation technique



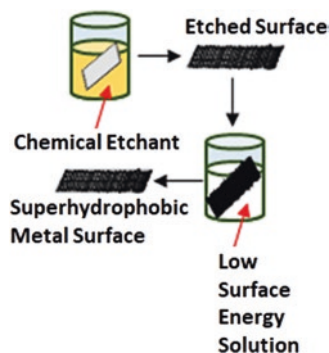
3.5 Etching

Etching is the process in which a desired roughness on the surface of the metal is created by various means. Different types of etching are created on a metal surface by chemical etching, plasma etching, sandblasting, etc. Chemical etching is a method where the surface roughness on the metal is carried out by exposing the surface to a solution of acid or base. Etching on the surface creates a desired roughness, after which the sample is exposed to a low surface energy material where metal surfaces achieve superhydrophobicity after drying. The process of achieving a superhydrophobic surface is shown in Fig. 9. In the case of plasma etching, the surface of the metal is bombarded with charged ions that create the roughness and also change the chemical composition of the metal's surface and thus change the wettability of the surface.

Kim et al. (2018) [39] created roughness on a stainless steel surface by chemical etching in a solution of hydrogen fluoride and sodium chloride. The roughed surface was then coated with trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane, which increased the contact angle to 168° and exhibited excellent self-cleaning properties with at least 1 month stability. Wang et al. (2017) [40] synthesized a superhydrophobic steel surface with mechanically stable and anti-corrosive properties. The steel surface was chemically etched in a solution of antiformin and hydrogen peroxide solution followed by 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane treatment that increased the contact angle to 163°. Liu et al. (2007) [41] chemically etched the surface of copper with nitric acid followed by surface treatment with n-tetradecanoic acid to achieve a noncorrosive superhydrophobic surface with a contact angle of 158°.

Park et al. (2011) [42] synthesized a superhydrophobic magnesium surface by chemical etching. The plate was immersed in 5% HCl, followed by depositing copper on the surface by immersion. After the deposition, the metal surface was treated with phenethyl-urea and hexyl-urea silane to achieve a contact angle of 155° and 150°, respectively. Jagdheesh et al. (2011) [43] studied the effect of roughness on the superhydrophobic property on stainless steel and Ti-6Al-4 V alloys. Roughness was created by a laser-induced beam followed by treating with perfluorinated octyl-trichlorosilane. It was observed that with an increase in the number of pulses, nano-roughness increased which increased the contact angle to 152.3°. Ta et al. (2015)

Fig. 9 Schematic diagram of the formation of superhydrophobic coating by chemical etching



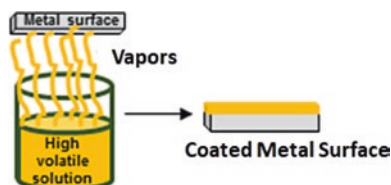
[44] fabricated hierarchical structure roughness on brass and copper surfaces by a nanosecond fiber laser. The prepared sample exhibited excellent self-cleaning properties and was used for sensing applications. Vilaro et al. (2017) [45] fabricated an anti-corrosive, superhydrophobic copper surface with a contact angle of 163° . Hierarchical roughness on copper was developed by O_2 and Ar plasma etching followed by coating with 1H,1H,2H,2H-perfluorodecyl acrylate-ethylene glycol diacrylate using initiated chemical vapor deposition (CVD).

3.6 Chemical Vapor Deposition (CVD)

Anti-corrosive coatings with superhydrophobic properties can be developed by chemical vapor deposition. In this process, the surface to be coated is exposed to the vapors of low-energy chemicals that are to be the coating. These vapors then get deposited on the metal surface making a protective film. The substances that are deposited are mainly volatile, which is represented in Fig. 10. Ishizaki et al. (2018) [46] created a chemically stable superhydrophobic film on a magnesium alloy with anti-corrosive properties. Magnesium alloy was coated with vapors of trimethylmethoxysilane using microwaved plasma CVD that increased the contact angle above 150° . Zhang et al. (2017) [47] changed the copper mesh surface by the CVD method to superhydrophobic/superoleophilic. First, the soot carbon is deposited on the surface using the flame of kerosene and then silica nanoparticles via CVD followed by removal of carbon at 500°C for 1 h in an oxygen atmosphere. The silica-deposited surface was further modified using HDMS to achieve a water contact angle of 158° . Besides superhydrophobicity, the coating exhibited excellent mechanical, thermal, and corrosion resistance. Lee et al. (2011) [48] synthesized vertically aligned multi-walled carbon nanotubes on stainless steel mesh. The mesh was coated by Al_2O_3 and iron catalyst followed by growing CNT via the introduction of C_2H_2 and H_2 . The contact angle was above 150° and was used for oil-water separation.

Li et al. (2013) [49] prepared a chemically stable, superhydrophobic coating for oil-water separation on stainless steel mesh. The CVD method was used to coat ZnO nanorods with a contact angle of 157° . Hozumi et al. (2011) [50] changed the wettability of an aluminum and titanium surface-coated Si substrate to superhydrophobic with a contact angle of 163° using CVD of 1,3,5,7-tetramethylcyclotetrasiloxane. Nicola et al. (2015) [51] grew multi-walled carbon nanotubes on stainless steel by CVD of acetylene at low temperatures ($<1000^\circ\text{C}$). The method increased the contact angle to 154° .

Fig. 10 Schematic diagram of the CVD technique for coating on the surface



3.7 *Electrochemical Deposition*

Electrochemical deposition is the process in which coating is carried out in the presence of electricity. In this method, the substance coated is placed in an electrolyte, and voltage is applied. The surface of the metal is then coated with the metal species present in the electrolyte, thereby changing the wettability. Kwon et al. (2014) [52] changed the wettability of the steel surface to superhydrophobic by laser treatment and electrodeposition. Microstructures were developed by laser treatment. The surface was then insulated, mechanically polished, and then followed by the electrodeposition of copper to form reentrant structures. Electroplating on copper surface was performed at high current density in the presence of a copper sulfate and sulfuric acid solution to replicate the surface roughness of a lotus leaf by Xi et al. (2009) [53]. The contact angle increased to 153.5° . Wu et al. (2014) [54] electrodeposited a solution of hybrid silica on mild steel to alter the surface to superhydrophobic. The prepared surface was chemically stable to acid and seawater and also exhibited anti-corrosive properties.

Zhang et al. (2016) [55] synthesized a superhydrophobic mild steel surface with a water contact angle of 155° by a two-step electrodeposited method. The surface was first electrodeposited with a SiO_2 film followed by immersion in dodecyltrimethoxysilane. Besides superhydrophobic properties, mild steel exhibited good mechanical abrasion resistance and anti-corrosive properties. Xi et al. (2008) [56] fabricated a superhydrophobic coating by electrodeposition on different metal surfaces. The surface of copper was coated with solution of ethanol and n-tetradecanoic acid. The water contact angle of surface increased to 154° and exhibited resistance to different pH solutions. Su et al. (2014) [57] developed a contact angle of 162° on a copper surface by the electrodeposition of nickel followed by treating the surface with (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane. Morphology of the sample showed a pin-like structure with excellent stability to mechanical abrasion, pressure, and different pH solutions. Besides this, the developed surface acted as an anti-corrosive barrier with self-cleaning properties.

3.8 *Hydrothermal Method*

The hydrothermal method is the process of developing a superhydrophobic coating on the metal's surface based on high temperature and high pressure. It is always associated with developing surface roughness on the metal surfaces. Wang et al. (2016) [58] developed an ultralow adhesive force coating on different metal surfaces (low alloy steel, zinc, copper, and aluminum). ZnO nanorods were grown on the surface by the hydrothermal method, followed by surface modification with PDMS that increased the contact angle to 154° . The prepared sample showed anti-corrosive properties. Wu et al. (2016) [59] developed a superhydrophobic coating on various surfaces including copper. The surface was coated with a solution of

nanoparticles, ethanol, and vinyltriethoxysilane and heated to 100 °C in a closed chamber along with the substrate. SiO₂ and TiO₂ nanoparticles were used for the experiment. The contact angle increased to 151° with excellent mechanical and chemical stability. The surface was used for the separation of oil from water.

Cho et al. (2015) [60] grew cerium nanorods on different substrates (aluminum, stainless steel, titanium, and silicon) by using the hydrothermal method. A solution of cerium nitrate hexahydrate, urea, and water was placed in an autoclave. The prepared sample exhibited a contact angle of 160°, 160°, 159°, and 159° for aluminum, stainless steel, titanium, and silicon, respectively. The coated cerium nanorods on the aluminum surface also showed excellent corrosion resistance. Similarly, Yao et al. (2012) [61] developed ZnO nanoflakes by hydrothermal treatment of zinc nitrate hexahydrate and hexamethylenetetramine along with the aluminum surface. The nanoflake surface was then immersed in stearic acid. After coating, the water contact angle of the aluminum surface reached 157°. The prepared sample was also stable toward different pH solutions and UV rays. Gao et al. (2014) [62] synthesized an anti-corrosive coating on a magnesium alloy. A fibrous szaibelyite coating was developed hydrothermally by coating with Mg(NO₃)₂·6H₂O, H₃BO₃, and water, followed by treating with fluoroalkylsilane which increased the contact angle to 166°.

3.9 Immersion Technique

The synthesis of artificial superhydrophobic metal surfaces is also reported to take place via the immersion technique. In this method, the substrate is immersed in a solution of low surface energy material for a more extended period of time, which causes the chemical to coat on the surface by deposition or by reaction with the surface ions, thereby making the surface superhydrophobic. Larmour et al. (2007) [63] coated a copper surface with another metal to achieve superhydrophobic property with a contact angle of 173°. The surface was first immersed in a solution of silver nitrate followed by a treatment with polyfluoroalkylthiol. Zhang et al. (2015) [64] synthesized a superhydrophobic-coated copper foam with a contact angle of 155° for oil-water separation. The copper foam was immersed in a solution of ethanol and n-dodecanethiol to achieve superhydrophobicity. Sarkar et al. (2010) [65] coated silver on a copper surface by immersing the surface in silver nitrate solution for different intervals in the presence of benzoic acid to achieve a contact angle of 162°.

Ishizaki et al. (2011) [66] developed a superhydrophobic, anti-corrosive, and mechanically durable magnesium alloy. The surface was first immersed in a solution of cerium nitrate hexahydrate. Then the magnesium alloy was again immersed in a solution of fluoroalkylsilane and tetrakis(trimethylsiloxy)titanium, which increased the contact angle to 152°. Escobar et al. (2014) [67] immersed an aluminum surface in a solution of HCl and lauric acid that changed the wettability to superhydrophobic with a contact angle of 153°. Wang et al. (2015) [68] fabricated an anti-corrosive, UV-resistant, and anti-icing coating for steel surfaces. The surface

was first chemically etched to get the desired roughness. Further, the surface energy was lowered by immersing the sample in a solution of *1H,1H,2H,2H*-perfluorodecyltriethoxysilane which made the surface superhydrophobic. Besides this, the coated surface also exhibited excellent mechanical abrasion resistance. Song et al. (2012) [69] immersed the aluminum on copper chloride solution for chemical etching the surface based on chemical substitution reaction. The etched surface was then immersed in tridecafluorooctyltriethoxysilane that increased the contact angle to 164° . Wang et al. (2010) [70] fabricated an anti-corrosive superhydrophobic magnesium surface by chemical etching with sulfuric acid followed by immersion in stearic acid. The structure after etching showed a flowerlike structure with contact angle of 154° .

4 Conclusions

This chapter reviewed the fabrication process of superhydrophobic metal surfaces and their properties and applications. It also discussed different long-term problems associated with metal surfaces such as corrosion, icing, the reason behind these problems, and different traditional methods used to overcome these problems and their limitations. The chapter also provided information about the superhydrophobicity, different models associated with it, and the factors that are essential for development of artificial superhydrophobic metal surfaces. Lastly, a brief discussion was provided about the various techniques that have been reported for the synthesis of superhydrophobic metal surfaces and their unique properties in multiple fields. Although several techniques are available for developing superhydrophobic coatings on metallic surfaces, they are not systematically accepted as few of them are inexpensive but tedious and some of them are simple but costly. Therefore, development of superhydrophobicity on metallic bodies is still a challenge. Improvement in superoleophobic metallic surfaces can enhance their industrial applications.

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Extreme Wetting Properties of Liquid Metal



Lei Wang and Jing Liu

1 Introduction

Gallium–indium (GaIn)-based liquid metal (LM), an attractive metal material with high electrical conductivity (GaIn₁₀, 3.4×10^6 S/m) and flow state at room temperature, has shown a significant promise for applications in soft robot, flexible electronics, cooling system, and so on [1–8]. As a novel liquid material, GaIn-based LM is characterized with higher density of ~ 6.9 g/cm³ (ten times of water) and larger surface tension of ~ 0.72 N/m (ten times of water) [9–12]. Due to the high density and easily oxidized properties of LM, it always stays in fixed shape and is hard to move briskly unless in solution system [13, 14]. For an example in the alkaline solution, the oxidation film on the LM surface is fast removed by the solution, and the fresh surface is exposed [15–17]. Without the limitation of solid oxidation film, the surface tension is increased. It induces the LM droplet in a quasi-spherical shape, and reduces the contact area between LM and solid surface, resulting in the decrease of drag [18–20]. With the assistance of surface tension gradient and other relative factors, the LM realizes self-motive in solution system like soft robot [21–25].

As a novel metal alloy with good conductor of electric current, LM has potential applications in soft electronic fields. But, due to the larger surface tension, LM hardly penetrates into the valley of the roughness topography of solid surface and wets the surface unless with the help of external factors. There are two methods to deal with this issue, i.e., lower the surface tension of LM for increasing the contact angle hysteresis, and enhance the wettability of solid bases. Researchers have figured out that the surface tension of LM could be lowered by doped magnetic metal particles, oxidation, direct current, and so on [26–28]. After those treatments, the LM could smoothly be written on some solid surfaces.

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2 Wettability of LM in Solution

GaIn-based LM is a kind of active alloy, whose outer surface is very easily oxidized at room temperature [29]. Just like sodium it is usually stored in the kerosene. To keep fresh surface, the LM must be preserved in a vacuum environment or in liquid solution for preventing oxidation. Alkaline solution could effectively remove the oxidation layer and keep the LM surface clean. With fresh surface, the LM performs with stable surface tension and flow condition, which offers it many functions like soft robot. The activity of GaIn-based liquid metal is very strong in alkaline, especially when it swallows aluminum. Zhang et al. find that aluminum flake as the fuel could drive the LM droplet run for a long time in alkaline solution [23]. Yuan et al. use the LM equipped with aluminum as a copper wire driver and realized the repeated movement [19]. In Wang's study, LM equipped with Fe nano-particles have been transferred from liquid state into the solid porous state due to its photore-sponse [30]. There are many interesting findings of LM in alkaline solution.

2.1 *Dynamic Hydrogen Generation*

Aluminum easily reacts with water and generates hydrogen due to its active property [31–33]. But this reaction is not always happening at nature. The passive oxide film on the Al surface plays a significant role for the continuous reaction. Gallium and indium alloy equipped with Al enhances the reaction between Al and water solution. In this complex system, the Al acting as fuel is used to generate hydrogen. The gallium-based LM performs good wettability with Al; it easily adheres on the Al surface and penetrates into the valley of the roughness topography of Al surface. The passive oxide film on Al surface is fast removed by the gallium, which promotes the reaction between Al and water solution. The quickly generated hydrogen changes the wettability of LM and generates powerful interaction on LM, inducing the self-motion of LM in solution [34].

2.2 *Self-Powered Motor*

Creatures of nature could not survive without energy. This special energy is always obtained by food. The GaIn-based LM equipped with Al could generate amount of hydrogen in a short time, which enhances interaction on LM. In Zhang's work, she discovered a self-propulsion mechanism of dynamic motors based on liquid metal [23]. In this system, feeding the LM with aluminum could induce the LM moving freely for a long term without any assistance of external energy in alkaline solution due to the surface tension gradient and H_2 propulsion performance [35, 36].

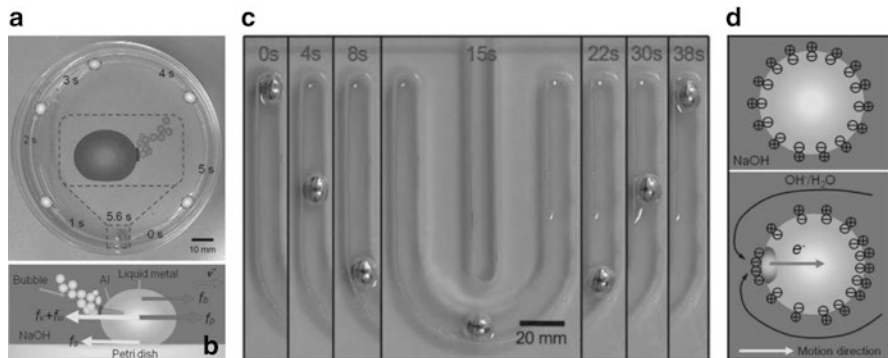


Fig. 1 Self-fueled LM motor running in a circular petri dish (a). (b) The sketch of driving force acting on the LM droplet. (c) LM runs in a circular channel. (d) Schematic of the electromigration and EDL alteration on LM. Reprinted with permission from Reference [23], Copyright (John Wiley & Sons, Inc.)

LM with volume of 60 μL swims autonomously in a circular petri dish containing NaOH solution (Fig. 1A-C). After adding LM with aluminum flake, the LM motor begins to swim with larger speed, accompanied by the generation of H_2 bubbles. Aluminum is split into pieces with smaller size, which accelerates the reaction with alkaline solution and H_2 production. The bubble recoil is one of the significant factors for driving the LM motion in solution. However, in the following work, researches find that the force from the bubble recoil is insufficient to drive the LM motion. There must be another more significant role for collaboratively promoting this function.

Another significant factor for improving the LM motion is surface tension gradient on LM surface, which is generated by the bipolar electrochemical reaction. The LM/aluminum system generates a galvanic cell. LM is anode, and aluminum works as the cathode in NaOH solution. In equilibrium state, Ga reacts with the alkali and generates $[\text{Ga}(\text{OH})_4]^-$, which induces the surface gallium negatively charged and cations accumulated. The electrical double layer diffuses uniformly on the LM surface (Fig. 1D). According to Lippmann's theory, the surface tension could be controlled by the potential difference across the electrical double layer [37–40]. The relationship of the two factors is characterized as

$$\gamma = \gamma_0 - \frac{1}{2} c V^2 \quad (1)$$

where γ is the surface tension, γ_0 is the maximum surface tension when $V = 0$. c is the capacitance of electrical double layer per unit area, and V is the potential difference across the electrical double layer.

The electrons transporting internally from aluminum to LM preferentially deoxidize the oxidized gallium neighboring aluminum, resulting in altering the distribution of charges across electrical double layer, which induces the potential gradient

along LM surface and asymmetric surface tension on LM surface. The smaller potential difference induces the larger surface tension. The surface tension at the rear is lower than that at the head region of LM droplet. According to Young-Laplace equation, the pressure difference p across the alkaline solution and LM can be expressed as $= \gamma \times \frac{2}{r}$, where $\frac{1}{r}$ represents the curvature of LM. The pressure difference between the head and rear of LM is formed, which realizes the LM droplet motion toward the head in alkaline solution.

3 Dynamic Motion of LM in Atmosphere Environment

Liquid metal is easily oxidized when it is exposed in atmosphere environment. The solid oxide layer decreases the flexibility of LM and limits its motion. For an example, the LM droplet could not rebound and detach from the surface after impact on the solid surface. The surface tension could not help the LM recover to its initial state due to the oxide layer and high density, resulting in rebound hysteresis. The larger surface tension and oxide layer of LM also limit its spreading behaviors on solid surface. Considering the unskillful actions of LM in the air condition, subsidiary factors are becoming more and more significant for improving the activity of LM. In our study, topography design and electricity are used to activate the motion of LM droplet as external factors.

3.1 *Dynamic Motion of LM on Flexible Needle Forest*

On the liquid-repellent surfaces such as natural lotus leaf, water droplet could easily rebound and detach from the surface due to the special topography of lotus leaf and wax coating, which has attracted much attention in recent years. As for water droplet, the larger surface tension and its lower density are the key issues for realizing the motion process. The liquid droplet can move far away without much energy loss by friction and hysteresis in the liquid/solid interfacial section [41–43]. A series of superhydrophobic surfaces have been successfully fabricated through enhancing the roughness and coating with low surface energy materials, who realize the droplet rebound off the surface after finishing the impacting process [44, 45]. Wang's and Yeomans' group studied the droplet motion on the superhydrophobic surface with details of the impact time and the rebound shape of droplet disclosed [46–48]. The theoretical studies about liquid water motions on superhydrophobic surfaces are very rich, while, as a kind of newly emerging functional liquid, the dynamic motions of liquid metal on repellent surfaces have not been discussed in details so far. In fact, the impact of liquid metal droplet on different surfaces has recently been found extremely important for a wide variety of practices such as material processing and characterization, flow driving, printed electronics, 3D additive manufacture, etc.

Liquid metal is characterized as having high conductivity and heat transfer efficiency and being fluidic at room temperature, which indicate its promising values in printed electronics and heat transfer fields [49]. $\text{Ga}_{90}\text{In}_{10}$ is one of the typical eutectic alloys; particularly its flow characteristic in room temperature enlarges the application in cooling system, while LM is easily oxidized when it is exposed to the atmosphere environment and the surface will be covered with oxide, which would result in bad flow regime and the decrease of electrical/thermal conductivity. Overall, the LM is hard to be driven in a long term when working outdoors and under atmospheric environment or on ambient solid surface. For dealing with this issue, Kim et al. made HCL-vapor-treated Galinstan droplet rebound on the Teflon-coated glass surface [50]. In this system, the component of LM had been changed. It is hard to realize untreated LM droplet rebounding and detaching from the solid surface. So, finding a new method to overcome this problem has become urgent.

Learning from nature, there is an energy conversion in the processes of falling droplet impacting on lotus leaf. The rain droplets with high speed impact the lotus leaf surface; its kinetic energy is almost transferred into the elastic energy of the leaf, which not only prevents the ruin of self-cleaning performance but also decreases the energy loss of droplets. Furthermore, the droplets rebound and detach from the leaf surface. The elastic energy of the leaf is transferred back to the kinetic energy of droplets [42, 51]. Inspired by that, a special flexible microstructure is designed, and the nano-particles are applied for reducing the adhesion force between solid and liquid interfaces. To date, the influence of LM on micro-/nanostructured needles has either been poorly studied or it has not been thoroughly examined. If the impact of LM on micro-/nanostructured needles is thoroughly determined, it may result in new discoveries and technology development in the area. As the earliest trial, we adopted here mainly the bare LM droplet with volume of $5\ \mu\text{L}$ to impact the designed surfaces. During the impacting process, the kinetic energy of LM transfers into the elastic energy of bent flexible needles (Fig. 2). After that, the LM droplet is driven to rebound and detach from the surface with the help of the stored elastic energy.

Under loading, the flexible needles (made by PDMS) are easily deformed. After release of the loading, the bent needles recover to initial state. It illustrates the

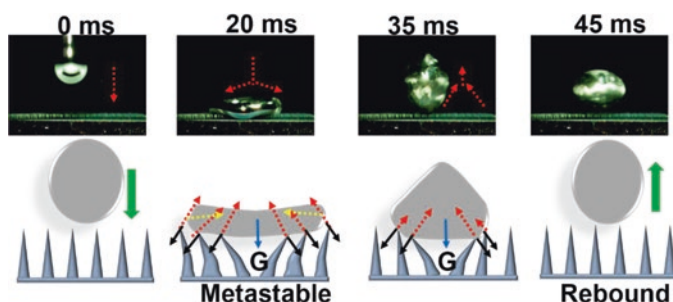


Fig. 2 The LM droplet rebounds and detaches from the surface after impact on the flexible needle forest. (Reprinted with permission from Ref. [42], Copyright (John Wiley & Sons, Inc.))

sensitive property of flexible topography. In this system, the elastic energy (Γ) contribution of PDMS needle to the droplets can be described by the following equation [52]:

$$\Gamma \propto \frac{\sqrt{K_{PDMS}}}{\sqrt{h}} = \frac{\sqrt{K_{PDMS}}}{\sqrt{h_0} \times \cos \theta} \quad (2)$$

where K_{PDMS} represents the elastic modulus of PDMS needles, h is the distance between the basement and air-LM interface (the vertical height of the bent needle), h_0 is the initial height of needle, and θ is the bending angle of needle. It indicates that the larger θ would induce the larger Γ .

During the impacting process, LM droplet bends the micro needles. Much energy is transferred into the elastic energy of flexible needles. Meanwhile, the bent needles resist the spread of LM in the impacting process. It decreases the energy loss in the spreading process.

In this research, we have investigated the LM droplet rebound motion on repellent flexible micro-/nanostructured surface. The surface is composed of flexible needles and carbon nano-particles. In this system, the flexible needles are applied to store the kinetic energy of LM. And the carbon nano-particles are used to lower the adhesion and contact angle hysteresis, which reduce the energy loss during the motions. The results indicate that the flexible needles could store elastic energy in the impacting process and release energy to drive the LM droplet to rebound and detach from the surface in their recovery process. In this technology, elastic energy is first applied in LM driving, and the LM droplet is successfully driven off without any modification, which suggests a new method for efficient driving of larger-density liquid materials.

3.2 Electric Wettability of LM

In electronic field, the conductivity is essential for applications. Along with science and technology advancement, soft electronic devices have also become more and more accustomed to our life. As electron-transporting materials, electronic wires play significant role for this field. In flexible electronics, solid metal wire could not meet the demand of flexibility, low heat generation, and high conductivity. LM could not perform as exclusive subject to realize multi-functions due to its unfixed forms.

In Liu's research, they find an ultra-compliant LM electrode that could transform with the electricity [53]. The LM shape is controlled by regulating direct current (DC). Figure 3 shows the forms of LM before and after the stimulation of DC. The spreading area is 3.6 times of the initial state. With the stimulation of DC, the LM overcomes the larger surface tension and spread into maximum. The extended

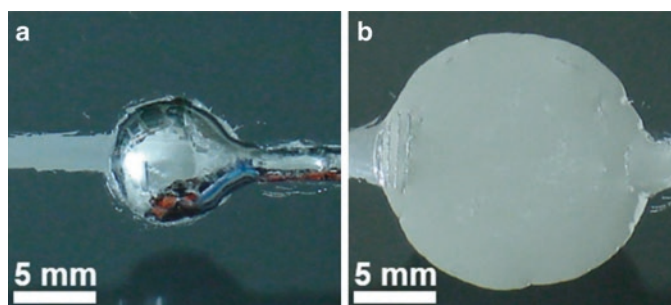


Fig. 3 The shape of LM electrode before (a) and after (b) the switch of DC voltage. With the stimulation of 3.5 kV DC voltage, the extended spreading area is 3.6 of initial state. (Reprinted with permission from Ref. [53], Copyright (AIP Publishing))

contact area effectively enhances the wettability of LM on the base. This research has potential applications for LM printing electronics.

4 Soft Electronics

Liquid metal with high electrical conductivity and flexibility at room temperature has been introduced into the printed electronics. But, due to the lower adhesion and larger surface tension of LM, it is hard to be printed on some surfaces, which limits its application in the electronic fields. In recent study, the GaIn-based LM has been successfully printed and written on various materials surfaces by three methods, i.e., controlling the wettability of substrate materials, adjusting the surface tension of LM, and using suitable buffer materials.

4.1 Surface Composition and Roughness

Paper-based electronic devices with excellent flexibility and low cost have aroused much attention of researchers. But LM with surface tension ten times larger than water is hard to write or print on solid surface. In order to solve this problem, buffer materials are applied to change the wettability of LM on the base.

Liquid metal (GaIn10) shows good wettability with polyvinyl chloride (Fig. 4A-B), but on the dry paper, it shows Cassie's state (Fig. 4C-D) [12, 54]. Due to the larger surface tension, the droplet shrinks into a sphere state. Paper and LM are both easily wetted by water. On the wetted paper surface, with the help of water in paper, the wettability of LM on paper is changed. It transfers from Cassie's state into Wenzel's state. The results reveal that as the wetting time increases, the LM droplet is hard to detach from the surface. After treated in humidity environment for 3 s, LM

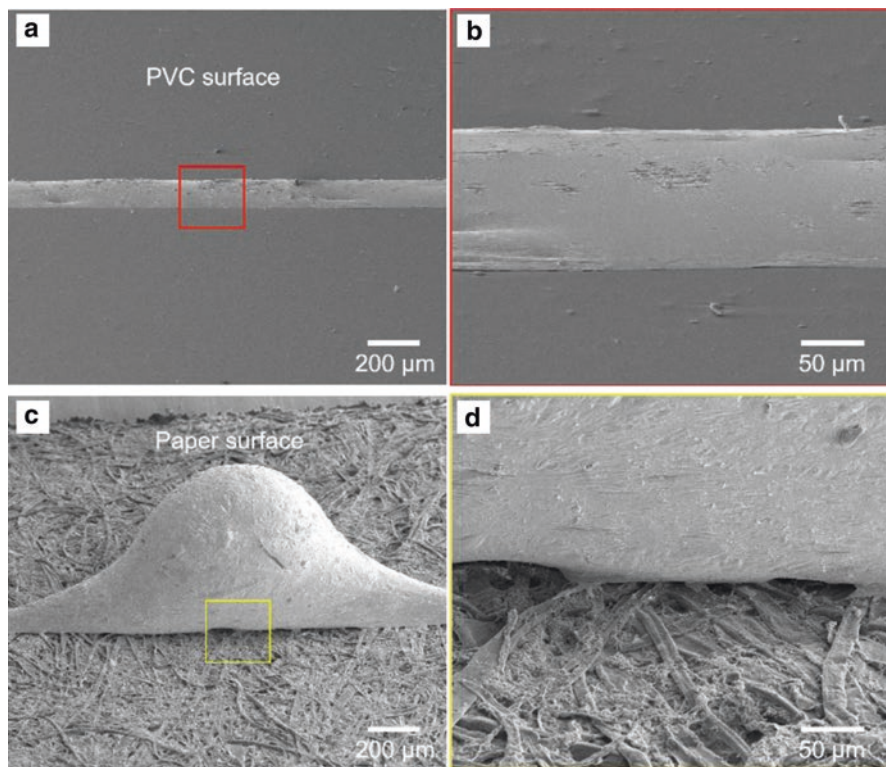


Fig. 4 The liquid metal line on the PVC surface (a–b) and paper surface (c–d). The PVC surface is wetted by LM (Wenzel's state). The paper surface could not be wetted by LM (Cassie's state). (Reprinted with permission from Ref. [12], Copyright (Elsevier))

could not detach from the surface due to larger adhesion. The liquid metal is torn with the force larger than 790 μN. According to the equation

$$F_{AF} = 2\sigma_{LM} \times L \quad (3)$$

where F_{AF} is the adhesion force between LM and paper, σ_{LM} is the interfacial tension force, and L is the length of three-phase contact line (TCL), respectively. As the wetting time increases, the wettability of LM on paper is enhanced. As a result, the TCL gets longer. F_{LM} is the surface tension of LM. On dry paper surface, $F_{AF} < F_{LM}$. As the L increases, F_{AF} becomes larger than F_{LM} . On that kind of wetted paper surface, LM electronic circuitry is smoothly written.

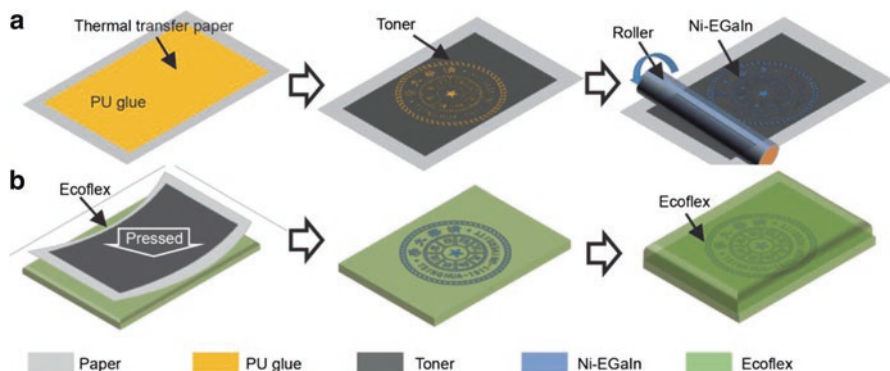


Fig. 5 The schematic diagram of semi-liquid metal rolling and transfer printing method. (Reprinted with permission from Ref. [55], Copyright (Springer Nature))

4.2 Bonding by Glue Buffer Materials

GaIn-based LM with good conductivity has potential application in electro printing fields. But its large surface tension (about ten times of water) limited its further application. The bare LM could not wet most of materials surface except PVC. For an example, the LM droplet keeps in sphere state on paper surface with larger contact angle and small adhesion force. After printing on the paper, the spread LM film shrinks and induces the destruction of whole circuit. Considering the bad wettability of LM on the base materials, finding a novel material that shows good wettability both with LM and the base materials has become more and more significant.

Guo et al. found a new way for dealing with the problem of the poor adhesion between LM and the base. Polyurethane (PU) glue as a kind of material with large viscosity shows good adhesion with many materials (Fig. 5) [55]. They use PU as the buffer material to overcome the bad wettability between LM and the base materials. The paper surface after modified by PU glue, the LM could easily be printed on the surface. This research provides a new way for fast and low-cost printing LM with electrical functions.

4.3 Control the Wettability by Oxidation

Due to the larger surface tension, LM could hardly be written directly on some surfaces, for example, on the paper surface. LM could hardly wet the paper surface. It easily shrinks and detaches from the surface, which limits the application in electronic circuit. Considering the bad wettability of LM on the substrate surfaces, finding an effective method that could lower the surface tension of LM has become one of the best solutions for this problem. In Gao's study, the surface tension and wettability of LM on paper surface was adjusted by the oxidation degree. The LM

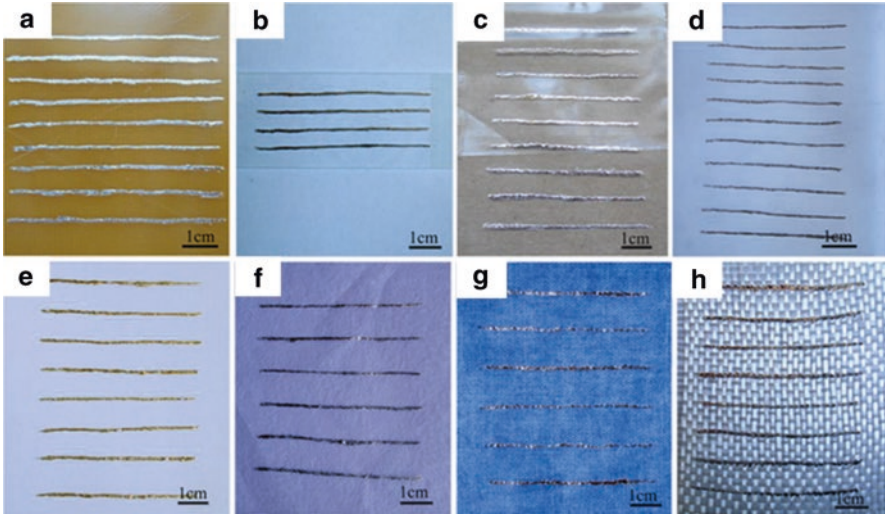


Fig. 6 Wettability of LM wire on different substrate materials. Epoxy resin board (a), glass (b), plastic (c), silica gel plate (d), typing paper (e), cotton paper (f), cotton cloth (g), and glass fiber cloth (h). (Reprinted with permission from Ref. [26], Copyright (Yunxia Gao))

(GaIn10) composed of 0.026 wt.% oxygen could easily be printed and written on many soft or rigid materials owing to its well-controllable wettability [26]. The increase of oxygen content in LM induces the decrease of surface tension, which directly increases the length of TCL. Based on Eq. 3, the oxidation decreases the surface tension of LM, resulting in the better wettability of LM on the solid surfaces. Figure 6 shows the performance of the LM electronic wires on different substrate materials.

After treated by oxidation reaction, the GaIn10-based LM is easily written on paper using brush and other relative tools. Various patterns could be smoothly drawn on flexible bases. In this experiment, the researchers find a novel way for writing LM electric topography directly on different substrates, which reduces the cost for electronics industry.

4.4 Control the Wettability by Doping Foreign Metal

Large surface tension of liquid is not good for printing due to its larger surface tension. The printing ink could not penetrate into the valley of the base and perform low adhesion, which limits the application in the electrical printing field. In recent study, we find that the wettability of LM could be adjusted by the acid solution, alkaline solution, oxidation, and buffer materials. Guo et al. found a new way to deal with this problem: doping foreign metal (Fig. 7A) [56–58]. They mix foreign Ni into the EGaIn. After that, the LM transforms from liquid state into semisolid state

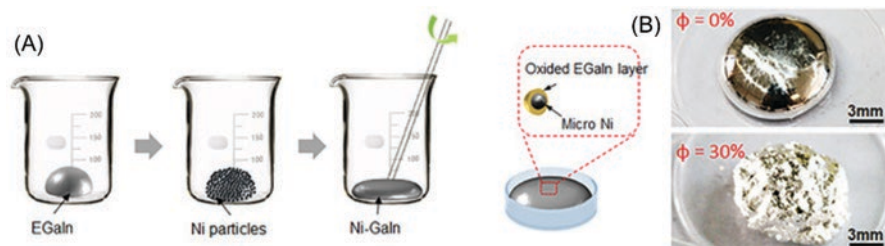


Fig. 7 The preparation process of Ni-GaIn amalgam. (Reprinted with permission from Ref. [56], Copyright (John Wiley & Sons, Inc.))

(Fig. 7B). This method could fast decrease the surface tension of LM and realize smooth writing and printing on paper surface.

LM is characterized with large surface tension, which is a bad role for printing electronic system. In this system, the methods for dealing with this problem are discussed. Researchers realize the LM printing by oxidation, foreign metal doping, and using buffer materials.

5 Conclusions

Liquid metal as a kind of liquid and special metal alloy has many functions in soft robot and printing electronic system. As a raw material, it could not realize capabilities without the external stimulation. Inspired by its special wettability, LM droplet is driven in solution and transforms in atmosphere environment. For realizing printing electronic, its wettability is changed, and the form is transferred from liquid state into semisolid state by oxidation, foreign metal doping, using buffer materials, and so on, which is easily printed on various base materials surfaces. By adjusting the wettability, LM could realize many more other special functions.

Acknowledgments This work is supported by the National Natural Science Foundation of China (No. 21805294).

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Superhydrophobic and Self-Cleaning Coatings for the Protection of the Cultural Heritage: A Case Study Using TiO₂ Nanoparticles



Ioannis Karapanagiotis, Ioannis Poullos, Aikaterini Chatzigrigoriou, and Tobin Kopp

1 Superhydrophobicity and Contact Angle Measurements

Rough surfaces with extreme wetting properties, which originate from structural features at the micro-/nanometer length scale, are found widely in nature. The most famous natural superhydrophobic surfaces are the lotus leaf [1] and the rose petal [2]. Another example from nature is provided in Fig. 1 which shows the superhydrophobic properties of the leaf of young fustic (*Cotinus coggygria* Scop.) [3]. It is interesting to note that the wood of young fustic has been a source to dye textiles since antiquity [4].

Superhydrophobic surfaces have been recognized since the beginning of the twentieth century [5], whereas the relative theoretical fundamentals were established in the middle of the same century [6, 7]. However, at that time, it was very hard, if not impossible, to control and manipulate the matter at the nanometer scale, and therefore superhydrophobic surfaces could not be fabricated for practical applications. With the development of nanotechnology in the late twentieth century, several strategies have been developed to produce surfaces with extreme wetting properties ranging from superhydrophilicity to superhydrophobicity, as described in several review papers [8–12].

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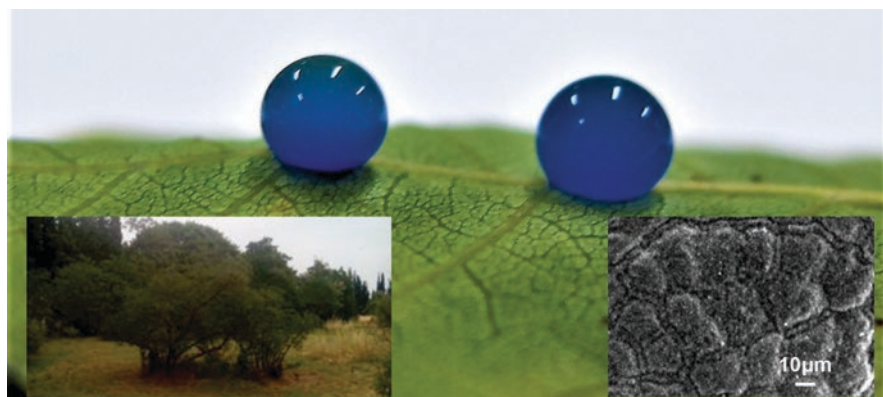


Fig. 1 Colored water drops on the superhydrophobic leaf of *Cotinus coggygia* Scop. The tree in the forest botanic garden of the Aristotle University of Thessaloniki, Greece, is shown in the photograph (left). The structure of the surface of the leaf is revealed in the SEM image (right)

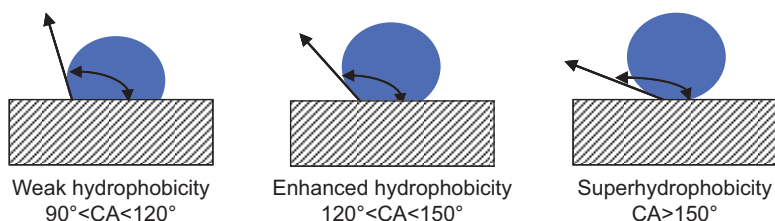


Fig. 2 Hydrophobic regimes

The static contact angle (CA), determined by the equilibrium shape of a resting drop of water on a solid, is one of the common ways to evaluate the wetting properties of the solid surface. According to typical definitions [13], surfaces with $CA < 90^\circ$ are hydrophilic, whereas surfaces with $CA > 90^\circ$ are hydrophobic. Recently, however, it was suggested that a lower CA ($\sim 65^\circ$) is more effective to divide the hydrophilic and hydrophobic solid surfaces, considering that long-range attractive forces are detected only between surfaces exhibiting a water CA $> 65^\circ$ [14, 15]. Following the typical definition, hydrophobicity is divided in Fig. 2 to smaller wetting regimes as follows: weak hydrophobicity, enhanced hydrophobicity, and superhydrophobicity corresponding to $90^\circ < CA < 120^\circ$, $120^\circ < CA < 150^\circ$ and $CA > 150^\circ$, respectively.

CA is determined by two parameters: (i) the intermolecular interactions between the molecules of the water drop and the solid surface and (ii) the morphology of the solid surface. The Young contact angle (CA_Y), which is used to define the inherent wetting properties of a surface, is influenced exclusively by the intermolecular interactions, as it is measured on an atomically smooth and passive surface. Consequently, CA_Y is assessed only by the chemical nature of the solid, provided that the chemical natures of the liquid (water) and vapor (air) are fixed. It is possible to fabricate

smooth surfaces of enhanced hydrophobicity. However, to achieve superhydrophobicity, it is necessary to have a contribution from the surface morphology to the measured (apparent) CA. On a theoretical basis, the significant role of surface morphology, and therefore roughness, in wetting phenomena was recognized first by Wenzel [6] and later by Cassie and Baxter [7]. For inherent hydrophobic surfaces ($CA_Y > 90^\circ$), superhydrophobicity is predicted by both models. However, only the Cassie-Baxter state is non-sticking corresponding to the famous lotus effect (bouncing drops), as a Wenzel drop interacts with many defects [16]. In the Cassie-Baxter scenario, air is trapped between the drop and the surface pores of the surface. Therefore, the drop only contacts the solid through the top of the surface asperities, on a fraction that is usually denoted as f_s . Because the drop is in contact with a small fraction (f_s) of the actual surface, friction is minimized, and motion of the drop on the surface becomes easy (non-sticking surface). As most of the superhydrophobic surfaces are non-sticking, the Cassie-Baxter model is most commonly used in the current literature:

$$\cos CA = 1 + f_s (\cos CA_Y + 1) \quad (1)$$

Figure 3 shows the variation of f_s with CA_Y according to Eq. 1 for two surfaces with $CA = 120^\circ$ and $CA = 150^\circ$. The CA_Y ranges from 90° (inherent hydrophobicity) up to 120° which is roughly the maximum contact angle that can be practically achieved on a smooth surface of very low surface energy (e.g., Teflon). The hydrophobic regimes which were defined in Fig. 2 are assigned in Fig. 3. The latter demonstrates that in order to enhance hydrophobicity, f_s has to be reduced, i.e., surface roughness must increase.

