Surfaces and Interfaces of Biomimetic Superhydrophobic Materials
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Preface

The field of surface wettability has had an extraordinary period of development in the last decade due to its potential applications. When a new field appears, its growth is judged by the number of publications, presentations, and patents. In the past decade year, more than 10000 papers have been published on surface wettability. It is well known that the surface wettability of a solid surface depends mainly on its surface structure and surface composition. Discovering the relationship between surface structure and surface properties is very important for scientists working in the field of surface chemistry.

The idea for this book titled *Surfaces and Interfaces of Biomimetic Superhydrophobic Materials* (SIBSM) came about in 2011 when I came back from Belgium to China and constituted my own research group in the Chinese Academy Sciences (CAS). More scientists paid attention to this field when more papers, preprints, talks, and words of mouth became available.

I am pleased to edit this book with Dr Fuchao Yang, who is now a lecturer in Hubei University, China, and who also was my PhD student in CAS during 2013–2016. SIBSM contains the recent progress, thoughts, and work of my group and many of the world’s foremost scientists who work in the field of biomimetic superhydrophobic materials. We discuss the theory, fundamentals, fabrication, properties, applications, and uses of these very special materials inspired by Nature.

SIBSM contains 10 aspects of the superhydrophobic story, covered in the following chapters: (1) Nature is a huge gallery of art involving nearly perfect structures and forms evolved over the millions of years development. Inspired by Nature, scientists have recently fabricated many biomimetic surfaces through various smart and easy routes. Many plants and animals in nature, showing water-repellent properties with fine microstructures, such as the lotus leaf, the water skimmer, and wings of the butterfly, are discussed. Some creatures with typical structures are also referred to, for instance, the rice leaf, desert beetle, rose petals, mosquito eyes, springtail, fish scale, shark skin, snail shell, lower surface of the lotus leaf, and clam’s shell. (2) We start the theory from the classical wetting models to the most recent theoretical advances of superhydrophobic surfaces (SHP5s) with regard to the wetting process, and some promising breakthroughs in the advancement of the theory are proposed. (3) Further study on the relationship between structures and properties will be conducive to better transferring the micro- and nanostructures to engineering materials so as to obtain the desired superhydrophobic performances and a wide range of applications. The methods
to fabricate SHPSs with micro- and nanostructures are varied and generally divided into two. One comprise top-down methods including etching, lithography, anodization, and laser processing. And the other is bottom-up methods containing electrodeposition, hydrothermal method, sol-gel process and electrospinning.. (4) Oil spills and industrial organic pollutants have induced severe water pollution, and special wettability materials have been developed over the past decade to separate oil/water mixtures. On this topic, we mainly focus on the development of materials with either superhydrophobic or superhydrophilic properties in oil/water separation applications. (5) The purification of oily water, especially oil/water emulsions, is one of the important topics of environmental protection. Traditional filter membranes, to some extent, are useful for the separation of oil/water mixtures, but they have many limitations and there is no effective way to achieve emulsified oil/water separation. Superwetting materials, based on bionics, have opened a brand-new door to membrane separation techniques. (6) The adhesion behavior of SHPSs has become an emerging topic to researchers in various fields as a vital step in understanding the interaction between materials and organisms. Controlling the chemical compositions and topological structures via various methods or technologies is essential to fabricate and modulate different adhesion properties, such as low adhesion, high adhesion, and anisotropic adhesion on SHPSs. We summarize the recent developments in both natural and artificial SHPSs with various adhesive properties and pay attention to SHPSs switching between low and high adhesion. (7) Superhydrophobic nanocoatings, a combination of nanotechnology and SHPSs, have received extraordinary attention recently, focusing both on novel preparation strategies and investigations of their unique properties. In this part we summarize the contributions to this field reported in recent literature, mainly including materials, fabrication, and applications. (8 and 9) Recently, particular attention has been paid to smart surfaces that can show switchable and reversible water wettability under external stimuli such as pH, temperature, light, solvents, and electric field. In this section, several kinds of smart SHPSs (pH-responsive wettable surfaces, photo-induced self-cleaning surfaces, solvent-responsive wettable surfaces, and magnetically controllable behavior of superhydrophobic microspheres) based on our and other groups’ published works are systematically summarized. (10) We primarily investigate the ice and frost formation mechanism for the rational design of anti-icing/anti-frosting surfaces. Significantly, the complex dynamics and thermodynamics of water droplets on the SHPSs under various freezing conditions that might be encountered in natural atmosphere (e.g., raindrops, condensation frosting) are comprehensively discussed. Critically, we explain why SHPSs play a fairly limited role in reducing ice adhesion strength. Furthermore, a family of novel superwetting materials termed  icephobic surfaces (IPSs) for effortless ice detachment is introduced. Finally, future challenges and possible breakthroughs in this field are pointed out. It is believed that under the unremitting efforts of scientists, the second generation of anti-icing/de-icing techniques based on superwetting interfaces will be put to practical applications in the near future.

