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Superhydrophobicity, Learn from the Lotus Leaf

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1. Introduction

As early as the eleventh century, the Song dynasty of China, one scholar named Zhou Dunyi (1017–1073), had planted the lotus all over the pool in his home and wrote an article named *Ode to A Lotus Flower*. From then on, in the East Asian countries and regions, especially the ancient China, the lotus flower and its leaves are frequently compared to one's noble spirit and purity because of "live in the silt but not sullied". Zhou Dunyi was thus memorized by this ode and the sentence "live in the silt but not sullied" was also came down to people today from that time.

This sentence displays an interesting phenomenon to us: the lotus' flowers and leaves unfold and stayed immaculacy by the pollution even when emerging from mud and muddy waters. Furthermore, in a pond after a rainfall, spherical water droplets on the lotus leaves, carrying effortlessly the contaminations attached on the leaves when the surface is slightly tilted, showing a self-cleaning function (Fig. 1a). The lotus, furthermore, is not the only type of plant in nature that the spherical water droplets can float on the leaves. Rice, for example, the main source of food for over half of the world population, is cultivated over a geographical range from 53°N to 40°S and to elevations of more than 2500 m (Guo & Liu, 2007). According to soil and water habitat, rice is generally classified into four broad categories: irrigated or paddy-grown rice, lowland rainfed rice, upland rice, and deep-water rice. Whatever the kind of rice is, we can easily find the interesting phenomenon that the rice leaf is very similar to the lotus leaves: their surfaces have the ability to resist water, and water droplets cannot wet on the leaf surfaces.

In addition to the leaves of plants, a number of insects, their wings also have the ability to resist water to spread on their surfaces. The most representative example is the water strider (*Gerris remigis*). The water striders are famous for their nonwetting legs that enable them to stand on water effortlessly (Fig. 2a). The maximal supporting force of a single leg is 152 dyn (1 dyn = 1×10^{-5} N), which is about 15 times the weight of the insect (Gao & Jiang,

2004). Furthermore, butterflies and cicadas, the evolution bestowed them the self-cleaning ability which can keep them uncontaminated by removing dust particles, dew or water droplets easily from their wings, and bestowed them water-repellent ability which can keep their wings not be wetting in the rain. Many poultry, such as the duck and the swan, have also the ability that their feathers can resist the water to spread out on the whole body surfaces when they are floating on the water.

On the surface of the lotus leaves, the almost spherical water droplets will not come to rest and simply roll off if the surface is tilted even slightly, which is now usually referred to as the “**Lotus Effect**”. This effect belongs to the subfield of the wettability of solid surface and is also named as the “**Superhydrophobicity**”. The wetting behaviour of solid surfaces by a liquid is a very important aspect of surface chemistry, which may have a variety of practical applications. When a liquid droplet contacts a solid substrate, it will either remain as a droplet or spread out on the surface to form a thin liquid film, a property which is normally characterized by means of the contact angle measurements. For a solid substrate, when the contact angle of water or oil on it is larger than 150° , it is called superhydrophobic or superoleophobic, respectively. On the other hand, when the contact angle of water or oil on a surface is almost 0° , it is called superhydrophilic or superoleophilic, respectively. Among the four kinds of surfaces, the superhydrophobic surfaces are referred to as self-cleaning surfaces and the contamination on them is easily removed by rolling droplets and as such this type of surface has obviously great potential uses, as water will not “stick” to it.