According to the above, there is a clear relation between CA and the morphology (i.e., roughness) of a solid surface. It should be stressed that surface roughness and f_s can be experimentally measured with confidence on micro-patterned surfaces with protrusions which have well-defined geometries [17] (e.g., squared pillars as shown in Fig. 3). On the contrary, roughness measurements of surfaces which

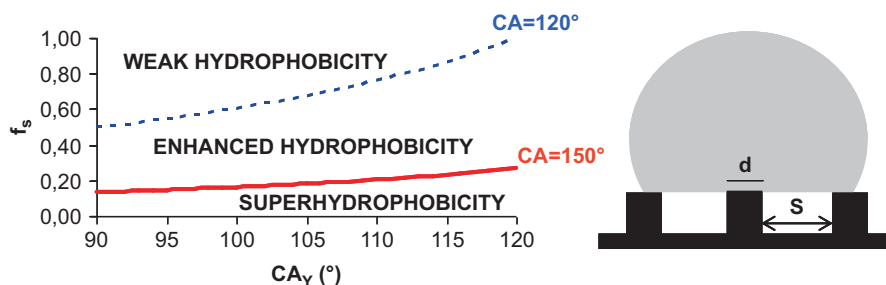


Fig. 3 The three regimes of hydrophobicity of Fig. 2 are assigned in the plot which was constructed using Eq. 1 (left). The Cassie-Baxter scenario where a water drop sits on a “composite” surface of air and solid is shown (right). For the patterned surface which is composed of squared pillars with side length d and separation distance S , f_s is as follows: $f_s = d^2 / (d + S)^2$

exhibit randomly distributed surface structures can be elusive, as the reported results are affected by the area which is selected for the measurement and, moreover, by the size of the selected area. For surfaces which are randomly rough, different areas and different area sizes lead to different roughness values. Consequently, roughness measurements which are commonly carried out by atomic force microscopy on randomly rough surfaces and are used in the literature to estimate the f_s parameter of Eq. 1 should be carefully considered.

From a technical point of view, the measurement of the CA of a water drop on a smooth solid surface is an easy process using a modern optical system equipped with a camera and software. The drop is placed on the surface, the drop image is acquired by the camera, and the drop shape is determined by the software. Gravitational effects are negligible provided that a small drop volume is used. Drops with volumes less than 10 μL are typically used. For the 10 μL volume, a nominal radius of 1.3 mm is calculated which is much lower than the capillary length l_c of water (2.7 mm). Consequently, the Bond number (Bo) which is given by $Bo = (R/l_c)^2$ is clearly <1 , and therefore surface tension forces dominate over the gravitational forces [18]. For drops on superhydrophobic square pillar surfaces, it was shown that the experimentally measured CA remained unchanged for drop volumes ranging from 0.5 to 19 μL [19]. The key point for a reliable measurement is to determine accurately the drop profile and the contact line of the drop with the surface. This process is sometimes difficult to execute with confidence on superhydrophobic surfaces. In particular, for non-reflective or macroscopically rough surfaces (e.g., textiles), it may be hard to resolve the contact line. Slight shifts of the substrate baseline during image processing may lead to a high deviation of the determined CA [20].

Nature shows that the evaluation of dynamic wetting properties is extremely important for a meaningful characterization of the wetting properties of a solid surface. The CAs of drops on lotus leaves and rose petals exceed 150° [1, 2]. Therefore, both natural surfaces exhibit superhydrophobicity. However, while drops easily roll off a lotus leaf [1], they are pinned on the surface of rose petal [2] implying high drop repellency and adhesion, respectively. Consequently, overall the wettabilities of the two plant surfaces are different and this is illustrated by the dynamic contact angles which are described next. The advancing contact angle (ACA) and the receding contact angle (RCA) are related to the force (F) needed to start a drop moving over a solid surface [21]. In particular, small contact angle hysteresis (CAH), defined as the difference of ACA and RCA, corresponds to small F . Consequently, small CAH implies that a water drop moves easily on the surface [22], which is therefore considered as a water-repellent surface (lotus leaf effect). When this surface is slightly tilted, the drop rolls off thus corresponding to a small sliding angle (SA). In contrast, when the water drop is pinned on a solid surface, then large CAH and SA are measured (rose petal effect).

Another process which is useful to characterize the wetting properties of a solid surface is the evaporation of a water drop from the solid surface of interest. It is of particular importance to measure the CA and the area of contact between the water drop and the solid surface during drop evaporation. Two distinct modes have been

described in the literature for the evaporation of a drop on a superhydrophobic surface [23, 24]: (i) the constant contact area mode, where the drop is pinned and is accompanied by a gradual decrease of CA during evaporation and (ii) the constant contact angle mode, where a gradual decrease of the drop-surface contact area is recorded. Water drop evaporation on typical superhydrophobic and water-repellent surfaces is usually dominated at the initial evaporation stages by the constant contact area mode, whereas at later evaporation stages, a transition to the constant contact angle mode is observed [23, 24]. The water drop's evaporation on a typical superhydrophobic and water adhesive surface (e.g., rose petal) is dominated exclusively by the constant contact area mode [25, 26]. This is because the water drop is pinned on the petal-like surface.

Figure 4 shows the results of the evaporation of a water drop on a surface which was prepared using a silane/siloxane commercial product (Silres BS290) and silica (SiO_2) nanoparticles. The latter were added to enhance the surface roughness and therefore the hydrophobic character of the resulting film [27]. The polysiloxane- SiO_2 film was deposited on glass support. A water drop was placed on the film surface, and the evaporation process of the drop was monitored. As shown in Fig. 4, the polysiloxane- SiO_2 surface exhibits superhydrophobicity, as right after ($t_{\text{evap}} = 0$) the deposition of the drop on the surface CA was $>150^\circ$. The evaporation process is dominated exclusively by the constant contact area mode implying that the drop is pinned on the surface. Consequently, the produced coating does not exhibit water repellency, which is a highly desirable property in many applications.

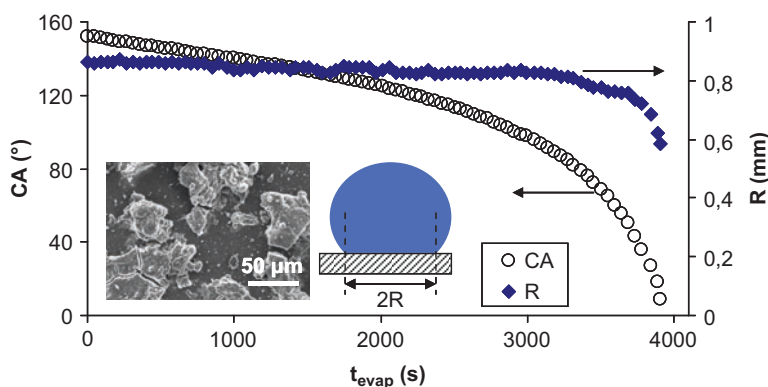


Fig. 4 Contact angle (CA) and contact radius (R) of a water drop on a polysiloxane-nanoparticle surface versus evaporation time (t_{evap}). Evaporation is dominated by the constant contact area mode: R remains constant with t_{evap} until the very last stages of the evaporation process; CA decreases with t_{evap} . The radius R is defined in the scheme. The SEM image reveals the enhanced roughness of the polysiloxane-nanoparticle surface. (Adapted with permission from [27], Copyright Elsevier)

2 Photocatalysis and Self-Cleaning

Semiconductor photoelectrochemistry and heterogeneous photocatalysis, two closely related fields, have been involved during the past decades in the movement toward a green, sustainable future. These efforts have included topics such as environmental protection, self-cleaning materials and surfaces, hydrogen or electric power production, CO₂ reduction, and chemicals synthesis [28, 29] to name a few.

Semiconducting materials mediating photocatalytic oxidation of organic or inorganic compounds can be an alternative to conventional methods for the removal of organic pollutants from water and air [30–32]. The illumination of these materials with light energy greater than the band gap energy of the semiconductor ($h\nu > E_g$) produces excited high energy electron and hole pairs (e^-/h^+) that can migrate to the surface of the semiconductor, where the holes as well as the electrons act as powerful oxidants and reductants, respectively (Fig. 5).

A variety of semiconducting powders (oxides, sulfides, etc.) acting as photocatalysts have been used. Most attention has been given to titanium dioxide (TiO₂) which is an excellent photocatalyst with applications in various fields. The main advantages of TiO₂ are its resistance to corrosion and photocorrosion, its biological immunity, its relatively low cost, and its highly oxidizing power, which make it a competitive candidate for many photocatalytical applications [33]. The highly oxidizing effect of TiO₂ under UV-A or solar light makes it suitable for the decomposition of organic and inorganic compounds at very low concentrations ranging from 0.01 to 10 ppm. The photocatalytic effect of TiO₂ can also be used for self-cleaning of surfaces, for decomposing atmospheric organic or inorganic pollutants or for self-sterilization. Studies involving photocatalytic inactivation of microorganisms are also of major interest because of the possible applications in water and air disinfection [34–37]. According to the literature, OH[•] radicals can act as strong biocides, due to their high potential of oxidation and their non-selective reactivity.

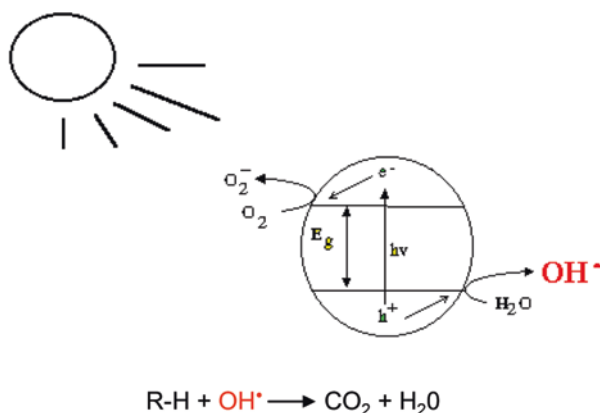
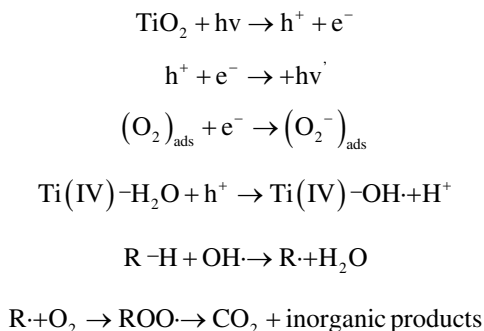


Fig. 5 Schematic illustration of the formation, onto a semiconductor surface, photogenerated holes and electrons, upon ultraviolet UV-A illumination

General description of heterogeneous photocatalysis under artificial or solar irradiation is presented in several excellent review articles and books [28, 33, 38, 39]. A brief summary is presented here only for the sake of completeness. It is well established that by the irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor ($E_g > 3.2 \text{ eV}$), conduction band electrons (e^-) and valence band holes (h^+) are generated. Part of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons, act as powerful oxidants and reductants, respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti(III) -sites, reducing it to the superoxide radical anion $\text{O}_2^{\cdot-}$, while the photogenerated holes can oxidize either the organic molecules directly or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $\text{OH}^\cdot$ radicals. These radicals together with other highly oxidant species (e.g., peroxide radicals) are reported to be responsible for the primary oxidizing step in photocatalysis. The $\text{OH}^\cdot$ radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with a standard reduction potential of 2.8 V. As a result, they can easily attack the adsorbed organic or inorganic molecules or those located close to the surface of the catalyst, thus leading finally to their complete oxidation.



Furthermore, the TiO_2 surface, when irradiated with UV light, becomes superhydrophilic with a water contact angle of less than 5° . It was found that the H_2O molecules adsorbed on the TiO_2 surfaces desorb during UV light irradiation by the heating effect of the light source. Since the amount of the H_2O adsorbed on the TiO_2 surfaces decreased, the distribution of the hydrogen bonds within the H_2O molecules decreased, resulting in a decrease in the surface tension of the H_2O clusters. The decrease in the surface tension of H_2O under UV light irradiation was found to be one of the most important driving forces in which the H_2O clusters on the TiO_2 surface spread out, forming H_2O thin layers (Fig. 6). The partial elimination of the hydrocarbons from the TiO_2 surface by the photocatalytic complete oxidation was seen to be the other important factor, providing free spaces on the surface where the H_2O clusters could spill over and spread out to form the thin H_2O layers. Moreover, the temperature changes of the TiO_2 samples during UV light irradiation were found to show a good correspondence with the changes in the contact angle of the H_2O drops on the TiO_2 thin film surfaces [40, 41].

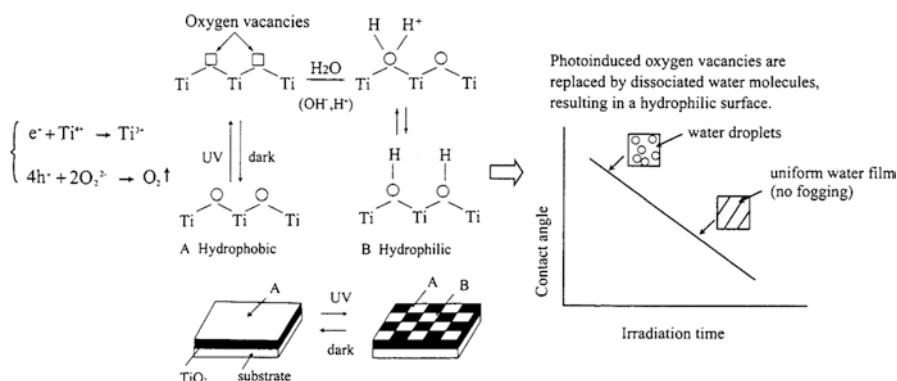


Fig. 6 Mechanism of photo-induced hydrophilicity. (Reprinted with permission from [41], Copyright Elsevier)

Because of its photocatalytic oxidation activity and photo-induced superhydrophilicity, the TiO_2 surface exhibits a self-cleaning property with excellent durability; thus, it has already been used in various industrial items including exterior tiles, glasses, plastic films, and tent materials [40]. Photocatalytic self-cleaning is probably the most widely used nano-function in building construction, with Japan leading the field. There are numerous buildings of all sizes around the world that make use of this function [42]. Its primary effect is that it greatly reduces the extent of dirt adhesion on surfaces. It is important to note that the term “self-cleaning” in this context is misleading and does not mean, as commonly assumed, that a surface need not be cleaned at all. The interval between cleaning cycles can, however, be extended significantly, a fact that is particularly relevant in the context of facility management. Fewer detergents are required, resulting in less environmental pollution and less wear and tear of materials. Likewise, reduced cleaning cycles lead to savings in personnel costs and the fact that the dirt adheres less means that it is also easier to remove.

3 Protection of the Cultural Heritage

3.1 Enhanced Hydrophobicity and Superhydrophobicity for Cultural Heritage Protection

Atmospheric water induces various decay phenomena to the surfaces of the exposed cultural heritage monuments and historical buildings which were made of natural stone. Moreover, water enters through the pore network to the interior of the stone causing further severe damages [43]. The application of hydrophobic conservation materials for surface protection of the stone or for consolidation purposes is necessary to reduce the rate of the water-induced degradation processes, as emphasized

by several review reports [44–53]. Organic polymers and polysiloxanes are usually inherent hydrophobic materials ($CA_Y > 90^\circ$) with good adhesive properties, and therefore they are reasonable choices for stone protection and conservation. In principle, polysiloxanes are advantageous, as they are generated by small molecules of silanes and siloxanes which have the ability to penetrate deep into the stone network, before they become highly viscous gels through the sol-gel process [54]. Moreover, polysiloxanes are more stable and more hydrophobic compared to typical organic polymers [54, 55].

Hydrophobization of a rough natural stone is relatively easy to achieve, as it is practically promoted by the intrinsic surface roughness of the stone. The latter affects the surface roughness of the deposited protective coating which follows the rough structure of the underlying stone substrate [56]. According to Eq. 1, roughness enhances the hydrophobic character of the coating's surface resulting in a CA which is larger than the CA_Y , measured on an atomically smooth surface. For example, CA measurements of water drops on Rhodorsil 224 films which were deposited on substrates with different roughnesses are summarized in Table 1 [44, 57]. Coatings on smooth glass and silicon wafers gave CAs which ranged within 102° – 105° . Spin coating should produce smoother films than spray deposition. Indeed, slightly larger CAs were measured on films prepared by spraying than spin coating, although the differences are almost within the experimental variations. The Rhodorsil film on the rougher marble gave a larger CA ($=108^\circ$), whereas the film on the very rough sandstone gave the largest CA ($=141^\circ$). Finally, it is interesting to note that the variation of the CA measurements in Table 1 increases with surface roughness, as randomly distributed surface instabilities give rise to the actual range of the measured CA.

Surface roughness and therefore hydrophobicity can be further promoted by embedding nanoparticles into the matrix of a polymeric material. Nanoparticles form clusters which enhance the roughness of the polymer surface at the micrometer/nanometer scale leading to enhanced hydrophobicity or even to superhydrophobicity [57]. For example, following this simple approach, SiO_2 nanoparticles (7 nm in mean diameter) were dispersed in a tetraethoxysilane (TEOS)-based product (Remmers KSE-100), and the dispersion was sprayed onto marble [58]. TEOS is widely used in stone consolidation [54, 55]. The CA of a water drop on the surface

Table 1 Contact angle (CA) measurements of water drops on Rhodorsil 224 coatings which were deposited on four substrates. The polysiloxane film was applied on smooth glass and silicon wafers by two techniques: spin coating and spraying. The latter was used to coat marble and sandstone [44, 57]

Substrate	Spin coating	Spraying
Glass	$102^\circ \pm 1^\circ$	$103^\circ \pm 1^\circ$
Silicon wafer	$102^\circ \pm 1^\circ$	$105^\circ \pm 1^\circ$
Marble	–	$108^\circ \pm 2^\circ$
Sandstone	–	$141^\circ \pm 4^\circ$

of the composite coating was 147° [58]. Therefore, by just adding a small amount of SiO_2 nanoparticles into the TEOS-based product, a highly hydrophobic nanocomposite material was produced [58].

Previously published reports which describe methods to impart enhanced hydrophobicity ($120^\circ < \text{CA} < 150^\circ$) or superhydrophobicity ($\text{CA} > 150^\circ$) onto stone surfaces are summarized in Table 2 [59–96]. Polymers and polymer precursors which were used for stone hydrophobization are also described in the table. In most suggested recipes, nanoparticles are included as indicated in the data of Table 2. In particular, SiO_2 and TiO_2 were most often used. Other nanoparticles which are reported in Table 2 are aluminum (Al_2O_3), tin (SnO_2), and zinc (ZnO) oxides and silver (Ag). For reasons which were described above, polysiloxane materials were preferred over typical polymers (e.g., polymethylmethacrylate, PMMA) and other acrylic polymers and copolymers (e.g., Paraloid B72). Finally, treated stones are described in Table 2.

3.2 Photocatalysis and Self-Cleaning for Cultural Heritage Protection

In several reports found in Table 2, photocatalytic nanomaterials were included to produce multifunctional materials which combined self-cleaning and enhanced hydrophobicity or superhydrophobicity. In most reports, TiO_2 was selected [50, 61, 64, 69, 70, 74, 81, 82, 87, 88, 91], but other photocatalysts such as ZnO [69, 80, 95] and Ag [73, 91] were also included in some investigations. It should be noted that these nanomaterials can inhibit the growth of microorganisms, thus inducing antimicrobial/antibacterial properties which can be promoted further by superhydrophobicity. Combining several useful properties in a single material is not an easy task. In some other investigations, enhanced hydrophobicity of conservation materials is not considered as priority, and attention is given only to self-cleaning and antimicrobial/antibacterial properties [97–104].

4 Case Study: A Polysiloxane- TiO_2 Composite Coating for the Protection of Marble

4.1 Experimental

TiO_2 nanoparticles (type P 25) with average diameter of 21 nm were dispersed in a water-based emulsion composed of amino-modified silanes and fluoro-modified siloxanes. The ratio of (silanes+siloxanes)/water in the emulsion was 1:6 (v/v). Several dispersions were prepared with various nanoparticle concentrations, as summarized in Table 3. The dispersions were stirred mechanically and sprayed onto

Table 2 Coating formulations for stone protection which led to enhanced hydrophobicity ($120^\circ < CA < 150^\circ$) and, in some cases, to superhydrophobicity ($CA > 150^\circ$). The latter is indicated in the following reference numbers [59, 60, 61, 64, 66, 68, 69, 72, 74, 77, 80, 81, 82, 83, 84, 85, 91, 96] in the table. Nanoparticle sizes are provided whenever they were reported

Materials for coating production		Treated stone	References
Polymer & polymer precursor	Nanoparticle		
Akeogard P (perfluorinated polyether)	SiO ₂ (7 nm)	Calcium carbonate	[59]
PMMA	SiO ₂ (7 nm)		
Akeogard P (perfluorinated polyether)	SiO ₂ (14 nm)		
PMMA	SiO ₂ (14 nm)		
Rhodorsil 224 (siloxane)	SiO ₂ (7 nm)	Marble (Pentelic, Naxos, Thassos)	[60]
Rhodorsil 224 (siloxane)	SiO ₂ (7 nm)	Sandstone (Opuka, Božanovsky, Hořický)	[61]
Porosil VV plus (siloxane)	SiO ₂ (7 nm)		
Rhodorsil 224 (siloxane)	Al ₂ O ₃ (40–50 nm)		
Porosil VV plus (siloxane)	Al ₂ O ₃ (40–50 nm)		
Rhodorsil 224 (siloxane)	SnO ₂ (22–43 nm)		
Porosil VV plus (siloxane)	SnO ₂ (22–43 nm)		
Rhodorsil 224 (siloxane)	TiO ₂ (5 nm)		
Porosil VV plus (siloxane)	TiO ₂ (5 nm)		
TEOS, PDMS and n-octylamine	–	Biocalcareous stone	[62]
Silres BS290 (silane, siloxane)	–		
Dynasylan 40 (TEOS)	Functionalised SiO ₂ (14 nm)	Limestone, Sandstone, Granite	[63]
Glymo 3-(2,3epoxypropoxy)-polytrimetoxysilane	Functionalised SiO ₂ (14 nm)		
Mixture of silane and siloxane oligomers	TiO ₂ coated SiO ₂	Sandstone	[64]
Fluorinated siloxane oligomers	TiO ₂ coated SiO ₂		
Fluorinated siloxane polymer	TiO ₂ coated SiO ₂		
TEOS (Silres BSOH100), PDMS and n-octylamine	–	Limestone	[65]
Silres BS 4004 (siloxane water soluble resin)	SiO ₂ (7 nm)	Marble, Sandstone, Lime mortar	[66]
Tecnoflon TN (fluoroelastomer)	–	Lecce stone	[67]
TES 40 WN (ethoxysilanes), PDMS and n-octylamine	SiO ₂ (40 nm)	Sandstone	[68]
n-isooctyltriethoxysilane, PDMS and emulsifier	TiO ₂ (15 nm)	Mortar (cement based)	[69]
n-isooctyltriethoxysilane, PDMS and emulsifier	ZnO (20 nm)		
Paraloid B72	SiO ₂ (50 nm)	Marble (Carrara)	[70]
Paraloid B72	SiO ₂ (50 nm) & TiO ₂ (15 nm)		
Baygard RT (fluorocarbon based organosilicate)	–	Calcareous sedimentary rock, Volcanic rock	[71]

(continued)

Table 2 (continued)

Materials for coating production		Treated stone	References
Polymer & polymer precursor	Nanoparticle		
Methyltrimethoxysilane	–	Travertine, Marble (Pentelic), Granite, Sandstone	[72]
n-isooctyltriethoxysilane, PDMS and emulsifier	Ag	Mortar (cement based)	[73]
Alpha®SI30 (trimethoxysilane, PDMS)	TiO ₂ (estimated 20–30 nm)	Marble (Carrara, Botticino), Angera stone	[74]
HEP (silanes, siloxanes, methacrylate)	–	Pietra Leccese (Lecce stone)	[75]
Antipluvial S (silanes, siloxanes)	–		
Antipluvial W (aqueous emulsion of silanes, siloxanes)	–		
TEOS and PDMS	–	Sandstone	[76]
Silres BS29A (emulsion of silanes, siloxane and organic fluoropolymer in water)	SiO ₂ (7 nm)	Marble, Sandstone	[77]
HYBRID _{SUN} (silanes, PDMS, methacrylic resin, photoinitiators)	–	Lecce stone	[78]
Copolymer of Fluorolink D-10H (perfluoropolyether) and the (racemic form) of polylactic acid	SiO ₂ (40 nm)	Marble (Macao)	[79]
Methyltrimethoxysilane	SiO ₂ (<35 nm)	Sandstone	[80]
Methyltrimethoxysilane	ZnO (<35 nm)		
Akeogard P (perfluorinated polyether)	TiO ₂ (25 nm)	Carrara marble, Noto calcarenite	[81]
Alpha®SI30 (trimethoxysilane, PDMS)	TiO ₂ (20 nm)	air-hardening calcic lime & hydraulic lime mortar	[82]
Bluesil®BP9710 (alkylpolysiloxane)	SiO ₂ (12 nm)		
TES 40 WN (ethoxysilanes), FS10 Fluorolink (perfluoropolyether) and n-octylamine	SiO ₂ (40 nm)	Sandstone	[83]
Silres BS29A (emulsion of silanes, siloxanes and organic fluoropolymer in water)	SiO ₂ (7 nm)	Marble, Sandstone, Concrete	[84]
Dynasylan F8815 (fluoroalkylsilane)	SiO ₂ (40 nm)	Limestone, Granite, Concrete	[85]
Dynasylan 40 (ethoxysilanes), polydimethylsiloxane and n-octylamine	–	Limestone	[86]
BSOH100 (TEOS)	–		
BS290 (silanes, siloxanes)	–		
Alkyl alkoxy silane oligomers in water	TiO ₂ (15 nm)	Apuan marble, Ajarte limestone	[87]
Alkyl alkoxy silane monomers	TiO ₂ (10 nm)		
BS290 (silanes, siloxanes)	–	Carrara marble	[50, 88]
Silo 112 (organosiloxanes)	TiO ₂ (40 nm)		
Fluoline PE (nanocomposite based on fluoropolyethers)	TiO ₂ (40 nm)		

(continued)

Table 2 (continued)

Materials for coating production		Treated stone	References
Polymer & polymer precursor	Nanoparticle		
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxyvalerate) (PHBVV)	–	Sandstone, Limestone	[89]
Sol-SIL (silanes, siloxanes)	–		
Emul-SIL (silane, siloxane water emulsion)	–		
n-propyl trimethoxysilane tris(propyltrimethoxysilyl)amine	–	Ajarte and Obernkirchen stones	[90]
2-methylpropyl trimethoxysilane, ethyl orthosilicate	–		
n-propyl trimethoxysilane tris(propyltrimethoxysilyl)amine	TiO ₂ (50 nm)		
2-methylpropyl trimethoxysilane, ethyl orthosilicate	TiO ₂ (20 nm)		
ESTEL1100 (TEOS & alkylsilanes), PDMS and n-octylamine	Ag grafted to functionalized SiO ₂	Lecce stone, Limestone, Granite	[91]
Water-based fluorine resin	SiO ₂ (40–50 nm)	Limestone (Trani stone), Lecce stone	[92, 93]
Trichloromethylsilane	–	Carrara marble	[94]
Alpha®SI30 (trimethoxysilane, PDMS) and TegoPhobe 1500 N (amino functional polysiloxane)	–		
Porosil VV plus (siloxane)	ZnO	Sandstone	[95]
Paraloid B72	SiO ₂ (7 nm)	Marble	[96]

Table 3 Concentrations (% w/w) of the TiO₂ nanoparticles which were dispersed in the silane+siloxane emulsion. No particles were added in the preparation of the Sil coating (reference sample). Coatings were deposited onto the marble specimens and labeled as indicated

Concentration of TiO ₂ nanoparticles (% w/w)	Coating
–	Sil
0.5	Sil + 0.5
1	Sil + 1
1.5	Sil + 1.5
2	Sil + 2
3	Sil + 3

marble specimens using an airbrush system with a nozzle of 660 µm in diameter. Thassos marble, which was used in the study, is composed of roughly 86% dolomite, 12% calcite, and 2% quartz [60].

After drying, the wettabilities of the surfaces of the deposited coatings were investigated by measuring contact angles of water drops (CA and SA) using an opti-

cal tensiometer apparatus (Attension Theta). Scanning electron microscopy (SEM; JEOL, JSM-6510) was used to study the surface structures of the coatings.

Colorimetric measurements were carried out on both coated and uncoated specimens using a Miniscan XE Plus (HunterLab) reflectance spectrophotometer. The results were evaluated by the use of $L^*a^*b^*$ coordinates of the CIE 1976 scale.

Capillary water absorption measurements were performed by the gravimetric sorption technique. The dried weighted sample blocks were placed (with the treated/coated sides) on a filter paper pad (1 cm of Whatman paper, No 4) partially immersed in distilled water and left for 1 and 19 h, thus creating two sets of samples. The samples were then removed and weighed again to determine the amounts of water absorbed by capillary forces. The same procedure was applied for uncoated marble samples.

4.2 Superhydrophobicity and Water Repellency

Figure 7 shows the effect of the nanoparticle concentration on CA and SA. CA initially increases with nanoparticle concentration and becomes very large ($>150^\circ$) for coatings which were prepared using high particle concentration, i.e., Sil + 1.5, Sil + 2, and Sil + 3. For these superhydrophobic coatings, CA is practically stable corresponding to the plateau of the curve in Fig. 7. Overall, the CA results of Fig. 7 suggest that the Sil coating corresponds to the weak hydrophobicity ($90^\circ < CA < 120^\circ$) regime and the Sil + 0.5 and Sil + 1 coatings induced enhanced hydrophobicity ($120^\circ < CA < 150^\circ$) to the treated marble, whereas the Sil + 1.5, Sil + 2, and Sil + 3 coatings exhibited superhydrophobicity ($CA > 150^\circ$). Figure 7 shows furthermore that SA decreases with nanoparticle concentration. It was not possible to measure the SAs for the Sil and Sil + 0.5 coatings, as water drops which were placed on these surfaces were pinned. For the Sil + 1 coating, the SA was 24° and became 11° for the Sil + 1.5 and 8° for the Sil + 2 and Sil + 3 coatings. The friction coefficient (μ) can be approximately estimated by the SA as $\mu \sim \tan(SA)$. Therefore, it is calculated that the friction force which is applied on the water drop by the Sil + 1 surface is roughly three times larger than the corresponding force applied by either the Sil + 2 or the Sil + 3 surfaces.

The origin of superhydrophobicity and water repellency which were achieved for the Sil + 1.5, Sil + 2, and Sil + 3 coatings is revealed by the SEM image of Fig. 7. The latter shows that nanoparticles form microscale clusters which enhance the roughness of the surface of the coating. The results shown in Fig. 7 agree with previously published reports which described the effect of nanoparticles on the surface of polymer-nanoparticle composite films [44, 46, 57, 59, 60, 61, 66, 77, 96]. Nanoparticles only contribute to surface roughness, while it is the polysiloxane (or organic polymer) material that is in the topmost layer all over the surface. The achieved superhydrophobicity is illustrated in the photographs of Fig. 8. Water was colored with green and blue pigments for demonstration purposes. Marble areas coated by the Sil + 3 coating exhibited superhydrophobicity as evidenced by the

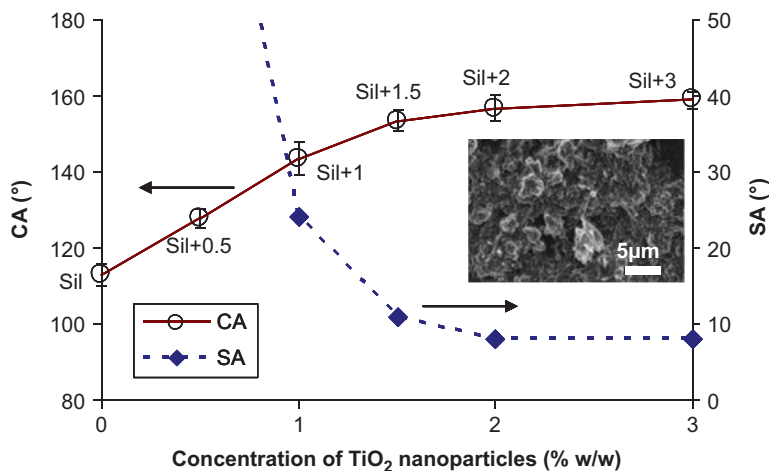


Fig. 7 Contact angle (CA) and sliding angle (SA) versus the concentration of the TiO_2 nanoparticles. The experimental data are connected with lines to guide the eye. Water drops on Sil and Sil + 0.5 coatings were pinned, and therefore no SA results are reported for these two coatings. The rough structure of the surface of the Sil + 2 coating is revealed by the SEM image

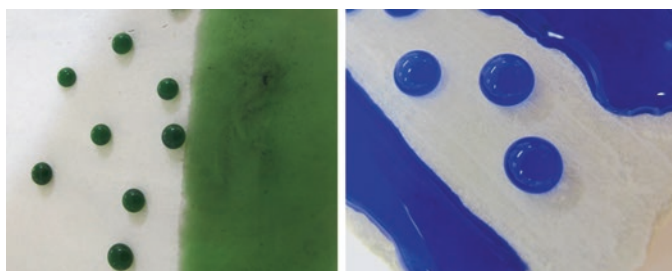


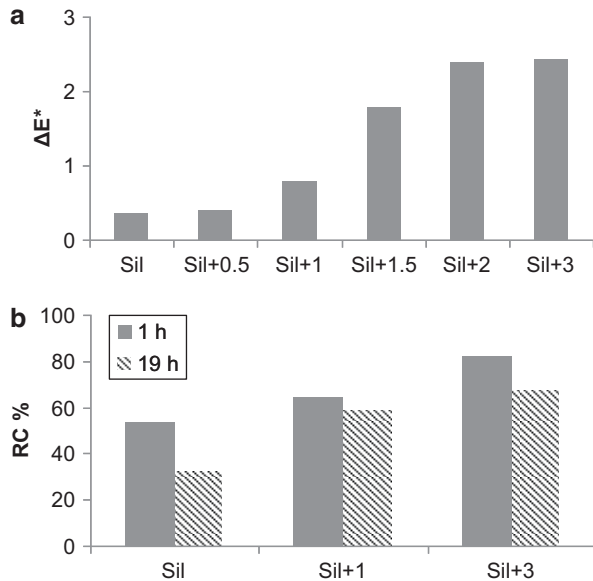
Fig. 8 Water drops colored with green (left) and blue (right) pigments on marble surfaces which were coated with superhydrophobic coatings (Sil + 3). Uncoated areas are included in the photographs, and these are completely wetted

spherical shapes of the resting water drops. Water is spread on the uncoated areas because of the hydrophilic nature of marble.

4.3 Color Changes and Absorption of Water by Capillarity

The optical effects of the coatings on marble appearance were evaluated through colorimetric measurements. The global color differences (ΔE^*) of marble specimens, induced upon coating application, were derived from the following equation:

Fig. 9 (a) Total color changes (ΔE^*) of coated marble specimens with respect to the uncoated marble. (b) Relative reduction of water absorption by capillarity (RC%) of coated marble specimens with respect to the uncoated marble. Two sets of measurements are included by leaving the specimens in contact with liquid water for 1 and 19 h



$$\Delta E^* = \sqrt{(L_t^* - L_u^*)^2 + (a_t^* - a_u^*)^2 + (b_t^* - b_u^*)^2} \quad (2)$$

where L^* , a^* , and b^* are the brightness, the red–green component, and the yellow–blue component of the CIE 1976 scale, respectively. The “u” and “t” subscript characters correspond to the untreated/bare and treated/coated specimens, respectively.

The results are presented in Fig. 9a which shows that the color change of treated marble increases with the concentration of the TiO₂ nanoparticles. Consequently, the presence of TiO₂ in the coating recipe has a negative optical effect but is not able to be perceived by the human eye, as ΔE^* is <3 for any of the coatings included in the study.

The reduction of water absorption by capillarity (RC%) was calculated for marble specimens treated with hydrophobic Sil, highly hydrophobic Sil + 1, and super-hydrophobic Sil + 3 coatings, using the following equation:

$$RC\% = \left(\frac{m_{uw} - m_{tw}}{m_{uw}} \right) \times 100 \quad (3)$$

where m_{uw} and m_{tw} are the masses of water absorbed by capillarity by the untreated/bare and treated/coated marble, respectively. Apparently, an ideal coating must eliminate the amount of water absorbed by capillarity, i.e., $RC\% = 100$.

The results are presented in Fig. 9b for the two sets of samples, i.e., samples which were left in contact with liquid water for 1 and 19 h. For any of the two sets

of samples, the results show that the RC% of treated marble increases with the concentration of the TiO₂ nanoparticles. For example, for the first set of samples (1 h in contact with water), the reductions in the amounts of absorbed water were 53.7, 64.1, and 82.0 for the specimens coated by Sil, Sil + 1, and Sil + 3, respectively. A similar increase of RC% is observed in Fig. 9b for the second set of samples, i.e., samples which were in contact with liquid water for 19 h. Consequently, the use of the TiO₂ nanoparticles has a positive effect on the resistance of the coating against water absorption by capillarity. This result agrees with the CA measurements (Fig. 7) which showed that nanoparticles promote the hydrophobic character of the coating. The comparison between the two sets of samples leads to the conclusion that longer contact with liquid water reduces the performance of the coatings. For example, for the marble sample coated by the superhydrophobic coating Sil + 3, RC% was 82.0 after being in contact with water for 1 h and became 67.0 when the time of contact with liquid water was extended to 19 h. Finally, it is noted that the achieved RC% results of Fig. 9b are comparable with RC% data which were reported previously using different polymer-nanoparticle coatings for the protection of marble. For example, a superhydrophobic coating composed of a polysiloxane material and SiO₂ nanoparticles was deposited on marble and gave RC% = 75.1 after being in contact with liquid water for about 4 h [84].

4.4 Photocatalytic Activity and Self-Cleaning

As discussed previously, the CA of a TiO₂ surface diminishes after irradiated by UV light. The effect of the sunlight on the wettability of the Sil + 3 coating is demonstrated in Fig. 10. A freshly prepared coating, which was not intentionally exposed to intensive UV light, showed superhydrophobicity as discussed above (Fig. 10a). However, the surface of the coating becomes superhydrophilic by the effect of the bright sunlight (Fig. 10b).

The self-cleaning process induced by the TiO₂ nanoparticles is shown in the photographs of Fig. 11. Ultramarine pigment was deposited on uncoated marble and marble specimens coated with Sil and Sil + 3. Prior to pigment deposition, the coated samples were left outdoors for several days, and therefore the Sil + 3 samples obtained superhydrophilic properties. The stained samples were exposed to sunlight for a total of 2 h. The self-cleaning process is evident for the Sil + 3 sample according to the relevant photos and color measurements. The reported ΔE^* (=0.6) describes the color change after exposing the stained sample to sunlight for 2 h with respect to the unstained sample. The very small value of ΔE^* shows that staining had practically a negligible effect on the color of the Sil + 3 sample, as the stain almost disappeared by the synergetic effect of sunlight and TiO₂.

On the contrary, the stain is visible on the surface of the uncoated marble specimen throughout the experimental process, as shown by the photographs of Fig. 11.

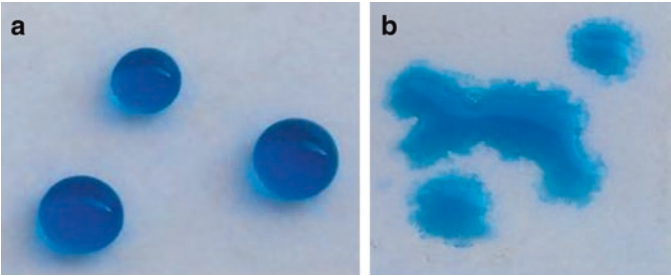
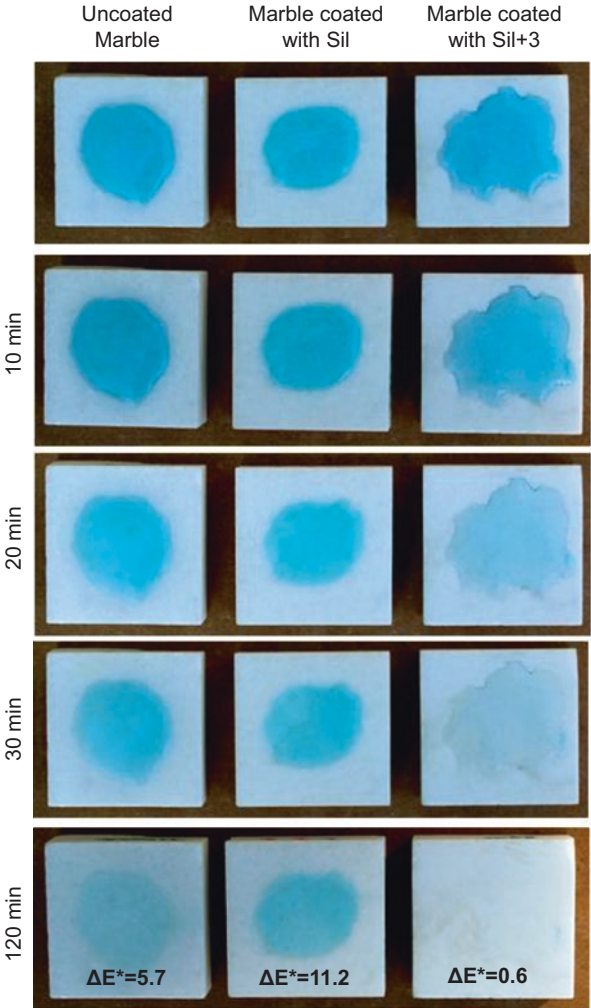


Fig. 10 Water on marble surfaces which were coated with Sil + 3 coatings. **(a)** Treated marble was kept in the laboratory; the Sil + 3 coating exhibits superhydrophobicity. **(b)** Treated marble was exposed to sunlight for 2 days; the Sil + 3 coating became superhydrophilic

Fig. 11 The self-cleaning process induced by the TiO_2 nanoparticles is visualized in the photographs. Three samples were intentionally stained by a pigment. Photographs were taken before (top) and after exposing the samples to sunlight for 10, 20, 30, and 120 min, as indicated. The ΔE^* results describe the color change after exposing the stained samples to sunlight for 120 min with respect to the unstained samples



After exposing the sample to the sunlight for 2 h, the color change induced by the pigment corresponded to $\Delta E^* = 5.7$. This is a considerable color change ($\Delta E^* > 3$) which can be perceived by human eye. An interesting result is reported for the marble specimen which was coated with Sil: the optical effect of the pigment was more dramatic for this sample compared to the uncoated marble. The color change after exposing the Sil coated sample to sunlight for 2 h was extremely high, corresponding to $\Delta E^* = 11.2$. The result suggests that the pigment was absorbed by the Sil coating, creating a permanent and durable stain. In the photographs of Fig. 11, the visual effect of the pigment on the Sil-coated specimen is evident throughout the experimental process and clearly visible after 2 h of sunlight exposure.

5 Conclusions

Superhydrophobicity accompanied by water repellency and self-cleaning induced by the photocatalytic activity of TiO_2 are properties which can be “added” to materials (e.g., polysiloxanes) used for the protection and conservation of cultural heritage monuments and historical buildings. This can be achieved using TiO_2 nanoparticles which have opened new avenues for the production of multifunctional coatings. Nanoparticles are added to the solution or emulsion of the conservation product, and the dispersion is then applied onto the natural stone. The nanoparticle concentration is a key parameter which has to be appropriately adjusted to obtain the desired properties, without affecting other requirements such as the preservation of the color of the original stone.

Based on the promising results which have been reported in the literature, it can be concluded that the useful properties of TiO_2 nanoparticles can lead to the production of very effective products for the conservation of natural stone. In general, nanoparticles can be effectively used as additives to modify and improve the properties of materials of conservation science and practice.

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Hydrophobic Carbon Soot Nanostructure Effect on the Coatings



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1 Introduction

There are many compositions of organic coatings which are utilized to protect against corrosion. Hydrophobic and superhydrophobic coatings were especially shown to provide a good protection due to their improved ability to slow down water. Besides, in the presence of liquid water, the superhydrophobic surfaces equipped with a self-cleaning property can clean the dirt and dust deposited spontaneously, thereby restoring the artistic features simultaneously [1]. When the hydrophobic coating is applied in marine conditions, metal structures have a long service life because these organic coatings can protect these structures against corrosion [2].