The book is aimed at the following readers:

- Advanced students and instructors in the fields of science and engineering.
Professional scientists and engineers, who may be trained in more traditional disciplines but who need to learn about this emerging area.

Policymakers and management experts looking for an understanding of the scientific challenges, prospective uses, and emerging markets for surface wettability.

The overall goal is to capture the multidisciplinary and multifunctional flavor of surfaces and interfaces of biomimetic SHPSs while providing in-depth discussions on select areas.

Importantly, I should show my appreciation to the contributors for their effort and dedication in preparing the chapters, to Hubei University, and to my PhD students, Mr Liwei Chen, Mr Yifan Si, Mr Gang Wen, Mr Lieshuang Zhong, Mr Pan Tian, Mr Zelinlan Wang, and Miss Xiaoyu Gao, for their continuous assistance and hard work in drawing the figures and putting the chapters together. I also thank Mr Hai Zhu and Miss Ting Jiang for correcting the proof. I also thank Dr Lifen Yang of Wiley, who gave me the idea of starting a book in the beginning this year, and her publication team for their continuous help and support. Finally, I am indebted to my wife, Yan Xin, and my two daughters, Zhehan and Zheyuan, for their kind and endless enthusiasm and support.

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Introduction for Biomimetic Superhydrophobic Materials

Wetting phenomena are found abundantly in our body, our surroundings, and our daily lives. Our eyes repel condensed water for a clear vision, and the articular cartilage is superwetting to achieve ultralow wear. When it is raining, we can glance the raindrop rolling down from some kinds of plant leaves while still leaving a trail of water trace on other kinds of plant leaves. Wetting behavior is also closely related to laundry, froth flotation, printing and dyeing, oil extraction, welding materials, lubricating systems, and so on.

Wettability is determined by the interaction of a surface and interface between a solid and a liquid. The interface is a transition region forming a boundary between two different phases of matter. Exactly speaking, a solid (liquid) surface means the interface between a solid (liquid) and vacuum or a gas. If the liquid is water, the wetting behavior falls into several categories, namely superhydrophilicity, hydrophilicity, hydrophobicity, and superhydrophobicity. As our book will show in detail in the following part, superhydrophobicity is usually defined as the contact angle (CA) of a water drop on a solid surface >150° and a sliding angle (SA) <10°. It is also possible to change a solid surface from hydrophilic (or hydrophobic) to superhydrophobic.

Tuning the wettability of a liquid drop on solid surfaces is an important issue attracting more and more interest from both fundamental and practical perspectives. The answers to such question do help us find the miracle and power of the biomimetic ideology.

Biomimetic materials mean mimicking organisms with the aim of designing artificial materials with desirable functions [1]. In Nature, there are many perfect functional materials with various structures, and the needs of adaptation and survival are indeed the result of esthetic functional systems. Geckos are known for their excellent ability to run on ceilings, and studying their feet would inspire technologists to design of a variety of dry adhesives [1, 2]. The water strider has a remarkable ability to stand, walk on, and even leap from a water surface effortlessly [3]. This skill derives from the superior water repellency of its legs, which possess thousands of tiny setae with fine nano-grooved structures. Investigating the water strider’s leg would be helpful in developing some water-standing/walking micro-devices employed in monitoring the activities on a water surface [4]. The lotus leaf with nanoscale details superimposed on a microscale structure is a typical example and has an impressive self-cleaning feature. This leaf surface is endowed with a large contact angle >160° and a sliding angle <3°, and this results in the well-known
“lotus effect” [5a]. Barthlott suggested that this property primarily originates from the cooperative effect of micrometer-scale papillae on the rough surfaces and hydrophobic epicuticular wax [5b]. This was a very interesting and important discovery. Learning from Nature, tremendous progress in biomimetic superhydrophobic architecture engineering has been achieved using a range of methods. The advantages, disadvantages, and typical examples of each main method will be introduced in this book.