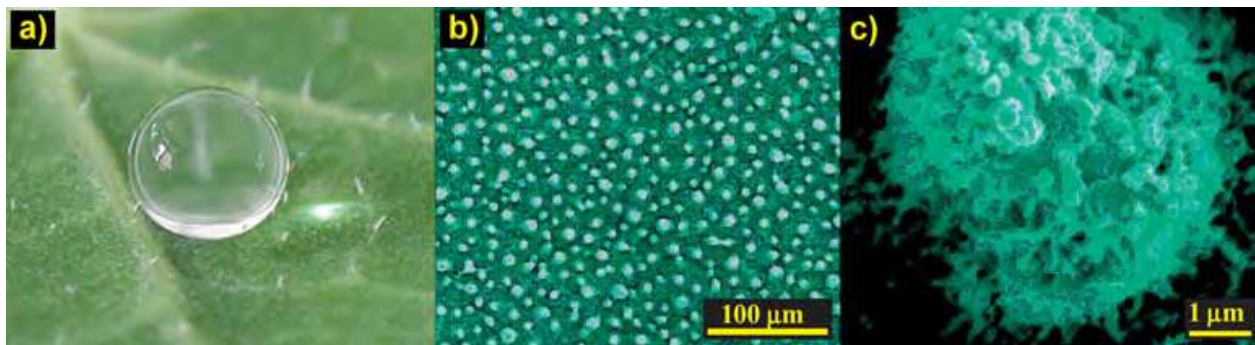


Fig. 1. (a) An almost ballshaped water droplet on a non-wettable plant leaf (Blossey, 2003). (b) Low- and (c) high-magnification scanning electron microscope images of the surface structures on the lotus leaf. Every epidermal cell forms a micrometer-scale papilla and has a dense layer of epicuticular waxes superimposed on it. Each of the papillae consists of branchlike nanostructures (Zhai et al., 2002). (Reproduced with permission from the Nature Publishing Group, Copyright 2003, and from the Chinese Physical Society, Copyright 2002.)

People have noticed these interesting nature phenomena quite a long time, while it is impossible to find out the essence under the science conditions at ancient time. The developments of analytical instruments are always promoting the level of human cognition. In the past two scores years, by means of scanning electron microscope, the studies of biological surfaces have revealed an incredible microstructural diversity of the outer surfaces of plants. Not until W. Barthlott and C. Neinhuis, Boon University, Germany, have research the lotus leaves systematically did people completely realized the mechanism of the lotus leaves to resist water. Barthlott and coworkers investigated the micro-structure of

the lotus leaves with a scanning electron microscope and hold that the surface roughness in micro-meter scale papillae and the wax layer of the surface were synergistic bestowed the superhydrophobicity to the surface of lotus leaves (Barthlott & Neinhuis, 1997). Further, detailed scanning electron microscopy images of lotus leaves indicated that their surfaces are composed of micro- and nanometer-scale hierarchical structures, that is, fine-branched nanostructures (ca. 120 nm) on top of micropapillae (5–9 μm) (Fig. 1b and 1c). The cooperation of these special double-scale surface structures and hydrophobic cuticular waxes is believed to be the reason for the superhydrophobicity (Feng et al., 2002; Zhai et al., 2002). Jiang and coworkers investigated the water strider's legs by the means of scanning electron microscope and revealed that the leg is composed of numerous needle-shaped setae with diameters on the microscale and that each microseta is composed of many elaborate nanoscale grooves (Fig. 2b and 2c). Such a hierarchical surface structure together with the hydrophobic, secreted wax is considered to be the origin of the superhydrophobicity of the water strider's legs (Gao & Jiang, 2004).