Most papers are devoted to the production of hydrophobic and superhydrophobic coatings. In these papers, nano-titanium dioxide, silica nanoparticles, carbon nanotubes, and fluoropolymers are employed to obtain hydrophobic and superhydrophobic coatings. Compounds based on aqueous solutions of nanostructured TiO_2

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fluoropolymer were produced by hydrophobic coatings. These mixtures prevent the destruction of stone buildings [3]. The presence of modified silica nanoparticles in a fluorinated acrylic coating provided fluorine enrichment on the film surface, which resulted in the improvement of surface hydrophobicity [4]. Multiwalled carbon nanotubes can be mixed with bisphenol – a diglycidyl ether (BADGE) which contains an epoxy resin. The multiwalled carbon nanotubes make the preparation of the superhydrophobic nanocomposite surface possible [5]. The other method includes the usage of many fluorinated polymers (e.g., polytetrafluoroethylene (PTFE, Teflon), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF)/fluoroethylene vinyl ether (FEVE)) for the production of hydrophobic coatings [6]. Soot is a material produced in large quantities and mainly utilized to retrofit the mechanical, electrical, and optical properties of building materials in the production of elastomers, dyes, dry power sources, paint and coatings, etc. [7]. During the combustion of hydrocarbon fuels, carbon soot particles were obtained. Fuel burning under specified conditions allows for the production of soot with desirable properties [7, 8]. To disperse carbon soot in the mixture of polyurethane and solvent 646 (the mixture containing 50% of toluene, 15% of ethanol, 10% of butanol, 10% of butyl/amyl acetate, 8% of ethyl cellosolve, 7% of acetone), an ultrasonic wave mixer was used.

Ultrasonic waves were produced in a liquid suspension by placing an ultrasound probe or “horn” into the suspension (when direct ultrasonic was used), and then the container with the suspension was placed into a bath together with a liquid. The ultrasonic waves spread through this container (when indirect ultrasonic was utilized). In a sonication bath (when indirect ultrasound was used), the ultrasonic waves should go through the liquid in the bath and then through the wall of the sample before reaching the suspension. When indirect ultrasonic is utilized, the probe is plunged directly into the suspension, thereby decreasing the physical obstacle to impart the dispersion with force. In the dispersion of dry powders, direct ultrasonic is more effective than indirect ultrasonic. Indirect ultrasonic can be utilized to resuspend ENMs (engineered nanomaterials) which are preliminary processed by direct sonication. It can be also employed for ENMs that may undergo change or damage (e.g., breakage of single-walled carbon nanotubes) when direct ultrasonic waves are used. Sonication is an extremely system-specific dispersion method that includes a variety of concomitant complex physicochemical effects and the reaction caused by cluster separation or further agglomeration, as well as other influences involving chemical reactions. For a specified system, the best sonication conditions should be determined by the influence of various sonication parameters on the dispersion conditions of the suspension in limited related conditions. In addition, the total significant acoustic energy is effective when disconnecting powder clusters are influenced by a system-specific parameter [9].

When sonication power and the experiment duration characterize the amount of energy transmitted to the suspension, the samples of different volumes and particle sizes can change the quantity of the energy delivered. At a fixed volume, the larger particle concentrations resulted in the growth of particle collision frequency. The growth of frequency can increase particle collisions. So, if enough local activation and sintering energies are obtained, increased collision frequencies lead to agglom-

eration in particle collision and coalescence. Therefore, both the energy transmission to the suspension and the physiochemical properties of the suspension influence the concentration [9].

In this paper, a one-component polyurethane air-drying system was stirred with solvent 646 at 20 °C using a pulsed ultrasonic mixer. Then the dispersed hydrophobic carbon soot contained in the resulting mixture led to the formation of a hydrophobic coating, which possessed thixotropic properties, normal dispersion, and adhesion ability for different surfaces such as paper, metal, wood, and tile.

2 Experimental

2.1 Materials

Polyurethane lacquer (“Elakor-PU,” TU 2312-009-18891264-2009 produced in the Russian Federation in compliance with ISO 51102-97) was applied to protect floors, walls, ceilings, building materials, etc., from the mechanical and chemical exposures. solvent 646 is a mixture containing 50% of toluene, 15% of ethanol, 10% of butanol, 10% of butyl or amyl acetate, 8% of ethyl cellosolve, and 7% of acetone. Hydrophobic soot was produced at the Institute of Combustion Problems by applying a 1 kV electric field during the combustion of a propane, butane, and isobutene mixture. The size of the soot particles was in the range of 30–40 nanometers with the main chain formation and a tertiary structure, and the contact angle was about 146° [10].

The 1 mm diameter nozzle supplied a working mixture at a gas flow rate of 425–500 cm³/min. Electric field voltage ranging from 0.01 to 1 kW was applied to the system. According to the polarity of the applied electric field, the cylinder may have connected to an anode or a cathode. Soot was placed on the surface of a stainless steel cylinder, which rotated at 1 rotation per second and was collected into the soot collector. After removing it from the surface of the rotating drum with a mounted scraper, it was collected into a soot container (Fig. 1.).

The wetting angle of the obtained soot was tested and controlled by drop shape analyzer (DSA25 KRÜSS). The soot was investigated by SEM, Raman spectroscopy, and EDS. Figure 2. shows SEM images of the soot samples.

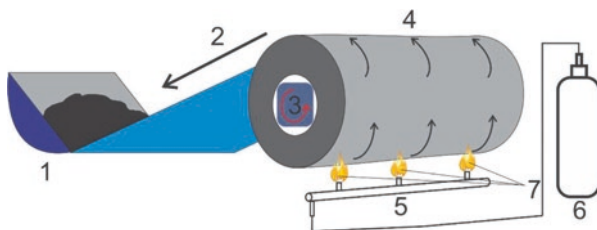


Fig. 1 The scheme of the apparatus for obtaining hydrophobic soot. (1) Soot collector, (2) carbon black tape, (3) retainer, (4) rotating drum, (5) tube, (6) propane-butane mixture, (7) flame

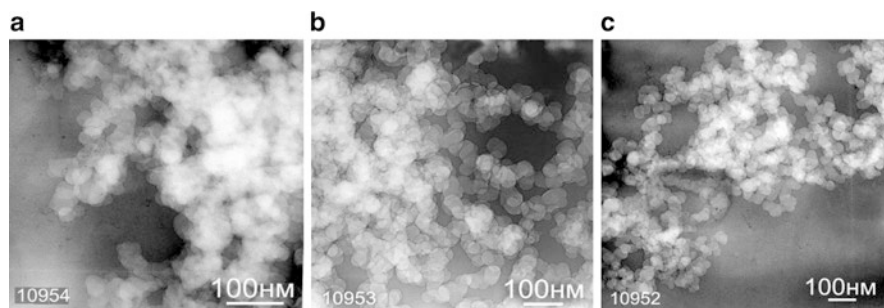


Fig. 2 Electron diffraction patterns of morphostructures

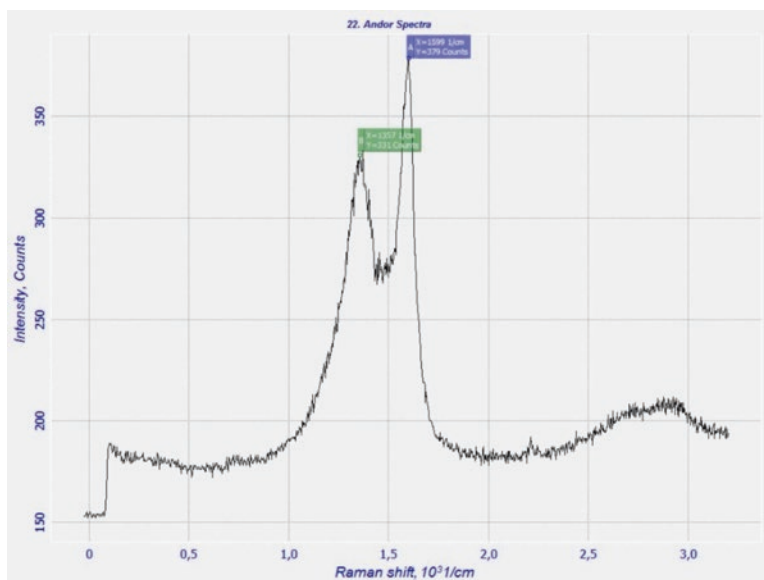


Fig. 3 Raman spectrum of soot

The sample substance is fairly homogeneous, the bulk of which consists of aggregates (Fig. 2a) of flattened rounded particles with fairly distinct boundaries. The visible particle diameter was 30–40 nm (Fig. 2b, c). Cloud and film particles were relatively rare.

Figure 3. illustrates the Raman results of the samples. The Raman spectra illustrate that the samples contain two peaks – 1350 cm^{-1} (D – amorphous) and 1590 cm^{-1} (G – graphite) – that corresponds to an amorphous carbon phase, which have been described in the literature [7, 12].

The existence of these two peaks with a comparable intensity is characteristic of graphitized materials consisting of disordered micro-crystallites with a size of up to 10 nm.

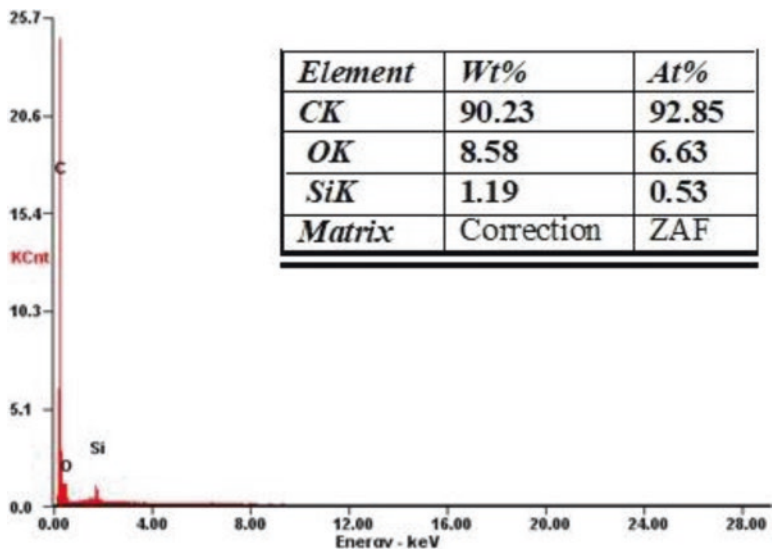


Fig. 4 EDAX analysis of soot

To determine the composition of the resulting soot, an elemental analysis was carried out. Figure 4 shows the elemental determination analysis of the composition of the resulting soot that had hydrophobic properties.

EDAX analysis of the soot samples showed that the resulting carbon material consisted of 90.23% of carbon atoms, 6.37% of oxygen, and 1.19% of silica atoms.

2.2 Preparation of Coatings and Dispersion of Soot in the Resin

Polyurethane and solvent 646 were mixed very well. Originally, polyurethane and solvent 646 were weighed and blended, and then the obtained soot was rapidly dispersed into the liquid mixture by an ultrasonic homogenizer (Fig. 5a) under various conditions. As illustrated in Fig. 5a), the ultrasonic homogenizer dispersed the hydrophobic soot without flocculation to polyurethane-solvent 646 mixtures. The instrument power and the time of mixing soot were changed by the control panel (Fig. 5b). To transmit ultrasonic waves to the mixture, a probe (Fig. 5c) was utilized.

Table 1 shows three samples of a coating composed of polyurethane resin (“Elakor-PU” lacquer, TU 2312-009-18891264-2009), solvent 646, and hydrophobic soot.

Samples were prepared in different containers and then applied on paper, tile, metal, and wood surfaces. To measure the wetting angle, a surface shape analyzer (DSA25 KRÜSS GmbH) was used. Three or four water drops were applied on the sample, and then the sample was measured and the average was calculated.

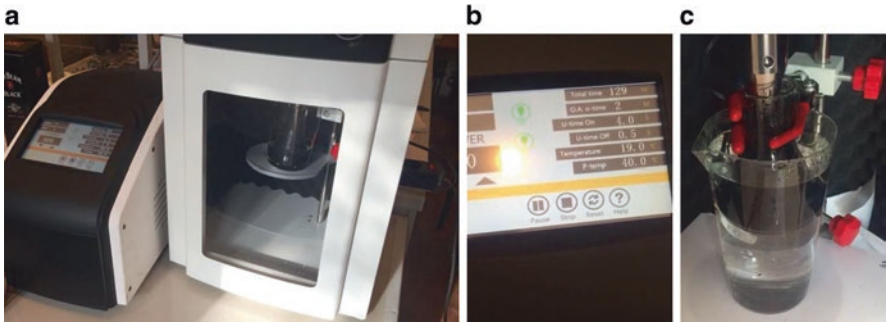


Fig. 5 Ultrasonic mixer (homogenizer) (a), control panel (b), ultrasonic probe (c)

Table 1 Different samples under different conditions

Number of the sample	Polyurethane, gr.	Solvent 646, gr.	Carbon soot, gr.	Ultrasonic power (25 Hz), watt	Ultrasonic on time (second working)	Ultrasonic off time (second not working)	Min
Coating-1	5	30	1	600	2	1	5
Coating-2	5	30	2	600	3	1	15
Coating-3	4	40	3	600	5	0.5	30

3 Results and Discussion

3.1 Comparison of Wetting Angle by Drop Shape Analyzer (KRUSS)

The wetting angle was measured on the surfaces of materials, such as tile, paper, wood, and metal without coating. The results of the wetting angle for the materials are shown in Table 2.

The obtained results show that the wetting angle is lowest on the metal surface and is greatest on the paper surface. Coating-1, coating-2, and coating-3 were applied onto tile, paper, wood, metal surfaces, and then the wetting angle was determined with data shown in Table 3.

The results of the comparison of different coating compositions, wetting angle, and soot concentrations are given in Table 3.

3.2 Comparison of Wetting Angle by Drop Shape Analyzer (KRUSS) Before and After Applying Coating-3

Figure 6 shows the comparison results of wetting angles on the tile surface before and after applying hydrophobic coating-3.

Table 2 The wetting angle of the tile, paper, wood, and metal surfaces without coating

Number of the sample	Measurement of contact angle on different materials without applying hydrophobic coating	Wetting angle
1.	Tile	47.8°
2.	Paper	98.6°
3.	Wood	40°
4.	Metal	29.9°

Figure 6 shows that before applying the hydrophobic coating on the tile surface, the wetting angle was 49.4°, whereas after applying hydrophobic coating-3, it rose significantly until reaching 141°. This rise is explained by adding 3 grams of soot to the polyurethane and solvent 646. Figure 7, illustrates the comparison of wetting angle on the wood surface before and after applying hydrophobic coating-3.

As Fig. 7 demonstrates before the application of coating-3, the wetting angle amounted to 53.6°, and then after applying coating-3, it changed to 137.3° because coating-3 created hydrophobic surface which enhances the wetting angle. Figs. 6 and 7 illustrate the adhesive ability of the wood and tile surfaces. By comparing the results presented in both figures, the adhesive ability of the tile surface is worse than that of the wood surface because wood is a porous material which possesses good adsorption properties, whereas tile is a smooth material that cannot adsorb coating-3. Figure 8 shows the comparison of wetting angle on the paper surface before and after applying hydrophobic coating-3.

Figure 8 shows that the wetting angle on the paper before applying hydrophobic coating was 96.1°, and after applying hydrophobic coating-3, the wetting angle was 143.6°. Hydrophobic coating-3 increased the wetting angle on the paper surface by adding 3 grams of soot to the composition of the polyurethane-solvent 646 mixture. Figure 9 illustrates the results of the wetting angle on the metal surface before and after applying hydrophobic coating-3.

Figure 9, reveals that the wetting angle on the metal surface before applying hydrophobic coating was 58.4°, and after applying hydrophobic coating-3, the wetting angle reached 135°, which was possible by adding 3 grams of soot to coating-3. Therefore, hydrophobic coating-3 on the paper surface has a better adhesive ability than on the metal surface. Figure 10, presents the results of WA on pure polyurethane and soot.

As it is seen from Fig. 10, when applied, the polyurethane lacquer imparts a good adhesive ability not only to glass but also to paper, metal, tile, and wood surfaces, whereas hydrophobic soot cannot be applied to any surface because of the lack of adhesive ability. The results of adding nanostructured soot showed that the hydrophobic properties of the surface increase due to the presence of carbon nanobeads in the soot.

Table 3 Comparison of different coating compositions, wetting angle, and soot concentrations

Number	Polyurethane, gr	Solvent 646, gr	Soot, gr	Ultrasonic action, min	Soot concentration, %	Wetting angle on the tile surface, degree	Wetting angle on the paper surface, degree	Wetting angle on the wood surface, degree	Wetting angle on the metal surface, degree
Coating-1	5	30	1	5	2.7	93	115	105	100
Coating-2	5	30	2	15	5.4	137	136	130	128
Coating-3	4	40	3	30	6.3	141	142	136	135. .

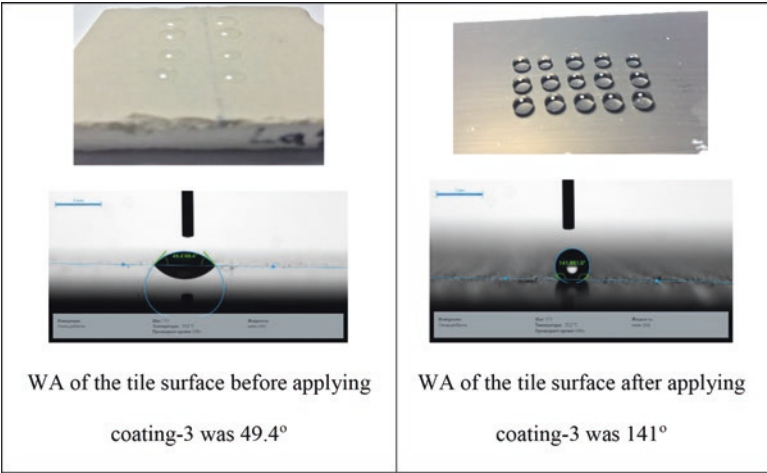


Fig. 6 Comparison of two tile surfaces without and with hydrophobic coating-3

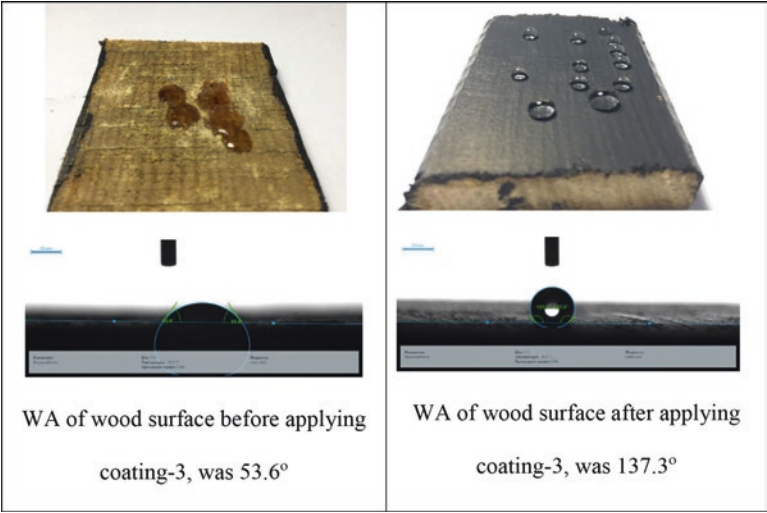


Fig. 7 Comparison of wood surfaces without and with hydrophobic coating-3

3.3 Comparison of Different Coatings by the Presence of the Thixotropic Properties

“Thixotropy” is a rheological phenomenon mainly found in many complex chemical materials. These materials are usually colloidal solutions. It is linked with different rheological properties during a certain time period, even when the applied stress rate is constant [11].

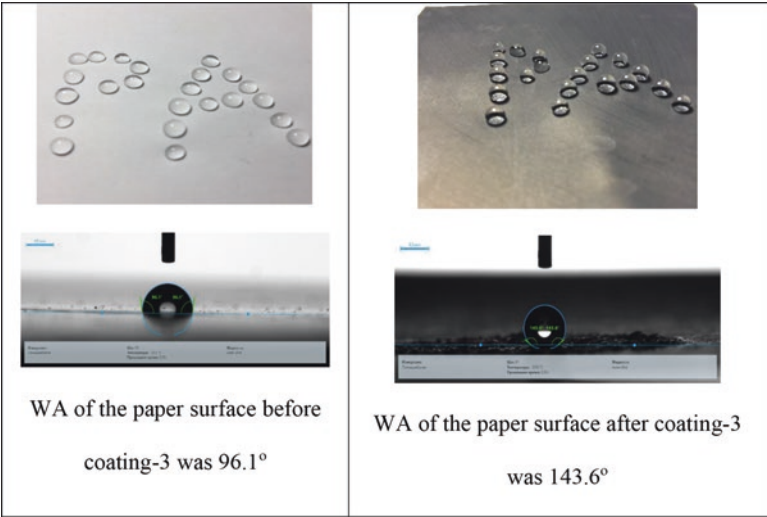


Fig. 8 Comparison of two paper surfaces without hydrophobic coating and with hydrophobic coating-3

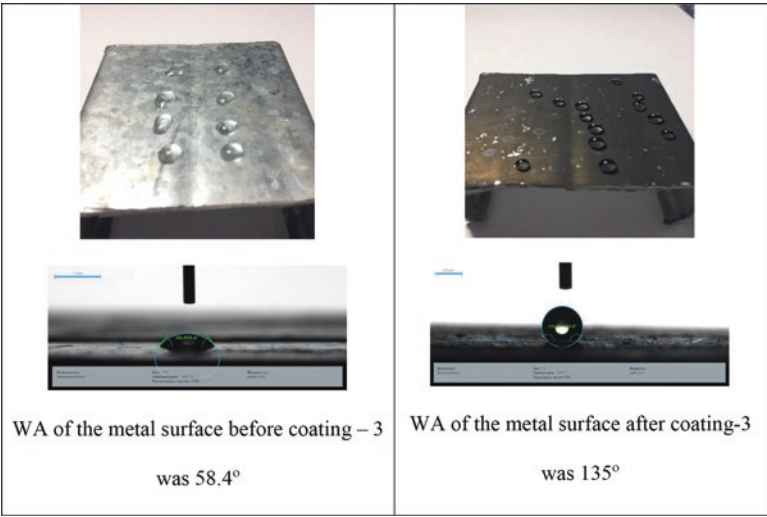


Fig. 9 Comparison of two metal surfaces without hydrophobic coating and with hydrophobic coating-3

This study showed that coating-2 and coating-3 have good thixotropic properties, and additionally, when these coatings were applied, settling and flocculation of soot were not observed (Table 4.).

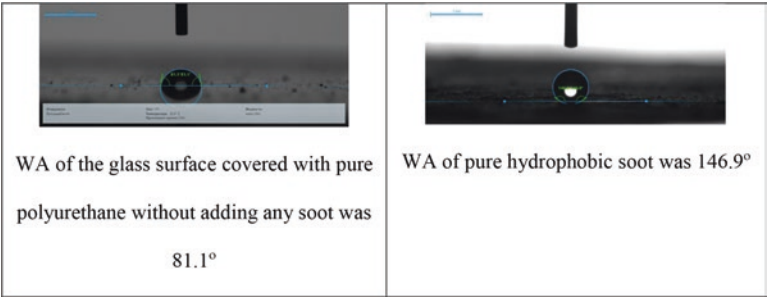


Fig. 10 Comparison of wetting angle of pure polyurethane and hydrophobic soot

Table 4 Comparison of soot concentration and thixotropic properties

Number	Soot, gr.	Flocculation	Use of dispersing agent	Thixotropic properties	Settling	Liquid stability	Concentration of soot in the composition, %
Coating-1	1	No	No	No	Yes	No	2.7
Coating-2	2	No	No	Yes	No	Yes	5.4
Coating-3	3	No	No	Yes	No	Yes	6.3

4 Conclusions

The addition of carbon soot to coating-3 improved the hydrophobicity of wood, tile, metal, and paper surfaces. Pure polyurethane was found to be acid and alkali material-resistant and had a good adhesive ability when applied to any surface. The mixing of polyurethane with hydrophobic soot in an ultrasonic homogenizer resulted in obtaining two hydrophobic coatings: coating-2 and coating-3. These coatings had good thixotropic properties which make the application of paint on wood, tile, paper, and metal surfaces efficient.

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Laser Surface Engineering for Boiling Heat Transfer Applications



Matevž Zupančič and Peter Gregorčič

1 Introduction

Global primary energy consumption grew at an average rate of 1.5% per year in the last decade, and the world's total power demand is estimated to increase from 18 TW (in 2018) to over 23 TW by 2040 [1, 2]. Since thermal energy plays a primary role in the world's total energy, the efficiency of thermal energy conversion is expected to be a very important factor in the technological progress of modern society. *Phase change* is considered to be the most effective and technically controllable mechanism of heat transfer due to the large change in enthalpy within a small temperature difference, allowing high energy transfer rates in high heat flux applications. *Liquid vapor phase change* in particular is a part of our everyday life and is utilized for cooling and general heat transfer in many applications on various scales – from boiling water reactors in large nuclear power plants [3] to small heat pipes, which are massively produced and are employed in computers, mobile phones, solar collectors, space applications and other fields [4, 5]. In addition to that, emerging technologies including electric vehicles, energy storage and renewable energy-based power generation systems will also need to consider phase-change heat transfer for cooling purposes [6]. Miniaturization and future development of high heat flux devices in terms of performance and safety concerns, therefore, depend on the enhancements in phase-change heat transfer.

Over the last century, *nucleate boiling* became one of the primary topics in liquid vapor heat transfer research [7, 8] with a constant goal of enhancing the boiling process in terms of minimizing the *surface temperature* and increasing the *critical heat flux* (CHF), which defines the maximum attainable heat flux in the nucleate boiling regime [9–14]. Finding the ultimate enhancement approach is a challenging task, since the boiling process is a complex phenomenon and its definite physical

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model is still not defined, which means that experimental approach to research is unavoidable.

Nucleate boiling depends on a multitude of factors, which can be divided into the following categories:

- *Surface characteristics*, including geometric and material properties, topography on the micro- and nanometre scale, surface chemistry, transient heat transfer inside the solid material, etc.
- *Fluid properties*, including physical and thermal properties, mixture composition, and impurities
- *The interaction between the surface and the fluid* through wettability and adsorption
- *Operating conditions*, such as surface orientation, pressure, liquid subcooling, gravity, electric and magnetic fields, etc.

For a given set of operating conditions and working fluid, the surface characteristics, including micro- and nanoroughness, wettability, surface chemistry and porosity all have a significant impact on boiling process. The main enhancement approach, therefore, is based on the modification (functionalization) of the boiling surface in order to achieve a lower surface temperature at the onset of boiling, alongside increasing the density of active nucleation sites, limiting the bubble growth and finally delaying the dry-out as much as possible. Surface modification methods, thoroughly summarized in recent reviews [15, 16], mostly include mechanical machining [17–19], sintering [9, 20, 21], electrodeposition [22–26], sputtering [27], oxidation [28, 29], growth of nanowires and nanotubes [30–33], (nanoparticle) coatings [34, 35], micro-/nanoelectromechanical techniques [36–39] or combinations of the above methods [40–45]. Usual drawbacks of the employed techniques are expensive production, mechanical and/or thermal instability of surfaces, problematic scale-up and difficult implementation on real three-dimensional surface geometries. As it will be presented in this chapter, *laser surface engineering* has the potential to overcome the current limitations for further miniaturization of microelectronic devices and to increase performance and safety in high heat flux systems [46].

The surface wettability in general significantly influences the boiling performance. For *ideal* surfaces (i.e. chemically homogeneous, chemically stable and completely flat), this is usually explained by using two limiting cases: superhydrophobic (very poorly wetted) and superhydrophilic (very well wetted) surfaces. Here, the prefix “hydro” is related to liquids in general [47, 48], while the prefix “hydro” is used when we specifically describe the results connected with water. (Super) hydrophobic surfaces prefer to be in contact with the vapor phase rather the liquid phase. This promotes the activation of nucleation, reduces the temperature of the onset of nucleate boiling and increases the heat transfer coefficient at low heat fluxes, *but* decreases the critical heat flux. On the contrary, the (super)hydrophilic surfaces delay the critical heat flux *but* increase the surface superheat at low heat fluxes. From these two limit cases, it clearly follows that surface wettability significantly changes the key boiling heat transfer parameters. However, as it will be

discussed in this chapter, the ideal surfaces practically do not exist in real applications. Thus, the measured boiling performance cannot be sufficiently explained without appropriate consideration of the surface topography. Additionally, the surface chemistry and, consequently, wettability may even change during boiling due to intense processes, including the vaporization of the working fluid, high surface temperatures and high frequency temperature variations due to bubble nucleation [49].

This chapter provides a background in nucleate pool boiling needed to explain the current understating of the effects of surface wettability on boiling heat transfer. Afterwards, it introduces direct laser texturing as an emerging technology to produce surfaces with different wetting properties and morphological features. With an emphasis on the results obtained by the authors, the capabilities of surfaces functionalized by nanosecond laser pulses to enhance saturated nucleate pool boiling with water and other fluids are demonstrated. It is also explained how laser surface engineering can be used to decrease the influence of the surface wettability on the key boiling heat transfer parameters and – in this way – to ensure a more stable heat transfer processes by utilizing functionalized surfaces.

2 Introduction to Nucleate Pool Boiling and the Effects of Surface Wettability

Pool boiling is a process of heat transfer between a heated surface and a seemingly stationary liquid in such a way that generation of vapor occurs. The necessary condition is that the temperature of the surface T_w exceeds the liquid's saturation temperature T_{sat} at the given operating pressure. In normal gravity, the growing bubbles detach from the surface mostly due to buoyancy forces, whereas the surrounding liquid near the surface is in motion due to free convection and periodic bubble growth/detachment. Another mode of boiling is forced convection boiling (also termed as flow boiling), where fluid motion is assisted by external flow. Another classification of boiling is through the temperature of the bulk liquid. In subcooled boiling, the temperature of the liquid is below the saturation temperature and the vapor bubbles typically condense before reaching the free surface. In saturated nucleate pool boiling, which is investigated in this chapter, the entire liquid is under saturated conditions, and the heat transferred from the solid to the liquid can be formalized with the Newton's law of cooling

$$q'' = h(T_w - T_{\text{sat}}) \quad (1)$$

where q'' is the heat flux typically expressed in W cm^{-2} or kW m^{-2} , h stands for the heat transfer coefficient usually given in $\text{kW m}^{-2} \text{K}^{-1}$ and $(T_w - T_{\text{sat}})$ is the wall superheat known also as the surface excess temperature in K.

In 1934, Nukiyama [7] studied boiling regimes through an experiment with Joule-heated, horizontally oriented nichrome and platinum wires in a saturated pool

of water. With further experiments by Drew and Mueller [50], it was possible to plot a so-called boiling curve depicting the relationship between the heat flux and the wall superheat, as presented in Fig. 1. At low heat flux, the natural convection sufficiently removes the entire heat from the surface, and no vapor is generated. In this region, heat is removed from the surface by superheating of the liquid, which subsequently travels away from the surface under the effects of buoyancy. As the wall superheat is increased to a few degrees above T_{sat} , bubbles eventually start to form, which is termed as the onset of nucleate boiling.

On a smooth, clean surface, this event usually causes a temperature drop as the heat transfer coefficient suddenly increases. At the onset of nucleate boiling regime, isolated bubbles periodically form on active nucleation sites and are buoying off the surface. Heat is removed from the surface in the form of latent heat of the phase change and enhanced convective heat transfer due to the agitation of the liquid near the surface. As the wall superheat increases further, nucleation site density and nucleation frequency also increase, causing horizontal and vertical coalescence of bubbles. When the bubble population becomes too high and there is virtually no

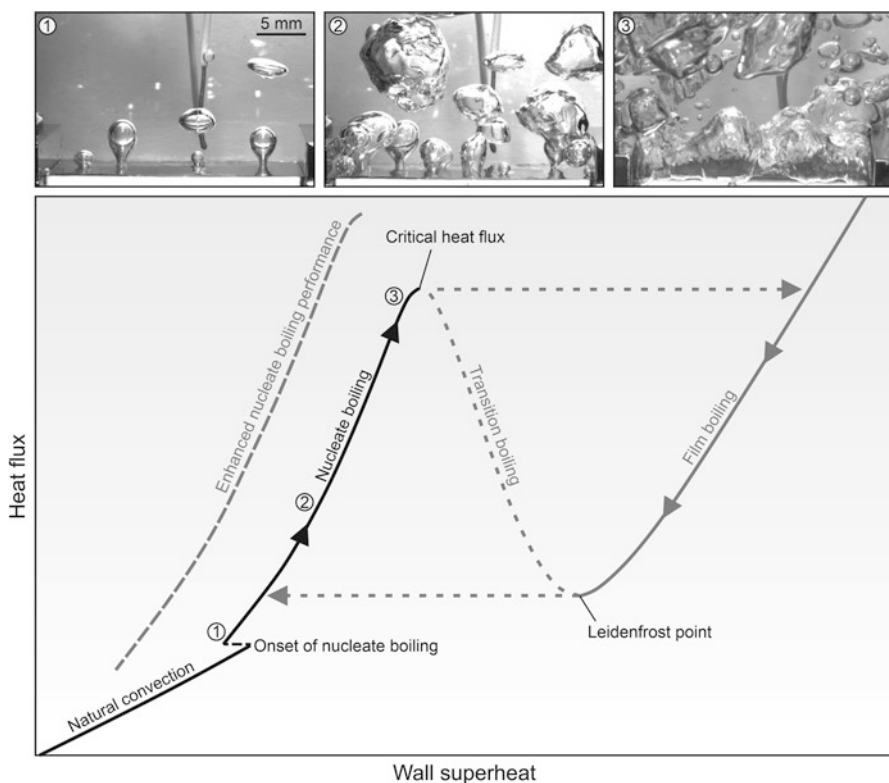


Fig. 1 Typical pool boiling curve (not to scale) and high-speed images at three different heat fluxes (50, 200, and 1150 kW m^{-2}) during saturated pool boiling of water at 1 atm on horizontal Joule-heated stainless steel surface

possibility to create more independent (non-coalescing) nucleation sites on the surface, the insulating vapor blanket entirely covers the surface and significantly decreases heat transfer coefficient. At the moment of reaching this boiling crisis, the heat flux is termed as the critical heat flux (CHF).

In typical boiling heat transfer applications, the heat flux is the independent variable, meaning that by increasing the heat flux just beyond the CHF, the wall temperatures suddenly increases and the film boiling regime ensues. When water is used as the working fluid, this direct transition usually causes the heater to reach its melting point and causes the eventual burnout. However, if the wall superheat is the controlled variable [50] or the surface material can withstand relatively high temperatures (e.g. platinum), the film boiling regime can be sustained. In this regime, the heat is transferred from the surface both by conduction and radiation through the vapor layer on the surface. When the heat flux is lowered again, the boiling curve follows a different path and reaches so-called Leidenfrost point. A further decrease in the heat flux causes a transition back to the nucleate boiling regime, accompanied by a sudden temperature decrease. This loop in a boiling curve is known as the boiling hysteresis and will not be further investigated within this chapter. Clearly, nucleate boiling is the region of interest for most practical applications with the CHF as the upper limit of operation. Hence, this chapter will only consider the nucleate boiling regime.

2.1 Bubble Nucleation

To initiate bubble growth, the primary requirement is the existence of a vapor nucleus inside the liquid. The formation of nuclei inside the superheated liquid resulting from thermal fluctuations of liquid molecules is called *homogeneous nucleation*. When the vapor is formed on the heated solid surface or a suspended nonwetted material, this is known as the *heterogeneous nucleation*. Based on either the thermodynamic or the kinetic limit, the required homogenous nucleation temperature for water at atmospheric pressure is around 300 °C (e.g. 200 K of wall superheat), which is at least one order of magnitude higher than the temperature normally observed in boiling applications. Clearly the surface itself serves as a catalyst and reduces the energy required for nucleation. In practice, heterogeneous nucleation initiates vapor formation, whereas the wettability and morphology of the surface play a key role.

When considering bubble formation on a completely smooth horizontal surface (Fig. 2a), the homogenous nucleation temperature is reduced by a factor $f(\theta)$ as proposed by Cole [51]:

$$f(\theta) = \sqrt{\frac{1}{4}(2 + 3\cos\theta - \cos^3\theta)} \quad (2)$$

where θ is the static contact angle of liquid. When liquid completely wets the surface ($\theta = 0$), the $f(\theta)$ equals 1 and the required nucleation temperature is the same as

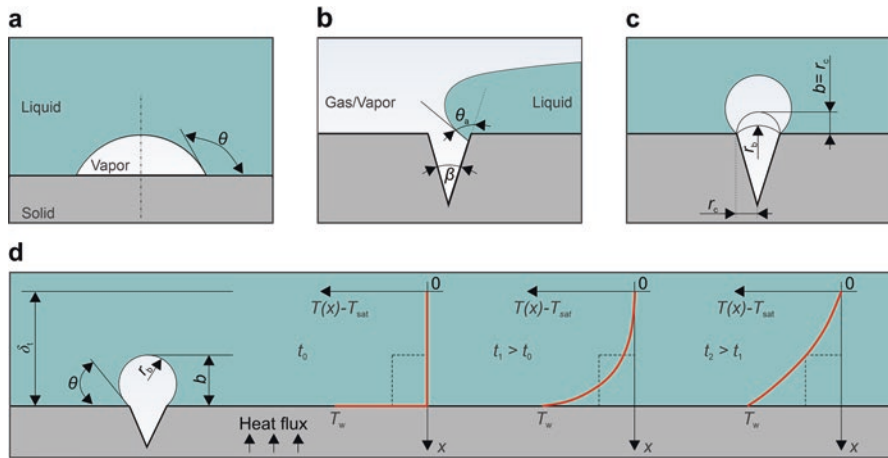


Fig. 2 (a) Bubble embryo on an ideal smooth surface; (b) trapping of gas/vapor inside a conical cavity; (c) presentation of the critical hemispherical condition; and (d) model of Hsu's nucleation criterion

for the homogenous nucleation. In the ideal nonwetting case (when $\theta = 180^\circ$), the $f(\theta)$ equals 0, and nucleation will occur at no superheat of the surface. Here, two facts should be pointed out:

- A completely smooth surface with ideal nonwetting behaviour has never been recorded and cannot be fabricated for practical use
- The reduction of temperature proposed by the $f(\theta)$ factor is not sufficient to explain the actual nucleation temperatures recorded in experiments.

The reason that the actual nucleation temperatures are lower than predicted is the existence of cavities on the heated surface. Naturally present or artificially produced cavities might trap vapor or gas that act as a nucleation embryo. If a certain cavity remains filled with vapor (also due to vapor spreading from neighbouring bubbles) and continues to be active once the nucleation is initiated, it is defined as an *active nucleation site*.

To initially entrap a gas inside the conical cavity, Bankoff [52] proposed that advancing contact angle θ_a must be larger than the groove angle β (Fig. 2b). In this situation, the liquid hits the opposite cavity wall before reaching the bottom, therefore entrapping a certain amount of gas or vapor. As the bubble grows from a cavity with a mouth radius r_c , it passes through the critical hemispherical condition [53], where the bubble tip is at the same distance from the surface as the cavity radius value (Fig. 2c). Here, the bubble radius is at its smallest, and the pressure inside is at its maximum as predicted by the Young-Laplace equation. In other words, the maximum amount of superheat is needed at this point to keep the bubble growing. For low-surface-tension fluids, however, the initial radius of a gas bubble inside the cavity might be smaller than the cavity radius. In this case, the wall superheat is larger than the value predicted by the critical hemispherical condition.

Analysis in the previous paragraph assumes a uniform and equal temperature of the liquid, the vapor and the wall. In practical boiling, however, the heat is transferred from a heated surface to the cooler liquid. When a bubble grows inside the liquid, it moves through the thermal boundary layer adjacent to the wall, and the criteria specified for uniform temperature are not necessarily sufficient. Experiments have shown that for a certain wall superheat, there is a certain size range of active nucleation cavities. This was taken into account by Hsu [54], who derived a nucleation criterion that later became one of the most commonly used in the pool boiling community. Let us assume a small bubble nucleus of a radius r_b sitting at the mouth of the vapor trapping cavity (Fig. 2d). The nucleus is leftover vapor from the previous bubble departure. At time t_0 , the entire liquid is in saturated conditions, and thermal boundary layer starts to form again following the previous bubble growth and departure cycle. With time, the liquid is heated up inside the boundary layer δ_t due to heat transfer from the hotter surface. Only when the liquid temperature reaches the saturation temperature of the vapor inside the bubble (which can be calculated from the Clausius-Clapeyron equation) over the entire bubble height at time t_2 , the bubble starts to grow. By accounting for all geometrical constraints and the transient temperature distribution inside the thermal boundary layer from Carslaw and Jaeger [55], Hsu derived the final equation to determine the size range of possibly active cavities

$$\{r_{c,\min}, r_{c,\max}\} = \frac{\delta_t \sin \theta}{2(1 + \cos \theta)} \left(1 \mp \sqrt{1 - \frac{8\gamma_{LV} T_{\text{sat}} (1 + \cos \theta)}{h_{LV} \rho_V \delta_t (T_w - T_{\text{sat}})}} \right) \quad (3)$$

where γ_{LV} is the liquid vapor surface tension, h_{LV} is the heat of vaporization and ρ_V is the vapor density. Figure 3 shows three different ranges (for three different wettabilities) of active cavity size versus wall superheat for saturated boiling of water at 1 atm. It is obvious that superhydrophobic surfaces provide the lowest needed superheat for the onset of boiling and allow nucleation from cavities with a radius from roughly 1 μm up to 1000 μm (pink region in Fig. 3). On superhydrophilic surfaces, however, the cavities should be significantly smaller, and the size range of possibly active cavities narrows down to about 0.2–10 μm (blue region in Fig. 3). It should be pointed out that the overlapping of different regions in Fig. 3 clearly shows that there exists a certain range of cavity size that are suitable as active nucleation sites for surfaces with different contact angles.

In the above analysis, it should be noted that the thermal boundary layer constantly changes during boiling and the optimal cavity size range is therefore subjected to perpetual change as well. Moreover, Hsu's model considers the static contact angle of the liquid, even though the receding contact angle is the one that is observed during a bubble growth. This was later addressed by Kandlikar et al. [56], who provided a modification of the criterion from Eq. (3) specifically for flow boiling processes [57–59]. Bubble nucleation is obviously a very complex phenomenon, and it would be impossible to even list the existing publications and their

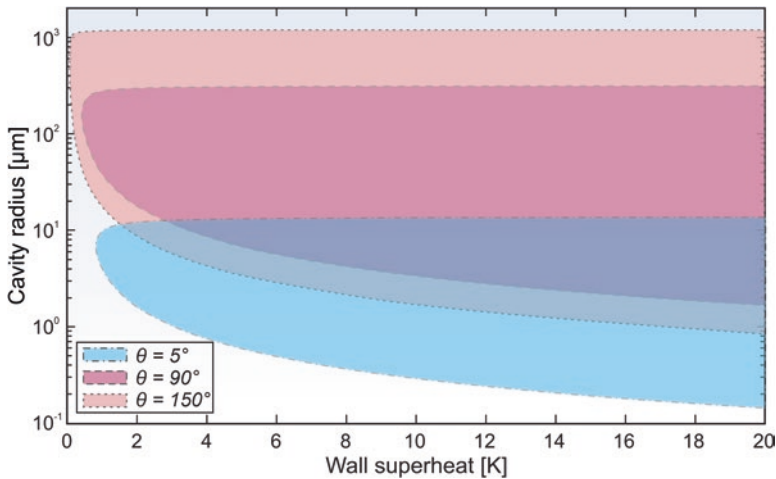


Fig. 3 Effective cavity radius range versus wall superheat for saturated boiling of water at 1 atm at three different contact angles. The calculation is based on the Hsu's nucleation criterion (Eq. (12.3)), while the thermal boundary layer thickness δ_t was assumed as the ratio between the thermal conductivity of the water ($0.679 \text{ W m}^{-1} \text{ K}^{-1}$) and selected value of the heat transfer coefficient for natural convection ($2.2 \text{ kW m}^{-2} \text{ K}^{-1}$)

findings within a single chapter. Instead, we will provide some key points that are also necessary for the further discussion of the experimental results:

- To initiate the boiling process at reasonably low superheats (e.g. up to 5 K), the surface must contain gas or vapor trapping cavities. The general rule is that poorly wetted surface will allow vapor trapping within steep and shallow cavities [51], whereas the well wetted surface will only allow trapping within steep cavities. The combination of a steep cavity and well wetted surface, however, makes it difficult to entrap vapor again after the cavity was completely filled with liquid. Hence, poorly wetted cavities have the greatest tendency to entrap gas or vapor and show the best potential to initiate boiling process.
- The boiling onset and the initial population of active nucleation sites depend greatly on the concentration of non-condensable gasses inside the liquid. This is especially important for poorly wetted surfaces. Furthermore, the nucleation process from non-condensable gas embryo (e.g. air) in comparison to vapor embryo is very different [52, 60, 61], which will be discussed later.
- Surfaces with strictly defined cavity size might only be optimal to provide nucleation under certain operating conditions. On the other hand, surfaces that incorporate cavities in a wide range of sizes might allow effective nucleation within the entire nucleate boiling regime (e.g. across a wide range of superheats), for different wettability states [62] and different types of fluids [46].
- Over two decades ago [63], atomic force microscopy (AFM) revealed the existence of so-called surface nanobubbles – spherical caps of gas (possibly even vapor) sitting on top of a poorly wetted surface. Observed nanobubbles with

diameters up to 1 μm and height up to several tens of nm exhibit extremely high contact angles in water (over 150° measured through the water), which makes it possible for them to become stable over a longer period [64, 65]. It was proved that nanobubbles can cause a relatively low temperature at the onset of nucleate boiling even on a nanoscopically smooth surface [66], which cannot be explained through existing heterogeneous nucleation models. In the near future, the emerging fluorescence microscopy techniques [67–69] with submicron spatial resolution might be able to provide a completely new understanding of the mechanisms behind bubble nucleation.