In this chapter, the fabrication methods of certain superhydrophobic materials will be mentioned succinctly, and the amazing applications of biomimetic superhydrophobic materials are explored and elaborately introduced. It is a fact that a full-scale introduction of the applications of biomimetic superhydrophobic materials is beyond us. So the adhesive behavior and oil/water separation properties of superhydrophobic materials, discussed in other chapters, are not intended to be presented repeatedly. The main relative aspects we focus on in this part will cover novel fields such as water harvesting, self-cleaning, corrosion resistance, photochromic superhydrophobicity, robust superhydrophobicity, conductive and transparent superhydrophobicity, anti-fingerprint superhydrophobicity, and the anti-icing ability of superhydrophobicity. We hope this arrangement can help arouse the readers’ interest and encourage the reading of other chapters.

### 1.1 Water Harvesting

An alternating pattern of superhydrophobic and hydrophilic hybrid materials has an important applied background. The available freshwater resources for humans in the poor and rural areas are extremely scarce. In recent years, learning from Nature has motivated extensive interest in the field of bioinspired superwettable materials [6], which show a huge potential to effectively address this very serious issue. Namib Desert beetles feature an interesting fog-harvesting property resulting from the alternating waxy hydrophobic and nonwaxy hydrophilic regions on their dorsal body [7]. Spider silk can collect fog from the atmosphere due to its periodic spindle-knots with a combined structure and chemical gradient [8]. These typical examples from Nature offer the inspiration to synthesize corresponding biomimetic water-collecting materials. Some representative works from our group and other laboratories are described in the following.

Because of their high surface energy, metal nanoparticles (NPs) are known to be extremely hydrophilic substances. Hydrophobic properties of the metal NPs can be obtained if these particles are pretreated with low-surface-energy chemicals. $n$-Octadecyl thiol, which possesses low surface energy, was selected as the modifier to obtain a superhydrophobic–superhydrophilic hybrid fabric depending on the thiol’s selective modification of NPs on the fabric. Based on this, two adjacent transition metals, Fe and Co, were selected and coated on a commercially available fabric via a facile in situ growth method [9]. The surface of Co NPs could be modified by $n$-octadecyl thiol and transformed into hydrophobic NPs. However, the Fe NPs could not be modified by $n$-octadecyl thiol under our
experimental conditions. Thus, they retained the hydrophilic property. The as-prepared fabric with these two kinds of NPs evenly distributed on the surface is termed a superhydrophobic–superhydrophilic hybrid fabric because it shows superhydrophobicity and possesses many superhydrophilic spots. These two kinds of NPs were evenly distributed on the fabrics, and their coating amounts were easily controlled by altering the concentrations and the proportion of the two kinds of ions in the precursor solution. Because of the selective modification, the wettability of the fabrics is linearly dependent of their concentration ratio and varies over a wide range from superhydrophilic to superhydrophobic. To obtain a superior water-harvesting fabric, the concentration ratio must be appropriate because values that are either too small (Fe NPs are dominant) or too large (Co NPs are dominant) are not beneficial for water harvesting. This kind of material might help in solving the global shortage of fresh water via an energy-saving strategy. This material has been found successful in realizing water harvesting similar to the desert beetle that collects micro droplets of water from the morning fog.