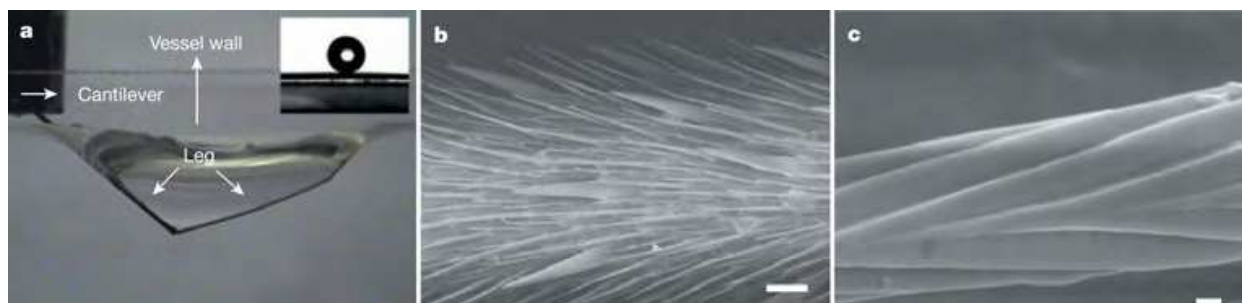


Fig. 2. The non-wetting leg of a water strider. (a) Typical sideview of a maximal-depth dimple (4.38 ± 0.02 mm) just before the leg pierces the water surface. Inset, water droplet on a leg; this makes a contact angle of $167.6 \pm 4.4^\circ$. (b), (c) Scanning electron microscope images of a leg showing numerous oriented spindly microsetae (b) and the fine nanoscale grooved structures on a seta (c). Scale bars: (b), 20 μm ; (c), 200 nm. (Gao & Jiang, 2004). (Reproduced with permission from the Nature Publishing Group, Copyright 2004.)

2. The Related Fundamental Theories

The shape of a liquid droplets on solid surface, may be flat, hemisphere or spherical, and is governed by the surface tensions. Figure 3 showed the two typical states of the liquid droplet on a solid surface. The surface tensions γ_{s-l} and γ_{v-l} attempt to make the droplet to shrink, while the tension γ_{s-v} attempts to make the droplet to spread out on the surface. When the droplets on surface reached equilibrium, the angle between the solid/liquid interface and the liquid/vapour interface was named as contact angle (θ). The value of the contact angle describes the degree of the liquid wetting the solid surface. The relationship between these parameters is commonly given by the famous Young's equation:

$$\cos\theta = (\gamma_{s-v} - \gamma_{s-l}) / \gamma_{v-l}$$

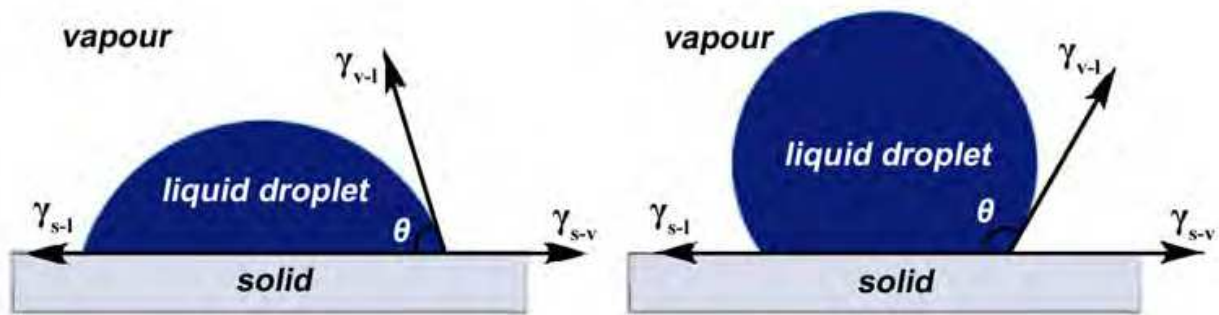


Fig. 3. The two typical states of the liquid droplets on a solid surface.

The Young's equation can be only applied for the chemical homogeneous and ideal flat surfaces. In actuality, few solid surfaces are truly flat, therefore, the surface roughness factor must be considered during the evaluation of the surface wettability. Wenzel and Cassie have developed Young's equation and worked out the Wenzel's equation and Cassie's equation, respectively. The two equations are commonly used to correlate the surface roughness with the contact angle of a liquid droplet on a solid surface. This improvement has made their application scope more wide than the Young's equation.

In 1936, Wenzel found that the surface roughness must be considered during the evaluation of the surface wettability (Wenzel, 1936). He hold that the liquid completely fills the grooves of the rough surface where they contact (Fig. 4a). The situation is described by equation:

$$\cos\theta_W = r (\gamma_{s-v} - \gamma_{s-l}) / \gamma_{v-l} = r \cos\theta$$

where θ_W is the contact angle in the Wenzel mode and r is the surface roughness factor. From this equation, it can be found that if the contact angle of a liquid on a smooth surface is less than 90° , the contact angle on a rough surface will be smaller, while the contact angle of a liquid on a smooth surface is more than 90° , the angle on a rough surface will be larger. These two situations can be described as: for $\theta < 90^\circ$, $\theta_W < \theta$; for $\theta > 90^\circ$, $\theta_W > \theta$.