2.2 Bubble Growth and Departure

Once the conditions to initiate a nucleation event are fulfilled and the bubble starts to grow, the bubble growth time t_g and waiting time t_w can be defined by analysing the surface temperature at the nucleation site and the bubble footprint radius r_f (Fig. 4). Start of the nucleation is observed as a sharp temperature drop with a high local heat flux [70, 71] where both the bubble radius r_b and the bubble footprint radius increase. After the buoyancy force starts to lift the bubble off the surface, the footprint decreases until finally the bubble is detached. The period between the start of nucleation and detachment is known as the bubble growth time t_g . After the bubble departure, cold liquid rewets the nucleation site and a thermal boundary layer starts to form again until the next nucleation occurs. This time is termed as the

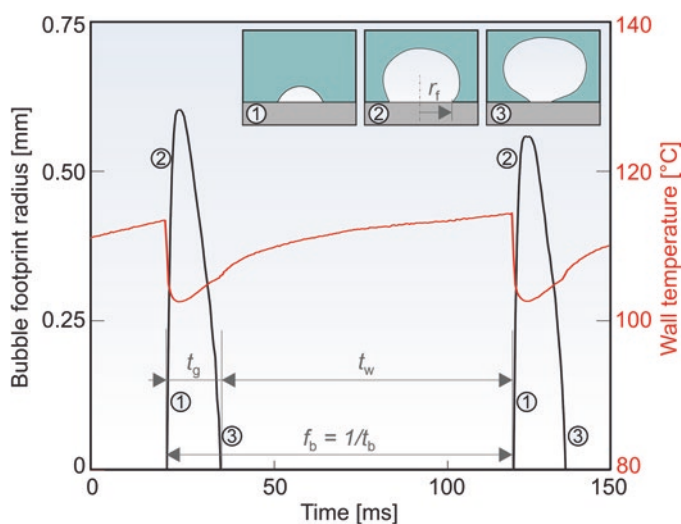


Fig. 4 Typical wall temperature and the bubble's footprint radius development during the bubble life cycle in the saturated pool boiling of water on smooth stainless steel at 50 kW m^{-2}

waiting time t_w . The period t_b is the sum of the growth and the waiting time, and the nucleation frequency $f_b = 1/t_b$ is inversely proportional to it.

As the heat flux is increased towards the CHF or if the nucleation requires relatively large superheats that result in very large bubbles, there is a chance that the liquid microlayer beneath the bubble dries out [72–74]. In this case, the local heat flux underneath the bubble is decreased dramatically followed by the formation of a local hot spot. In order to keep the entire boiling surface at a low temperature and to avoid the burnout of the heater, the hot spot formation should be avoided or delayed as much as possible.

Fritz [8] was the first who correlated the bubble departure radius r_d and contact angle as a result of balancing the buoyancy with the surface tension force, as schematically presented in Fig. 5a:

$$r_d = 0.0104\theta \sqrt{\frac{\gamma_{LV}}{g(\rho_L - \rho_v)}} \quad (4)$$

where g stands for the amplitude of the gravitational acceleration and θ is the static contact angle in degrees. This correlation suggests that bubble departure diameter linearly increases with the contact angle. However, Phan et al. [75] analysed the situation from another perspective (Fig. 5b). When considering two ideally spherical bubbles with the same footprint and different contact angles, the one with a larger contact angle will always be bigger due to simple geometric reasons. They

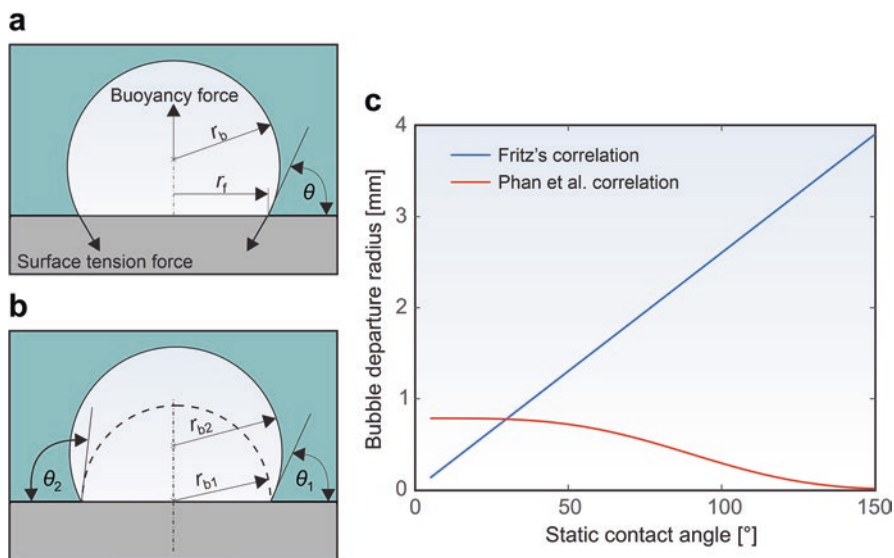


Fig. 5 (a) Illustration of buoyancy and surface tension forces acting on a growing bubble; (b) effect of the contact angle on the size of a spherical bubble; and (c) comparison of two correlations (Eq. (12.4), the blue curve, and Eq. (12.5), the red curve) for the bubble detachment radius for saturated pool boiling of water at 1 atm

modified the Fritz's model by taking into account the energy factor $f(\theta)$ needed to form a bubble from Eq. (2). In this way, they developed a new correlation for the bubble departure radius:

$$r_d = 0.3135 \frac{(2 + 3 \cos \theta - \cos^3 \theta)}{4} \sqrt{\frac{\gamma_{LV}}{g(\rho_L - \rho_V)}} \quad (5)$$

From Fig. 5c, it follows that the correlations by Eqs. (4) and (5) provide completely different trends for the bubble departure radius as a function of the static contact angle. However, the experimental results on surfaces with specific wettability, roughness, fluid type and operating conditions have shown that both correlations can be valid under certain conditions. This indicates that all of these factors play an important role in bubble growth, and despite numerous investigations, there is still no uniform model to accurately predict the bubble size and its growth time for a variety of applications. Even so, one can summarize the most important conclusions, which are mostly based on the experimental results:

- Investigators usually observe a decrease in the bubble departure diameter when a surface is engineered in such a way that lowers its static contact angle [34, 76–78]. On a well wetted surface, the adhesion of the liquid limits the bubble growth, which in turn results in smaller bubbles and higher nucleation frequency assuming the nucleation site density is kept constant. Looking from another perspective, poorly wetted surface will produce larger bubbles and provide longer growth times [79–81], which increases the possibility of formation of undesired local dry-outs and hot spots.
- While maintaining the same pressure and gravity, a decrease in bubble diameter can also be achieved by lowering the fluid's surface tension, which can be achieved either by using a different type of fluid [46, 82], by adding an additional miscible fluid with low surface tension [83–85] or by adding nanoparticles [86]. These techniques can be used to decrease the bubble size, even though this does not necessarily result in an enhanced heat transfer coefficient as the required wall superheat for the bubble nucleation might also increase.
- Discussion about the effects of wettability on the bubble growth is often limited to the static contact angle, as the difference in advancing and receding contact angle in pool boiling is within only $\pm 5^\circ$ based on the results from Ramanujapu, Dhir [87]. Recent findings [76], however, proved that some types of poorly wetted surfaces can exhibit low receding contact angles, which allows low temperature at the onset of boiling and – at the same time – prevents vapor spreading. This enhances the heat transfer coefficient and does not decrease the critical heat flux, which will be discussed in Sect. 4.4.
- Bubble size and bubble dynamics depend not only on wettability, surface roughness and fluid properties, but are influenced also by temperature fields in the solid and the liquid, contribution of microlayer evaporation and complex interactions with neighbouring bubbles. Therefore, tailoring the surface to provide the highest possible nucleation frequency and the nucleation site density does not

necessarily result in the best boiling performance. Distribution of active nucleation sites has to be considered as well, which will be partially discussed in the next section.

2.3 *Pool Boiling Enhancement*

Topographical features and wettability of the boiling surface play an important role in the nucleation, growth and departure of vapor bubbles. Therefore, specific surface characteristics can be used to enhance the heat transfer coefficient (HTC) and the critical heat flux (CHF). Increasing the surface wettability generally increases the CHF but also increases the activation energy for bubble nucleation, which leads to decreased HTC. On the other hand, increasing the nucleation site density and lowering the bubble activation temperature by decreasing the surface wettability and providing appropriate nucleation cavities will increase the HTC, while the CHF is typically decreased on such surfaces. One of the best approaches to enhance both the HTC and the CHF is by locally altering the surface features and chemistry to achieve controlled nucleation, low onset of boiling, effective removal of bubbles and fast liquid replenishment in such a way that formation of large vapor patches is delayed and average surface temperature is maintained as low as possible.

Despite several decades of research, there is still no universal model to accurately predict the HTC and CHF for the wide spectrum of possible boiling conditions [88, 89]. The early hydrodynamic model [90] suggest that CHF value in saturated pool boiling of water is around 1.2 MW m^{-2} . The later developed force-balance model [91] that also includes the effects of the contact angle predicts a decrease in CHF with increasing contact angle. Both of the aforementioned models somewhat accurately predict the measured CHF values on smooth untreated surfaces, which are in the order of $0.6\text{--}1.4 \text{ MW m}^{-2}$ at about $17\text{--}35 \text{ K}$ of superheat (Fig. 6a). The maximum reported HTC values on untreated surfaces are usually in the range of $20\text{--}60 \text{ kW m}^{-2} \text{ K}^{-1}$. Using water as the working fluid, the CHF alone can be enhanced by coupling the hydrophilicity and micro-/nanoroughness via nanowires or nanotubes [31, 92, 93], bio-templating [12], sintering [9, 20, 21], hierarchical structuring [42, 94, 95] or oxidation [28]. These kinds of surfaces can provide enhanced capillary force or wicking [96] to effectively rewet the surface and push the CHF to about $2\text{--}3 \text{ MW m}^{-2}$ with generally limited enhancement in HTC.

To answer the need for simultaneous enhancement of HTC and CHF, researchers developed different surface engineering approaches that include heterogeneous surface chemistry and geometry from macro- to nanoscale in order to gain control over the bubble nucleation. One of the most straightforward techniques shown in Fig. 6b was introduced by Rahman et al. [97], who fabricated alternating regions with low and high thermal conductivity on a copper surface. Heat is conducted mostly through the copper, which represents the active boiling surface, while the insulating epoxy is cooler, thus preventing bubble nucleation and providing a downward pathway for the liquid. Despite the decrease in active boiling area compared to untreated

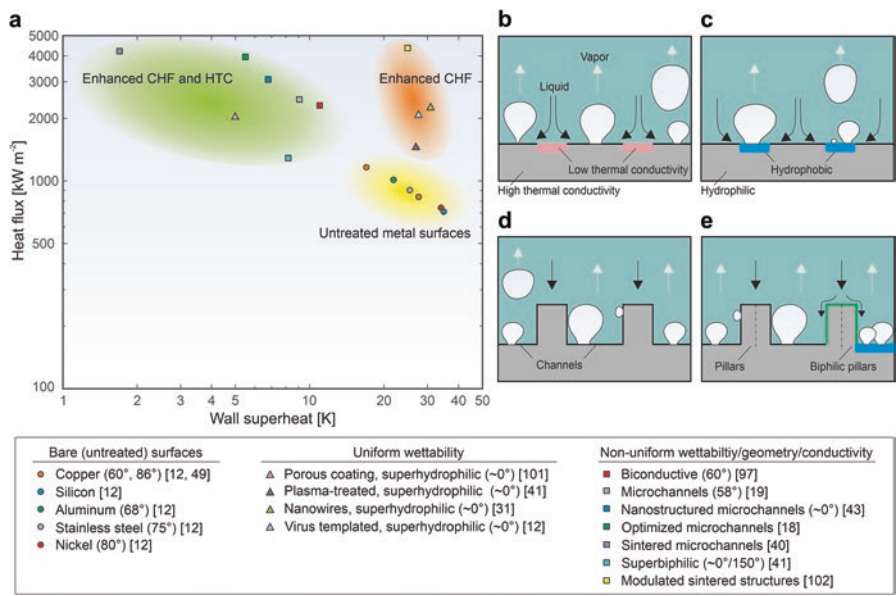


Fig. 6 (a) CHF values recorded on bare metal surfaces and various engineered surfaces reported in the literature [12, 18, 19, 31, 40, 41, 43, 49, 97, 101, 102], achieved under atmospheric saturated pool boiling of water. Where applicable, values in round brackets in the legend represent the reported static contact angles of water. Schematic depiction of how boiling enhancement is achieved by the spatial control over bubble nucleation on (b) biconductive surfaces, (c) biphilic surfaces, (d) open mini-/microchannels and (e) mini-/micropillars

copper, the fivefold enhancement of the HTC ($210 \text{ kW m}^{-2} \text{ K}^{-1}$) and twofold enhancement of the CHF (2.3 MW m^{-2}) was demonstrated on such biconductive surfaces. The authors also show that the optimal pitch of the low-conductivity array is close to the capillary length of water (2.5 mm). Similar control over the nucleation can be achieved on surfaces with mixed hydrophilic and hydrophobic regions (so-called biphilic surfaces), which are shown in Fig. 6c. Surfaces with hydrophobic islands and a hydrophilic background have shown the best enhancement in CHF (up to 1.9 MW m^{-2}), while superbiphilic surfaces demonstrated the HTC of more than $200 \text{ kW m}^{-2} \text{ K}^{-1}$ [41, 98]. In this case, the hydrophobic regions promote bubble nucleation, while the surrounding hydrophilic areas prevent the expansion of the vapor and drive the liquid towards nucleation sites [34].

Effective separation of the vapor and the liquid can also be achieved with mini-/microchannels or pillars (Fig. 6d, e). The bottom of the channel is closer to the heating source and thus hotter making it favourable for nucleation, while the top structures are cooler and less likely to promote bubble formation. This effect can also be enhanced with hydrophobic/hydrophilic patterning. Open microchannel structures with relatively smooth surface demonstrated the CHF of more than 2.4 MW m^{-2} and HTC of $270 \text{ kW m}^{-2} \text{ K}^{-1}$ [19], while the sintered channels were able to dissipate 4.2 MW m^{-2} at the superheat of only 1.7 K ($\text{HTC} > 2400 \text{ kW m}^{-2} \text{ K}^{-1}$) [40]. The

characteristic length scales of optimal surface geometries for biconductive, biphilic or channeled surfaces span from several millimetres down to the micrometre range, indicating that several complex mechanisms are governing the boiling enhancement. This is likely the reason why the universal model of the boiling process is still not defined. Despite great efforts to control and enhance nucleate boiling, the reported CHF values are still far below the kinetic evaporation limit [99, 100], which remains the ultimate goal for future generations.

Currently available techniques for surface engineering provide numerous possibilities of their combinations to develop hybrid surfaces with even better performances. Unfortunately, this usually sacrifices the scalability and increases the complexity as well as the production costs. From this perspective, it seems that further steps should focus on simplified approaches that still have the potential to result in significantly enhanced nucleate boiling performance. We believe that *laser surface engineering* is a promising alternative approach for functionalization of surfaces for controlled and enhanced nucleate boiling, offering both scalability and environmental friendliness. Thus, the next section introduces laser surface engineering and briefly describes how it can be used for the modification of surface topography, chemistry and, consequently, wettability.

3 Laser Surface Engineering

Due to intrinsic properties of laser radiation, its interaction with solid material can induce topographical and chemical modifications on the micrometre and nanometre scale [103–106]. A number of studies have shown that this can be efficiently done using femtosecond [107–110], picosecond [111–113], and nanosecond [114–117] laser pulses as well as continuous-wave laser radiation [118]. These solid surface modifications depend on several parameters, such as light polarization, wavelength, pulse duration, average power, pulse fluence and pulse overlap.

To tailor the functionalized surfaces for specific applications, a new research field, known as *laser surface engineering* [119], emerged in last decade. In general, it comprises the following steps:

- Designing surfaces for various applications
- Modelling and choosing of the laser-processing parameters
- Modifying the surface properties by laser radiation
- Characterizing the fabricated surfaces using different analytical methods
- Testing the engineered surfaces in proposed applications.

The laser surface engineering represents a flexible, scalable and chemical-free method. Thus, it opens up completely new possibilities for the development of new advanced materials that are important for a wide range of engineering applications. We will limit this chapter to engineering of metal surfaces with multiscale μ -cavities as well as variable and/or unstable wettability for boiling heat transfer [46, 49, 62] by using nanosecond laser texturing at pulse fluences significantly exceeding the

threshold fluence for laser ablation [104]. However, this section also briefly presents a general concept of changing the surface wettability through the morphology and chemistry modification by laser-surface interaction. This concept is – in addition to the boiling heat transfer – important also for biomedical [106, 120–122], corrosion [123–126], tribological [127–130] and fluid-flow [131] applications.

3.1 Laser Texturing of Two-Dimensional Surfaces

For laser texturing, a laser system is needed. It consists of (i) a laser source, (ii) focusing optics, (iii) a scanning head, (iv) a controller and (v) the graphical user interface. *The laser source* is characterized by the wavelength λ given in nm, pulse duration t_p , average power P_{avg} , repetition rate f and the beam quality factor $M^2 > 1$ defining how close is the laser-beam profile to the diffraction-limited beam, also called the Gaussian beam. Pulsed laser sources irradiate light in optical pulses, where the pulse duration t_p goes from several femtoseconds to several milliseconds. In this chapter, we will limit ourselves to laser texturing by nanosecond laser pulses.

A laser pulse is a “package” of a certain number of photons, each carrying the energy of $E_0 = hc/\lambda$, where Planck constant equals $h = 4.14 \times 10^{-15}$ eVs, while the speed of light in vacuum is $c \approx 3 \times 10^8$ m s⁻¹. Thus, most commonly used lasers radiate photons with energies in the range 0.1–10 eV. Not only the photon energy but also the absorption of the laser light in a certain material depends on the wavelength. The pulse energy equals the number of photons, irradiated within a single laser pulse, multiplied by the photon energy. Laser pulses are separated by a time interval, t_0 (Fig. 7). The pulse repetition rate is defined as $f = 1/t_0$ and typically goes from a single pulse to several MHz.

Power is the measure for the temporal flow of the energy. Thus, the average power of the laser radiation is defined as the product of the number of pulses N_p , and the pulse energy E_p divided by time t , needed to irradiate this number of pulses. Since the ratio N_p/t equals the repetition rate, the average power is simply

$$P_{\text{avg}} = E_p f \quad (6)$$

However, the pulse power is changing during the pulse, i.e. it goes from zero to peak power P_p and back to zero (the blue curve in Fig. 7). By using a square approximation, we can define the peak power P_p as

$$P_p = E_p / t_p \quad (7)$$

where the pulse duration t_p is usually measured at full width at half maximum (FWHM) of the pulse-power curve (Fig. 7). If we assume that the pulse power can be described by a Gaussian beam, the peak power, estimated by the square approximation (Eq. (7)), is $1/2\sqrt{\pi/\ln(2)} = 1.06$ times higher than the real peak power (the dashed violet square in Fig. 7).

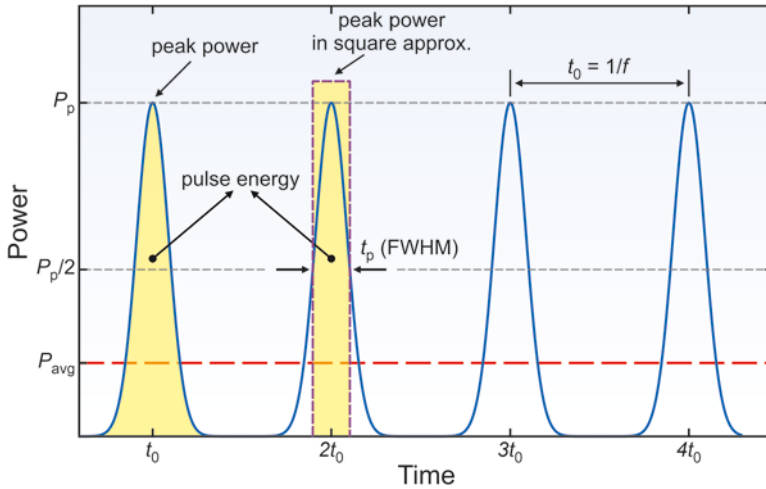


Fig. 7 Schematic presentation of pulse power as a function of time (the blue curve) for the pulse duration of t_p and the pulse repetition rate $1/t_0$. The pulse energy E_p equals the yellow area. The square approximation (with the same pulse energy) is shown by the dashed violet curve, while the dashed red line shows the value of average power

The *focusing optics* is an important component of the laser system, since it defines the area of the beam spot on the processed surface and, consequently, the fluence F given in J cm^{-2} or intensity I in W cm^{-2} . In general, the focusing optics of a laser system consists of a beam expander and a focusing (F-theta or telecentric) lens. The beam expander is usually used to increase the beam diameter D on the focusing lens. This decreases the beam radius in the focus of the lens, called also the beam waist radius w_0 , since the following relation is valid

$$w_0 = \frac{2f_L \lambda}{\pi D} M^2 \quad (8)$$

where f_L stands for the focal length of the lens. It can be observed that the beam quality factor, which is an inherent property of the laser source, significantly influences the smallest attainable beam waist radius. High beam quality is one of the most important advantages of the fibre lasers versus other types of lasers [132].

The *scanning head* usually consists of two mirrors that lead the laser pulses over a two-dimensional surface. Instead of using a scanner, the sample can also be moved using an appropriate x-y positioning system. Both approaches allow processing of the sample in two dimensions. Here, the following three processing parameters are important: the scanning speed v , the scanning line separation Δy and the scanning strategy. The combination of the scanning speed and the repetition rate defines the distance between the centres of consecutive pulses (Fig. 8a):

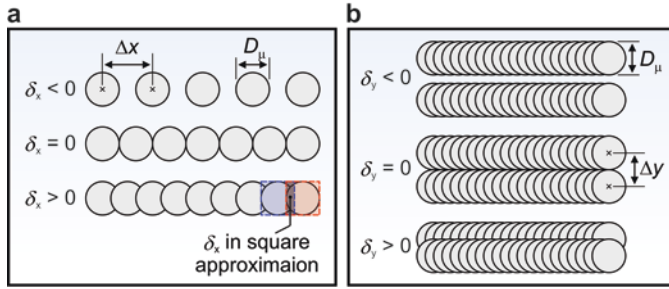


Fig. 8 (a) Overlapping between pulses (in the x direction). The square approximation is schematically presented. (b) Overlapping between μ -channels (in the y direction)

$$\Delta x = \frac{v}{f} \quad (9)$$

Consequently, the pulse overlap (Fig. 8a) is defined as

$$\delta_x = 1 - \frac{\Delta x}{2D_\mu} \quad (10)$$

where D_μ stands for the diameter of the hole (damage) ablated by a single pulse. It should be noted that Eq. (10) is valid for a square approximation (see the last two pulses for $\delta_x > 0$ in Fig. 8a). Some authors use the beam diameter on the surface w instead of D_μ in Eq. (10). However, in this case, this is not the overlap of the laser-induced craters but is instead related to the overlapping of the laser pulses. As we will show later, the crater diameter is not necessarily equal to the beam diameter (in general, $D_\mu \neq w$). When $\delta_x > 0$, the craters overlap and form a micro(μ)-channel, while $\delta_x < 0$ leads to separate μ -craters, as sketched in Fig. 8a.

To process the whole two-dimensional surface, multiple μ -channels need to be fabricated across the surface. Here, the scanning line separation Δy is another important parameter. Like the overlap of consecutive pulses, the overlap of the consecutive lines (Fig. 8b) can be defined as

$$\delta_y = 1 - \frac{\Delta y}{2D_\mu} \quad (11)$$

In Eq. (11), D_μ stands for the width of individual μ -channels.

The two-dimensional surface can be textured in many different ways. The most common *scanning strategies* are schematically shown in Fig. 9 and can be used to control the surface wettability for different applications:

- *0° texturing with equidistant spacing* (Fig. 9a) represents the simplest scanning strategy. Therefore, it was used in plenty of experiments, including the production of laser-textured hydrophobic surfaces for chemical sensing applications

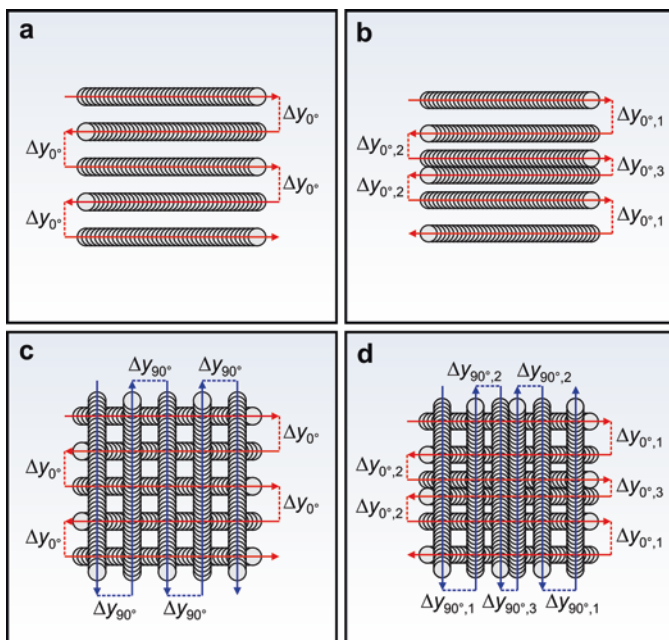


Fig. 9 Schematics of the most common scanning strategies. (a) 0° texturing with equidistant spacing, (b) 0° texturing with variable spacing, (c) $0^\circ/90^\circ$ texturing with equidistant spacing and (d) $0^\circ/90^\circ$ texturing with variable spacing. The direction of the scanning passes is shown by the arrows, and the laser is switched off when leading at the dashed lines

[114], laser texturing of wettability gradients [133], modifying the surface wettability for friction control [128] and the development of biodegradable materials by producing hydrophilic FeMn surfaces that trigger self-driven corrosion [121].

- 0° texturing with variable spacing (Fig. 9b) is a modification of the previous scanning strategy leading to multiscale μ -cavities. Gregorčič et al. [46] used this approach to enhance boiling heat transfer for a diverse range of fluids, independent on their polarity or surface tension, while Zakšek et al. [84] have shown that this approach enhances boiling parameters also for binary mixtures.
- $0^\circ/90^\circ$ texturing with equidistance spacing (Fig. 9c) is the combination of the simplest scanning strategy (0° texturing) in two perpendicular directions—the surface is textured first in x and then in y direction. Trdan et al. [123] used this scanning strategy to study the influence of superhydrophilic-to-superhydrophobic transition on corrosion resistance of laser textured stainless steel. They have shown that this strategy leads to open μ -channels along the last laser scanning direction (90°) and partially closed μ -channels in the perpendicular direction (0°) enabling faster fluid motion in the last scanning direction (90°).
- $0^\circ/90^\circ$ texturing with variable spacing (Fig. 9d) is a modification of the previous scanning strategy. Zupančič et al. [62] used this strategy to produce surfaces with multiscale μ -cavities and non-uniform wettability.

In many cases [111, 117, 134], the surface modification does not depend only on the pulse fluence but also on the total energy irradiated to the surface area, F_{tot}

$$F_{\text{tot}} = N_A \frac{P}{v\Delta y} \quad (12)$$

where the integer N_A tells how many times the whole area is processed (the number of the repetitions across the whole processed area). In case of a single repetition of 0° texturing, $N_A = 1$, while for a single repetition of the $0^\circ/90^\circ$ texturing, $N_A = 2$. If the same surface is processed twice using the $0^\circ/90^\circ$ strategy, $N_A = 4$.

3.2 Influence of Laser Fluence on Surface Topography

It is widely known that laser ablation leads to topographical and chemical modifications of the surface [103–105, 115]. Since the particular change of the surface properties significantly depends on the intensity and/or fluence of laser radiation, laser texturing of metals in an oxygen-containing atmosphere can be classified into the following three regimes:

- *The regime of very low fluences* (i.e. below the threshold fluence for surface ablation), where the oxidation of the metallic surface represents the main modification during the processing. In this case, the topographical modifications of surface on the micrometre level almost disappear and the chemical modification manifests itself the formation of ten or hundred nanometre thick oxide layer that is visible as colorized metal [117, 135].
- *The regime of fluences near the ablation threshold* by polarized laser pulses. In this case, the so-called laser-induced periodic surface structures (LIPSS) [136] appear on the surface as a regular ripple structure with a period scaling from well below to well above the laser wavelength, while its orientation and shape depend on the pulse polarization [111, 137]. LIPSS can be formed using various pulse durations, including femtosecond [138–141], picosecond [111, 142] and nanosecond pulses [116, 143] as well as continuous-wave radiation [144].
- *The regime of high fluences* resulting in ablation and melting of the material. Here, the overlap of craters forms μ -channels, as visible on SEM micrographs in Fig. 10a and a hierarchical structure appears due to the melting and oxidation of the material [104, 106]. Additionally, the remolten material is deposited around the textured μ -channel.

This chapter considers only the laser texturing in the high fluence regime and in the air atmosphere. Figure 10a shows μ -channels on a stainless steel surface induced by a Nd:YAG laser ($\lambda = 1064$ nm) radiating 30 ns long pulses. The sample was textured in the x direction (0° texturing) in the focus. The scanning line separation was constant ($\Delta y = 50$ mm), while the peak fluence was varied in the range of $4.51\text{--}25.1$ J cm $^{-2}$ by changing the average power at a constant repetition rate. The

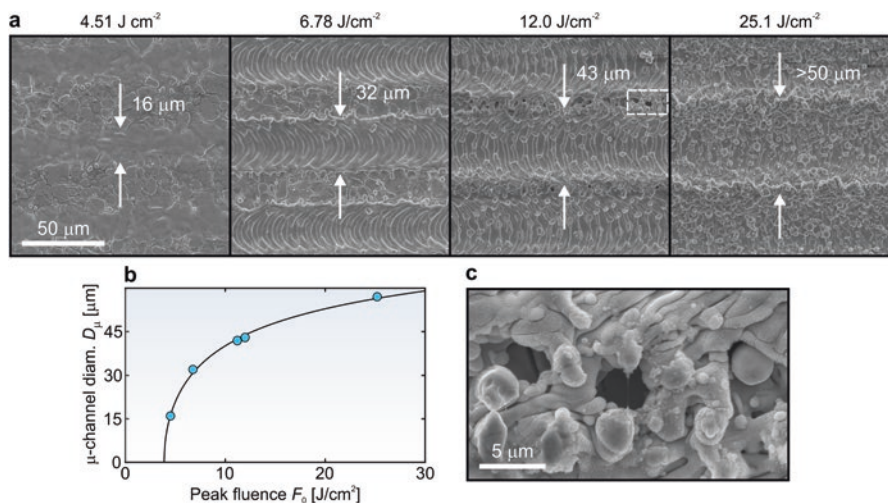


Fig. 10 SEM micrographs of μ -channels at different peak fluences F_0 (shown on the top of each micrograph); scanning line separation in all cases equals $\Delta y = 50 \mu\text{m}$. **(b)** Experimental (points) and theoretical (line; see Eq. (17)) dependence between the μ -channel diameter and the peak fluence F_0 . **(c)** Magnification of the selected area in **(a)** showing the appearance of μ -cavities. (Reproduced and adapted from Ref. [134]. Creative Commons Attribution 4.0 International License)

scanning speed of 150 mm s^{-1} and the repetition rate of 25 kHz resulted in the distance between the consecutive pulses of $\Delta x = 6 \mu\text{m}$, while the beam diameter equalled $w_0 = 29 \mu\text{m}$. Considering $D_\mu = w_0$ in Eq. (9), the overlap of laser pulses equalled $\delta_x = 0.90$. However, it is clearly visible that the μ -channel diameter D_μ depends on the pulse fluence and – for the given processing parameters – goes from 16 to 56 μm . If the real μ -channel diameter is taken into account, Eq. (10) gives that the overlap δ_x changes in the range 0.81–0.95.

The dependence between the μ -channel diameter and the laser fluence can be described by considering a Gaussian beam profile [134], where the fluence $F(z, r)$ is a function of the axial distance from the beam's focus z and radius r is given by

$$F(z, r) = F_0 \frac{w_0^2}{w^2(z)} \exp\left(-2 \frac{r^2}{w^2(z)}\right). \quad (13)$$

In Eq. (13), F_0 stands for the peak fluence at $r = 0$ and $z = 0$, w_0 is the $1/e^2$ beam waist radius in the focus (at $z = 0$) and the beam radius as a function of z is defined as

$$w(z) = w_0 \sqrt{1 + z^2 / z_R^2}. \quad (14)$$

Here, the Rayleigh length, i.e. the distance between the focus and the position z_R , where the area within the beam diameter is doubled, is calculated as

$$z_R = \frac{\pi w_0^2}{\lambda}. \quad (15)$$

Equation (13) can be used to predict the radius of the ablated area $R_\mu = D_\mu/2$ on a surface placed at z , if the following assumptions are made:

- The region of the irradiated surface, where $F(z, r) \geq F_{th}$ is damaged (textured).
- The region with $F(z, r) < F_{th}$ is not damaged (not textured).

Under these assumptions, the radius R_μ of the damaged (textured) surface equals the radius r , where $F(z, r = R_\mu) = F_{th}$. Putting this condition into Eq. (13) gives

$$R_\mu = w_0 \sqrt{\frac{1 + (z/z_R)^2}{2} \ln \left(\frac{F_0 / F_{th}}{1 + (z/z_R)^2} \right)}. \quad (16)$$

Figure 11 shows how the radius of the ablated area changes, when the surface is moved out of the focal plane for different ratios between the peak fluence and the fluence for the ablation threshold F_0/F_{th} . Note that the dimensionless radius R_μ/w_0 is given in the y axis and that the dimensionless distance $|z|/z_R$ is shown in the x axis. It is evident that the radius of the μ -structure, textured in the focal plane, equals the beam waist radius ($R_\mu/w_0 = 1$) only for the ratio $F_0/F_{th} = e^2$. For the ratios $F_0/F_{th} < 3$, the μ -structure radius is *always smaller* than the beam waist radius, and it *decreases* when the surface is placed out of the focal position. However, for $F_0/F_{th} > e^2$, the μ -structure radius is *larger* than the beam waist radius, and it first *increases* by moving the surface out of the focal position. However, if the surface is further moved out of the focus, the R_μ starts to decrease until surface damage is no longer observable.

If the surface is processed in the focus ($z = 0$), Eq. (16) is simplified to

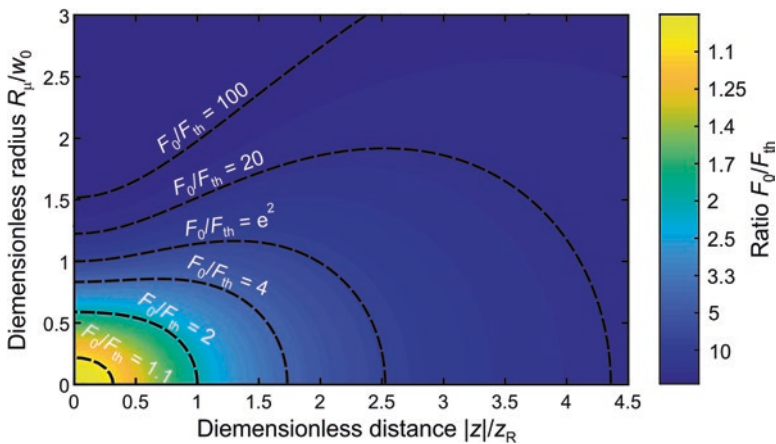


Fig. 11 The theoretical dependence (calculated by Eq. (16)) of the μ -structure radius as a function of the axial distance from the beam's focus for different ratios F_0/F_{th}

$$R_\mu = w_0 \sqrt{\frac{1}{2} \ln \left(\frac{F_0}{F_{th}} \right)}. \quad (17)$$

Equation (17) can be used to calculate the threshold fluence for a given material under given processing parameters. To do this, one should put the surface in the focal plane and should texture the lines or holes at different peak fluences (e.g. by changing the average power at a constant repetition rate). The result for stainless steel is shown in Fig. 110b, where the measured radii are presented by the points. Fitting Eq. (17) across the measured points gives the fluence threshold that in this case equals 3.8 J cm^{-2} . The fit further enables the estimation of the μ -channel diameter at $F_0 = 25.1 \text{ J cm}^{-2}$ that cannot be measured otherwise due to overlapping of the μ -channels. Fit gives that $D_\mu = 56 \text{ }\mu\text{m} > \Delta y$. This calculated result is experimentally confirmed by μ -channel diameter measurements at the same fluence, but for $\Delta x = 100 \text{ }\mu\text{m}$ [134].

Since the surface topography significantly depends on the combination of the peak fluence and scanning line separation, the variation of these two parameters can be used for structuring different surface topographies. In a special case, when D_μ is just slightly smaller than scanning line separation Δy , the μ -cavities appear on the border between two adjacent μ -channels as clearly visible from Fig. 10c, which is the magnification of the selected area (marked by the white rectangle) in the third micrograph of Fig. 10a. As we will show later this approach enables production of the μ -cavities that play an important role in engineering of surfaces for enhanced heat transfer [46, 62].

It should be noted that several definitions of pulse fluence are used in the literature. This may lead to confusion, if the authors do not explicitly state how they calculate (define) the beam fluence. Usually, the fluence is calculated as a pulse energy per area within the beam waist radius

$$F = \frac{E_p}{\pi w_0^2}. \quad (18)$$

However, one should consider that the laser radiation is theoretically not limited to the radius of the beam. This radius is defined as the distance from the centre to the radius, where the beam intensity decreases to the $1/e^2$ peak intensity. Thus only $(e^2 - 1)/e^2 \approx 0.86$ of the pulse energy is included into this area of the beam cross section. The average fluence within the beam radius w thus equals

$$F_w = \frac{e^2 - 1}{e^2} F. \quad (19)$$

The peak fluence F_0 is also commonly provided. In this case the following relation is valid:

$$F_0 = 2F. \quad (20)$$

As we can see by comparison of Eqs. (18), (19), and (20), any type of the fluence definition enables comparison of the results obtained by different authors, but the authors should *always* reveal how they define it.

3.3 The Role of the Scanning Line Separation

Not only the fluence but also the scanning line separation Δy and the scanning strategy determine the surface morphology modifications [104, 128, 134]. Moreover, when one would like to produce surfaces with different roughness, changing the scanning line separation is more appropriate approach as changing the pulse fluence, since pulse fluence – when well above the threshold fluence for laser ablation – has only minor effect on surface roughness, as follows from Eqs. (16 and 17).

The influence of the scanning line separation on surface topography is clearly evident from the SEM micrograph in Fig. 12a that shows the surface morphology of stainless steel for different Δy at a constant fluence $F_0 = 31 \text{ J cm}^{-2}$. It is observable that under very small scanning line separation ($\Delta y < D_\mu$), the processed surface becomes highly porous with no specific (long) μ -channels (Fig. 12a for $\Delta y = 25 \mu\text{m}$). On the contrary, large scanning line separation (i.e. $\Delta y > D_\mu$) leads to the well separated μ -channels, as visible in Fig. 12 for $\Delta y = 200 \mu\text{m}$.

Similar behaviour of the surface morphology as a function of the scanning line separation (at a constant pulse fluence) has been observed by several authors [128, 134, 145], who used the surface roughness parameter S_a as the main evaluation metric of the surface morphology after the laser texturing. They all show (similarly as

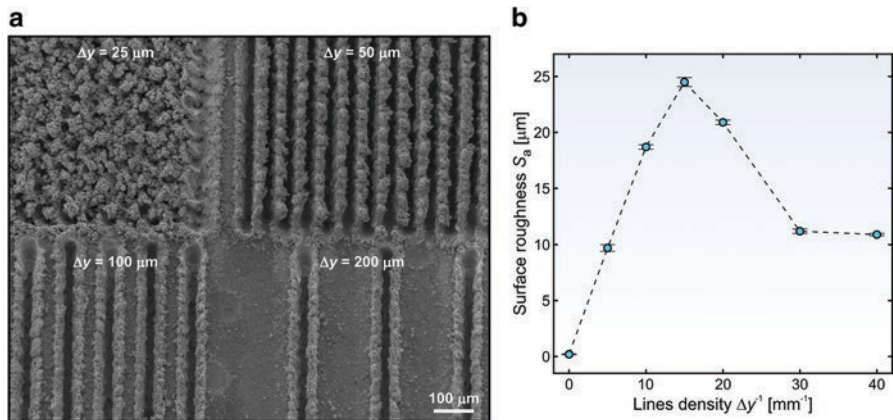


Fig. 12 Influence of the scanning line separation on (a) surface topography and (b) average surface roughness S_a . Note that in (b) the line density Δy^{-1} (i.e. the inverse value of the scanning line separation Δy) is used for better presentation; here, the unprocessed surface corresponds to $\Delta y^{-1} = 0$. (Panel (a): Reproduced and adapted from [104] with permission from Springer. Panel (b): Reproduced and adapted from [128]. Creative Commons Attribution 4.0 International License)

in Fig. 12b) that S_a increases by decreasing Δy until $\Delta y > D_\mu$, since under this condition the laser-textured μ -channels are (well) separated (as for $\Delta y \geq 50 \mu\text{m}$ in Fig. 12a). However, a further decrease of Δy leads to a decrease of the average surface roughness parameter, since S_a measures the arithmetical mean of differences in the height of each point compared to the arithmetical mean of the entire surface. Therefore, it is not sensitive to the increased porosity (as visible for $\Delta y = 25 \mu\text{m}$ in Fig. 12a) induced by a further decrease of Δy [128]. Note that the line density Δy^{-1} (i.e. the inverse value of the scanning line separation Δy) is used for better presentation in the ordinate axis of Fig. 12b. The non-processed surface corresponds to $\Delta y^{-1} = 0$ and in case of Ref. [128], where Fig. 12b is taken from, its surface roughness equalled $S_a = 202.7 \text{ nm} \pm 5 \text{ nm}$.

Higher SEM magnification (the inset in Fig. 13a) reveals that the tops of μ -channels are covered with bumps with the dimensions in the range of 1–7 μm [104]. This bimodal surface is also clearly visible from the cross section in Fig. 13b, while the electron backscatter diffraction (EBSD) analysis of the cross section (Fig. 13c) reveals that both the bulk and the processed material (on the tips) have no specific grain orientation. The austenitic grains of the bulk (unprocessed) material have typical dimensions between 20 and 30 μm , while the laser texturing results in much finer grains with typical dimension below 10 μm [104].