Inspired by Nature and beyond it, Peng et al. fabricated a new kind of material that could achieve fog harvesting even under windless conditions [10]. They dispersed 200 mg Co MPs in the microscale with an average diameter of 2 mm into each mechanical hole of the array. Poly(dimethylsiloxane) (PDMS) pre-polymer containing 0.1 equiv. of curing agents was cast on the template filled with cobalt magnetic particle (Co MPs) with the help of a vacuum pump. Here, mechanical perforation and template replica technology were also applied, whereby Co MPs were added in the latter step. Meanwhile, a magnet of 60 mm diameter and 50 mm thickness was prepared. The sample was placed on the top of a permanent magnet with a superficial magnetic field intensity of about 0.9 T during the process of degassing and curing so as to make the Co MPs vertically aligned in the holes. As shown in Figure 1.1a, the conical array responded to the magnetic field. Using a high-speed (charge-coupled device) CCD camera, the movements of cone arrays responding to the magnetic field were recorded (Figure 1.1b,c). When the magnet was placed directly over the sample, the cactus-spine-like cones were totally upright. The cone arrays could collect fog in a spontaneous and continuous way if a moving magnetic field was provided (Figure 1.1d). However, no water drop deposited on the arrays without the magnetic field (Figure 1.1e). By integrating cactus-inspired spine structures with magnetically responsive flexible conical arrays, magnetically induced fog harvesting under windless conditions was achieved. To meet the urgent demand for the basic water requirement, a much larger scale of the as-prepared, magnetically induced fog collector should be fabricated. In windless and foggy regions, the magnetically induced fog harvesting system has great advantages and promising applications. Furthermore, it may serve in our daily lives as an effective method for further optimization of oil mist purification and fog harvesting strategies.

Using the fluid coating method, Jiang and coworkers developed bioinspired fibers with periodic spindle-knots on a large scale [11]. The nylon fibers in the polymer solution reservoir were fabricated by capillary tubes (about 400 μm inner diameter), which were composed of poly(methyl methacrylate) (PMMA) dissolved in N,N-dimethylformamide (DMF) with a weight percentage of 11%, and
Figure 1.1  (a) Schematic of the fabrication of cactus-inspired conical arrays and (b) the magnetically induced conical array responses. (c) Charge-coupled device (CCD) camera observations in response to a magnet. Scale bar: 1 mm. (d) Magnetically driven cone and (e) a static cone placed in the same fog chamber at different time periods. (Peng et al. 2015 [10]. Reproduced with permission of John Wiley and Sons.)
the end of the fiber was connected to a motor. At the same time, the solution container was controlled to be $2\text{ cm} \times 3.5\text{ cm} \times 3\text{ cm}$ (width $\times$ length $\times$ height) in size. As it moved out of the reservoir, the polymer solution was coated on the fiber. The cylindrical polymer film was broken up into droplets because of the Rayleigh instability, and periodic spindle-knots on the fiber were obtained after solvent evaporation. In Figure 1.2a, when the concentration of PMMA/DMF solution increased, the critical velocity ($V_{\text{critical}}$) decreased. The spindle-knots on the fiber could be formed only if the drawing velocity was more than $V_{\text{critical}}$. In Figure 1.2b, the spindle-knot attained the largest size at a velocity of $1.44\text{ mm s}^{-1}$ (13% by weight PMMA/DMF solution). The solution parameters and fiber-drawing velocities were proved to play very important roles in the formation of the spindle-knots. As shown in Figure 1.2c–g, the bioinspired fiber was endowed with directional water-collecting ability. Inspired by the beautiful sight of a spider’s web decorated with shiny water droplets, novel and functional fiber materials were designed and fabricated that were endowed with water collection abilities.

Figure 1.2 (a) Relationship between the critical velocity ($V_{\text{critical}}$) and the concentration of the PMMA/DMF solution. The spindle-knots could be constructed when $V > V_{\text{critical}}$, or vice versa. (b) Size of the spindle-knots as a function of the drawing velocity. (c–g) Directional water-collection process on a bioinspired fiber with a PMMA spindle-knot. (Bai et al. 2016 [11]. Reproduced with John Wiley and Sons.)
Also, TiO₂ has been used in a water collection system. It is well known that TiO₂ manifests switching wettabilities under UV light irradiation, attributable to its excellent photocatalytic property [12]. By integrating the water-collecting mechanisms of both desert beetles and spider silk, Zheng et al. successfully designed and fabricated TiO₂-based materials with star-shaped wettability patterns [8a]. In our study, TiO₂ was also introduced in fabricating water-collecting materials, which mainly utilized the alternative modifications between Cu, TiO₂, and thiols [13]. Cu can easily be modified by thiols and can act as the hydrophobic areas, while TiO₂ cannot be modified by thiols and serves as hydrophilic sites. The hybrid engineered surfaces therefore inspired their synthesis. At a precursor molar rate (Cu:TiO₂) of 9:1, the as-prepared sample, with a water contact angle (WCA) and rolling angle (RA) of 155.1° and 4.5°, respectively, exhibited the highest water collection rate (WCR) of 1309.9 mg/h/cm². The fabrication of superhydrophobic hybrid materials may show new directions for future fog collection projects and be indicative for mass production, demonstrating promising applications to solve the growing global water shortage. In another study [14], we synthesized successfully a superhydrophilic sample with two embedded superhydrophobic circles, and the fabrication process could be accomplished by a simple and quick route at room temperature. Importantly, this material showed high efficiency for fog capture with a WCR of 1316.9 mg/h/cm², which is an advantage over uniformly superhydrophobic and superhydrophilic samples. It is worth mentioning that the water collection of these samples could be repeated over 10 times without obvious variations in the WCR.