In 1944, based on Wenzel's model, Cassie further developed and revised the Young's equation. He presented that the solids rough surface should be regarded as a solid-vapour composite interface and the vapour pockets were assumed to be trapped underneath the liquid (Fig. 4b). In this case, the solid-liquid-vapour three phase contact area can be represented by the f_s and f_v , which are the area fractions of the solid and vapour on the composite surface. Defining the contact angle in the Cassie mode as θ_C , θ_C can be correlated to the chemical heterogeneity of a rough surface by equation:

$$\cos\theta_C = f_s \cos\theta_s + f_v \cos\theta_v$$

Since $f_s + f_v = 1$, $\theta_s = \theta$, $\theta_v = 180^\circ$, the above equation can be written as equation:

$$\cos\theta_C = f_s (\cos\theta + 1) - 1$$

From the above equation it can be easily found that for a true contact angle more than 90° , the surface roughness will increase the apparent angle. This is unlike the Wenzel case, because even when the intrinsic contact angle of a liquid on a smooth surface is less than 90° , the contact angle can still be enhanced as a result of the as trapped superhydrophobic vapour pockets.

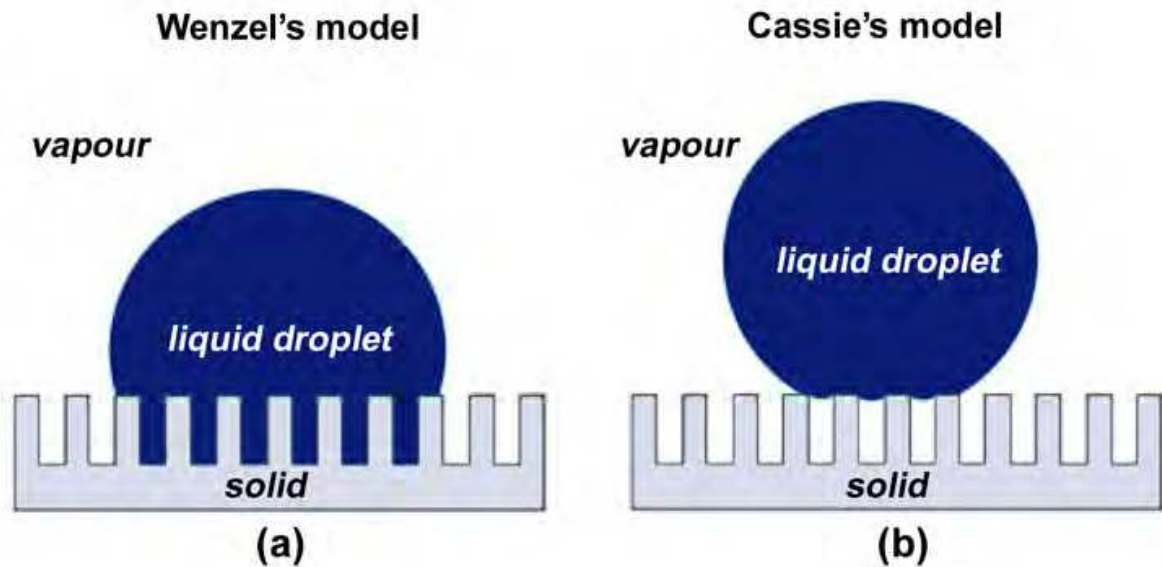


Fig. 4. (a) Wetted contact between the liquid and the rough substrate (Wenzel's model). (b) Non-wetted contact between the liquid and the rough substrate (Cassie's model).

The achievements of the Wenzel's and Cassie's models are that they have expressed the contact state between the liquid and the rough solid surface more realistically and exactly. Heretofore, Wenzel's and Cassie's models and equations are numerous applied for illustrating the mechanism of the superhydrophobic surfaces which were prepared by the material researchers in their articles.