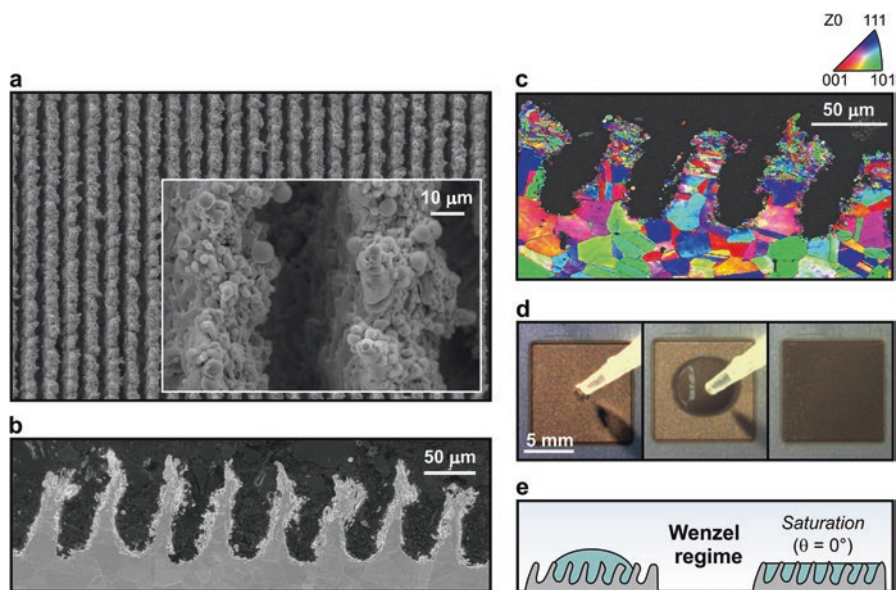


Fig. 13 Stainless steel surface morphology, microstructure and wettability after high fluence laser texturing with $\Delta y = 50 \mu\text{m}$ and $F_0 = 31 \text{ J cm}^{-2}$. (a) SEM micrographs of the surface and (b) its cross section. (c) EBSD measurement (Z direction IPF colouring orientation map). (d) Surface in a saturated Wenzel regime immediately after the laser texturing. (e) Schematic presentation of the saturated Wenzel regime. (Panels (a)–(d): Reproduced and adapted from [104] with permission from Springer)

3.4 Surface Wettability Immediately After Laser Texturing

As shown by several authors [114, 134, 146], the scanning line separation and surface roughness after nanosecond laser texturing significantly influence the surface wettability. Immediately after the laser texturing (with high fluences), the water droplet shows complete wetting of the entire processed surface and forms a thin film, as visible in Fig. 13d. This indicates that laser texturing turns the surface superhydrophilic and causes the appearance of the saturated Wenzel regime with a contact angle $\theta = 0^\circ$ (see schematics in Fig. 13e).

In the Wenzel regime, the liquid-solid interaction results in homogeneous wetting. Thus, the liquid completely penetrates into the solid surface asperities and the Wenzel contact angle θ_w depends on the Young angle θ_Y for an ideal (i.e. flat, perfectly smooth, chemically homogeneous, insoluble, non-reactive, and rigid [48, 147]) surface and the surface roughness r , defined as the area of the rough surface and the area of the corresponding smooth surface [148]:

$$\cos(\theta_w) = r \cos(\theta_Y). \quad (21)$$

The Wenzel state (Eq. (21)) predicts saturation of an ideal hydrophilic surface with the Young angle θ_Y below 90° to a film ($\theta_w = 0^\circ$) when roughness r exceeds the saturated roughness r_s [149, 150]:

$$r_s = \frac{1}{\cos(\theta_Y)}. \quad (22)$$

Gregorčič et al. [104] have measured the Young's contact angle on a polished stainless steel sample before laser processing to be $\theta_Y = 81.6^\circ$. From this value, it follows that the saturated roughness (Eq. (22)) for their material equals $r_s = 6.8$. From the cross section of the surface after the laser texturing (Fig. 13b), they measured that the surface roughness after laser processing equalled only $r = 4.5 < r_s$, yet the surface was already in the saturated Wenzel state. This additionally confirmed that the laser texturing in an oxygen-containing atmosphere changes the surface chemistry and, consequently, the intrinsic contact angle.

They have additionally confirmed this conclusion by the EDS measurements, presented in Fig. 14b. Figure 14a shows a bump with a broken oxide layer – the EDS measurements were performed in points 1–6 and within areas A (without the oxide layer) and B (covered by the oxide layer). The measured weight percentage of the oxygen within the selected points and/or areas is revealed in graph in Fig. 14b. This measurement clearly proves that laser texturing results in surface oxidation.

Formation of oxide layer on metal surfaces significantly affects wetting. Usually, rough metallic oxide surfaces tend to be highly hydrophilic [151]. This explains why the saturated Wenzel regime happens already with roughness smaller than r_s , predicted by Eq. (22) for the Young's angle of the base (unprocessed) material. The laser processing does not only change the surface morphology, but it also

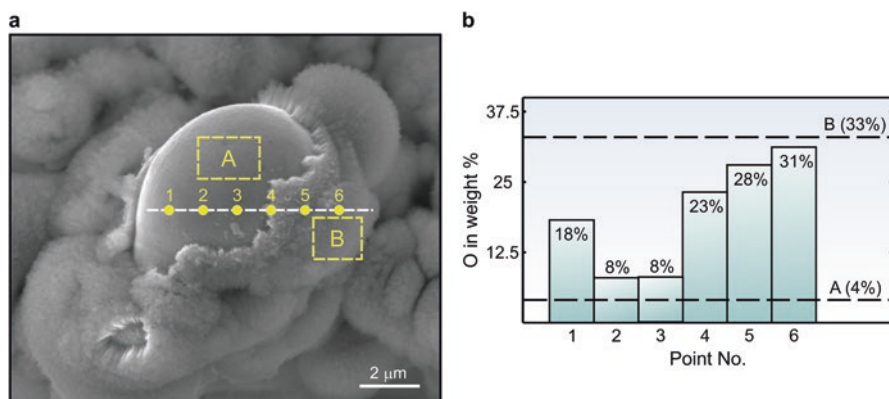


Fig. 14 (a) SEM micrograph of a bump with broken oxide layer on a stainless-steel surface after laser texturing and (b) EDS analysis of the oxygen content element. (Reproduced and adapted from Ref. [104] with permission from Springer)

significantly modifies the surface chemistry [103, 105, 106, 126] leading to a decrease in Young's angle due to metal oxidation. Thus, not only the morphological modification but also the modified surface chemistry increases the metallic surface wettability after laser texturing.

3.5 The (Super)Hydrophilic-to-(Super)Hydrophobic Transition

The initial (super)hydrophilic state of the laser-textured surface is not stable. Several authors [104, 114, 123, 134, 145, 146, 152, 153] have reported that the (super)hydrophilic-to-(super)hydrophobic transition occurs if the laser-textured sample is exposed to atmospheric air for an appropriate period (usually from several days to several weeks). The underlying mechanisms responsible for this transition are still under debate [154]. Different (even contradictory) mechanisms have been proposed, including decomposition of carbon dioxide into carbon with active magnetite [152]; partial surface deoxidation [155] and creation of hydrophobic functional groups [153]; as well as the absorption of organic matter from the atmosphere, where the processed samples are stored (i.e. the hydrocarbon contamination) [151, 156, 157].

We have several reasons to believe that the wettability transition of the laser-textured metallic surfaces happens mainly due to the hydrocarbon contamination, although it seems that contradictory results exist in the literature [105]. Long et al. have shown that the time needed for the (super)hydrophilic-to-(super)hydrophobic transition after laser processing of aluminium [112] and copper [151] remarkably depends on the atmosphere, where the surfaces are stored after the processing. Similar behaviour was observed also by Yan et al. [158] for laser-textured brass that was stored in different media (including liquids) after texturing. They all found that the organic-rich environments significantly shorten the time needed for the

transition toward hydrophobicity. Their XPS analysis also revealed that the C/metal ratio corresponds well with trends in measured contact angles. Larger contact angles always appeared in combination with relatively high C/metal ratio. Additionally, the analysis of the relative atomic percentage of nonpolar C-C(H) bonds that serve as hydrophobic regions suggested that high C/metal ratios and high atomic percentage of C-C/C-H value may be an indicator of a hydrophobic surface [112, 151]. However, it should be pointed out that such wettability transition is not observed solely on the laser-induced oxides, since similar effects due to airborne hydrocarbons have also been discussed by Takeda et al. [159], who studied the increase of the contact angle on metal oxide films deposited on soda-lime-silica glass by magnetron sputtering; by Strohmeier [160], who exposed plasma-treated aluminium foil to the atmospheric air; as well as by Seshardi et al. [161] who studied the effects of gamma (ionizing) irradiation of metallic surfaces on their wettability.

Since the low-temperature annealing could remove the surface modified monolayer [162], different authors annealed at low temperatures the aged laser-textured samples that have already developed (super)hydrophobicity [112, 151, 156]. Their results show that the low-temperature annealing (in the range of 250–350 °C) recovers the initial (super)hydrophilicity. Additionally, the XPS measurements [112, 156] after the annealing process revealed a *decrease* of C/metal ratios as well as *decreased* content of C-C/C-H bonds. This leads to a conclusion that thermal annealing partially removes the adsorbed organic contaminants.

Several authors have convincingly demonstrated that spontaneous (super) hydrophilic-to-(super)hydrophobic transition under ambient conditions happens for a number of laser-textured metals and metal alloys with different chemical and catalytic activity as well as different crystallographic structure. These samples were textured by femtosecond [152, 163], picosecond [112] and nanosecond [104, 114, 134, 146] laser pulses. Moreover, similar transitions have also been observed on oxides that were not induced by laser radiation [159–161]. All of this indicates that the mechanism of wettability transition after laser texturing should be universal and should not characteristically depend on a specific metal or metal alloy as well as on specific (laser-)processing parameters [154].

However, some observations reported in the literature are at the first sight not consistent with the above-reviewed results. In this context, Chun et al. [164], Ngo et al. [165] and Lian et al. [166] reported that they *accelerated* the hydrophilic-to-hydrophobic transition of laser-textured samples by low-temperature annealing. Unfortunately, they do not reveal enough details of the chemical analysis (of a thin surface layer), which would explain, why they observed the exact opposite of what was shown very convincingly by Long et al. [112, 151]. Thus, we have repeated similar low-temperature annealing experiment with (i) fresh, still superhydrophilic laser-textured surfaces and with (ii) aged, already superhydrophobic laser-textured surfaces [105]. If the furnace was *free of contaminants*, the result of the low-temperature annealing was *always* a hydrophilic surface. When a fresh, still hydrophilic surface was annealed, the water repellency has not developed, while the low-temperature annealing led to increased wettability (turned off the hydrophobicity) on aged, already hydrophobic laser-textured surfaces. On the contrary, if the

furnace was *contaminated* by organic compounds, the low-temperature annealing universally (i.e. independently on metal used) resulted in hydrophobic surface [105].

Figure 15a shows the stainless steel surface, processed by the parameters described in Ref. [104], immediately after the texturing, when the surface was in a saturated Wenzel state ($\theta = 0^\circ$). The SEM image of the same surface in a superhydrophobic state ($\theta = 153^\circ$, the roll-off angle $< 7^\circ$) 3 months later is shown in Fig. 15b. The comparison of these two images reveals that the suggestion of some authors [114] that surface morphology does not change during aging the samples might only be true on the micrometre scale and not necessarily on a sub-micrometre scale. Figure 15 clearly demonstrates the development of an additional nanostructure on the oxide layer in the scale of 200–700 nm. In this example, the nanostructure immediately after the laser-texturing looks like a “closed flower”, while 3 months later, it looks like an “opened flower”. Although this sample was already superhydrophobic 30 days after the laser texturing, the nanostructure was still developing in a fractal-like manner, as shown on the SEM image acquired on the same sample 10 months later (Fig. 15c).

To additionally confirm the results of low-temperature annealing experiments by Long et al. [112, 151], this superhydrophobic sample was put into an uncontaminated furnace at 350°C for four hours. After the low-temperature annealing, the superhydrophobicity was turned off, and the surface was returned into the saturated Wenzel regime ($\theta = 0^\circ$). The morphology on the micrometre and nanometre scale has not changed significantly, as visible from Fig. 15d, while the content of C atoms was significantly reduced. This suggests that the mechanisms proposed by Long et al. for aluminium [112] and copper [151] surfaces are also valid for stainless steel. Moreover, it additionally confirms that the wettability transition after laser texturing is governed mainly by the surface chemistry modification. The (sub-micrometre) morphology modification during surface aging is not negligible, but it seems that its influence on the overall wettability behaviour is insignificant.

Similarly, at the first sight contradictory effect is observed, when the laser-textured surfaces are exposed to vacuum [151, 167]. Long et al. [151] reported that

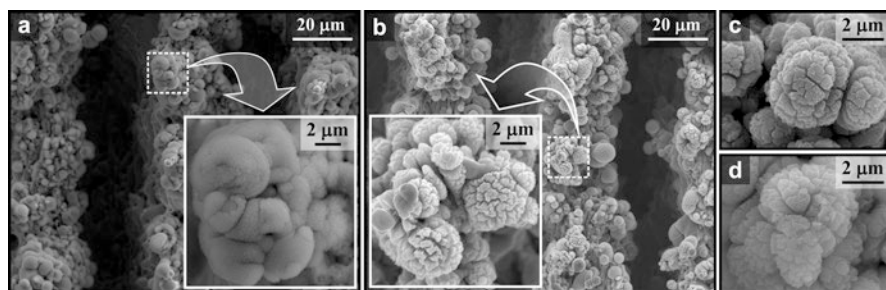


Fig. 15 SEM micrographs revealing the surface nanostructure evolution of stainless steel: (a) one day after laser texturing ($\theta = 0^\circ$); (b) 3 months after laser texturing ($\theta = 153^\circ$); (c) 10 months after laser texturing and before low-temperature annealing ($\theta > 150^\circ$); (d) sample from (c) after low-temperature annealing ($\theta = 0^\circ$)

“vacuum” accelerates the hydrophilic-to-hydrophobic transition just like an organic-rich atmosphere. This corresponds well with findings by Yan et al. [168], who examined the wettability of a Fe_2O_3 nanoflakes film. They observed a remarkable acceleration of the temporal contact angle increase, when the film was exposed to vacuum. In this case, the surface became ultrahydrophobic with a contact angle of 160° , compared to 0° for the sample that was stored in a nitrogen atmosphere. They explained that this happens due to the chemisorption of organic molecules such as oil droplets from vacuum pumps.

These findings clearly show that the contamination of the atmosphere, where the surfaces are aged and/or annealed, plays a significant role in the wettability transition. Moreover, the existing experimental results also clearly indicate that the *ambient conditions* should be appropriately controlled during aging of the samples and that an analysis of surface chemistry is required to correctly interpret the experimental observations.

As shown by Gregorčič et al. [134], the *long-term examination* of wettability transition after laser texturing is another important factor that should be taken into account to develop pertinent conclusions. In this study, the authors compared the contact angles after a short- (up to 40 days), intermediate- (100 days) and long-term (1 year) superhydrophilic-to-(super)hydrophobic transition of laser-textured stainless-steel surfaces exposed to atmospheric air. The measured contact angles as a function of time for different scanning line separations are shown in Fig. 16. According to Eq. (12), smaller scanning line separation means higher total energy irradiated to a surface. The results in Fig. 16 clearly indicate that solely the short-term consideration of the wettability transition (many authors [104, 114, 123, 133, 146, 153, 169] that usually indicate “stable conditions” after 1 or 2 months of the contact angle analysis) may lead to the wrong conclusion that the “final” contact angle is strongly influenced by the scanning line separation, since in the short-term period, the smallest Δy (Fig. 16a) results in a still hydrophilic surface. Such a conclusion was developed by Ta et al. [146] who evaluated the surface wettability for only 15 days following laser texturing. However, as shown by Gregorčič et al. [134], an intermediate-term evaluation (i.e. after 3 months) already reveals that such hydrophilic state is not stable, since hydrophobicity is achieved on all the samples, independent of the scanning line separation (see the contact angles within “intermediate-term” in Fig. 16). Moreover, a long-term examination of the wettability transition reveals that after one year, all the samples expressed a successful transition from superhydrophilic to superhydrophobic state. After the long-term period, even the surfaces that were processed by the smallest scanning line separation (Fig. 16a) achieved a lotus leaf-like state with $\theta > 150^\circ$ and a roll-off angle $< 5^\circ$ [134].

In contrast to the short-term evaluation [146], the long-term results in Fig. 16 suggest that the highest final contact angle is achieved for the highest value of the total absorbed energy per unit area, defined by Eq. (12). A long-term evaluation of the wettability transition is especially important, when high total energy per unit area is used due to (i) high average power (P in Eq. (12)), (ii) slow processing speeds (v in Eq. (12)), and/or (iii) small scanning line separations (Δy in Eq. (12)). In this case, immediately after laser texturing, the surface is in a highly saturated

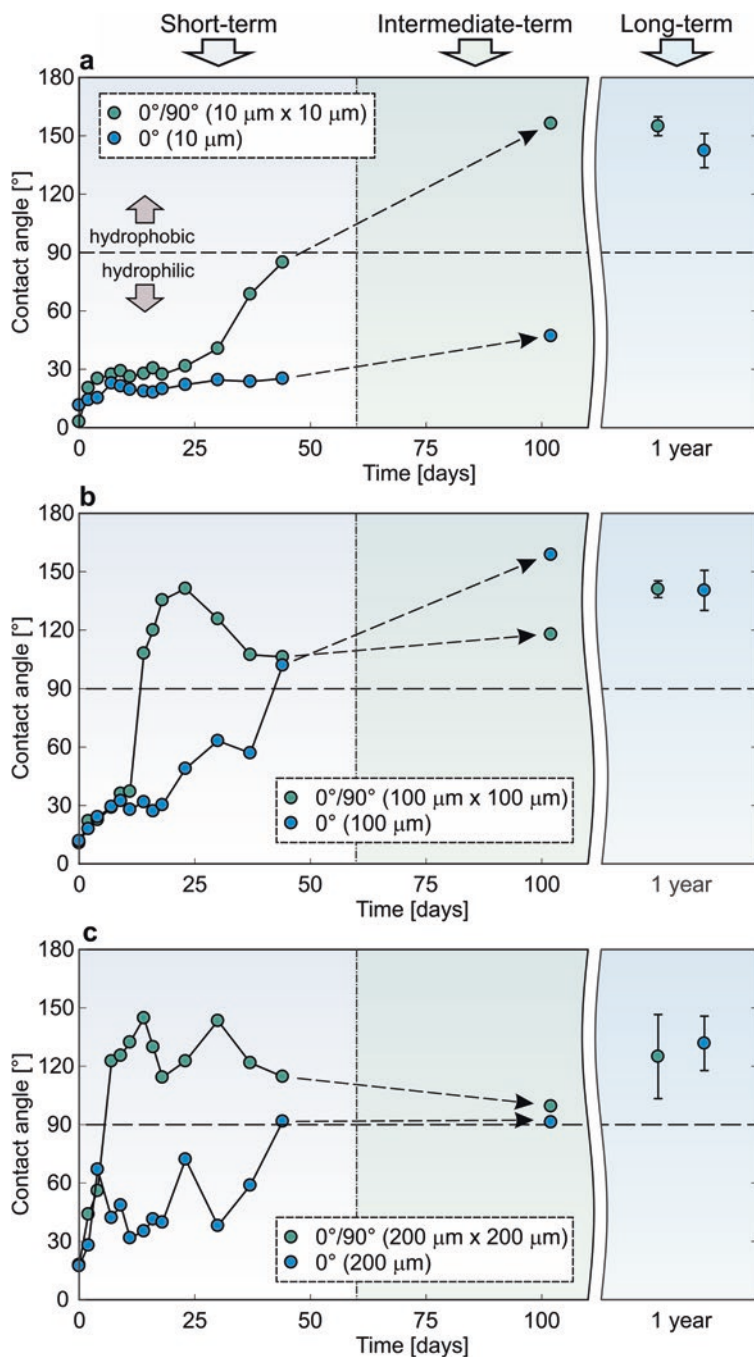


Fig. 16 Short-term, intermediate-term and long-term static water contact angle development on surfaces with the following scanning line separations: (a) $\Delta x = \Delta y = 10 \mu\text{m}$; (b) $100 \mu\text{m}$; and (c) and $200 \mu\text{m}$. The results are shown for the 0° texturing (blue points) and for the $0^\circ/90^\circ$ texturing (green points) with $F_0 = 25.1 \text{ J cm}^{-2}$. (Reproduced and adapted from Ref. [134]. Creative Commons Attribution 4.0 International License)

Wenzel state ($\theta = 0^\circ$), making it impossible to evaluate different surface wettabilities through the contact angle. Thus, other approaches for the wettability characterization (e.g. measuring the wicked volume flux [44] or droplet spreading [170]) should be used to distinguish different wettabilities of such surfaces immediately after the texturing. As shown by the results in Fig. 16, a higher amount of total absorbed energy per unit area does not lead only to a more hydrophilic surface, but it also causes a *slower* development of hydrophobicity. However, the slower development usually results in a *higher* final contact angle (i.e. a more hydrophobic surface) [134].

3.6 Fabrication of Multiscale μ -Cavities by Laser Texturing

- As we have discussed in the Sect. 2, the surface wettability significantly influences the boiling performance. However, there are several reasons why solely the modification of surface wettability cannot represent the ultimate heat transfer enhancement approach in the nucleate boiling applications.
- The wettability significantly depends on fluid properties, and different working fluids are used in a diversity of boiling applications. Water, a polar liquid with high surface tension, is used in boiling water nuclear reactors, while dielectric, non-polar liquids with almost one order of magnitude lower surface tension and small capillary lengths are usually employed for phase-change heat transfer in heat pipes and refrigeration systems.
- As has been shown by Može et al. [49], the surface wettability may change during boiling due to intense processes, such as the vaporization of the working fluid, high surface temperatures and high frequency temperature variations due to bubble nucleation (further discussed in Sect. 4.5).
- As already described, the wettability can also change due to hydrocarbon contamination, which does not happen only in contaminated gas atmospheres [112, 151] but also in liquid atmospheres [158].
- When surfaces are exposed to ionizing radiation, this also significantly influences surface wettability [161, 171, 172].

Therefore, when developing different functionalization approaches for surfaces in boiling heat transfer applications, it is highly desirable that such functionalization will also decrease the influence of the wettability on boiling performance and stability. In this context, Zupančič et al. [62] have shown that surfaces with laser-induced multiscale μ -cavities enable enhanced and controlled saturated nucleate boiling performance. This was proven further by Gregorčič et al. [46], who successfully used such surfaces for enhanced and controlled boiling heat transfer in a wide range of fluids (further discussed in Sect. 4.3), independent of their polarity or surface tension, as well as by the experiments by Zakšek et al. [84], who demonstrated that this kind of surfaces enable controlled boiling also in binary liquid mixtures. All these results confirm that functionalization of the heating surfaces by multiscale μ -cavities

can decrease the influence of the surface wettability on the key boiling heat transfer parameters and, consequently, leads to more stable heat transfer processes that are independent of (i) fluid properties, (ii) hydrocarbon contaminants and (iii) ionizing radiation.

Two possible strategies can be utilized to produce surfaces with multiscale μ -cavities by (fibre) laser texturing in a straightforward, compact, robust, flexible, chemical-free and cost-effective way. The first one is *the very high fluence approach*. When high pulse fluences are used, laser ablation leads to a high amount of remolten and solidified material around the μ -channels, as visible in Fig. 17a. Here, the μ -cavities with *diverse* radii appear due to significant ejection of this remolten material. However, this strategy is not appropriate for processing thin foils (e.g. with a thickness of 25 μm) that are required when measuring the transient temperature fields using an IR camera on the backside of the foil, as performed in several experimental studies [34, 46, 62, 84, 174], since very high fluences may lead to up to 100 μm deep μ -channels (Fig. 13b). Even so, this strategy can be successfully employed in experiments with heating blocks [49, 175] as well as in real production including modification of different types of heat exchangers, where much thicker surfaces are used.

The second approach is *the (variable) scanning lines approach*. Here an appropriate combination of (lower) pulse fluences and scanning line separation, as suggested in Fig. 10c, is used. Typical surface microstructures obtained by this approach are shown in Figs. 18b–e. However, using this strategy, only small variations in scanning line separation and/or pulse fluence can lead (according to Eq. (17) in combination with the equidistant spacing sketched in Fig. 9a) to (i) closed gap

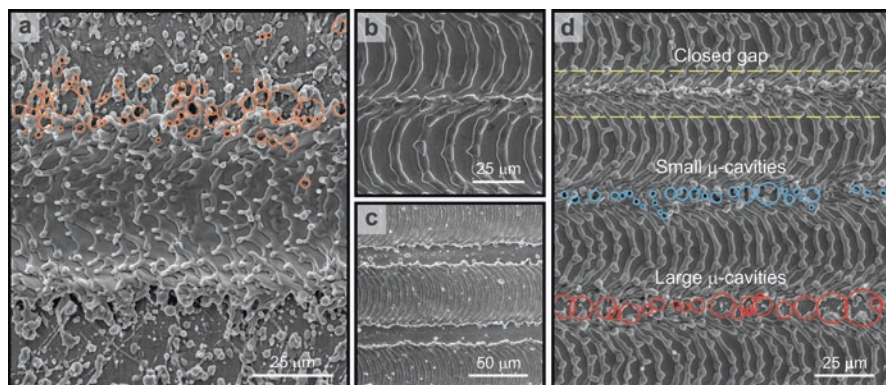


Fig. 17 (a) Surface modification using the very high fluence texturing approach. The identified μ -cavities on the top edge of the μ -channel are marked by the orange circles with their radii corresponding to the largest dimension of the identified μ -cavity. The variable scanning approach with (b) closed gap without μ -cavities, (c) gap that is too wide and thus lacks appropriate μ -cavities and (d) with multiple scanning line separations leading to higher diversity of the μ -cavities' radii. (Reproduced and adapted from Ref. [173]. Creative Commons Attribution 4.0 International License)

without μ -cavities due to too small distance between two consecutive μ -channels (Fig. 17b) and (ii) too wide gap lacking appropriate μ -cavities (Fig. 17c).

Although lower fluences may be used with the *scanning lines approach*, they should not be too low, since this leads to less ejection of the remolten material. In this case, the μ -channel edge is smooth and even overlap will not lead to appropriate μ -cavities. An example of this situation is demonstrated in Fig. 17c, where very smooth edges of the μ -channels are clearly visible. The surfaces from Fig. 17c, d were processed with the same laser parameters, but the beam diameter at the focusing lens was changed. In case of the surface on Fig. 17c, the beam diameter on the F-theta lens D equalled 5 mm, while in case of Fig. 17d, it equalled 7.5 mm. According to Eq. (8), the ratio between the beam waist radii, therefore equalled 1.5, which means that (according to Eq. (18)) the surface on Fig. 17c was processed with 2.25 times lower fluence as the surface in Fig. 17d.

- The robustness of the (variable) scanning lines approach can be significantly improved by using multiple scanning line separations (e.g. see Fig. 9b), as

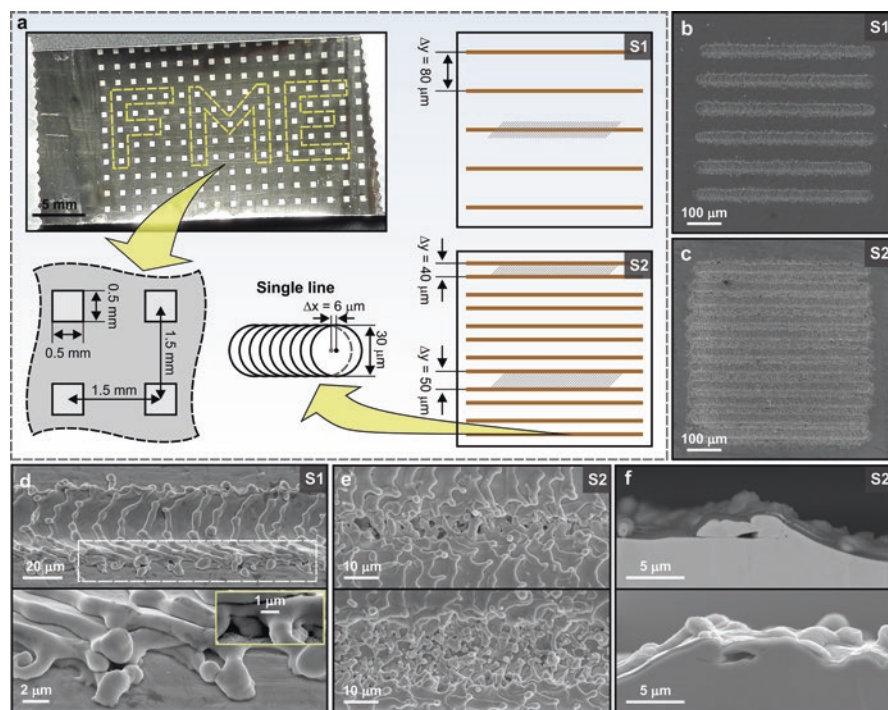


Fig. 18 (a) Stainless steel foil with laser textured array and schematic presentation of the laser-texturing method. SEM images of the square, textured by (b) S1 and (c) S2 structure. Magnified SEM images of (d) S1 structure [marked area in S1 in (a)] and (e) S2 structure on the border between two channels [marked areas in S2 in (a) – top for $\Delta y = 40 \mu\text{m}$, bottom for $\Delta y = 50 \mu\text{m}$]. (f) Cross section of S2. (Reproduced from Ref. [46]. Creative Commons Attribution 4.0 International License)

reported by Gregorčič et al. [46], where the surface was processed by two different Δy . This strategy makes it possible also to use low-cost scanners with lower angular (positioning) resolution. Moreover, such approach additionally leads to a higher diversity of μ -cavities' radii and, thus, enables higher degree of enhancement of the boiling process (according to the theoretical results presented in Fig. 3).

- To demonstrate the boiling performance of such surfaces, Gregorčič et al. [46] fabricated two types of structures on stainless steel foils. The first one was labelled S1 and consisted of well-separated channels, as shown in Fig. 18b. The other one was labelled S2 and was fabricated using a scanning line separation that alternated between two values, as shown in Fig. 18c. A SEM image, acquired on the surface S1, tilted for 60° , reveals that μ -cavities are formed even on the edges during the solidification of the remolten material after laser ablation (Fig. 18d, the white dashed rectangle). This indicates that the very high fluence approach is additionally effective, since the μ -cavities do not appear only on the top of the surface but also at the intersection between the drilled μ -channel and the ejected, solidified material. As was shown in [46], the radii of μ -cavities, induced on well-separated μ -channels with lower fluences, are typically in range from approximately hundred nanometres up to $1\text{ }\mu\text{m}$. The situation is slightly different for S2, where the scanning line separation is decreased to the values just slightly larger than the channel width. Here, the range of μ -cavity radii is significantly increased due to overlapping of the solidified material at the edges of the neighbouring channels (Fig. 18e). Thus, the radii go from approximately hundred nanometres up to $5\text{ }\mu\text{m}$. Additionally, this approach results in a more porous structure as the cavities are much deeper compared to the well-separated μ -channels, where the ejections of the solidified material from parallel μ -channels do no overlap. The overlapping of the solidified material may also lead to interconnected μ -cavities, as revealed by a surface cross section in Fig. 18f.

4 Applications of Laser Engineered Surfaces in Pool Boiling

4.1 Experimental Boiling Performance Determination

Evaluation of nucleate pool boiling performance on different surfaces requires a carefully designed experimental setup that allows accurate monitoring of the boiling surface temperature (wall temperature) and the heat flux while maintaining the homogeneity of the bulk liquid at the desired pressure and temperature. In the most common experimental configuration, the boiling surface is heated through conduction from an external heating source, and the heat flux and the wall temperature are calculated from several temperature measurements along the heated block [40, 49, 175–178]. This configuration is suitable to determine the spatio-temporal averaged

wall temperature and heat flux in order to obtain reliable values of the HTC and CHF that are also observed in real applications.

However, to study specific parameters like nucleation frequency, distribution of the active nucleation sites, bubble growth characteristics and local heat fluxes, the transient wall temperatures on the boiling surface should be determined. This can be achieved using the liquid crystals [179, 180], microthermocouple arrays [181, 182], temperature sensitive paints [183, 184], fluorescence microscopy [69] or infrared (IR) thermometry [30, 70–72, 185, 186]. Since the IR thermometry is used most commonly, it is a well-developed technology able to detect small temperature differences (~ 20 mK) with pixel-to-pixel resolution down to about $10\text{ }\mu\text{m}$. To successfully detect transient temperature fields underneath a growing bubble, the heater should have relatively small thermal capacitance, which is generally achieved by depositing a thin metal layer atop of an IR transparent substrate or by using a thin metal foil. Boiling on Joule-heated metal foils supported by the high-speed IR thermography (framerate ≥ 1 kHz), which is specifically studied in this section (Fig. 19), can provide an accurate estimation of the wall temperature, bubble footprint area and its growth time, locations of active nucleation sites and local heat fluxes [187]. However, the measured CHF values on such foils (usually their thickness is below $50\text{ }\mu\text{m}$) are significantly smaller compared to thicker heaters due to conductance/capacitance effects [188, 189]. After optimizing a specific surface structure on a thin heater, the actual CHF value should be experimentally determined on the heater with the thickness above the asymptotic limit (with thickness typically above $500\text{ }\mu\text{m}$).

4.2 Laser-Induced μ -Cavities as Active Nucleation Sites

Based on the nucleation criteria explained in Sect. 2.1, the optimal cavity radius for water on superhydrophilic surfaces is within the range of $1\text{--}10\text{ }\mu\text{m}$. This is below the generally achievable spatial resolution of the IR thermography, which is limited by diffraction. Despite that, Zupančič et al. [62] demonstrated that appropriate post-processing of IR data can be used to confirm the effectiveness of μ -cavities. They laser-textured a stainless-steel surface (Fig. 20a) by using the $0^\circ/90^\circ$ texturing with a variable spacing (Fig. 9d), where Δy varied from 10 to $200\text{ }\mu\text{m}$ in both directions (the left-hand side of Fig. 20a). In the regions, where the scanning line separation was in the range of $30\text{--}50\text{ }\mu\text{m}$, the multiscale μ -cavities were induced. Their existence was confirmed by SEM micrographs, and their radii were measured to be in the range of $0.1\text{--}3\text{ }\mu\text{m}$ (SEM images in Fig. 20a), while the surface exhibited a non-uniform wettability with contact angles ranging from 66° to 142° .

Contrary to (super)hydrophilic surfaces, superhydrophobic ones would theoretically require cavities with radii in the range of $100\text{--}1000\text{ }\mu\text{m}$. However, low thickness of the foil prevents the fabrication of such large cavities with appropriate depth. Therefore, only cavities in the micrometre range are significant in the described situation. Post-processing algorithm of the transient temperature fields, acquired by

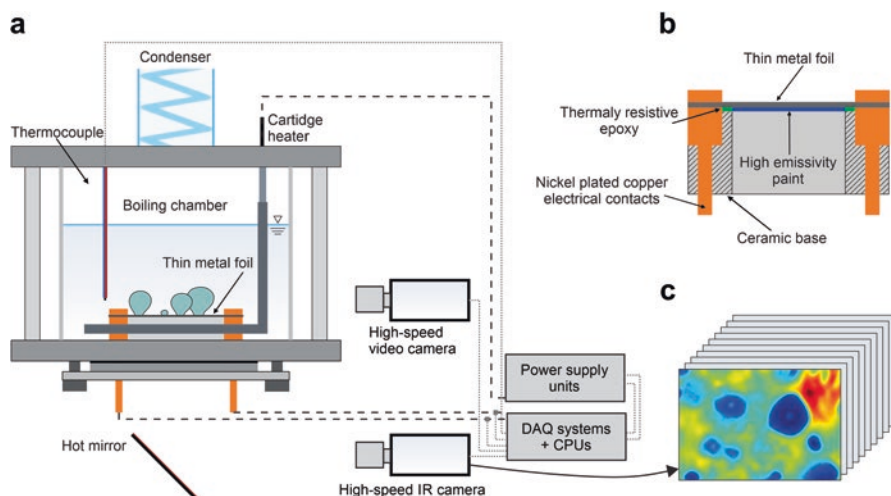


Fig. 19 (a) A simplified schematics of the pool boiling experimental setup for thin metal heaters and (b) cross section view of the thin-metal-foil heater unit. (c) Representation of consecutive temperature fields of the boiling surface obtained by the high-speed IR camera – note that cooler regions are represented by blue colour and therefore indicate the bubble footprints

the IR thermography, is explained in Fig. 20b. The result of the processing in Fig. 20c clearly shows that the active nucleation site density is periodically distributed across the entire surface and exactly matches the spatial distribution of the μ -cavity regions. The presence of the μ -cavities increases the active nucleation site density, lowers the onset of nucleate boiling for more than 5 K compared to bare stainless steel and improves the overall HTC for more than 110%. The combined effect of μ -cavities, increased surface roughness and modified wettability increased the nucleation frequency for at least 200% and nucleation site density for two orders of magnitude compared to untreated material [62]. Slightly lower enhancement was also observed by Kruse et al. [14], who studied nucleate pool boiling on stainless steel surfaces (type AISI 304) processed by femtosecond laser pulses. The superhydrophilic sample S4 (Fig. 20d) incorporated circular pits (cavities) with radii up to about 5 μm .

4.3 *Decreased Influence of Surface Wettability on μ -Cavity-Induced Boiling Performance Enhancement*

The ability of the surfaces with multiscale μ -cavities to provide control over the boiling process in a diverse range of fluids, independent of their polarity and surface tension, was demonstrated by Gregorčič et al. [46]. They fabricated two surfaces (labelled S1 and S2) using nanosecond laser pulses and different scanning line separations, as shown in Fig. 18. The first surface (S1) was textured with well-separated

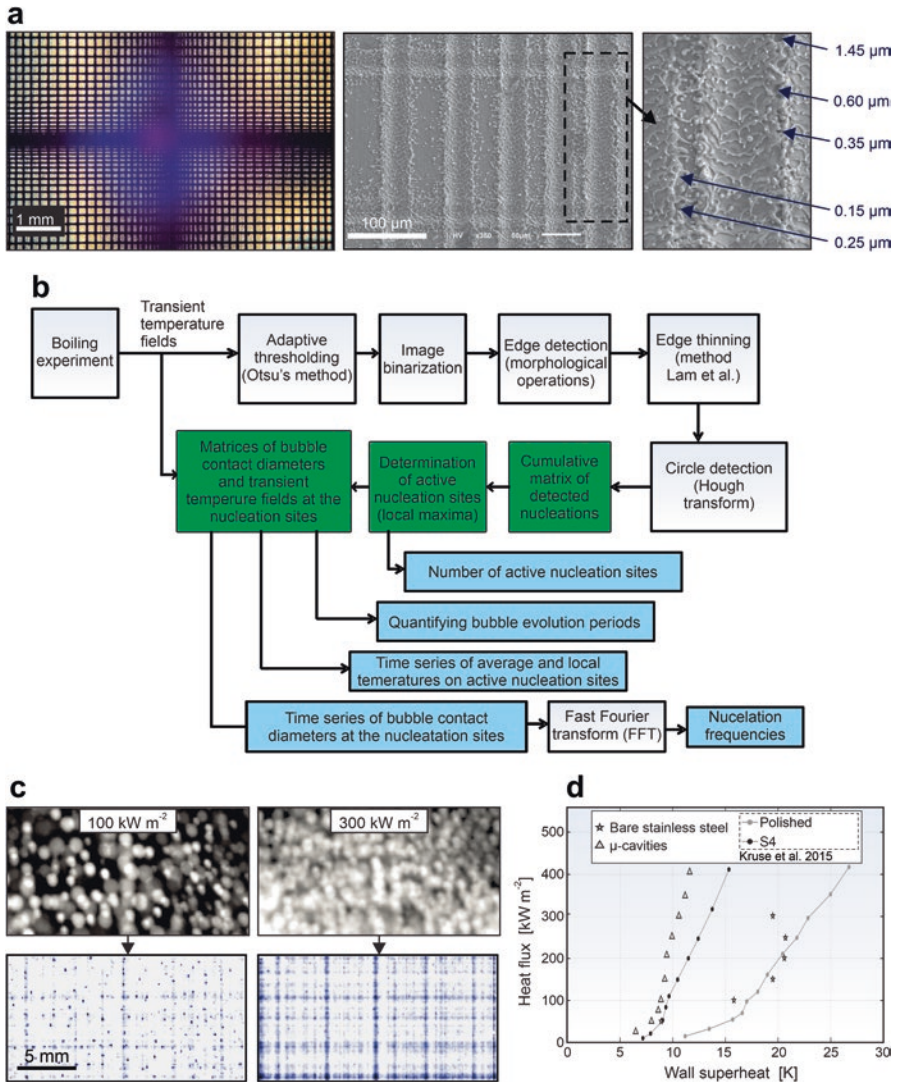


Fig. 20 (a) Microscope image of laser-textured, 25- μm -thick stainless-steel foil with variable scanning line separation and SEM micrograph of the μ -cavity regions with some representative values of cavity radii. (b) Flowchart of the data processing algorithm to detect the active nucleation sites. (c) Cumulative matrix of detected bubble footprints (top) and distribution of active nucleation sites (bottom) over the entire laser-textured foil. (d) Boiling curves during the saturated pool boiling of water for bare stainless steel and laser-textured stainless-steel foil measured up to 400 kW m^{-2} . Results using femtosecond laser-textured surfaces reported by Kruse et al. [14] are shown for comparison. (Panels (a), (c) and (d): Reproduced and adapted from Ref. [62] with permission from Elsevier)

μ -channels, thus containing only small μ -cavities with radii in the range of 0.1–0.75 μm . On the contrary, the variable scanning line separation used for S2 resulted in multiscale μ -cavities with radii in the range 0.1–5 μm . To demonstrate the capability of such surfaces to control boiling, a stainless steel foil (type AISI 316 L) was textured in regions of $0.5 \times 0.5 \text{ mm}^2$ squares forming the shape of the “FME” (Faculty of Mechanical Engineering; see Figs. 18a and the top of Fig. 21).

The textured surfaces were tested in two very contrasting fluids: water, which is polar with high surface tension (58.9 mN m^{-1} at T_{sat} and 1 atm) and high heat of vaporization, and the non-polar, dielectric tetradecafluorohexane (FC-72) with low surface tension (8.0 mN m^{-1} at T_{sat} and 1 atm) and much lower heat of vaporization. It should be emphasized that FC-72 exhibits extremely low contact angles with most practical materials (also superhydrophobic materials) except of some special superrepellent surfaces with re-entrant structures [190]. Although the boiling performance of FC-72 is completely different compared to water, experiments in Ref. [46] convincingly show that surface structure with a wide range of μ -cavity size can provide control over the nucleation locations for different types of fluids with completely different wetting characteristics. The time-averaged temperature fields of the boiling surface in Fig. 21 show the comparison of the active nucleation sites distributions on both surfaces for water and FC-72.

The S1 structures with smaller cavity radii in the range of 0.1–0.75 μm was only able to provide the active nucleations for FC-72 (the left-hand side in Fig. 21), since this range of the μ -cavities radii is not optimal for water according to the Hsu’s nucleation criterion (Eq. (3)), but falls within the desired range for FC-72 and other low-surface-tension fluids. On the other hand, the S2 structure with one order of magnitude larger range of the μ -cavities radii (from 0.1 to 5 μm) resulted in clearly

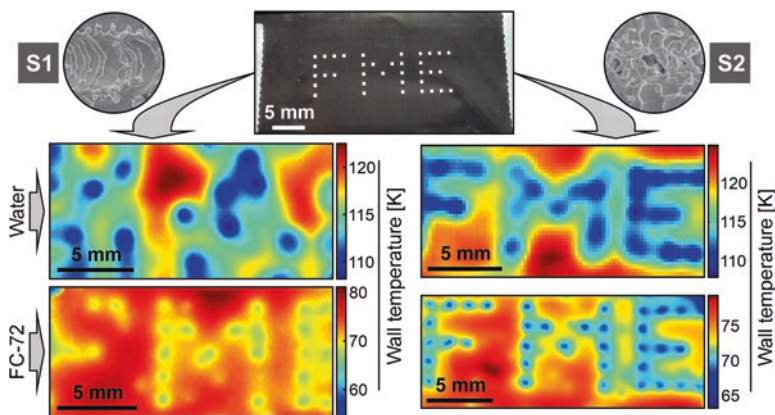


Fig. 21 Controlled nucleate boiling performance of water and FC-72 on laser textured “FME” pattern. Time-averaged temperature fields were taken at 150 kW m^{-2} for water and 15 kW m^{-2} for FC-72. On the laser-textured regions, the static contact angle of water equalled around 16° and for FC-72 around 13° . The S2 structure provides on average 11 K (for water at 150 kW m^{-2}) and 7 K (for FC-72 at 15 kW m^{-2}) lower surface temperature compared to the surrounding inactive regions. (Reproduced from Ref. [46]. Creative Commons Attribution 4.0 International License)

visible “FME” structure for both fluids as a low-temperature region due to constant boiling activity. In addition to water and FC-72, similar behaviour was also confirmed with pure ethanol and water-ethanol mixtures [83, 84].