Functional surfaces with superior water collection, as promising materials, are required for the abatement of water shortage. Though a number of water-collecting materials have been fabricated, there are still some problems that need to be solved. Also, the gap between basic research and applied technology should be bridged, which is of great importance in realizing the transformation between experimental results and industrial achievements. It is believed that water-collecting materials will pave the way for functional practical applications to solve the current severe water shortage in dry and less economically developed areas of the earth.

1.2 Self-Cleaning

No dust can reside on a lotus leaf after rain because of its effective water repellency. Bearing this in mind, we tried to biomimetically construct artificial superhydrophobic materials to study their self-cleaning effect. We have fabricated a kind of transparent liquid that can form transparent superhydrophobic films on various substrates by spraying [15]. The results showed that the spray exhibits excellent self-cleaning properties, which are very vital for their promising applications in industry. To evaluate the effect of antifouling, Figure 1.3a shows muddy water poured on a white fabric with a superhydrophobic coating. Figure 1.3b shows that the coated fabric was well kept and had no muddy water trail on the surface, while the uncoated fabric on the left had much muddy water on it. The coated fabric exhibits surface properties like the lotus leaf, which lies in silt but is
not imbrued. We have also developed a facile, low-cost fabrication strategy for strong amphiphobic coating [16]. The detailed procedure included the construction of a CuO hierarchical structure on porous substrates (nickel foam and fabric) and the subsequent modification with perfluorodecanethiol. The CuO-coated nickel foam and fabric showed excellent repellency to water and oils at the same time. Water and oil droplets on their surface can easily roll off from the surface. Furthermore, these samples exhibited strong oleophobicity for different types of oils such as ethylene glycol, rapeseed oil, hexadecane, glycerol, and decane. It is worth mentioning that the surface of as-prepared samples showed excellent oil-self-cleaning properties, which would extend its potential applications in some oily surroundings. Self-cleaning effect of a surface with liquid repellency plays an important role in many practical applications. In order to investigate the self-cleaning behavior, chalk powder was employed as contaminant that was dusted on the surface of a lotus leaf and CuO-coated fabric (Figure 1.3c–e). For the CuO-coated fabric with superhydrophobicity and strong oleophobicity, the liquid droplets could take away the chalk dust on the surface when sliding on the surface, as shown in Figure 1.3c–e. Importantly, ethylene glycol and rapeseed oil were observed to easily move from the contaminated surface and take the chalk

Figure 1.3 (a, b) Digital photographs of a coated white fabric used in antifouling (Dong et al. 2015 [15]. Reproduced with permission of The Chemical Society of Japan). (c) Description of the self-cleaning ability of strong amphiphobic fabric through the removal of chalk dust from the surface by the movement of water, ethylene glycol, and rapeseed oil. (Zeng et al. 2014 [16]. Reproduced with permission of The Chemical Society of Japan.)
dust away effortlessly, suggesting that the CuO-coated fabrics possessed good self-cleaning property against both water and oil, which is attributed to the high contact angle and low sliding angle of the constructed surface.

Photoinduced self-cleaning is another kind of smart self-cleaning property. In our work [17], TiO$_2$ coatings with hierarchical rutile TiO$_2$ flowers on fluorine-doped tin oxide substrate were fabricated through a simple one-step hydrothermal method. The flower-like coatings exhibited superhydrophilicity in air and superoleophobicity under water with a contact angle of 157° (Figure 1.4a, left column), presenting good underwater self-cleaning performance. The as-prepared films were contaminated with an $n$-pentane solution containing oleic acid to study its photoinduced self-cleaning. Because of the high surface free energy of the TiO$_2$ material, the film was superhydrophilic in air and superoleophobic