In addition to stainless steel [14, 46, 62, 191], laser texturing for enhanced boiling applications can be also applied to other important materials, like copper [49, 192], silicon [193], Inconel [192], aluminium, titanium and zirconium alloy. Figure 22a shows an example of the laser-textured zirconium alloy type 702. The textured areas with dimensions of $0.5 \times 0.5 \text{ mm}^2$ are distributed in a hexagonal pattern to reach an optimal filling factor. Similar to the previous example, each textured area consists of multiscale (interconnected) μ -cavities with radii ranging from 60 nm up to 3 μm . These areas were superhydrophilic prior to boiling experiments due to the reasons explained in Sect. 3.4. However, superhydrophilic surface is not ideal to lower the temperature of the onset of nucleate boiling. Despite this, the boiling initially took place only on the μ -cavity regions as presented in Fig. 22b. Significant enhancement of the nucleation site density, nucleation frequency and equal distribution of the nucleation sites on Zr- μC sample resulted in 3–5 K lower superheat (Fig. 22c) and significantly smaller wall-temperature deviation (Fig. 22d) in comparison to the untreated surface. Light-tailed and narrow probability density function is a clear indicator of stable boiling performance [194], which is required to maintain relatively homogenous surface temperature. This is especially important for applications, such as cooling of microelectronic chips.

Figures 21 and 22 convincingly demonstrate that laser surface engineering can be used to develop surfaces with well-defined nucleation sites on diverse materials and for a wide variety of fluids. This represents a tremendous capability to study the optimal distribution of active nucleation sites in the context of (i) achieving a uniform temperature field and high heat transfer rates at low superheats and (ii) delaying the horizontal coalescence of bubbles that prevents a generation of large vapor patches (i.e. to reach high CHF). Some studies [97, 174, 195] have shown that the optimal distance between the active nucleation sites (regions) that leads to the maximal enhancement of the HTC and CHF roughly corresponds to the capillary length of the working fluid. However, a possible deviations from this theory [84] might be attributed to the fact that the growth time, nucleation frequency and bubble size are not the same for all nucleation sites. Recent work by Zhang et al. [196] considered this near-wall stochastic behaviour of individual bubbles and proves that the boiling crisis is a percolative and scale-free phenomenon that can be delayed by optimization of the nucleation site density, the product of the nucleation frequency and bubble growth time ($t_g f_b$) and the time-dependent bubble footprint radii without additional consideration of macroscale hydrodynamic instabilities or microscale fluid-solid interactions. This (rather radical) idea could completely change the future approach in finding the surface engineering solution(s) to optimally enhance the boiling performance. In this context, the demonstrated capability of laser texturing to create well-defined nucleation sites is worth to be investigated further.

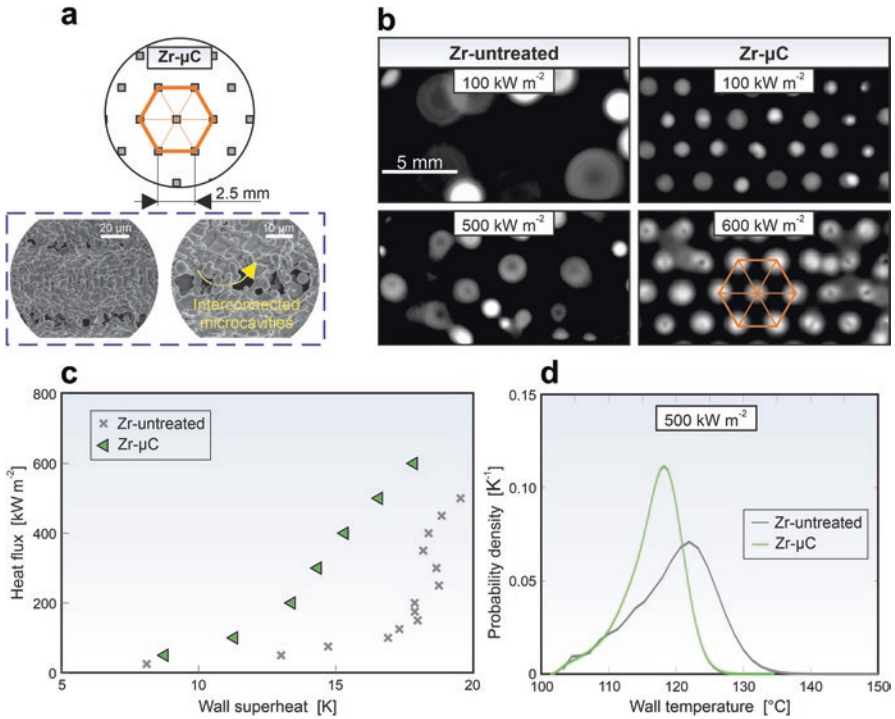


Fig. 22 (a) Laser-textured pattern design on zirconium alloy and SEM images of corresponding μ -cavities. (b) Cumulative matrix of detected bubble footprints on untreated and laser-textured samples at two different heat fluxes. (c) Boiling curves during saturated pool boiling up to 600 kW m^{-2} (note that untreated samples experienced burnout at roughly 540 kW m^{-2}) and (d) wall-temperature distributions for both samples at 500 kW m^{-2}

4.4 Pool Boiling on Laser-Textured Superhydrophobic Surfaces

Numerous publications have shown [34, 79, 81, 197, 198] that superhydrophobic surfaces significantly reduce the temperature at the onset of boiling and the CHF, which was often observed immediately after the boiling incipience. For that reason, superhydrophobic surfaces were not considered to be a good choice in practical (high heat flux) applications. Since the initially superhydrophilic laser-textured surfaces tend to become superhydrophobic over time due to the reasons discussed in Sects. 3.5 and 3.6, the boiling behaviour on surfaces with time-dependent wettability has to be carefully analysed. To evaluate this behaviour, the laser texturing was initially performed on three 25- μm -thick stainless steel foils (type AISI 316 L) to create μ -cavities over the entire surface. The surfaces were then aged at room temperature or in a *contaminated* furnace at 100°C .

Sample, labelled as SHPO, was left exposed to the normal open atmosphere for 82 days and became superhydrophobic with a static contact angle of 158° (Fig. 23b). A similar contact angle of 154° was achieved on the sample SHPO*, which was kept in a contaminated furnace for 17 h, while the sample HPI reached a contact angle of 34° after 2.5 h in a contaminated furnace. As discussed in Sect. 3.5, the aging of the laser-textured metallic surface results in a formation of a thin film of hydrophobic organic compounds due to airborne hydrocarbon, while during the low-temperature annealing, the contamination in form of a thin polydimethylsiloxane (PDMS) coating arose from the silicone components of the furnace [105].

Figure 23a shows the results of two consecutive pool boiling experiments for each sample, first up to 500 kW m^{-2} and second up to the burnout point. Both superhydrophobic surfaces exhibited the same boiling behaviour. During the first run (open circles in Fig. 23a), the onset of boiling was reached at only about 3 K of superheat ($< 25 \text{ kW m}^{-2}$) and provided significant HTC enhancement compared to the untreated sample. However, in the second run (full circles in Fig. 23a), the onset of boiling was increased to about 10 K of superheat, and both boiling curves follow a slope otherwise unexpected for superhydrophobic surfaces until they reached the burnout at $\sim 1300 \text{ kW m}^{-2}$. On the contrary, the HPI sample exhibited the same trends during both experimental runs and provided lower HTC and CHF compared to the superhydrophobic samples.

Such behaviour can be a consequence of several possible reasons. First of all, it was experimentally determined that the contact angle after the first and the second boiling run decreases to about 25° on all laser-textured surfaces. This demonstrates that the naturally occurring superhydrophobicity on the macroscopic scale is not stable during boiling applications. Nevertheless, both superhydrophobic samples provided overall enhancement in HTC in comparison to the hydrophilic one. This indicates that some (super)hydrophobic micro-/nanostructures may be stable and still present on the surface. This kind of structures could lower the nucleation temperature, but their existence cannot be confirmed solely by the macroscale contact angle measurements. Thus, further surface analysis on different scales, including the atomic and molecular scale, is required.

The second important observation is the difference in the onset of boiling temperature between the first and the second experimental run for superhydrophobic samples. Figure 23c,d shows that the early nucleate boiling during the first run takes place at multiple nucleation sites, while the bubbles nucleate at relatively high frequencies and cause small surface temperature fluctuations ($\pm 1 \text{ K}$). However, during the second run, the nucleation site density is decreased, bubble activation temperatures increase by about 5 K, and the temperature profile underneath the bubble follows the recognisable pattern as previously shown in Fig. 4. This behaviour may be explained by the influence of entrapped gasses on the surface before it is exposed to the boiling process for several hours. Shen et al. [199] proved that presence of the non-condensable gas on the hydrophobic surface causes an early transition to nucleate boiling and results in completely different bubble dynamics compared to a fully degassed surface. Additionally, Allred et al. [60] explained that initial Cassie-Baxter wetting state on a superhydrophobic surface results in low surface superheat and

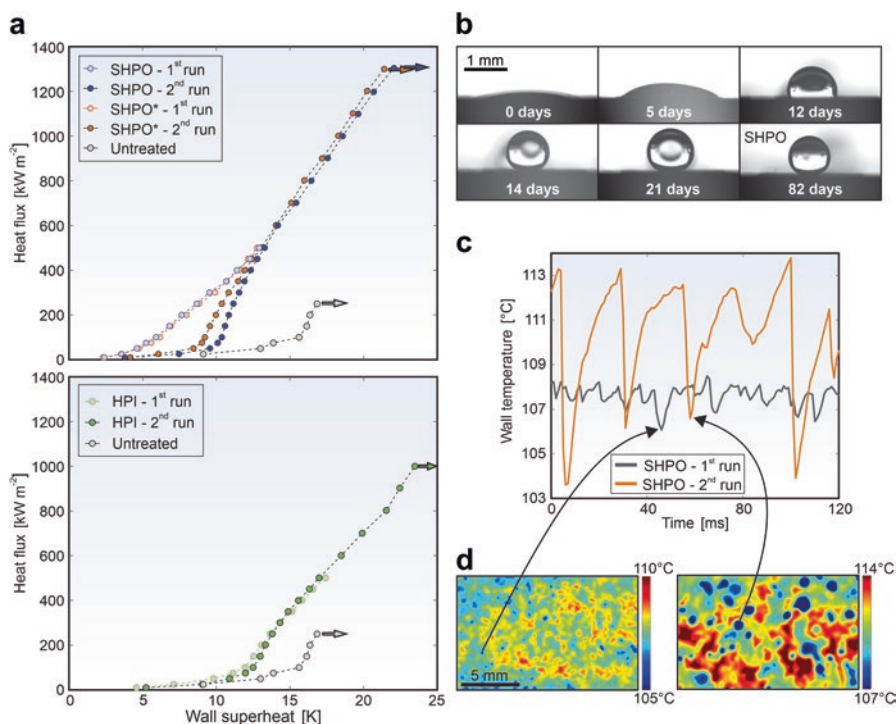


Fig. 23 (a) Pool boiling curves for saturated boiling of water on superhydrophobic and hydrophilic laser-textured surfaces in comparison with untreated stainless steel. (b) An example of naturally developed superhydrophobicity on the SHPO sample under atmospheric conditions (air, 20–25 °C, RH 40–60%). (c) Wall temperature fluctuations underneath an active nucleation site at 200 kW m^{-2} for the first and second boiling run on SHPO sample and (d) corresponding time-averaged temperature fields of the boiling surface

low CHF, matching the values commonly observed in the literature [34, 79, 81]. This Cassie-Baxter boiling regime takes place when the surface structure is initially covered with non-condensable gas (commonly air) or a vapor layer that spreads in all directions as the heat flux is increased, which may be so far the best explanation behind extremely low CHF values reported for most of the superhydrophobic surfaces.

To support the arguments of Shen et al. [199] and Allred et al. [60], we performed additional boiling experiments on a 3×3 array of the laser-textured areas (Fig. 24). High-speed IR thermography and a microthermocouple were used to synchronously monitor the wall and liquid temperature in the vicinity of the active nucleation site. The temperature measurements acquired from the central nucleation area (the left-hand-side of Fig. 24) indicate that bubbles emerge from the non-degassed surface with high periodicity, while the microthermocouple measurement indicates the saturation temperature value (vapor phase temperature) during most of the 0.5-s time frame. This confirms that vapor/gas layer was constantly present on

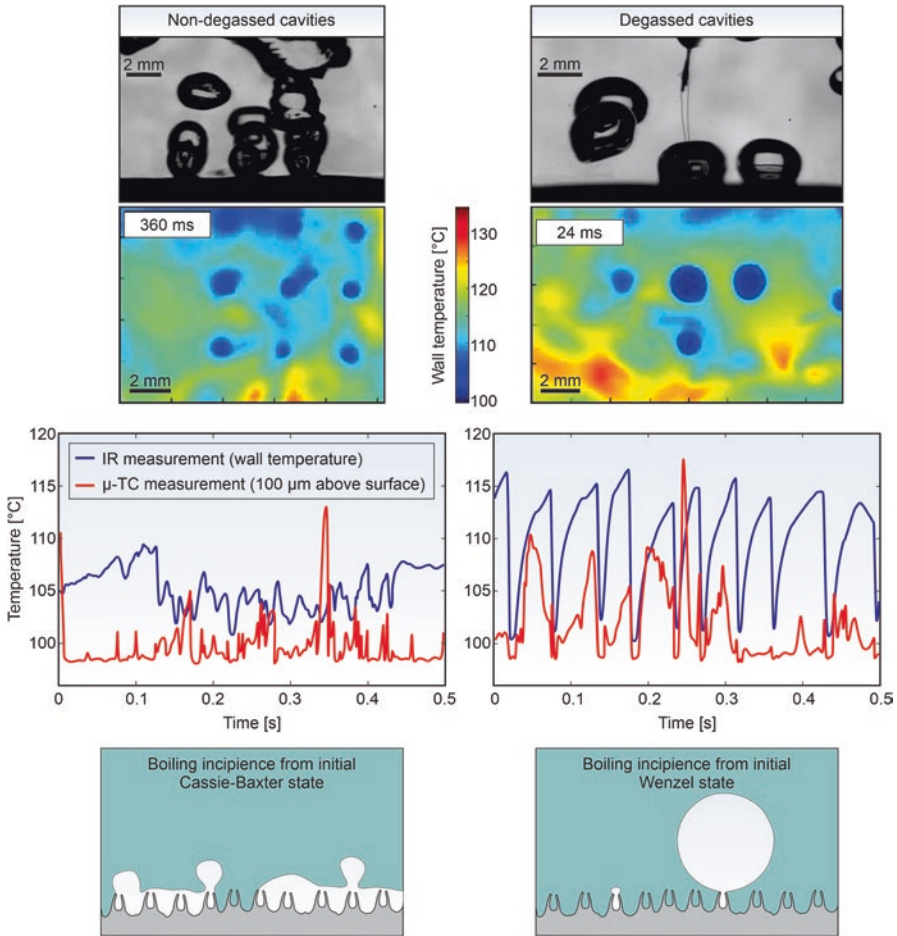


Fig. 24 High-speed images and corresponding temperature fields during the saturated pool boiling of water (pressure slightly below 1 atm) at 100 kW m^{-2} on a stainless steel surface with 3×3 array of the laser-textured areas with μ -cavities for (left) non-degassed and (right) degassed conditions. The size of laser-textured areas is $0.5 \times 0.5 \text{ mm}^2$ and the pitch between them is 3.5 mm. The wall temperature measurements (1 kHz, IR camera) and the liquid temperature measurements (10 kHz, micro-thermocouple placed $100 \mu\text{m}$ above the surface) are provided for the central laser-textured area for a selected 0.5-s time frame. Illustrations below the graphs are showing the bubble growth from μ -cavities in the initial (left) Wenzel and (right) Cassie-Baxter state

the laser-textured areas and provided virtually uninterrupted bubble growth and departure with minimal or no waiting time in between nucleations.

On the other hand, if the surface is successfully degassed either by pressurization, vacuuming or several repeated boiling runs with intermediate condensation of the vapor by slightly subcooling the liquid, the initial Wenzel wetting state is observed. In this situation, as visible from the right-hand side of Fig. 24, the bubble life cycle is initiated by substantial superheating of the surface followed by the

nucleation event and bubble growth (sharp temperature drop associated with high local heat fluxes). After bubble departure, the surface temperature is gradually increased during the waiting time until the nucleation conditions are reached again. The IR thermography proved that non-degassed surface allowed almost simultaneous activation on all nine laser textured areas, which was not observed with the fully degassed surface.

Finally, recent publication by Može et al. [175] convincingly demonstrated that pool boiling of water can be significantly enhanced (in terms of HTC and CHF) on superhydrophobic laser-textured surfaces coated with nanoscale hydrophobic fluorinated silane. Results confirm that the Wenzel wetting regime is possible during boiling on apparently superhydrophobic surface. What is not completely clear, however, is why the vapor layer does not spread around the entire boiling surface at relatively low superheat (i.e. low heat flux) after the boiling incipience. One of the possible reasons is that the underlying micro- and nanostructure, even though covered with hydrophobic layer, prevents the microlayer dry-out and delays the CHF. This would still need to be experimentally confirmed.

The following conclusions can be drawn from the discussed observations and the results reported in the literature [60, 76, 175, 199]:

- Hydrophobic or superhydrophobic surfaces with low receding contact angles benefit from the low-superheat boiling incipience but prevent the vapor spreading. Thus, they do not decrease the critical heat flux. This type of surfaces was termed as parahydrophobic.
- Superhydrophobic surfaces tend to exhibit the Cassie-Baxter boiling regime leading to film boiling immediately after incipience, which is not desirable for practical boiling applications. However, if the boiling on the superhydrophobic surface can be initiated from the Wenzel state, vapor spreading can be suppressed. An important reason behind the Cassie-Baxter boiling behaviour is incomplete degassing of the surface (rather than the liquid alone), which can be avoided in the laboratory environment and has to be seriously considered in practical applications as well.
- The laser-textured surfaces with μ -cavities and time-developed superhydrophobicity show a significant increase in the heat transfer coefficient and maximum attainable heat flux compared to untreated surfaces, which implies the Wenzel boiling behaviour. This is attributed to the appropriate degassing procedure and the fact that superhydrophobicity is not stable during the nucleate boiling. Initially superhydrophobic surfaces showed a static contact angle of $\sim 25^\circ$ after exposure to boiling but still provided lower superheats compared to hydrophilic samples. This proves that (super)hydrophobic properties might still be locally present even after the boiling, which needs a further analytical confirmation.
- Despite the unstable wetting behaviour of laser-textured surfaces, the μ -cavities were shown to enhance bubble nucleation and can provide control over the locations of active nucleation sites regardless of the initial contact angle between the fluid and the surface. This is particularly important for future implementation in real applications.

4.5 *The Influence of Boiling on Surface Chemistry and Wettability*

There are few research papers that discuss the specific changes in surface chemistry and wettability as well as long-term stability of surfaces when used in boiling conditions [49, 200–202]. Despite the importance for real applications, it is presently still not understood well, how newly developed functionalized surfaces are affected by periodic bubble nucleation and associated temperature variations as well as by the relatively high (local) temperatures near the CHF or during the transition to film boiling. In this context, the results by Može et al. [49] are of great importance, since they show the chemical and morphological changes that are induced on the molecular and atomic level due to the critical heat flux incipience as well as the stability of boiling performance on laser-textured copper surfaces in pool boiling of water. It was shown that, similarly as for other materials [46, 62, 84, 175], the laser-textured copper surfaces with μ -cavities enhance the HTC and CHF for 115% and 90%, respectively (Fig. 25a). Moreover, their results convincingly demonstrate better stability (repeatability) of nucleate boiling process on laser-textured surfaces compared to the untreated sample. However, when the surfaces reached CHF and underwent a controlled transition into the film boiling regime with surface temperatures in the range 210–320 °C, the surface experienced a deoxidation through conversion of Cu (II) oxide and hydroxide species into Cu(I) oxide and Cu metal. This was confirmed by high magnification SEM imaging (Fig. 25b) and XPS analysis (Fig. 25c-e).

Changes in surface chemistry and nanostructure constituted the transition from the initial hydrophilic (before reaching CHF) to hydrophobic (after reaching CHF) state, which greatly affected the boiling performance. After exceeding the surface temperature of 200 °C for the first time, the later experiments showed decreased CHF and increased HTC, which corresponds well with the hydrophilic-to-hydrophobic wettability transition.

Contrarily to the observed deoxidation of copper during pool boiling, Trojer et al. [200] intentionally pre-oxidized low-carbon steel samples to simulate the natural oxide layer observed on a reactor pressure vessel wall in light-water reactor nuclear power plants. Oxide layer rendered the surface superhydrophilic and capable to wick water. Flow boiling experiments performed over a wide range of testing conditions proved a consistent increase in the CHF (up to 70%) on pre-oxidized samples compared to the untreated one, which is again in-line with the extreme surface wettability properties. However, to convincingly conclude this CHF enhancement is permanent, additional long-term tests are still required.

Surface wettability and multiscale topography significantly influence the nucleate boiling phenomena. Thus, the stability of the surface from the chemical and topographical perspective will directly affect the boiling performance. Generalization of the long-term boiling performance for numerous combinations of materials,

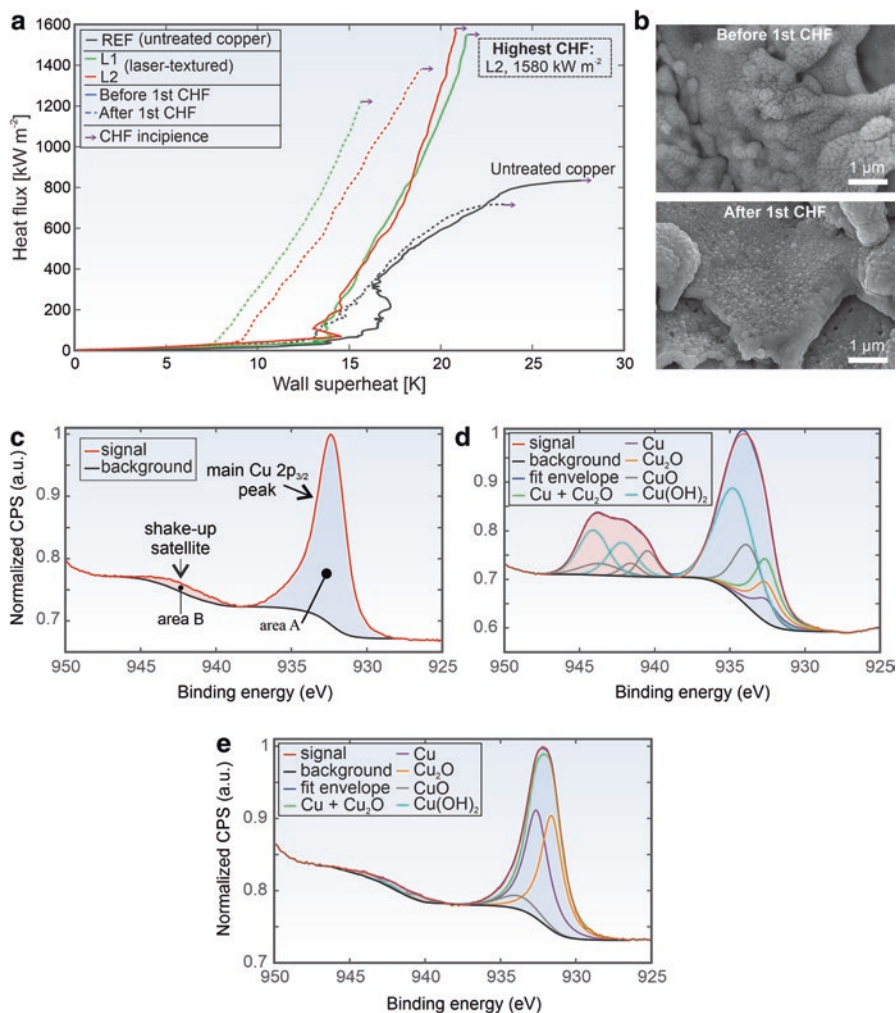


Fig. 25 (a) Pool boiling curves before and after the first incipience of CHF on the untreated and laser-textured copper in air (L1) and argon (L2) atmosphere. (b) SEM images of the L1 sample before and after the first CHF incipience. The narrow XPS scans of the Cu $2p_{3/2}$ main peak and its shake-up satellite on the (c) untreated copper surface prior to boiling with additional deconvolution on L1 sample (d) before and (e) after the CHF incipience. (Reproduced and adapted from Ref. [49] with permission from Elsevier)

possible surface engineering methods, working fluids and operating conditions is, however, practically impossible and requires individual studies, which are necessary for later implementation in real phase-change heat transfer applications.

5 Outlook

Undoubtedly, the *surface wettability* influences the nucleate boiling process, but the relation between the boiling performance and wettability is not as straightforward as it looks from a very simplified picture. This commonly used simplified theoretical approach considers solely the preference of the (super)hydrophilic surface to be in the contact with the liquid phase rather than with the vapor phase. Thus, it leads to the conclusion that such surface should delay the attainable critical heat flux, while at the same time it should increase the surface overheat at low fluxes. Conversely, this very simplified view explains that the (super)hydrophobic surface should lower both the temperature of the onset of nucleate boiling and the attainable critical heat flux due to its preference to be in the contact with vapor rather than liquid. The main problem of such simplification is that its validity is limited only to the *ideal* (i.e. chemically homogeneous, chemically stable and completely flat) surface. Unfortunately, ideal surfaces practically do not exist in real applications. Thus, as reviewed in this chapter, neglecting the influence of the surface topography and/or surface chemistry modification during the intense boiling process *inevitably* leads to conclusions that are not consistent with the commonly observed and measured boiling behaviour.

The presented results demonstrate that multiscale surface μ -cavities – when their radii fall within an appropriate range – practically universally enhance the boiling performance with the same surface capable of working well with a various fluids, independent of their polarity, surface tension and heat of vaporization. Moreover, they can ensure stable, controlled and enhanced boiling performance even in combination with binary fluid mixtures. This is of great importance in *real applications*, since diverse boiling systems often use very different working fluids. Additionally, this leads to the stabilization of the boiling process, which is not possible when modified wettability alone is used for surface functionalization. As has been shown, the wettability of the surfaces may change during boiling due to different reasons, including the intensive boiling processes, hydrocarbon contamination and/or ionizing radiation. In this context, it is of great importance that the laser-induced μ -cavities enable enhanced bubble nucleation and provide control over the locations of the active nucleation sites regardless of the contact angle between the fluid and the surface. The ability to produce well-defined areas with different nano-/microtopographies and modified wettability on the micro- and macroscale is of great importance also in *fundamental research*. The unprecedented spatial control over active nucleation sites can be used for the optimization of the active nucleation sites distribution. The results of such studies will, surely, push the heat transfer coefficient and the critical heat flux to even higher values.

Although currently available technologies for surface engineering provide numerous possibilities for their combinations to develop hybrid surfaces with practically any imaginable performance, this usually sacrifices the scalability and increases the complexity as well as the production costs. In this context, *laser surface engineering* represents a straightforward, compact, robust, flexible,

chemical-free and cost-effective alternative. Additionally, laser texturing avoids adding extra surface layers, as is the case when performing surface modification by application of different coatings, and, consequently, such boiling interfaces do not increase the overall thermal resistance of the surface. Due to these reasons, laser surface engineering has the ability to open new possibilities for overcoming the current limitations for further miniaturization of microelectronic devices and has a high potential to increase the performance and safety in high heat flux systems. As always in new emerging technologies, the important still open question remains the *long-term stability* of new types of surfaces for the boiling heat transfer enhancement. This question is of a great importance, since in real applications, the surface and, consequently, boiling stability is measured in years and not in hours as in the everyday scientific experiments.

Acknowledgments The authors would like to express a special thanks of gratitude to Prof. Dr. Iztok Golobič for inspiration, encouragement and his continuous support. The authors would also like to acknowledge Dr. Matej Hočevar from the Institute of metals and technology for his support in SEM characterization of the selected samples as well as Matic Može from Faculty of Mechanical Engineering (University of Ljubljana) and Mao Takeyama from Kyoto University for providing the microthermocouple measurements.

The authors acknowledge the financial support from the state budget by the Slovenian Research Agency (research core funding No. P2-0223 and P2-0392 and project No. J2-1741) and SPI Lasers Ltd. for their support of the research project *Surface functionalization by nanosecond fiber laser texturing (nsFLaT)* by loan of their fibre laser.

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Optimal Design of Flexible Micro Multi-level Topographies for Enhancing Durability of Superhydrophobic and Icephobic Functions



Lei Wang and Yan Xing

1 Introduction

To survive in the cruel world, organisms in nature need to arm themselves with kinds of abilities to adapt to the surrounding environment, like self-cleaning ability [1–3]. Lotus, for example, pure and fragrant water plant growing in the dirty mud, needs to keep their leaves clean to absorb more sunlight and prevent corrosion [4, 5]. Over the last few decades, researchers have taken some investigations on the attractive self-cleaning ability through theories and experiments to explore the insight physical mechanisms based on lotus leaves [6–9]. The exploring history can be summarized as follows. At first, researchers find that water droplet can keep its spherical shape on and easily roll off (just like a wheel without any block) from the lotus leaves, which seem to be the apparent reasons for the plant's self-cleaning ability [10]. Then, they find that the essential factors for self-cleaning ability should be attributed to the specific surface topography and surface chemical property, resulting in spherical droplets and low contact hysteresis. It has been reported that particular micro-/nano-structures lie on the lotus leaves covering with low surface tension wax, which makes droplet suspended effectively on the top of the structure and air layer lying under the droplet, showing a nonwetting state [11–16]. The specific micro-/nano-structures on the lotus leaf consist of micro-papillae (diameter, 5–10 μm ; distance, 10–20 μm) and nano-rods (diameter, ~ 50 nm; height, 300–500 nm). Under nonwetting state, droplets roll off the surface easily when subject to gravity through a small tilt angle of substrate. Here, with this property, the

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lotus leaf surface was named superhydrophobic surface with superhydrophobic ability. What's more, if some pollutants, such as dirt which has a larger diameter than the micro-/nano-structure distance, fell on the superhydrophobic surface, the rolling off droplet will take the dirt away, leaving the surface clean, which can be called the self-cleaning ability [17, 18]. Not only lotus but also many other creatures in nature have the superhydrophobic ability and self-cleaning ability, such as bamboo leaf, bird feather, insect wings, and so on [19–25]. With functional superhydrophobic surface, animals and plants can keep their functional surface clean and surviving in the high-humidity environment.

Inspired by the natural lotus leaf, many superhydrophobic and self-cleaning surfaces are duplicated [26–31]. On these artificial surfaces, the liquid droplets could not penetrate into the valley and can be suspended on the top region of topographies due to the protected air between the rough micro-/nano-structures. Researchers find that this air layer not only prevents the surface to be wetted by water but also effectively enhances the thermal isolation between the environment and the base, resulting in the liquid droplet to not freeze fast on the superhydrophobic surface at low-temperature environment. This extra extended function is called “icephobicity” [32–35].

Researchers focused on the rigid superhydrophobic surface for a long time due to the fact that it is hard to fabricate soft micrometer-scale and nano-scale topographies based on technologies that already exist, though easy to build rigid micro-/nano-structures, which significantly limits the wide application of biomaterials. On the rigid superhydrophobic surface, the functional topographies are easily ruined by the sequent impact of water or the freezing droplet at low temperature [36–38]. Figure 1 shows a steel needle after freezing test [39]. Experiments show that the apex region will be cut by the extended volume of freezing droplet. Focused on this phenomenon, researchers took various researches. Results show that in the freezing process, the droplet freezes and extends its volume, which generates smaller displacement and larger stress on the steel needle surface, which is proved to be the real reason why superhydrophobic surfaces always fail in the icephobic process. At low temperature, the formation and condensation of small-size droplets from the atmosphere is a ticklish issue [40, 41]. The condensed droplets with small diameter easily penetrate into the valley of the nano-structures and wet the surface. At the same time, the liquid droplet transfers their wetting states from Cassie's state into Wenzel's state, and the superhydrophobic function fails [42–45]. Then, the freezing process ruptures the micro-/nano-structures, which is a long-term and irreversible damage. This section elaborates on the flexible micro multi-level topographies on superhydrophobic surfaces for enhancing durability of superhydrophobic and icephobic functions, offering a theoretical and experimental basis for enhancing stabilities of functional micro multi-level topographies.

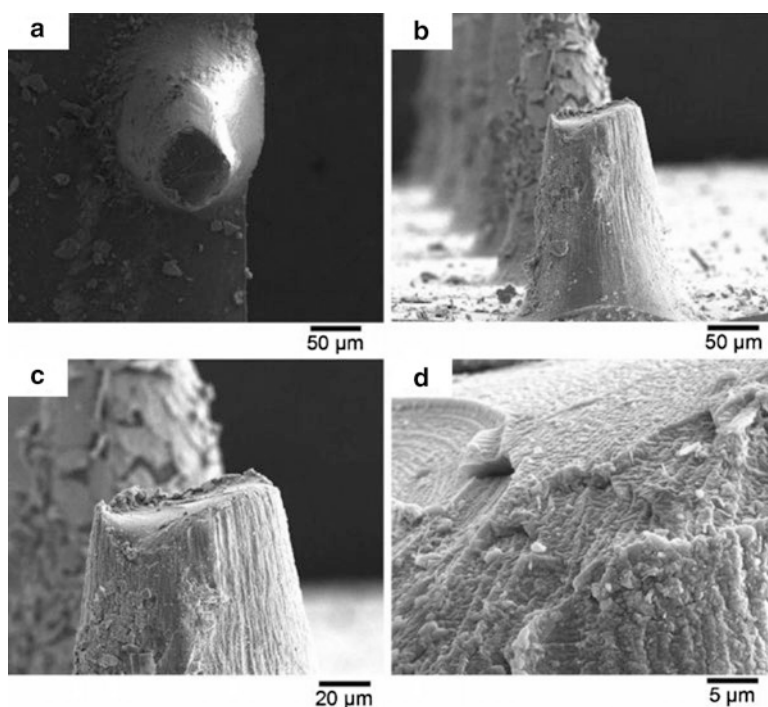


Fig. 1 SEM images of the micro pillar after more than 50 icing tests. (a–b) The top view and side view of the rigid surface. (c–d) Magnified views of the nano-topography of the rigid micro pillar. The micro-structure and nano-structures are destroyed. (Reprinted with permission from Reference [39], Copyright (John Wiley & Sons, Inc.))

2 Superhydrophobic and Icephobic Surfaces

In the current studies, researchers claim that self-cleaning ability of superhydrophobic surface is achieved mainly through the effect of the micro-/nano-structures. It is known that surfaces with low surface energy component can be hydrophobic [46]. Common hydrophobic surface will be superhydrophobic if we add some roughness. Due to the roughness of micro-/nano-structure, droplet will not penetrate into the structures and sit on the top of the structures, staying in Cassie's state. According to Cassie's equation, droplet wetting ability decreases with the increase of the roughness, meaning it will be more hydrophobic, and it can become even superhydrophobic in the end [47, 48]. Furthermore, based on the structures and corresponding superhydrophobic phenomena, researchers find that there is some pocketed air at the solid-liquid interface when droplet sits on the superhydrophobic surface, which will effectively reduce the heat transfer between solid and liquid interfaces, resulting in icing-delay time [49, 50]. On the surface with much pocketed air, the liquid droplet could not freeze in a short time at low-temperature environment. That's the way that superhydrophobic functions and icephobic functions are bound together.

2.1 Superhydrophobic Surface

According to Jiang's explanation, generally speaking, superhydrophobic surfaces can be defined as the surfaces with static CA higher than 150° [51]. However, more details should be illustrated when roughness and CA hysteresis are taken into consideration. In general, roughness is an essential element in designing the superhydrophobic surface (the largest CA of most surfaces without roughness can be up to 120°) and plays an important role in deciding the CA hysteresis (existing in a dynamic process). On rough superhydrophobic surface, three kinds of states can be simply divided based on the wetting state: Wenzel's state, Cassie's state, and the transitional state between Wenzel's state and Cassie's state [51]. Wenzel's state is a state with high CA hysteresis owing to the penetration of the droplet into the structures, presenting a wet-contact mode on the surface (Fig. 2a). On the contrary, the droplet in Cassie's state can sit on the top of the rough structure and roll easily with low CA hysteresis, showing a nonwet-contact mode (Fig. 2b). The intrinsic difference between Wenzel's state and Cassie's state can be known as the difference of the wetting state of droplet in structures. However, the most popular state in nature should be the third one: transitional state between Wenzel's state and Cassie's state (Fig. 2c). In this transitional state, surface water droplet can slide on the surface when the substrate is tilted with a small angle.

Except for these three fundamental states, researchers also find two special states. The first one is Gecko state, a kind of special Cassie's state (Fig. 2d). Gecko state is a superhydrophobic state with high adhesive force, like gecko's foot [52]. The high adhesive force can be attributed to two different states of air layer. For Cassie's state, droplet sits on the top of the structure, and the air layer is connected to the

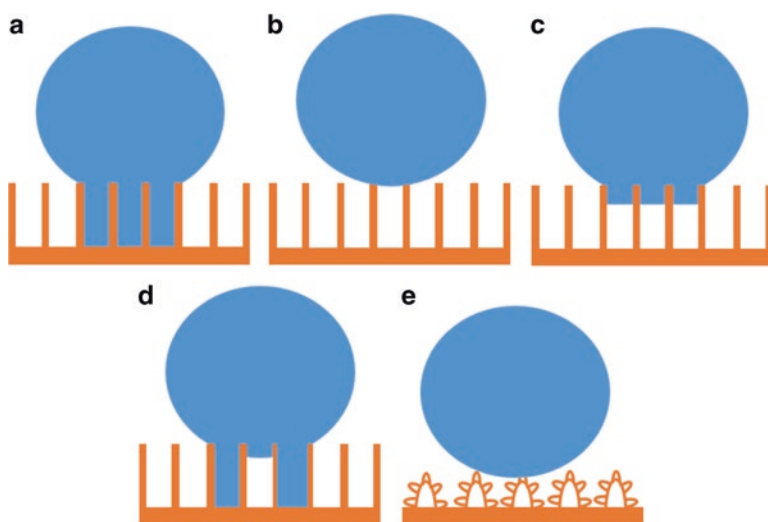


Fig. 2 Superhydrophobic states of droplet on rough surfaces in nature

atmosphere. As for Gecko state, except for the existing connected air layer, there is also another kind of air layer locked completely in the pores of the structures. The completely enclosed air layer will conduct the high adhesive force through negative pressure induced by the volume change of the air. Naturally, here a special Cassie's state with both high CA and high hysteresis can be noticed, not wetting the structure. The second one is the lotus state (Fig. 2e), which can also be seen as another kind of special Cassie's state. Due to the micro-/nano-structures on the lotus leaf, droplet can get higher CA and lower CA hysteresis than the normal Cassie's state, and the corresponding surface can be armed with better self-cleaning functions.

The self-cleaning effect of lotus leaf is arousing much interest for practical applications. Researchers reported the possible relationship between micro-/nano-structures and took some investigations. Feng et al. have given some structure parameters of lotus leaf and constructed a mathematical relationship between CA and its structure parameters based on the Koch curve in fractal geometry [2]:

$$\cos \theta_f = f_s (L/l)^{D-2} \cos \theta - f_v \quad (1)$$

where θ_f is the CA on a rough surface while θ is the CA on smooth surface of the same substance. f_s and f_v are the occupying percentages of the solid and air parts exactly under the supported droplet, respectively ($f_s + f_v = 1$). $(L/l)^{D-2}$ is described as the structural parameter. L and l are the size of the diameter of micro-papillae and nano-branch-like structures. D is the fractal dimension. According to the theories of triadic Koch curve model, D in three-dimensional is defined as value of 2.2618, while the L/l can be recognized as 3^n . In Eq. (1), f_s , f_v , and θ can be measured by the SEM and Dataphysics directly; then θ_f can be calculated as 147.8° , 149.7° , 152.4° , 156.5° , and 163.4° for $n = 0, 1, 2, 3$, and 4 , respectively.

2.2 Icephobic Surface

Air is a poor heat transfer medium in our daily life due to its low thermal conductivity. In view of the poor thermal conductivity in thermodynamics and universality in daily life of air, researchers decided to introduce it into the icephobic system and conducted series of experiments to demonstrate the reliability of the novel design [52–54]. It is incidental that, according to the previous studies on superhydrophobic surfaces with roughness, there are great deal of air pockets at the liquid-solid interface, which are the most important factor for self-cleaning process. Based on the air at the liquid-solid interface, thermal isolation can be well done in the superhydrophobic system. Naturally, superhydrophobic surfaces with micro-/nano-structures are employed extensively as the icephobic surface, which can effectively prolong the icing-delay time.

Zheng's group firstly applied the artificial surface with micro-/nano-structures in icephobic. When the artificial surfaces with micro-/nano-structures were compared with the natural surfaces with micro-structure or nano-structure, the

natural surface with micro-/nano-structures showed a higher CA and longer icing-delay time [32, 47, 55]. Besides, they give some explanations from the theories. In order to analyze the phenomenon of heat transfer, we should understand how things are working in this system. In this droplet and solid substrate system, there are two external mediums for droplet heat transfer. The first one is the air-surrounded droplet, while the second one is the solid substrate under the droplet. High-temperature air and low-temperature solid substrate result in heat gain from air and heat loss to solid substrate through heat transfer and thermal radiation. They can be described in unit time respectively with h_g , $h_{g'}$ and h_l , h_r , and the net heat gain in unit time of droplet is equal to:

$$\Delta h = h_g + h_{g'} - h_l - h_r \quad (2)$$

With the decrease of the temperature of substrate, the decrease temperature of the droplet can be described as:

$$t_f = \frac{\rho_w C_p (t_0 - t_s)}{\Delta h} \quad (3)$$

From the equation 3, t_f is decided by Δh . Furthermore, they find h can be influenced a lot by the number of contact area. Assuming that the volume of the droplet on these different surfaces is the same, there is no doubt that the contact area between air and liquid on micro-/nano-superhydrophobic surface is higher than surfaces with other kinds of structure according to the previous studies, while there is lower solid-liquid contact area. That is, there are more heat gain from air and less heat loss in the system of superhydrophobic surface with micro-/nano-structures.

In conclusion, superhydrophobic surface with micro-/nano-structures plays an important role as an icephobic surface and has more potential in kinds of icephobic applications.

2.3 Hollow Superhydrophobic and Icephobic Surface

Benefitting from the outside surface roughness, the liquid could not penetrate into the micro-valley and be suspended on the apex region of topography, which generates much pocketed air at the solid-liquid interface and enhances the ability to decline the conductivity. The increase of pocketed air between the solid and liquid interface could effectively enhance the superhydrophobic and icephobic function. It is known that surface roughness plays an important role in the outside structure of the surface which can influence the superhydrophobic and icephobic function. However, the inside structure of the surface has rarely been mentioned in previous studies. Obviously, there will be higher efficiency for icephobicity if internal and external structure can be integrated together. A novel design for increasing thermal isolation was proposed which can make use of air layer outside and inside the surface: hollow micro-topography [56].