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**Figure 1.4** (a) Photographs of an oil droplet on the TiO$_2$ flower coatings after contamination treatment and UV irradiation. (b) Reversible changes of OCA on the sample during cyclic alternations of contamination treatment and UV irradiation.
under water before oil contamination. As for contamination, the sample was dipped into the above solution for 5 s and then withdrawn at a speed of 9.5 mm/s, followed by drying at 60 °C for 10 min. After the contamination treatment, the film lost its superwetting property, with the WCA increasing to 137° and the oil contact angle (OCA) decreasing to 64° (Figure 1.4a, right column). In this case, the underwater oil–solid contact can be termed as a homogeneous wetting state. However, the film turns hydrophobic in air and oleophilic under water if it is discretely contaminated by oleic acid spots. The surface free energy decreased after the contamination, resulting in the increase of WCA (from 0° to 137°). Because of some oleic acid spots trapped between the oil and the film, the underwater oil–solid contact in this situation is the so-called heterogeneous wetting regime. After irradiating by UV light (for 2 h), the film recovered its superamphiphilic and underwater superoleophobic properties. This shows that the TiO₂ coatings exhibit excellent self-cleaning ability under UV irradiation. Furthermore, as shown in Figure 1.4b, this process could be continuously repeated for several cycles without the loss of its responsivity, and the as-prepared self-cleaning surface had good stability.

Surfaces with self-cleaning property can remove contaminates on superhydrophobic materials, which is of great importance for water repellency. Moreover, self-cleaning is a decisive factor for applications of superhydrophobic materials.

1.3 Corrosion Resistance

Corrosion due to various active metals is of great importance in deciding the lifetime of some engineering materials. Interestingly, superhydrophobic coatings on the surfaces of metals can bring about superb corrosion resistance, which expands their scope of application and prolongs the service life of the metallic materials. On the basis of this, we have reported a simple method for preparing a two-dimensional material based on commercially available stainless steel mesh and copper mesh substrates functionalized by depositing nanoscale polypyrrole (PPy) particles, followed by modification of a low-surface-energy material such as fluoroalkylsilane (FAS) [18]. Such superhydrophobic samples are endowed with good anticorrosion properties for several metals to a greater extent. We applied several corrosive liquids, such as acidic, basic, and salt aqueous solutions, to test the corrosion resistance. Corrosive liquids on the surface of superhydrophobic PPy-coated substrates stood uniformly on the surface and maintained a spherical shape. All samples’ WCAs were >150°. Utilizing polarization measurements, we also compared the anticorrosion properties of superhydrophobic PPy-coated metal meshes with those of bare metal samples. The corrosion characteristics of such samples in 3.5 wt% NaCl aqueous solution, 0.5 M H₂SO₄ solution, and 1 M NaOH solution are given in Table 1.1. According to Table 1.1, the \( i_{corr} \) values of uncoated surfaces appear to be relatively high. This is because the bare substrate surfaces are in an unstable state and copper or iron becomes ions quickly, thus promoting corrosion.

Generally, a lower corrosion current density or a higher corrosion potential corresponds to a lower corrosion rate and better corrosion resistance. From
Table 1.1, we can find that the corrosion potential and the corrosion current of the superhydrophobic PPy-coated copper meshes were 0.9716 V and 4.172 × 10^{-6} A, respectively, whereas the corresponding values for bare copper meshes were 0.1643 V and 7.817 × 10^{-5} A. The shift of the corrosion potential (by ~1.13 V) in the positive direction indicates that the superhydrophobic PPy coatings act as the effective anodic protective coating rather than offering sacrificial corrosion protection. By the deposition of superhydrophobic coating on copper mesh substrates, the corrosion current decreases by one order of magnitude, showing the significant improvement of corrosion resistance. When bare copper mesh substrates are immersed in corrosive media, the passive oxide breaks down and severe corrosion begins. Importantly, the corrosion resistance of the superhydrophobic coating was achieved by coating the bare substrates with nanoscale PPy and modifying them with a low-surface-energy material. The reason for this is that air can be easily trapped in the pits and cavities between the PPy particles, and the trapped air can serve as a first barrier layer; then the conductive polymer coating can act as the second effective barrier to the inward diffusion of Cl\(^{-}\), thus inhibiting the corrosion of the substrates. In the same way, the \(i_{\text{corr}}\) of superhydrophobic stainless steel mesh samples show a decrease compared to the corresponding bare substrates while the \(E_{\text{corr}}\) increases (Table 1.1), meaning a better anticorrosion behavior of superhydrophobic samples than the bare substrates. It is believed that the double barrier layers, which consist of the trapped air layer and the PPy layer, on the substrates could guard against the outside corrosive ions, and thereby improve the corrosion resistance of such substrates to a great extent.