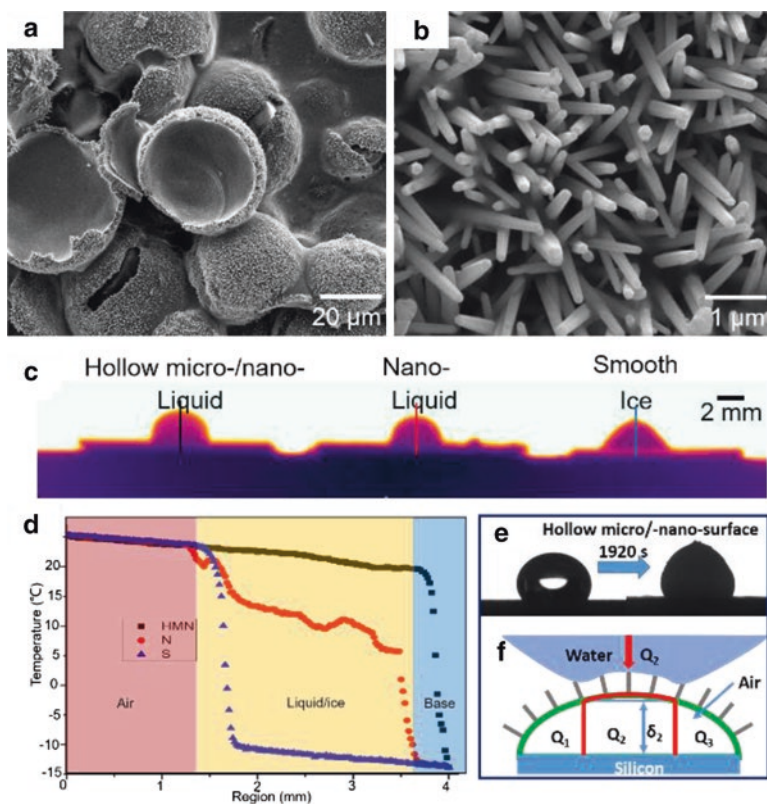


Fig. 3 Topography of hollow micro-/nano-structured (HMN) surface and the heat transfer process at low temperature. The SEM image of the HMN (a) and the magnified image of the nano-structures (b). (c–d) The temperature distribution at the solid-liquid interface for 20s (-15°C). (e–f) The icing test on the HMN surface. (Reprinted with permission from Reference [56], Copyright (Elsevier))

ZnO-based hollow micro-/nano-structured (HMN) topographies are achieved on the polymer surface and silicon wafer surface. After modified by the fluoride, the surface obtains superhydrophobic, self-cleaning, anti-fogging, and anti-icing properties. Figure 3a shows that the HMN surfaces with diameter of $\sim 30\ \mu\text{m}$ and thickness of wall of $5\ \mu\text{m}$ distribute uniformly on the silicon wafer surface. The magnified observation shows that the diameter of nano-rods is $100\ \text{nm}$ and its length is $1\ \mu\text{m}$ (Fig. 3b). With the contribution of the hollow micro-sphere, the droplet performs better anti-icing than the other two surfaces (Fig. 3c–d). The temperature distribution on three solid-liquid interfaces is different. On the HMN surface, the temperature could not decline fast due to the bed thermal transfer in the hollow micro-sphere.

From the top surface to the base, HMN is divided into three layers, i.e., base, air layer inside of the HMN, and the ZnO wall. Meanwhile, the top layer (ZnO wall) is composite composed of ZnO nano-rods and pocketed air. The total thermal resistance is:

$$R_{HMN} = \left[R_{(Si)} + R_{(Air)} + R_{(ZnO)} \cdot f_{HMN} + R_{(Air)} \cdot (1 - f_{HMN}) \right] \quad (4)$$

$$= \delta_1 / \lambda_{(Si)} A + \delta_2 / \lambda_{(Air)} A + \delta_3 / \lambda_{(ZnO)} A \cdot f_{HMN} + \delta_3 / \lambda_{(Air)} A \cdot (1 - f_{HMN})$$

where $R_{(Si)}$, $R_{(Air)}$, $R_{(ZnO)}$ is the thermal resistance of silicon, air, and ZnO, respectively, and δ_1 , δ_2 , and δ_3 represent the thickness of the three layers (Fig. 3e–f). $\lambda_{(Si)}$, $\lambda_{(Air)}$, and $\lambda_{(ZnO)}$ represent the thermal conductivity of three materials. A represents the contact area between liquid and solid. Apparently, the R_{HMN} is larger than the R_N and R_S . Figure 3d shows linear distribution of temperature from the top of droplet to the base (along the solid line in Fig. 3c) on three surfaces. HMN shows the minimal decline speed. The total heat flux to silicon wafer on HMN surface contains three layers: Q_1 , Q_2 , and Q_3 . Q_2 , the heat flux of a droplet from water to silicon wafer, is calculated according to the Fourier heat conduction law [57, 58]:

$$Q_2 = \frac{T_{base} - T_{Top}}{R} \quad (5)$$

where T_{base} and T_{Top} are the temperature of the environment and the base (silicon), respectively. Sequentially, the heat flux on HMN surface is shown in Eq. 6:

$$Q_2 = \frac{T_{base} - T_{Top}}{R_{HMN}} = \frac{T_{base} - T_{Top}}{\delta_1 / \lambda_{(Si)} + \delta_2 / \lambda_{(Air)} + \delta_3 / \lambda_{(ZnO)} f_{HMN} + \delta_3 / \lambda_{(Air)} (1 - f_{HMN})} A_{HMN} \quad (6)$$

The heat transfer happens mainly at the interface of liquid-solid; it happens between droplet and the cold base and forms temperature fluctuation. Subsequently, the relation of liquid-solid contact area ratio is $S (A_S) > N (A_N) > HMN (A_{HMN})$. The minimal contact area limits the thermal conductivity, which indicates the best thermal resistance on HMN. This is a novel method for enhancing the anti-icing performance by introducing the hollow micro-topographies at the interlayer region.

3 Flexible Multi-level Topographies for Enhancing Durability

Various artificial superhydrophobic and icephobic surfaces have been achieved based on the studies of researchers on the lotus micro-/nano-structures. However, functional surfaces will easily fail in applications. For example, functions will be lost after longtime water impact and several icing cycles.

In Kulinich’s work, they find that the ice-repellent properties of surface roughness appear to be gradually damaged during icing/deicing cycles [36]. On the rigid surface, the freezing droplet extends its volume and generates stress concentration on the nano-structures. When it gets the ultimate stress, the nano-structures rupture and induce the failing of superhydrophobic property. He first tested the ice-repellent properties systematically in different conditions and over time. The conditions even include outdoor ice accretion during “freezing rain,” and the icing cycle number is more than 20. The results show that contact area of ice on the solid will be reduced due to the air layer in superhydrophobic micro-/nano-structures, but with the increase in icing cycles, ice on the same surface will sit on the lower position with the damage of the micro-/nano-structures.

It can be concluded that rigid structures cannot survive for a long time in the process of icing due to the damage caused by ice shedding. Figure 4 shows the simulation of icing process on rigid micropillar surface. The rigid micro pillar generates smaller deformation and larger stress on the contact region, resulting in the rupture of topography. Considering the larger stress concentration on the rigid

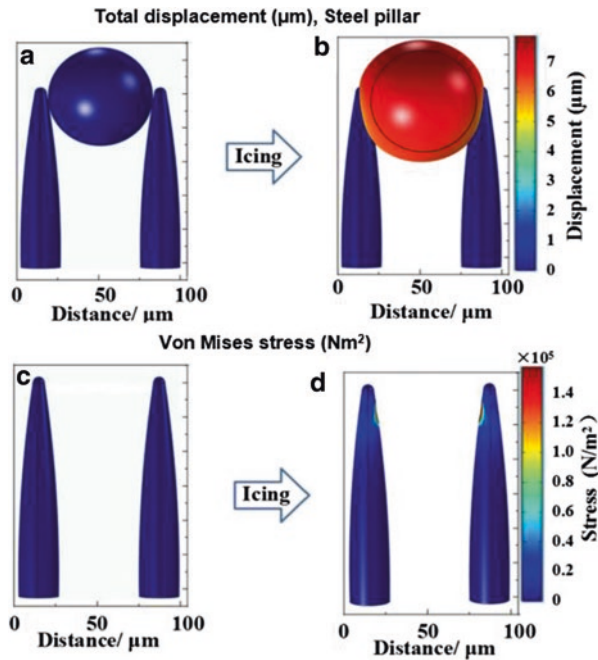


Fig. 4 The simulation for rigid micro pillar with icing test. (a–b) The displacement change of topography with icing test. There is no larger bending for the rigid micro pillar. (c–d) The stress distribution on rigid micro pillar. The stress concentration generates at the contact region. The extended volume of icing particle generates larger stress and smaller deformation on the rigid surface, resulting in the rupture of topography. (Reprinted with permission from Reference [39], Copyright (John Wiley & Sons, Inc.))

surface under loading, finding an effect method for dealing with this problem has become more and more urgent.

3.1 *Flexible Topography in Nature*

Flexibility is one of the significant roles for natural surface, which is very easily to be ignored in the duplication process. Lotus leaf survives in storms and maintains their superhydrophobic ability for a long time not only because of its micro-/nano-structure but also because of its flexibility. It can be described visually as Chinese philosophy “overcoming firmness by gentleness.” The lotus leaf under heavy rain transforms its shape to match the external force. Most of the kinetic energy of the rain or wind is transferred into the elastic energy of the leaf and its stem, resulting in the protection of rough micro-/nano-topographies on the leaf surface. It is the reason why lotus leaf could keep its self-cleaning performance for long time (Fig. 5).

Another leaf, lady’s mantle leaf, is a natural hydrophobic leaf with some hydrophilic hairs. There is no doubt that flexibility of hairs plays an important role in the maintaining of hydrophobic ability not only because the hairs are hydrophilic but also because the flexible hairs can bend themselves to store energies when subjected to the external pressures, returning to original shape when the pressure was removed [59, 60].



Fig. 5 The flexible lotus leaf in nature. The flexible leaf could deform to match the deformation generated by the falling droplet

3.2 Bio-fabricated Flexible Topography

Bioinspired by natural flexible functional structures, the surface superhydrophobic and anti-icing were realized by using PDMS as the flexible micro-structure and ZnO as the nano-structure. For enhancing the durability of superhydrophobic and ice-phobic functions, Wang et al. find a new design method in which they cover ZnO nano-rods on the soft PDMS-based papillae (Fig. 6a–d) [61, 62]. Even if the surface is in flat state or curved state, the droplets could not wet the surface for a long time at low-temperature and high-humidity environment (Fig. 6e–f). For illustrating the contribution of soft micro-papillae to the protection of nano-structures on their surface, the mechanical test is conducted on three surfaces, i.e., flexible micro-/nano-structures, flexible nano-structures, and rigid micro-/nano-structures, respectively. Under loading and releasing process, the nano-structures could not be broken on flexible micro-/nano-structures (Fig. 6g), while on the flexible surface without micro-structures, the nano-structure is broken (Fig. 6h, the breakpoint of the curve).

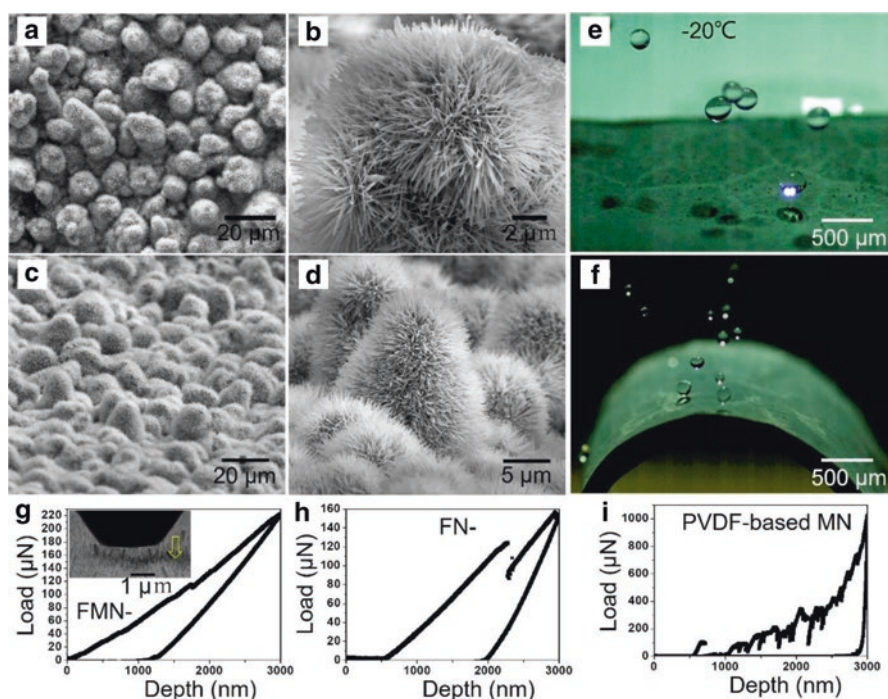


Fig. 6 The SEM images of the topography and the mechanical test of the nano-structures. (a–b) The top view of the flexible micro-nano-structure (FMN), (c–d) the side view of the topographies. (e–f) Motion of droplet on the FMN surface (on flat and curved surface). (g–i) The mechanical test of nano-structures on the three surfaces, i.e., FMN, flexible nano-structured (FN) surface, and rigid surface (PVDF-based micro-nano-structured surface). (Reprinted with permission from Reference [61], Copyright (John Wiley & Sons, Inc.))

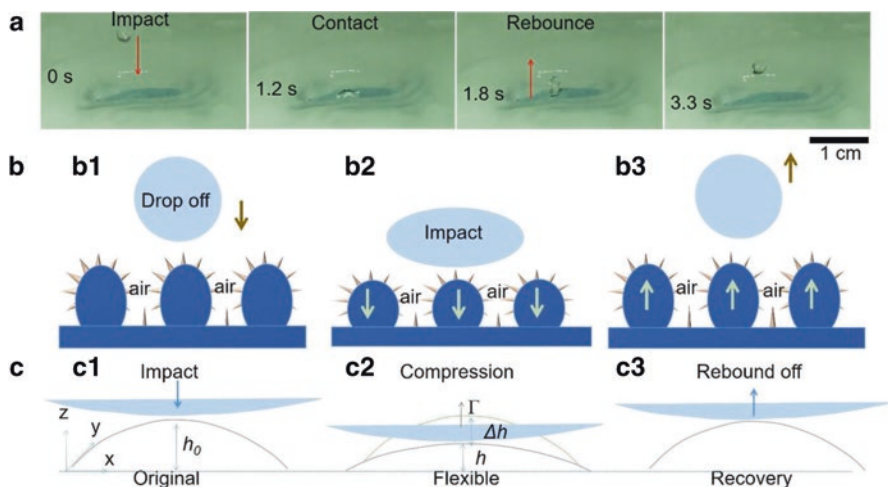


Fig. 7 Dynamic motion of supercooled droplet on the flexible micro-nano-structured surface. (a) The droplet with temperature of 0 °C impacts on the FMN surface. The temperature of the surface is −20 °C. (b) Under impact, the flexible micro-papilla transfers its size to match the deformation generated by falling droplet. (c) The kinetic energy of falling droplet is transferred into the elastic energy (Γ). After release, the elastic energy of the base is fed back to the kinetic energy of rebounding droplet. (Reprinted with permission from Reference [61], Copyright (John Wiley & Sons, Inc.))

The stability of nano-structures on the rigid surface is much worse (Fig. 6i) – the structures generate serious destruction. The results indicate the special contribution of flexible micro-structures to the stability of nano-structures.

When the falling droplet impacts on the flexible surface (Fig. 7a–b), its kinetic energy is transferred into the elastic energy of the flexible base (Γ). The contribution of Γ to the topography's stability can be described by Eq. 7:

$$\Gamma \propto \frac{\sqrt{K}}{\sqrt{h}} = \frac{\sqrt{K}}{\sqrt{h_0 - \Delta h}} = \frac{\sqrt{K}}{\sqrt{h_0 - x}} \quad (7)$$

where K is the elastic modulus of the base, h is the distance between the base and the air/liquid interface, h_0 is the initial height between air/liquid interface, Δh is the change of height (x), and $h_0 = h + \Delta h$, respectively. As the Δh increases, the larger elastic energy is generated. Most of the kinetic energy is transferred into the elastic energy of flexible micro-papilla, resulting in the less stress concentration on the nano-structures, which protects the surface roughness and enhances the durability of multi-functions.

An ideal system for icephobicity is that the freezing droplet could not ruin the micro-/nano-topography. The flexible setae of insect will always be stable in harsh environment due to its elastic property. Excellent mechanical property of micro-topography is the most critical factor for long-lasting superhydrophobic and anti-icing performances. The stable micro-topography could provide air layer, which

decreases the solid-liquid contact area and enhances the heat isolation. To enlarge and observe the details of the dynamic motion of the flexible topography under loading process, superhydrophobic flexible needles are achieved [39]. Fig. 8a shows

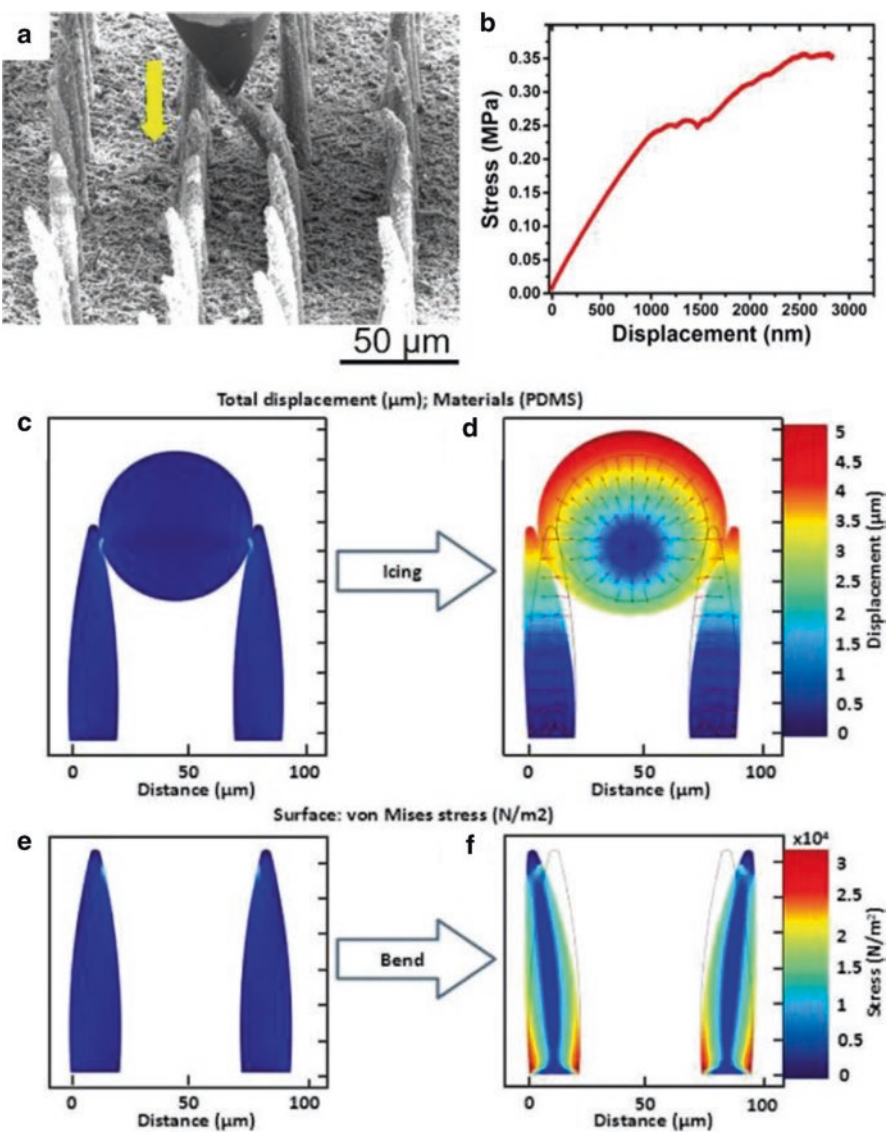


Fig. 8 The loading test and simulation process on flexible needles. (a) The SEM image of the loading test. (b) The stress-strain behavior of flexible needle. The flexible needle bends with plastic deformation. (c–f) The simulation of the icing process on flexible needles. The displacement (c–d) and stress distribution (e–f) of flexible needles. (Reprinted with permission from Reference [39], Copyright (John Wiley & Sons, Inc.))

the loading test on the flexible needle. The stress-strain curves illustrate the needle is bent with plastic deformation (Fig. 8b).

Flexible surface can deform itself to reduce the influence of freezing process (Fig. 8c–d). Meanwhile, the icing particle generates smaller stress on the bent topography, resulting in the protection of nano-structures on its surface. By converting the external energy into the elastic potential energy of its own flexible surface, the damage of the functional nano-structure can be reduced, thus improving the durability of the functional structure and maintaining the function.

3.3 Bio-fabricated Hollow Interlayer Topographies

To enhance the superhydrophobic and icephobic ability, hollow interlayer can be introduced into this system except for the optimal design of the surface structure. After displaying a strategy of robust nano-topography protection on flexible multi-level micro ellipsoid with optimal topography, efforts should be made to find an optimal structure of hollow interlayer topography. Hollow interlayer topography is a functional structure universal among animals, for example, the fly of insects [63–66]. The hollow interlayer structure not only reduces their weight but also enhances the mechanical performance and has some influences on the elastic modulus of the flies. R. M. Spriggs took some investigation in the relationship between porosity and elastic modulus on flexible structures [65]; the results of the effect of porosity on elastic modulus can be described as [63, 64]:

$$E = E_0 e^{-bP} \quad (8)$$

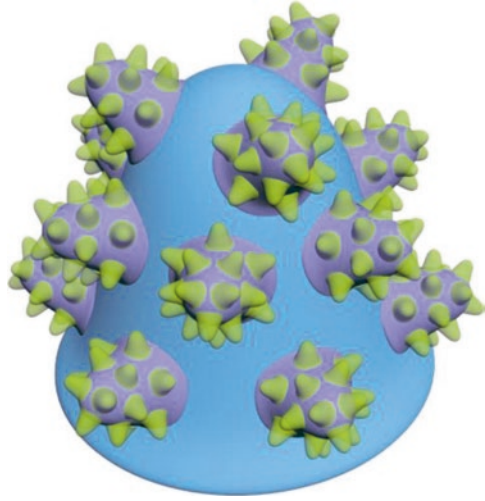
where E is elastic modulus of porous structure, E_0 is the elastic modulus of nonporous structure, e is the Napierian number, b is an empirical constant, and P is the volume fraction of porosity ($P = \frac{\text{void volume}}{\text{total specimen volume}}$). From the equation above,

it can be determined that the volume fraction of porosity has a negative effect on the elastic modulus, that is, with the increase of the volume fraction, the elastic modulus will decrease gradually. Therefore, the flexibility of the total structure can be enhanced via reducing the elastic modulus to transfer more energy into the elasticity energy of itself when the structure is subjected to the external impact and finally protect the structure efficiently.

3.4 Multi-level Flexible Topographies

Multi-level structures effectively enhance the superhydrophobic ability and icephobic ability of superhydrophobic surfaces through the increased percentage of air layer, which induces the low heat transfer efficiency. Figure 9 shows a sketch of the

Fig. 9 Sketch of the flexible multi-level topography. The load acting on the minimal structure decreases as the topography levels increase



multi-level flexible topography. However, the existing artificial surfaces with micro-/nano-structures have limited mechanical property compared with the natural surface. Therefore, what kind of multi-level structure superhydrophobic surface is better for icephobic? Experimental studies and simulations were conducted to make a detailed analysis on this topic.

It was concluded that not only flexibility of micro-structures is a significant factor on deciding the durability of the functional surface, but also the level number of the micro-structure plays an important role in the durability of the functional structure. Up to now, the reports about the level number of flexible topography that could enhance the functional sensitivity and topography stability are still rare. When the flexible surface is composited with n -level, the equivalent stiffness is shown in Eq. 9:

$$k_n = \frac{E_1 E_2 E_3 \dots E_{n-1} E_n}{E_1 E_2 E_3 \dots E_{n-1} + E_1 E_3 E_4 \dots E_n + \dots + E_2 E_3 E_4 \dots E_n} \quad (9)$$

$$= \frac{n E E_1^{n-1} A A_2 A_3 \dots A_{n-1} A_n}{n E E_1^{n-2} A A_2 A_3 \dots A_{n-1} + n E E_1^{n-2} A A_3 A_4 \dots A_n + \dots + E_1^{n-1} A_2 A_3 A_4 \dots A_n}$$

where k is the equivalent stiffness of the composite surface with n -level, E_x is the elastic modulus of x th-level surface, and A_y is the area of y th-level surface, respectively. With the increase of level number, the equivalent stiffness of the composite surface decreases. The load acts on the minimal topography (nano-structure) are calculated and showed in Eq. 10:

$$P_{dn} = k_n \left(\frac{mg}{k_n} + \sqrt{\left(\frac{m}{k_n} g \right)^2 + \frac{m}{k_n} v^2} \right) \quad (10)$$

where P_{dn} is dynamic load act on the nano-structures on the $(n-1)$ th-level surface, m is the mass of solid particle, g is gravity, and v is the impact velocity. When $\frac{A_n}{A} \ll 1$, with the increase of structural levels, the stiffness distribution decreases, and the load acting on nano-structures decreases. So, the multi-level of flexible topography is more valuable for durable superhydrophobicity and icephobicity.

4 Conclusions

The durability plays a significant role for the application of superhydrophobic and icephobic functions. In this chapter, a novel principle for designing the robust stable micro-nano-structured surface for preventing the stress concentration in the loading test was proposed. On the flexible multi-level topography surface, the icing particles or other loading styles acting on the surface could generate larger deformation and smaller stress, resulting in the protection of functional micro-/nano-topography.

Acknowledgments This work is supported by the National Natural Science Foundation of China (No. 21805294).

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Superhydrophobic Coatings for Marine Corrosion Protection



Ri Qiu and Peng Wang

1 Introduction

Wettability is one important aspect of the material. Commonly, from the wettability property, the materials are divided into different categories, including the hydrophilic and hydrophobic surface. However, with the join of the roughness, the apparent wettability of the surface will remarkably change, and the extreme wettability will perform. For the material having the static contact angle larger than 150° with water droplet, the surface is regarded to have superhydrophobicity (SHP). Primarily, SHP phenomenon is found from the natural plants and some animals. Lotus leaf is the representative surface to illustrate SHP. In one ancient Chinese essay, the leaf was praised as “the lotus leaves grow up from the sludge. However, they are not fouled”. Therefore, the self-cleaning effect is used to describe the noble sentiment of the literati. The self-cleaning effect is based on the SHP wettability from the leaf. Until late twentieth century, the intrinsic reason for lotus leaf to perform SHP is revealed by Barthlott et al. [1]. Later, by adopting the biomimetic strategy, the artificial SHP materials have been largely developed. When the surface possesses the roughness into certain extension, with the assistance of the intrinsic hydrophobicity of the material, SHP will exhibit. Therefore, the roughness plays the role to magnify

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the pristine wettability. When the surface is enabled SHP, different usages have been proposed to possess due to the extreme wettability, such as anti-icing [2, 3], anti-fouling [4, 5], anti-corrosion [6–9], and so forth [10–15].

2 The Development of SHP to Protect Underlying Metal

Since the last decade, SHP has been introduced into the corrosion community, and now it has been one hot spot in material protection field [6, 7]. For the corrosion, except the high temperature oxidation, mainly it needs water phase to carry out the electrochemical process. Without water, the corrosion based on electrochemical process cannot occur. Moreover, depending on the state of water phase, the corrosion can be divided as the atmospheric corrosion and corrosion in bulky aqueous phase. For the atmospheric corrosion, it depends on discrete or the continuous liquid film. In this chapter, we will take the marine environment as the harsh environment for interpreting the corrosion inhibition from the SHP coatings. The marine environment contains both the atmosphere and the seawater phase corrosion, and they all represent the harsh environment for the metal constructions. For the bare metal underneath the liquid film, the corrosion will be easy to occur. The corrosion is enhanced with the thin layer of the electrolyte film, which enables the rapid mass transfer of the corrosive species, e.g., oxygen, to diffuse onto the underlying metal surface, so that the corrosion rate increases. For corrosion in bulky phase of the aqueous solution, the corrosion process is different. The seawater corrosion is based on the natural electrolyte, which contains oxygen, Cl^- , and so forth for improving the corrosion reaction. With the water phase, the electrochemical reaction will be easy to proceed due to the separation of the anodic and the cathodic reaction.

Ordinarily, to protect metal from the different corrosion, mainly the coating and the cathodic protection are used. For the coatings, they can be categorized as inorganic and organic texture, and they are applicable for the atmospheric and water phase corrosion inhibition. The coatings are featured by the screen effect to the external corrosive environment. With the coating on metal surface, the corrosive species dissolved in the water phase can be blocked. Due to the tightness and inertness from the coating, it is hard for the existing corrosive species to reach the metal surface to trigger the corrosion process. For the corrosion environment of bulk seawater, except the coating protection, the cathodic protection method can also be used. The principle lies in that the cathodic current is supplied from the external facility or active metal electrically connected to the protected metal substrate. Therefore, the targeted metal will be protected by consuming the externally imposed current or the sacrificial metal, and the underneath metal itself will not be corroded in the corrosive environment, e.g., the well-known harsh seawater environment. However, the cathodic protection is mainly used in the bulky water phase state. Normally, in atmospheric condition, the cathodic protection is not used for the corrosion inhibition.

2.1 *Preparation of SHP onto the Metal Surface*

Mainly, the corrosion is a specific consideration to the metallic materials. To prepare SHP coating onto the metal surface, various approaches are reported. The main route can be divided into two main categories. One is to directly obtain SHP surface via the certain approaches, and the other one is to get SHP via the multiple steps. For the one-step approach, during the preparation process, the roughness and the hydrophobicity should be constructed at the same time. For the multiple steps to construct SHP, building the rough architecture and modifying the surface to enable hydrophobicity is separated, so that many routes can be the available options. For the one-step strategy, SHP can be constructed onto the metal surface via different approaches, and the electrochemical route is one important method. For example, the electrodeposition can be used for building the SHP. In previous studies, Wang et al. have used an electrochemical dissolution-coordination-deposition approach to realize SHP coating onto different metal surfaces. Cu, Zn, and so forth have enabled the extreme wettability due to the compound layer formed on the surface [16–23]. Although the mechanism for SHP coating formation includes several aspects, they are completed and integrated in one-pot style. However, several disadvantages still exist. Since the solid structures are made of the organic coordination compounds, the as-built rough structure is intrinsically weak and fragile to the external force. Other methods, e.g., hydrothermal method, are also used for fabricating SHP [24–28]. However, for the practical usage, it can be potentially used for building SHP onto some small parts, for example, the bolts, nuts, and so forth. However, for the large work parts to be coated with SHP, such as the ship hull, the hydrothermal method cannot be applicable. In this situation, more advanced technologies can be potential candidates. For example, the spraying technology reported previously is one potential applicable method to enable the surface coating [29–34]. Moreover, the sol-gel method and the other reported routes can also be applicable for use in the future [35–40].

2.2 *Corrosion Inhibition Evaluation of SHP to Metal*

Field Exposure Method

To know the real protection efficiency from the certain coating, the field exposure method is inevitable. The samples should be exposed in the real severe environments, such as marine atmosphere or the natural seawater environment, to understand the practical protection performance from the coating. However, up to now, exposure of SHP coating to the natural field is seldom found from the reports. This is mainly attributed to the low protection efficiency of the coating in the practical environment. For marine atmosphere, the airborne salt particle and the hydrophilic dust particles will deposit onto the SHP surface, so that the surface wettability will

remarkably change, leading to the deterioration of corrosion inhibition. When the coupon endures the immersion in natural seawater, especially in the living seawater, the complex physical (e.g., wave effect, the splash effect from the seawater), chemical and even biological factors (e.g., the formation of the biofilm or the biofouling) will rapidly destroy the SHP coating, and the corrosion of the underlying metal will follow. The current SHP coatings developed are still not endurable to the natural harsh environment.

Microscopy Method

Optical microscopy is also used for investigating the degradation process of SHP, although the target is for the general principle of the coating failure instead of the corrosion inhibition. By using the confocal microscopy, the failure of SHP has been revealed by Poetes et al. [41]. Using the optical image method can visually obtain the failure process from the image perspective. In a previous study, SHP Co dendrite matrix was built onto Cu surface [42]. For monitoring the failure process of the SHP in seawater environment, the optical camera is employed. The changing scenario is illustrated in Fig. 1. After 6 h, the as-immersed SHP surface still shows the silver color. Elongating immersion time to 12 and 18 h, the brightness has continuously faded. The immersion in seawater for 24 h has failed SHP, and the silver color has completely disappeared, indicating the failure of SHP. However, the real failure process is still ambiguous, since the microscopy technique cannot give the view from molecular scale. Moreover, the sudden change cannot be indicated based on optical microscopy. Therefore, to really monitor the failure process, sophisticated strategies are needed.

Electrochemical Approaches

For in situ observation of SHP coating degradation, electrochemical approaches including open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and polarization curve technique have been used for characterizing the corro-

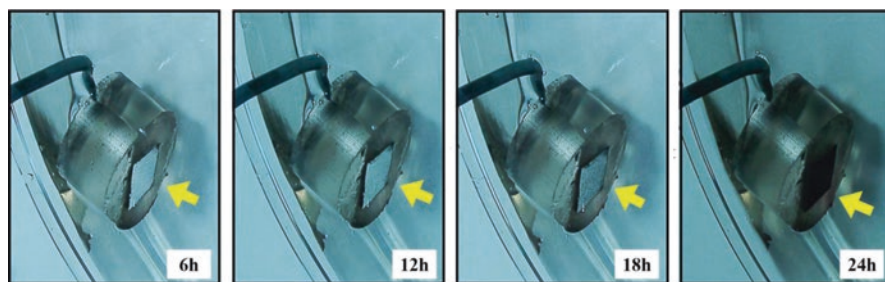


Fig. 1 The failure process of SHP coating in seawater environment revealed by the optical microscopy. (Reproduced with permission from Reference [42], Copyright Elsevier)

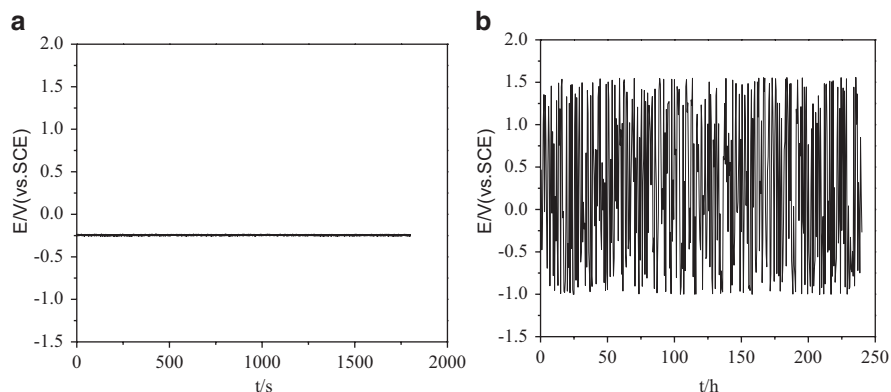


Fig. 2 The OCP test results of (a) bare copper and (b) superhydrophobic copper. (Reproduced with permission from Reference [43], Copyright Elsevier)

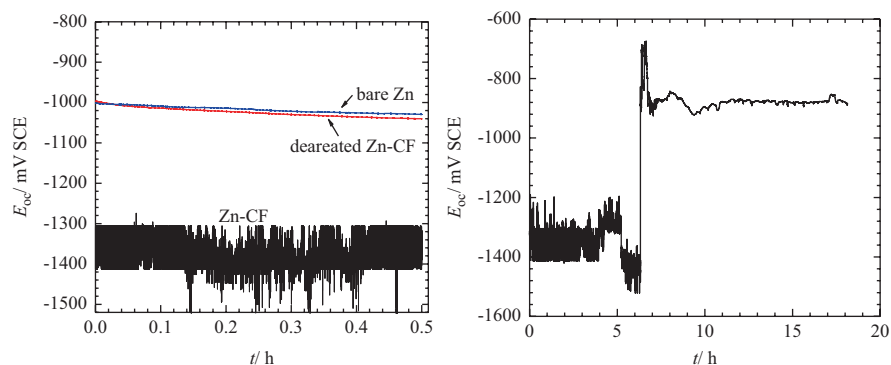


Fig. 3 Eoc-t plots of Zn, Zn-CF, and deareated Zn-CF in 3.5 wt.% NaCl solution. Eoc-t as a tool for monitoring the process of superhydrophobicity failure in 3.5 wt.% NaCl solution. (Reproduced with permission from Reference [8], Copyright Elsevier)

sion inhibition effect from the coating. The electrochemical approaches have their own advantages. By using the electrochemical method, the tiny change at the interface can be revealed. It is very sensitive to the coating integrity and the surface variation, which highly relates with the SHP coatings. OCP is mainly used for characterizing the interfacial potential of the metal in water phase. In previous studies [8, 43], OCP is widely used for knowing the surface change during immersion in seawater environment or in 3.5 wt% NaCl solution. It is very surprising that the OCP value has drastic vibration during immersion in water phase (Figs. 2 and 3). This is a typical phenomenon to feature SHP coating at its initial immersion stage. The vibration is correlated with the surface property of SHP coating, and up to now there is no persuasive explanation existing. We assume that the air cushion formed on the surface of SHP matrix is responsible for OCP vibration. With the long-term

immersion of SHP coating, the vibration vanishes. EIS works as another tool for measuring the corrosion inhibition effect from the SHP coating. For newly fabricated material, the surface is covered by the air cushion, so that the impedance is very high. The currently utilized electrochemical workstation has the difficulty to obtain the accurate impedance value. For EIS measurement, two kinds of data will be obtained, including both Nyquist and Bode diagrams. By using Nyquist diagram, the detailed kinetic information during the electrochemical process will be obtained with the assistance of the fitted equivalent circuit. However, when the impedance of the surface coverage is too large, the additional potential stimulation (ordinarily tens of millivolt) will not accurately achieve the response, so that the data will be very scattering. The scattering points are not useful for obtaining the equivalent circuit. (For example, the impedance is as high as the 10^{10} ohm, and the imposed additional potential is 20 mV. At the low frequency, the electrochemical process is similar to the electrolysis process by direct current. The current is calculated as $I=U/R = 20 \times 10^{-3} \text{ V}/10^{10} \Omega = 2 \times 10^{-12} \text{ A}$. If the value is beyond the sensitivity of the electrochemical apparatus, the instrument cannot regularly sense the current, and the scattering will come out. Without the fitting plots, the simulated electrical circuit cannot be obtained, and the failure process of SHP coating will not be revealed.). However, the Bode plots can give out the total impedance of the coating. Especially, the impedance corresponding to the low frequency is one feature parameter to quantitatively compare protection efficiency from the coating, although the detailed components in the impedance are unknown.

In other aspect, for rapidly knowing the protection efficiency from the air cushion during immersion in the water phase, another method can be used. Using organic liquid such as ethanol or acetone, SHP coating will be wetted. After being rinsed by water phase, the added organic liquid will be dissolved, and the primary SHP coating will be wetted by the water phase. Therefore, corrosion inhibition effect to the underneath metal from the coating with and without the air cushion can be revealed and compared directly by using OCP, EIS, or polarization curve technique. Using organic solvent to wet SHP coating can be regarded as an accelerated method to rapidly fulfill the target of air cushion degradation, since it needs very long time to dissolve the air cushion in SHP coating by the natural immersion.

Moreover, with the application of the microscale probe technique, the surface property of SHP coating can be locally characterized. For example, the scanning Kelvin probe (SKP) has been widely used for getting the local surface coating property on the metal surface. However, the probe is mainly used for knowing the surface potential distribution in the atmospheric condition, and the corrosion tendency of the metal can be revealed by making the comparison between the bare and the treated metal with SHP coating. As shown in Fig. 4, the as-formed SHP surface has been characterized with SKP to illustrate the surface potential difference between pristine and the as-modified Cu surface [43]. It is observed that the potential of bare Cu is very negative, so that it is susceptible to be corroded (left part). However, after being covered by SHP layer, the Volta potential positively shifts 400 mV, indicating the higher resistance to corrosion (right part of Fig. 4). Using SKP technique, SHP surface is locally characterized to have higher corrosion inhibition capability than

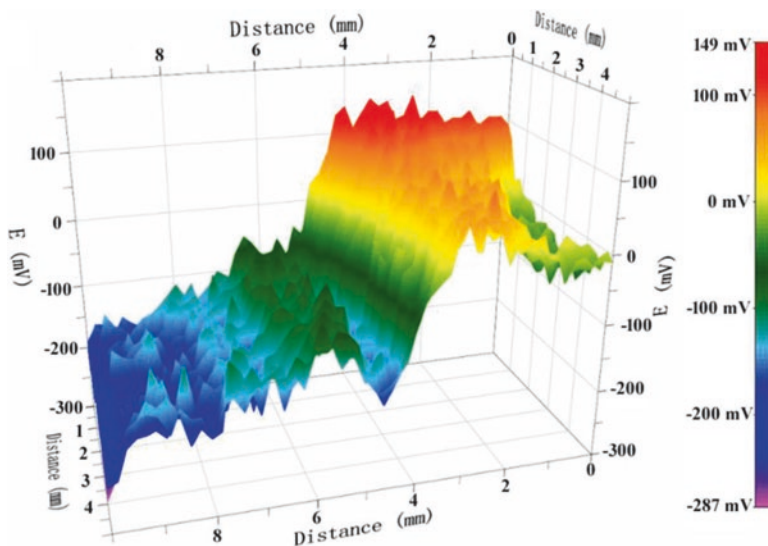


Fig. 4 The potential map of superhydrophobic copper-bare copper junction area achieved via SKP measurement. (Reproduced with permission from Reference [43], Copyright Elsevier)

bare metal. In other studies by us, SKP are also adopted to make the comparison between the bare metal and the as-covered metal by SHP coating. However, this method is not a highly accurate tool, since the thickness of the coverage is not considered during the measurement, especially for the deposit obtained by the dissolution-coordination-deposition approach. Based on this approach, the metal has been attenuated due to the dissolution of the meal. Therefore, the bare metal surface and the electrolyzed metal surface are not at the same plane. Moreover, the accumulation of the deposit on the metal surface will narrow the gap between the probe tip and the surface, further impacting the measured SKP results. Therefore, SKP is not an exactly accurate method to reveal the surface potential. Another widely used micro-scale probe technique is scanning vibrating electrode technique (SVET), and it can be applicable for underwater SHP coating investigation. Up to now, to know the SHP coating efficiency, SVET is widely used [44, 45]. Also, in some results, the scanning electrochemical microscope (SECM) is also employed for revealing the protection efficiency of the coating [46].

Mechanical Stability of the SHP Coating

Except the corrosion inhibition, other aspects of the coating have also been investigated these years. As a coating, the mechanical stability is required. During the initial stage for developing the SHP coatings, this aspect has been largely neglected. With the development for about two decades, currently this property is a critical aspect requiring development. However, it is not an easy task to manage. If the coat-

ing is targeted to achieve SHP wettability, it should be porous, rough, or loose. However, when it has such properties, the robustness will be a problem. Some previous reports have considered mechanical stability of SHP as one important parameter. For example, combining chemical etching and surface modification obtains an SHP steel surface [47]. The authors proposed that the SHP steel performs a good mechanical durability by using different degree sandpapers with loading weights. Peng et al. fabricated SHP Al surface with excellent stability against physical damages [48]. The fabrication process is not based on one-step protocol, either. Combination of both micro- and nanostructure and surface hydrophobization obtains SHP wettability, which performs excellent mechanical durability. Multiple physical damages such as finger-touch, scratch by sharp blade, peeling, abrasion tests, and so forth will not destroy the extreme wettability. Using electrodeposition method, Su et al. prepared SHP on Cu metal [49]. The pine-cone-like micro-nanostructure and the hydrophobic moiety lead to SHP, which exhibits high micro-hardness and excellent mechanical abrasion resistance. After mechanical abrasion against SiC sandpaper, SHP still maintains. In our own studies [43, 50, 51], we also measured the mechanical stability of the as-prepared SHP surface, including dendritic cobalt matrix on Cu surface, $\text{Cu}(\text{OH})_2$ nanoneedle matrix on Cu surface and $\text{Co}(\text{OH})_2$ nanowall on stainless steel. Mechanical stability measurement of the superhydrophobicity was conducted by abrasion between abrasive paper and sliding SHP surface. To increase the interaction between the abrasive paper and SHP surface, additional weight was placed onto SHP coupon. Using abrasive paper, various SHP endured abrasion under certain pressure. Afterward, contact angle was accordingly measured to reveal the wettability response to the abrasion length. Based on the previous reports, to get the mechanically stable SHP surface, two strategies can be adopted. Firstly, the solid phase to realize SHP should be mechanically stable. It can have high hardness or toughness. Secondly, the structure can be intrinsically hierarchical, and the scale might cover the micrometer and nanometer. When external mechanical damage destructs micrometer structure, the nanometer architecture can still stand to maintain the superhydrophobicity. In addition, during constructing the structure, the geometry should be optimized.

2.3 Corrosion Inhibition Mechanism of SHP to Metal

Atmospheric Corrosion

For water droplet, SHP has the high repellent effect. However, in the atmospheric condition, water is not always in the droplet state. Instead, the water mainly exists as the vapor phase. However, the definition of SHP is only based on the water droplet (i.e., the contact angle between the droplet and the surface is larger than 150°). It never considers the vapor phase, and SHP is not the super-vapor-phobic surface. Previous reports [21, 22] have used SHP as the coating to inhibit the atmospheric

corrosion, and certain scale water droplet and salt are specifically selected. In real natural environment, the aerosol can be as small as nanometer. The air cushion will not be formed between the underlying rough structure and the aerosol. Therefore, if the water droplet from salt fog and aerosol is smaller than the feature scale of the rough structure, the air cushion will not be sealed. The incoming water droplet and aerosol will accumulate inside of the porous structure. The as-deposited water phase can keep its humid property, so that it will work as the adsorbent for further collecting the water in the air phase. In atmospheric condition, the water vapor is everywhere, and the porous structure from SHP acts as a humid collector. Definitely, possessing the high capability, the rough structure in SHP is more efficient to collect the water molecule from the air than the planar hydrophobic material. The vapor condensation effect leads to the condensation of water phase into the porous structure. Under atmospheric condition, it is hard for SHP coating to have sufficient corrosion inhibition to the underneath metal.

In underwater environment, the air cushion of SHP acts as an insulating barrier for the invasion of corrosive species. However, it is not a long-term strategy for inhibiting the corrosion, either. Although an air cushion can be formed between the water phase and the SHP coating, the air will spontaneously dissolve into the water phase. Moreover, the cushion will perform as the channel for water molecule to go through. The vapor from the bulk water phase will condense in the cavities and rough structure to form the water layer (Fig. 5). When the immersion time is long enough, the condensed water film will merge with the external bulky water phase, so that SHP will see the failure. In other words, for underwater environment, SHP endures the similar process as in atmospheric condition. However, it is much more severe than the atmosphere. Firstly, the bulk water will consume the air. Unlike the atmospheric condition, even air is consumed, huge amount of the air exists, and the air can be continuously supplemented to avoid the exhaust of the air. Moreover, bulky water phase will afford higher vapor pressure to SHP. It means the air cushion has larger humidity than that of the ordinary atmospheric condition. Therefore, the water layer will be easy to form. When rough structure surface is covered by the water film, the wettability will surely change, and SHP property will vanish.

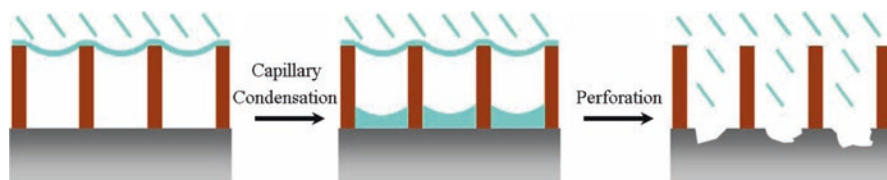


Fig. 5 Schematic illustration of the superhydrophobic carbon fiber film losing corrosion inhibition efficacy during immersion in 3.5 wt.% NaCl aqueous solution. (Reproduced with permission from Reference [8], Copyright Elsevier)

3 Focus of the Current Study

Currently, for protecting the underneath metal, the coverage mainly adopts the film form, so that the metal will be protected by the coating. The thickness is mainly micrometer to the millimeter scale. For maintaining the long durability, previous reports [52, 53] have tried different ways to realize the long-term SHP. For supplement the consumption of the air stored inside of SHP, researchers give out the route [52]. In their report, they developed a self-controlled gas generation approach to maintain the SHP condition under high liquid pressures (up to 7 atm), thus removing a fundamental barrier against the implementation of SHP surfaces for drag reduction. Lee et al. [53] introduce a novel method to regenerate a continuous air interlayer on superhydrophobic ZnO nanorod/Si micropost hierarchical structures (HRs) via the combination of two biomimetic properties of natural leaf: superhydrophobicity from the lotus leaf effect and solar water splitting from photosynthesis. The designed n/p junction in the ZnO/Si HRs allows stable gas interlayer in water and regeneration of the underwater superhydrophobicity due to the unique ability of the surface to capture and retain a stable gas layer. Up to now, there are sparse studies focusing the long-term sustainability, however, the breakthrough is still suspended.

For developing SHP coating to protect the underlying metal, the first is to develop the SHP having long-term duration. After that, the robustness can be considered, since advantage of the coating is based on SHP. If SHP is not able to sustain for a long time, the material cannot find its point to exist. For making the long-term sustainability of SHP, several points should be addressed. In the atmospheric condition, the water condensation should be avoided. To decrease the condensation tendency, firstly, the air can be dry enough. However, to dry the air is not easy, and probably it is not a practically available route. The other strategy is to enhance the surface temperature. Increasing the temperature of SHP surface will avoid the surface condensation. The water molecule will exist as the vapor phase instead of the water fluid, so that the water film will not be built on SHP surface. SHP wettability will keep for long time. During exposure in atmospheric condition, the ambient energy can be changed into the thermal energy, so that it is a versatile route to get the long-term SHP. For the underwater scenario, to maintain SHP is another challenging task. The proposed two routes including the supplying of drying air and enhancing the substrate temperature are not applicable for the film state of the coating. However, by changing the film coverage into the cushion state as the corrosion inhibition barrier seems an available option. For example, in our previous research, we have developed the cushion style SHP, i.e., superhydrophobic sponge to protect steel from corrosion [9]. We used a superhydrophobic sponge as cushion to isolate metal from bulk water phase. The superhydrophobic sponge matrix drastically alleviates underwater immersion corrosion. Water vapor from bulk seawater can be transported outside by inletting dry air, so that dry environment is kept as long as the existence of ventilation. Compared with bare steel and the steel covered with the sole superhydrophobic sponge, the ventilated superhydrophobic sponge matrix can effectively inhibit corrosion of steel to occur.

For illustrating the corrosion inhibition performance, a slit perpendicular to one facet was cut on the SHP sponge to accommodate the steel coupon. The bare steel and the steel wrapped in the sponge were exposed in indoor atmosphere and seawater for enduring the corrosion. For seawater immersion experiment, the five facets of as-modified sponge were immersed in seawater, only leaving the top facet to connect with the external atmosphere. Slight corrosion has occurred on metal surface after the exposure of bare steel to the indoor atmospheric environment for 4 days (Fig. 6, Row 1). When the steel is stored in an SHP sponge, the corrosion can be effectively inhibited. The airborne moisture in atmospheric environment entering into the matrix will be absorbed onto sponge skeleton surface, and the residual water diffusing onto the metal surface will remarkably decrease, leading to the dry steel surface. The corrosion rate is relative slow, when water amount is decreased (Fig. 6, Row 2). However, SHP sponge does not perform good corrosion inhibition environment for bare steel (Fig. 6, Row 3). The moisture from air will not be efficiently absorbed due to the low affinity to water molecules from SHP sponge. Water molecule will diffuse into the inner side of the matrix without significant loss. When contacting with the hydrophilic steel surface, the water molecules will spontaneously condense to form a thin liquid film, resulting in corrosion. In contrast, SHP sponge supplies the inter-connecting three-dimensional space and channels for the gaseous drying air or water

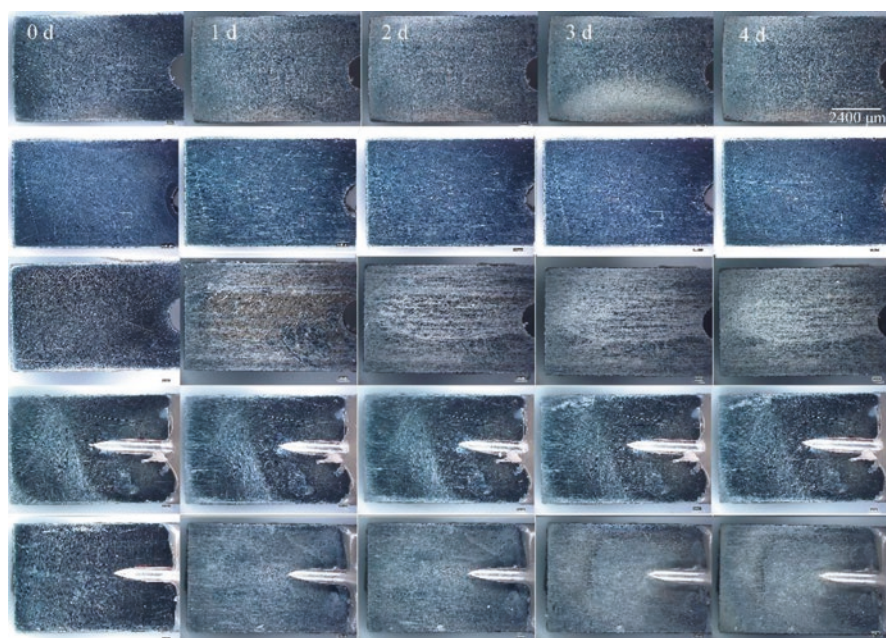


Fig. 6 The surface status of bare steel exposed for 4 days under the different coverage condition in atmospheric environment. Row 1: free atmosphere without coverage, Row 2: superhydrophilic sponge, Row 3: superhydrophobic sponge, Row 4: ventilated superhydrophilic sponge, Row 5: ventilated superhydrophobic sponge. Column 1–5 corresponds to the exposure in atmosphere for 0–4 days. (Reproduced with permission from Reference [9], Copyright Elsevier)

molecule to pass through. When water vapor is brought out of the matrix, the corrosion will be efficiently suppressed. Therefore, a facile ventilation approach can be used to bring out the moisture. Rows 4 and 5 in Fig. 6 show the protective effect of dry-air ventilation to the steel in superhydrophilic and superhydrophobic sponge matrix. For superhydrophilic sponge with ventilation, the steel can be protected even better, and bright surface can be observed after the test, indicating no corrosion occurring on metal surface. With ventilation, the water molecule on the surface will be removed, thereby retaining the metallic state even after 4 days. Therefore, the sole SHP sponge matrix does not exert remarkable protection to low-alloy steel in atmospheric environment. Its corrosion inhibition effect is even lower than a superhydrophilic sponge during a short exposure time, i.e., 4 days. However, the corrosion inhibition from SHP sponge will be firmly enhanced by using ventilation.

Ordinarily, seawater leads to more severe corrosion than the atmospheric environment. Accompanied with different surface coverage, the steel is immersed in natural seawater to endure the harsh corrosive environment; the corrosion status during 5 days is shown in Fig. 7. Severe corrosion occurs for the bare steel without any protection, showing brown corrosive product on the surface (Fig. 7, Row 1). The use of a superhydrophilic matrix as the cushion has no effect for corrosion inhibition. Based on water droplet measurement, an SHP sponge prohibits the liquid water to go through the matrix, unless the water pressure is larger than its tolerance to the hydrostatic pressure. The corrosion has been drastically decreased by wrapping the steel in SHP matrix, even immersed in seawater for 5 days (Fig. 7, Row 2). Only discrete corrosion pits can be found on the surface, and the large area product is absent, indicating the relief of the corrosion caused by SHP cushion covering on the metal. Therefore, SHP sponge changes the mechanism of underwater marine corrosion to corrosion in air. Only water and oxygen participate in the corrosion reaction. Dry-air ventilation transports vapor from SHP matrix, thereby eliminating the impact of water on corrosion. The mechanism of harsh seawater corrosion changes to slow oxygen oxidation in a dry environment because of the absence of water and Cl^- .

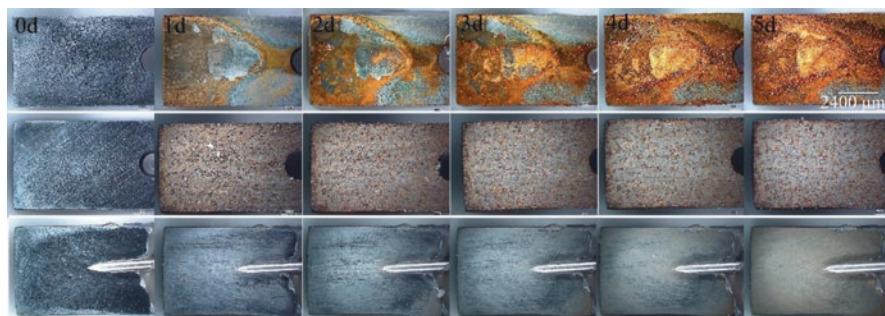


Fig. 7 The surface state of bare steel under the different covering condition in seawater environment for 5 days. Row 1: freely immersed in seawater without coverage, Row 2: superhydrophobic sponge, Row 3: ventilated superhydrophobic sponge. Column 1–6 corresponds to the immersion in seawater for 0–5 days. (Reproduced with permission from Reference [9], Copyright Elsevier)

There are many materials that can be finally manufactured into the cushion form, which can be constructed onto the surface to become the mantle for protecting the underneath metal phase. Introducing cushion structure seems a progress of SHP for corrosion inhibition. For SHP of film state, the air stored in the matrix is very limited. However, when the cushion material is adopted as the protection material, the as-sealed air inside of the matrix is much larger than that. Meanwhile, for the cushion mantle, due to the large space, further additional management can be imposed. The mantled metal surface can be especially applicable for the buried structure in underground soil environment. When the ventilation or heating is used, the humidity can be eliminated, and the drying state will be maintained, even originally there is the water vapor. Also, for the underground mine characterized by the humid atmosphere, this strategy will be applicable for corrosion inhibition from the harsh environment. In this chapter, we propose a new coating system for the material protection. The inner layer is covered by SHP layer, which can be built by the aforementioned fabrication processes. Alternatively, the coating can also be the traditional coatings, such as the epoxy coatings and so forth. With the SHP cushion to cover the coating, a reinforced protection system can be installed.

Another important focus is to develop the mechanically stable SHP coatings to meet the mechanical robustness requirement. For example, by using the stiff and mechanically robust micrometer scale structure, such as the metal of Ni, the mechanical stability will be enhanced. These years, focusing on the tolerance to the mechanical damage, the self-healing philosophy has been introduced to the fabrication of SHP coating [44, 46]. The self-healing will afford another strategy to endure the external mechanical damage. Even being damaged by the external force, it can still restore corrosion inhibition due to the certain composition in the coating. Therefore, in general, it can still withstand the external mechanical damage, showing the high tolerance to the external impact.

4 Perspectives

Corrosion is a practical issue. Proposing the usage of SHP in corrosion field is nearly two decades. However, the practical usage still has a long way to go. From the status of the development, it can be regarded that SHP for corrosion usage is still at its impetus stage. We elucidate the following two aspects as the perspective along the way from the lab to practical corrosion inhibition usage.

4.1 Standardization

During the test, the investigation, and the development of SHP, the standards remain absent [54]. Therefore, it is very hard and inconvenient to give comparison between the different results. For the corrosion usage, the two aspects remain to develop.

One is the mechanical robustness, and the other is the durability evaluation. For measuring the mechanical stability, mainly the abrasion process is used. Combining the contact angle measurement, the degradation of the extreme wettability will be achieved, so that the durability to the external mechanical damage is obtained. However, different researchers will use different load and different abrasive media for conducting the test. Also, the electrochemical techniques, including EIS, polarization, and so forth, are used for knowing the remaining corrosion inhibition effect, when SHP material is proposed for the corrosion inhibition. However, the parameters, such as the thickness of the SHP coatings and the variables for conducting electrochemical test, are not standardized, so that it is hard to know the prominent SHP coating developed via the different routes.

Another important factor to feature SHP coating is the tolerance capability to peeling off. However, for understanding this aspect of the coating, there still lacks the appropriate approaches. For the typical method to peel off the coating from the solid substrate, the adhesive tape is often used. However, for SHP, it is characterized by the low surface energy, and the force between the tape and the SHP surface is low, so that the peeling off process is hard to exert. Therefore, the efficient method to characterize the anti-peeling off capability of SHP coating is needed to develop in the future work.

Moreover, the definition of the SHP should be further clarified and standardized. Currently, the definition of SHP phenomenon is originated from the contact angle between water droplet and the surface. However, the volume of the water droplet is not defined. The current definition is still semi-quantitative. Therefore, in future, the definition of SHP should be standardized, and the relative communities (e.g., ISO, ASTM, and so forth) are proposed to participate in the relative work.

4.2 The Up-Gradation of SHP

Although SHP surface is hydrophobic from the macroscopic perspective, it can still adsorb the water molecule from the atmosphere or underwater condition. The porous structure will reinforce the adsorption effect from the structure due to the cavities and channels inside of the structure. Liquid layer will be formed on the inner wall of the hydrophobic cavity. Elongating the exposure time in the atmospheric and underwater condition, the accumulation will be even enhanced. Later, the SHP will fail, and it degrades as a rough coating, which is even inferior to the regular traditional coating without many defects. The corrosion inhibition effect of the failed SHP is far weaker than that. Therefore, the inhibition is mainly based on the thin layer of the air. If other immiscible fluid is used, the corrosion inhibition is expected to elongate. Following this orientation, researchers have developed the liquid infused surface (LIS) onto the metal substrate [55, 56]. Instead of air as the cushion between the substrate and water phase, the infused oil phase will not dissolve in water. The oil barrier will certainly prohibit the water layer formation onto the underlying metal substrate, showing much higher corrosion inhibition than SHP

coating. In our own study, the corrosion inhibition efficiency between SHP and LIS has been compared. LIS performs much higher corrosion inhibition effect than SHP in underwater environment. Therefore, a new paradigm for corrosion inhibition is installed.

5 Conclusions

In this chapter, superhydrophobicity (SHP) coating for usage in the corrosion protection field is reviewed. Taking the extremely harsh marine environment as the representative, SHP has been proposed to use for corrosion protection. The originality of the protection from SHP is analyzed. In seawater environment, the air cushion is formed between SHP matrix and the bulky water phase. The insulating barrier will hurdle the transportation of the water phase, so that the corrosion will be prohibited. However, the inhibition is only temporarily applicable. Elongating the immersion time, the water layer will be formed in the inner wall of the rough structure, which leads to the SHP wettability. Therefore, SHP will finally fail. For the marine atmospheric environment, the airborne aerosol and moisture deposition leads to the failure of SHP. Therefore, finding the efficient SHP is still the main task in the future. Moreover, the improvement of the mechanical stability is one important aspect during these years, and that is also reviewed in this chapter. Therefore, SHP coating is still on its impetus stage, and there is still a long way before its practical usage. Since the current researches are based on the different evaluation protocol, in this chapter we also propose to set the standard for evaluating SHP coating to propel the practical usage. Moreover, the up-gradation is also proposed to develop the further versatile coating for corrosion inhibition.

Acknowledgments The authors gratefully acknowledge the funding support from National Natural Science Foundation of China (41576079, 41922040), Qingdao National Laboratory for Marine Science and Technology (QNL2016ORP0413), and AoShan Talent Program Supported by Qingdao National Laboratory for Marine Science and Technology (2017ASTCP-ES02).

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Investigation of Conditions for the Creation of Hydrophobic Sand



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and Zulkhair Aimukhametovich Mansurov

1 Introduction

A surface that exhibits a large wetting angle, more than 150° , called a superhydrophobic surface [1]. Such surfaces have properties of extremal hydrophobicity and less wetting angle hysteresis. These properties occur from having an excessively less area of the solid surface coming into contact with water.

To obtain a superhydrophobic surface, two requirements should be satisfied. First of all, the surface should have roughness. The second is the material should have a low surface energy [2]. If these two conditions are contented, a water droplet on the surface matches to the Cassie law.

Currently, there is a wide range of modern hydrophobic coatings that provide reliable protection against the effects of aggressive environmental components, as well as reduce the water absorption of the surface of materials, but their main disadvantage is the high cost of production. In addition, over time, water leaches hydrophobic compounds and, therefore, with a certain interval, they need to be restored. Considering the expensive cost of these materials, the economic part of this issue plays an important role. Therefore, today there is a need for hydrophobic composite materials, the fabrication of which would be profitable, and their application would be effective [3, 4].

In recent decades, there has been a steady demand in the world for materials with hydrophobic properties. Because such kinds of materials have a number of exceptional functional properties, such as water resistance, resistance to bio corrosion, as well as resistance to pollution of organic and inorganic origin [3]. According to the

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above properties, the advantages of using such materials in everyday life and in technology are obvious. For example, with the penetration of water in building structures, corrosion and deformation can occur. Such destruction for traditional materials is primarily associated with the action of stresses that occur when water gets into defects and splits in the surface layer of the material and its subsequent freezing [4]. However, this problem can be solved using hydrophobic water-repellent materials, which can provide materials such as brick, concrete, plaster, gypsum, and asbestos cement water-repellent properties. The composition of all types of mortars, concrete, and asphalt concrete includes sand. It is also used in the form of a sandy “pillow” in the construction of foundations of buildings, in the road construction industry, and when laying pavers and paving slabs. Sand is also widely used for drainage.

In early studies, conditions were obtained for the formation of hydrophobic sand based on synthesized soot during the combustion of propane-oxygen mixture/waste oils. The results showed that the obtained sand covered with polyurethane glue and soot having hydrophobic properties was not wetted by water and the surface grains of the hydrophobic sand were fully enveloped by a nanoscale layer of superhydrophobic soot [5–7]. The results showed a decrease in water shortages and an increase in water conservation for the irrigation of crops [6–8].

Therefore, an urgent task is to impart hydrophobic properties to the sand. Sand with such properties will find wide application not only in construction but will also be able to solve the problem of acute water shortages in many regions. It is able to reduce water consumption for irrigation, and in desert territories it takes up to 80% of water for irrigation. Hydrophobic sand can be used as a protective barrier between the upper layer of the earth, which is agriculturally viable, and the rest of the soil. A hydrophobic sand layer of 10 cm would not allow water to seep, which would significantly reduce water consumption for irrigation. Such discovery allows for the purification of water from oil and other fatty substances. Hydrophobic sand repels water but allows molecules of oil and oil to react with it and penetrate into the sand. Due to this, oil and oil are absorbed into the sand, and at the outlet there is clean water. This will make it feasible to purify/filter water if it is polluted with oil. Hydrophobic sand is also useful for irrigation. It is able to hold oily substances and prevent groundwater contamination. It can be coated with pipes and cables to prevent humidity and corrosion.

An efficient way to prevent water absorption by a material is to modify its surface – hydrophobization. It is known that the hydrophobicity of materials is characterized by the structure and qualitative specifications of the surface layer [4]. Giving hydrophobic properties to materials is possible through the application of coatings with lower energy. The aim of the present work is to identify the conditions for the creation of a hydrophobic coating on quartz (river) sand using recycled silicon-containing waste.

It is known that firing waste organosilicon polymers can be used to obtain mechanically stable hydrophobic material in the form of a powder [9, 10]. For this purpose, the spent silicone products were placed in a metal container and then burned, where the resulting material was subjected to grinding to the necessary particle size [9].

Research in the field of nanoscale effects shows that the hydrophobic properties of surfaces are based on a regular structure of particles, protrusions or tips of sub-micron and nanometer size, arranged on the surface in an ordered manner. Such surfaces can be obtained by chemical or ion etching or by the method of growing nanoscale materials from the bottom up. Methods have been developed for growing vacuum “carpet” hydrophobic coatings from ordered carbon fibers. Water on such a coating, having contact only with the tips of protrusions or fibers, is fragmented into droplets by surface tension. A similar effect exists in wildlife. A striking example is the surface of the lotus leaf, dotted with numerous microscopic protrusions, giving the surface of the leaves exceptional superhydrophobic properties.

2 Materials and Methods

This study also revealed that soot obtained under certain conditions of hydrocarbon fuel combustion has a superhydrophobic property and can be used as a filler in the creation of hydrophobic coatings. The main disadvantage of soot is that its interaction with water initiates the mobility of nanostructured carbon components and new structural formations appear which lead to a loss of hydrophobic properties. However, if soot is obtained under certain conditions of fuel combustion, the obtained soot retains hydrophobic properties even after interaction with water, and it can be used to impart waterproofing properties to various materials. The optimal conditions for advancing the hydrophobic properties of carbon nanomaterials (soot, carbon nanotubes, carbon fibers) obtained during combustion and pyrolysis of associated gases from oil fields were determined [5]. Thus, silicone waste was burned. As a result, a gray polydisperse powder was obtained. The method developed for producing nanodispersed powder for the study herein is simple. The method is based on the method of burning silicone waste (supports made of silicone, various forms made of silicone); as a result, a mechanically durable hydrophobic nanodispersed powder is formed, Fig. 1a, b.

The burning method does not require additional energy costs, and the developed method yields a nanodispersed powder with a contact angle of over 155° . Thus, a method has been developed that allows simple combustion to produce a white-gray colored nanodispersed powder, which does not have an odor and does not have a harmful effect on the skin. Figure 2 shows the resulting powder with droplets of water on its surface.

Figure 3 shows the nanodispersed superhydrophobic powder, obtained during the burning process of waste of silicone materials, with a thin layer rubbed onto the surface of cardboard. The behavior of water droplets on its surface shows the exceptional hydrophobic property of the powder. This test shows that to give the surface a hydrophobic property, a sufficiently small amount of powder is used as a consumable.

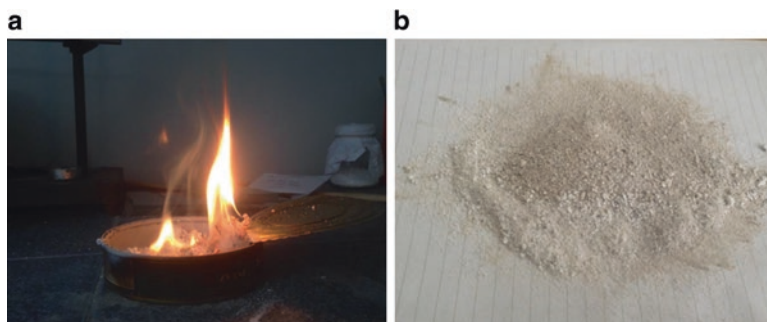


Fig. 1 The burning of waste organosilicon polymer compounds (a), the resulting superhydrophobic powder (b)

Fig. 2 The contact angle of the powder with the surface



Fig. 3 A droplet of water on the surface of superhydrophobic sand



Microscopic examination showed the presence of particles of various sizes from 10–12 microns to 100–200 microns. The contact angle of the powder surface exceeded 150 degrees, i.e., wetting practically does not occur.

The obtained hydrophobic agent (silicone ash) was used to create a bulk hydrophobic material based on quartz sand, which is 85–90 wt.% silicon dioxide. The sand was previously cleaned and sieved, where a fraction of 0.5–1 mm was selected. Then it was dried at a temperature of 50–70 °C. The prepared sand was intensively

mixed with the synthesized hydrophobic agent in a mixer at a speed of 300 rpm for 4–6 min. The role of the hydrophobic powder is to increase the degree of adhesion of the hydrophobic film on the surface of the grains of sand. In order to determine the optimal amount of hydrophobic agent, mixtures of a hydrophobic agent and sand were preliminarily prepared in the following ratios: 0.5:100, 0.75:100, 1:100, 1.25:100, 1.5:100, 1.75:100, and 2:100. As a result of the studies, bulk material was created, characterized by good water-repellent properties and resistance (Fig. 3).

The advantage of this sand based on silicone ash compared to the sand obtained on the basis of soot is that, in this case, it does not require the addition of polyurethane glue in its creation [3, 4].

3 Results and Discussion

To measure the contact angle of the hydrophobicity of the obtained material, a KRUSS tensiometer was used. The initially obtained mixtures of hydrophobic agent and sand were compressed into tablets. Next, a drop of water in a volume of approximately $\sim 2 \mu\text{l}$ was placed on the tablet surface. A high-speed camera recorded the process of droplet formation on the surface, which allows for the macro images of the surface. Using the mathematical calculation and the advance program, the exact contact angles were calculated using the method of lying drop. Thus, the contact angle for a mixture of hydrophobic agent and sand in various ratios: 1:100, 1.5:100, 2:100, and 3:100, is shown in Fig. 4.

As can be seen from Fig. 4, the contact angle for a mixture of hydrophobic agent and sand in a ratio of 1:100 was 157.8° , respectively, 1.5: 100 was 162.4° , 2:100 was

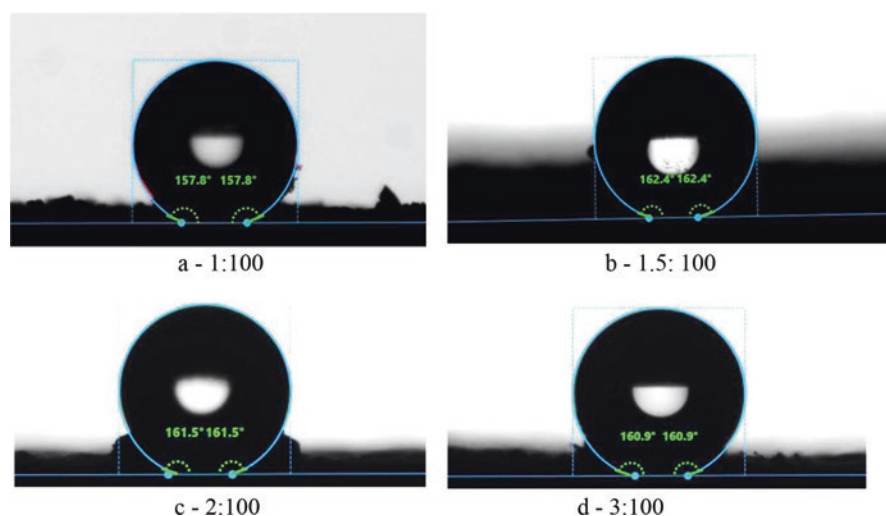


Fig. 4 The contact angle for a mixture of a hydrophobic agent and sand in different ratios

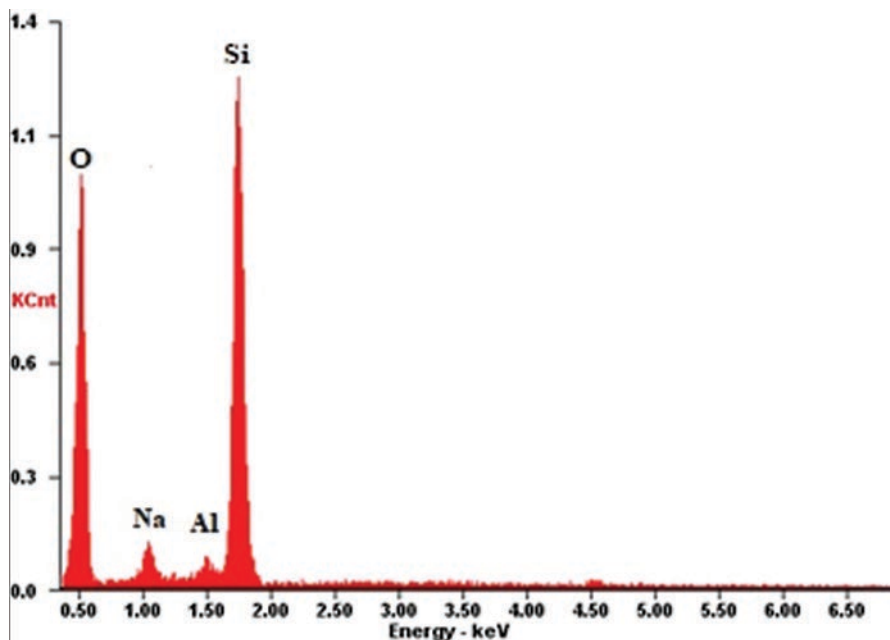


Fig. 5 EDAX analysis of hydrophobic agent

161.5°, and 3:100 was 160.9°. The amount of hydrophobic agent did not affect the hydrophobic properties of the material. This suggests that the sand should contain a sufficient amount of hydrophobic agent and the surface of the sand should be completely covered.

To obtain a quantitative analysis, samples of a hydrophobic agent and sand based on hydrophobic agent were studied by EDAX. The results of the analysis showed the appearance of four peaks, corresponding to oxygen, sodium, aluminum, and silicon, and were observed in the composition of the hydrophobic agent (Fig. 5).

Table 1 shows the elemental composition of the hydrophobic agent obtained by burning silicone waste. The data indicates that the composition of the resulting ash depends on the starting materials that were burned. The silicon content was 29.94%.

EDAX analysis of sand based on hydrophobic agent is shown in Fig. 6.

Three peaks were observed in the X-ray diffraction pattern: O, Al, and Si; the most intense of which were silicon. Table 2 shows the mass ratio of silicon, oxygen, and aluminum.

According to the obtained data, it can be considered that the main component in the composition of quartz sand and hydrophobic agent is silicon dioxide.

The above studies of the elemental composition of the hydrophobic agent and of the sand based on hydrophobic agent were confirmed by X-ray fluorescence analysis. The obtained X-ray diffraction patterns of the materials are shown in Figs. 7 and 8.

One intense peak corresponding to silicon is observed on the X-ray diffraction pattern of the hydrophobic agent.

Table 1 The elemental composition of hydrophobic agent (silicone ash)

Element	Wt., % (by weight)	At, % (atomic mass)
C	20.68	29.73
O	45.39	48.99
Na	2.81	2.11
Al	1.18	0.76
Si	29.94	18.41

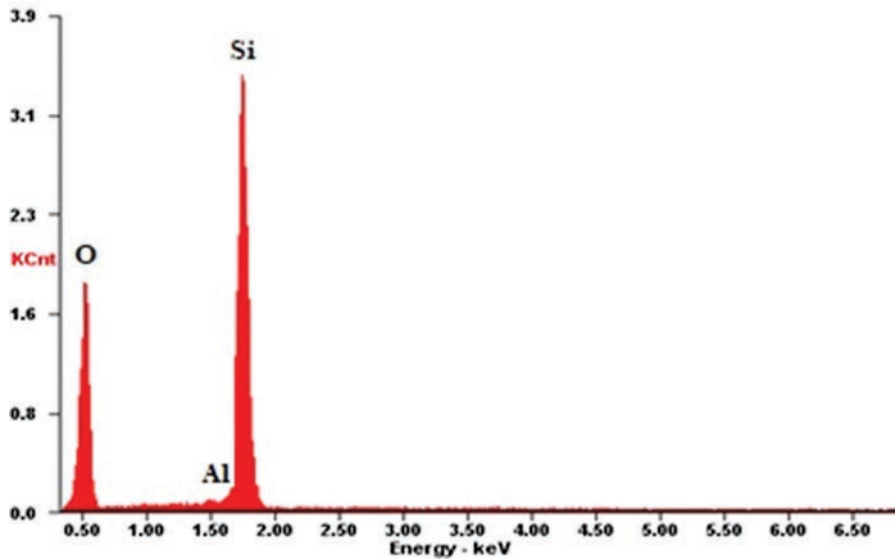


Fig. 6 EDAX analysis of sand based on hydrophobic agent

The created sand contained silicon at 43.77%; aluminum, 26.76%; iron, 15.33%; potassium, 6.03; calcium, 5.66%; and titanium, 1.47%. The remaining elements (manganese, copper, zinc, rubidium, strontium) made up less than 0.5%.

Morphological features of the studied objects were studied by optical and scanning electron microscopy (SEM), as seen in Fig. 9.

Fig. 9 shows that the surface of the hydrophobic agent is inhomogeneous, the size of the microparticles varies over a wide range, and a large number of defects were observed that can reduce the mechanical strength of the sample. An optical image of hydrophobic sand shows how microparticles of silicone ash are located on the surface of sand, but due to the limitations of the method, it cannot give a complete picture. Therefore, to further study the surface structure of the objects, SEM analysis was used.

As can be seen from Fig. 10, the particles of the hydrophobic agent are not evenly distributed, but the surface of the obtained sand is completely covered, the particle size varying from 3 to 6 microns.

Table 2 The elemental composition of sand based on hydrophobic agent

Element	Wt., %	At, %
O	47.77	61.61
Al	0.70	0.53
Si	51.53	37.86

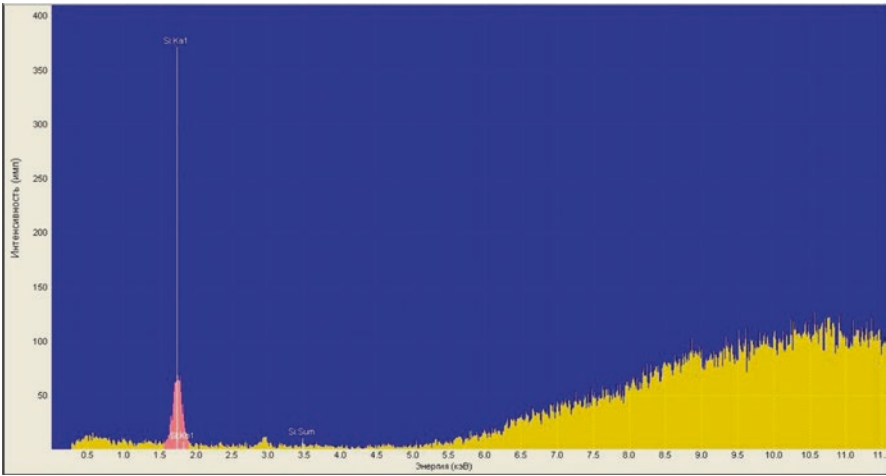


Fig. 7 Radiographs of the hydrophobic agent

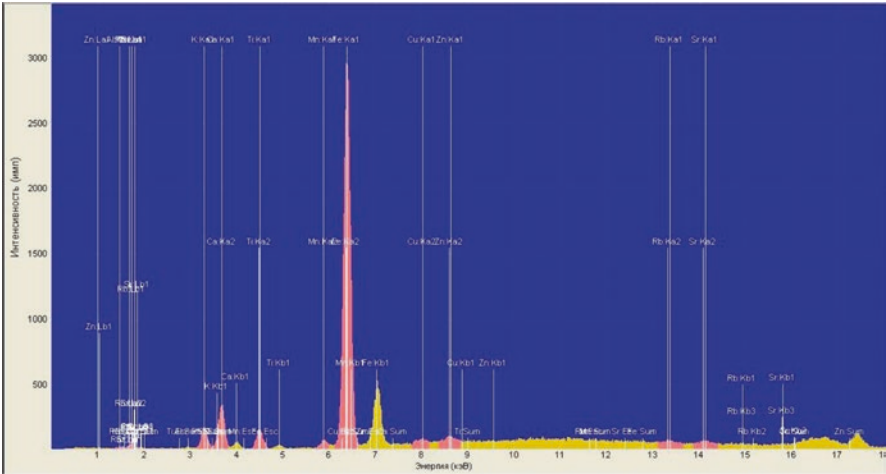


Fig. 8 Radiograph of quartz sand based on hydrophobic agent

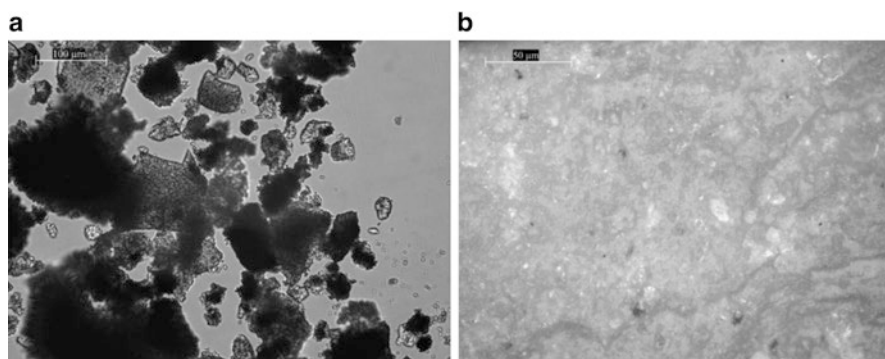


Fig. 9 Photographs (optical images) of the samples: (a) hydrophobic agent; (b) hydrophobic sand

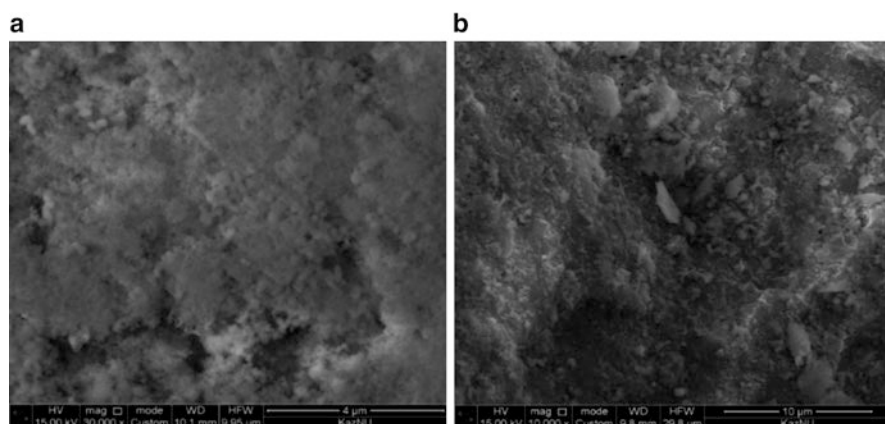


Fig. 10 Electron microscopic images: (a) hydrophobic agent obtained by processing waste organosilicon polymers, (b) hydrophobic sand

As can be seen from the above studies, the particles of the sample of hydrophobic agent are aggregated from smaller particles, the size of which is about 100–300 nm. According to the color scheme, it can be said that, mainly, silicon (light spots), as well as organic compounds (dark places) are present in the powder. The sample contains particles of two types, the large sizes of which are about 150–200 microns and the small are about 0.1–0.3 microns. At a larger magnification, it can be seen that the particles have asymmetric shapes and small particle sizes, indicating the porosity of the powder's structure.

Electron microscopic studies of the surface of the hydrophobic sand showed that the hydrophobic agent covers the entire surface of the sand. This coating is heterogeneous, and it is characterized by roughness. The average particle size is in the range of 3–6 microns. As it is known from the literature [1], the heterogeneity of the surface is one of the reasons for its hydrophobicity.

Table 3 The results of the analysis of measurement of the specific surface of the studied objects

Substance	Specific surface, m ² /g	Specific pore volume, cm ³ /g	The average pore size, nm
Sand	1672	0,001	–
Hydrophobic agent	87,277	0,037	1713
Hydrophobic sand	60,517	0,026	1713

One of the factors determining the contact angle along with the nature of the surface is the specific surface. Research data on the specific characteristics of the hydrophobic agent and hydrophobic sand are represented in Table 3. The specific surface area was determined by the BET method (Brunauer-Emmett-Teller).

According to the BET analysis, the specific surface of hydrophobic sand is the average value between the hydrophobic agent and hydrophobic sand.

To study the stability of the water-repellent properties of the obtained hydrophobic sand, experimental work was carried out in laboratory conditions. Hydrophobic sand made in various proportions of hydrophobic agent was poured into a glass of water. When hydrophobic sand was immersed in water, it did not sink but floated on the surface of water. The tests showed that the obtained hydrophobic sand remained absolutely dry for a long time without losing its hydrophobic properties (30 days). Only a sample with a low content of hydrophobic agent (100: 0.5) on day 29 lost the hydrophobic property.

In the next series of experiments, the stability of the water-repellent properties of the hydrophobic sand was studied under different temperature conditions. To study the effect of low temperature on the hydrophobic properties of sand, it was kept at – 24 °C for 28 days. Then, its wettability with water was checked (Fig. 11).

To study the effect of high temperature on hydrophobic sand, a sample of hydrophobic sand was placed in an oven. The stove was heated at a rate of 10 °C/min. Starting from a temperature of 250 to 300 °C, the appearance of white smoke was observed, which is explained by the decomposition of silicone waste, and the sand loses its hydrophobic properties.

A three-layer structure was created on a Petri dish to check the water permeability of the obtained hydrophobic sand (Fig. 12).

The first layer of the structure was well wetted by water. This layer, consisting of a mixture of sand and clay, was an indicator of water, i.e., when water passes, it gives a certain visible signal.

The second layer was a separator, which is a filter paper. Its main role was to separate the first and third layers, and it does not create obstacles to the movement of water. Third layer consisted of synthesized hydrophobic sand, on the surface of which water was periodically poured, since some of it was lost due to evaporation. The experiment lasted 32 days. It was found that the third layer was waterproof, since the indicator did not detect the presence of water in the first layer.

The obtained sand that had hydrophobic properties is recommended to be used as a filler in construction for external decoration and in agriculture to protect irrigation water from seeping into the lower layers of the soil or its evaporation. Hydrophobic

Fig. 11 Photo of the behavior of a drop of water on the surface of hydrophobic sand at temperature – 24 °C



Fig. 12 Three-layer structure for determining the water resistance of synthesized hydrophobic sand

sand can also be used to isolate the soil around plants from salty soil and groundwater, which otherwise can lead to the destruction of the root system of plants.

4 Conclusion

In this work, a method for producing hydrophobic sand using silicone waste was developed. Additionally, the conditions for formation of a water-repellent coating on the sand surface were investigated and the properties of the hydrophobic sand were examined. Hydrophobic sand was created which was based on a hydrophobic agent obtained by the combustion of silicone waste. It was experimentally established that mixtures of the hydrophobic agent and sand with the ratios 1:100, 1.5:100, 2:100, and 3:100 were suitable for the creation of hydrophobic sand. The tests showed that the created sand remains absolutely dry for a long time without losing its hydrophobic properties over a period of months.

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