Aluminum alloys are important engineering materials. Feng et al. fabricated superhydrophobic aluminum alloy surfaces by a facile and environmentally friendly method, including boiling water treatment and polymer chain modification [19]. The corrosion resistance of the superhydrophobic Al sheet was evaluated by electrochemical experiments, and the resulting potentiodynamic polarization curves of the Al sheet samples in 3.5 wt% of NaCl solution were obtained using the Tafel extrapolation method. The corrosion resistance can be described by the corrosion current density \(i_{\text{corr}}\) or the corrosion potential \(E_{\text{corr}}\). The obtained superhydrophobic aluminum alloys, with a CA of 153.6°, showed excellent corrosion resistance, as shown in Figure 1.5. In detail, the \(E_{\text{corr}}\) and \(i_{\text{corr}}\) of the cleaned Al sheet were −1.35 V and 1.74 × 10^{-4} A/cm\(^2\), respectively. By contrast, the \(E_{\text{corr}}\) and \(i_{\text{corr}}\) of a polystyrene (PS)-modified Al sheet increased to −0.95 V and decreased to 1.16 × 10^{-5} A/cm\(^2\). The corrosion potential of the superhydrophobic Al sheet is more positive, while the corrosion current density is much lower than that of the cleaned Al sheet. The increase of \(E_{\text{corr}}\) in the positive direction and the decrease of \(i_{\text{corr}}\) can be linked to the protective function of the superhydrophobic film formed on the Al surfaces. Why does the superhydrophobic Al sheet show excellent corrosion resistance? This phenomenon can be explained by the fact that the superhydrophobic surface can repel any hydrophilic molecules or ions coming into contact with it. That is to say, the corrosive ions (Cl\(^{-}\) in NaCl solution) cannot migrate and penetrate the Al surface. So the corrosion resistance of the Al sheet is improved greatly by its acquired superhydrophobic property.
Table 1.1 Corrosion characteristics on the surfaces of bare copper mesh, superhydrophobic PPy-coated copper mesh, bare stainless steel mesh, superhydrophobic PPy-coated stainless steel mesh.

<table>
<thead>
<tr>
<th>Samples</th>
<th>3.5 wt% NaCl solution</th>
<th>0.5 M H₂SO₄ solution</th>
<th>1 M NaOH solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{corr}$ (A)</td>
<td>$E_{corr}$ (V)</td>
<td>$i_{corr}$ (A)</td>
</tr>
<tr>
<td>Bare copper mesh</td>
<td>$7.817 \times 10^{-5}$</td>
<td>0.1643</td>
<td>$1.017 \times 10^{-4}$</td>
</tr>
<tr>
<td>Superhydrophobic copper mesh</td>
<td>$4.172 \times 10^{-6}$</td>
<td>0.9716</td>
<td>$7.160 \times 10^{-6}$</td>
</tr>
<tr>
<td>Bare stainless steel mesh</td>
<td>$6.821 \times 10^{-5}$</td>
<td>−0.3037</td>
<td>$2.400 \times 10^{-4}$</td>
</tr>
<tr>
<td>Superhydrophobic stainless steel mesh</td>
<td>$2.224 \times 10^{-5}$</td>
<td>0.1224</td>
<td>$3.726 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Also for the corrosion protection, Xu et al. reported a simple approach for the preparation of superhydrophobic polyaniline (PANI) [20]. In their work, PANI was synthesized by oxidative polymerization of aniline with ammonium persulfate (APS). Subsequently, PANI was modified by different surfactants (sodium dodecylbenzenesulfonate, poly(ethylene glycol), and cetyltrimethylammonium bromide), showing excellent surface superhydrophobicity. By using Tafel polarization curves and electrochemical impedance spectroscopy, the corrosion protection performance of PANI with different wettability degrees was evaluated in 3.5% NaCl electrolyte. Electrochemical tests were conducted to investigate the effect of surfactant addition on the anticorrosion performance of PANI coating.

Before starting, both bare stainless steel and those coated with PANI were immersed in a corrosive medium for 30 min. Corrosion resistance was studied by plotting the polarization curves, as shown in Figure 1.6. The polarization curves for stainless steel electrodes coated with PANI showed remarkable potential shifts to positive values, and their corrosion current density decreased slightly compared to that of the uncoated electrode. The role of PANI coating is to prevent access by corrosive species into the substrate. Superhydrophobic PANI modified with the surfactant displays much better corrosion protection performance. In Figure 1.6, the PANI-PEG1 sample shows the highest corrosion potential ($E_{\text{corr}}$) and the lowest corrosion current density ($i_{\text{corr}}$), indicating the best corrosion protection performance. The corrosion potential increased with the increase of the contact angle, and better hydrophobicity corresponded to better corrosion resistance. From the foregoing, it is clear that the various superhydrophobic PANI coatings have better anticorrosion performance compared to the hydrophilic PANI.

Chromium(VI) ions with their anti-corrosion properties are often used in most anticorrosive coatings, and alternative strategies have to be tested to replace them because of their toxicity. To keep the anticorrosive property on the surface is important for practical applications in industry.
1.4 Photochromism

It is novel and interesting to endow biomimetic superhydrophobic materials with photochromic property. After activation by a light source, photochromism refers to the reversible color transformation. And, via a facile and substrate-independent route, superhydrophobic tungsten oxide (TO) coatings with a WCA of 155° were developed by us for photochromism [21]. The preparation of superhydrophobic TO particles was based on two-step precipitation method, and the preparation of superhydrophobic coating could be achieved using a mixed resin solution. In this way, a superhydrophobic TO coating with photochromic property was prepared. After UV irradiation for 30 min, the original yellow color of the coating automatically changed to dark blue, and the intrinsic color could be fully reversed by irradiating with visible light. The reversible photochromic switch can be realized by alternating irradiation cycles.

By an inexpensive and simple electrochemical deposition process, Wang et al. prepared rough and photochromic TO films [22]. In their procedure, Na$_2$WO$_4$ aqueous solution was chosen as the electrolyte for the electrodeposition of TO films along with oxalic acid to adjust the solution pH in the range 3.1–8.6. Indium tin oxide (ITO) glass was used as the working electrode (with platinum as the counter-electrode and Ag/AgCl as the reference electrode), and electrochemical deposition was conducted at 1.5 eV in the single-potential time-based mode. The results indicate that the oxide films become rough with a remarkable increase of the size of the NPs upon increasing the pH value, whereas a smooth film composed of NPs is formed at low pH. When the pH of the precursor solution was ~8.6, a rough brown film was obtained that exhibited a pebble-beach-like morphology made up of many nanoprotuberances with diameters in the range 40–350 nm, as shown in Figure 1.7a,b.
TO’s photochromic behavior was also studied because it is an excellent photochromic material. After UV irradiation, the as-prepared film became yelloish green from the initial brown, and when this film was placed in the dark, it recovered the brown color. As shown in Figure 1.7c, the UV spectra show a change in absorbance, with the greatest absorbance change of 0.34 occurring at ~372 nm. In addition, good reversibility was observed for many cycles of coloration and decoloration. The authors pointed out that the photochromic behavior of the as-deposited film is due to the variation of the tungsten valence as well as the number of oxygen vacancies and water molecules. Importantly, the photochromic behavior and wettability change are linked to the adsorption of atmospheric water by the film, and this work is indeed great.

The elaboration of one-dimensional nanostructures of semiconductors, such as nanorods, nanoneedles, nanowires, nanotubes, or nanobelts, can yield unique properties including photochromism. Therefore, the deposition of these nanostructures on superhydrophobic surfaces should be carried further.

![Image](a) (b) 500 nm 500 nm

Figure 1.7 (a) Top view and (b) side view of typical SEM images of tungsten oxide films deposited from the electrolyte at a pH of ~8.6. (c) Absorption spectra of an electrodeposited tungsten oxide film before (solid line) and after (dashed line) UV light irradiation. The insert shows the photochromic switching of the absorption change (monitored at 372 nm) during consecutive cycles of UV irradiation and storage in the dark. (Wang et al. 2006 [22]. Reproduced with permission of John Wiley and Sons.)