With the emergence of the nanometer materials in 1960's, it promoted greatly the progress of the science and technology. Preparation and studies on the surface properties of the nanomaterials are the foundation of the nanoscience research. The emergence of the nanometer materials provides a good platform for the biomimetic materials research. Inspired by the microstructure of the natural water-resister, and based on the rapidly developed nanoscience and technology, material researchers have strong motivation to mimic the structure and the chemical component of the lotus leave surface for the biomimetic preparation of the superhydrophobic materials.

Heretofore, a variety of methods have been reported for constructing superhydrophobic surfaces by mimicking the surface of lotus leaves. These artificial superhydrophobic surfaces have been fabricated mostly by controlling the roughness and topography of hydrophobic surfaces and using techniques such as anodic oxidation, electrodeposition and chemical etching, plasma etching, laser treating, electrospinning, chemical vapour deposition, sol-gel processing, phase separation and so on. The materials that were used to fabricate the surface morphology ranged from carbon nanotubes, nanoparticles and nanofibers, metal oxide

nanorods, polymers to engineering alloys materials. In the following text, some most common and important preparation methods and the categories of the artificial superhydrophobic surfaces are introduced.

3. Methods for the Preparation of the Superhydrophobic Surfaces

3.1 Layer-by-Layer and colloidal assembly

The Layer-by-Layer assembly technique, which was developed by Decher's group, has been proved to be a simple and inexpensive way to build controllable chemical composition and micro- and nanometer scale (Decher & Hong, 1991). The greatest strength of the Layer-by-Layer technique is to control the thickness and the chemical properties of the thin film in molecular level by virtue of the electrostatic interaction and the hydrogen bond interaction between the molecules. Cohen, Rubner and coworkers prepared a surface structure that mimics the water harvesting wing surface of the Namib Desert beetle by means of Layer-by-Layer technique. The *Stenocara* beetle, which lived in the areas of limited water, uses their hydrophilic/superhydrophobic patterned surface of its wings to collect drinking water from fog-laden wind. In a foggy dawn, the *Stenocara* beetle tilts its body forward into the wind to capture small water droplets in the fog. After these small water droplets coalesce into bigger droplets, they roll down into the beetle's mouth, providing the beetle with a fresh morning drink. Cohen, Rubner and coworkers created the hydrophilic patterns on superhydrophobic surfaces by selectively delivering polyelectrolytes to the surface in a mixed water/2-propanol solvent to produce surfaces with extreme hydrophobic contrast (Zhai et al., 2006). Potential applications of such surfaces include water harvesting surfaces, controlled drug release coatings, open-air microchannel devices, and lab-on-chip devices. Sun and coworkers reported a facile method for preparing a superhydrophobic surface was developed by layer-by-layer deposition of poly(diallyldimethylammonium chloride)/sodium silicate multilayer films on a silica-sphere-coated substrate followed with a fluorination treatment. The superhydrophobic surface has a water contact angle of 157.1° and sliding angle of 3.1° (Zhang et al., 2007). The easy availability of the materials and simplicity of this method might make the superhydrophobic surface potentially useful in a variety of applications.

3.2 Electrochemical reaction and deposition

The electrochemical reaction and the electrochemical deposition are widely used for the preparation of the superhydrophobic materials. Zhang and coworkers reported a surface covered with dendritic gold clusters, which is formed by electrochemical deposition onto an indium tin oxide electrode modified with a polyelectrolyte multilayer, shows superhydrophobic properties after further chemisorption of a self-assembled monolayer of *n*-dodecanethiol (Zhang et al., 2004). When the deposition time exceeds 1000s, the contact angle reaches a constant value as high as 156° . Yan, Tusjii and coworkers reported a poly(alkylpyrrole) conductive films with a water contact angle larger than 150° (Fig. 5). The films were obtained by electrochemical polymerization of alkylpyrrole and are stable to temperature, organic solvents and oils. The surface of the film is a fractal and consists of an array of perpendicular needle-like structures (Yan et al., 2005).

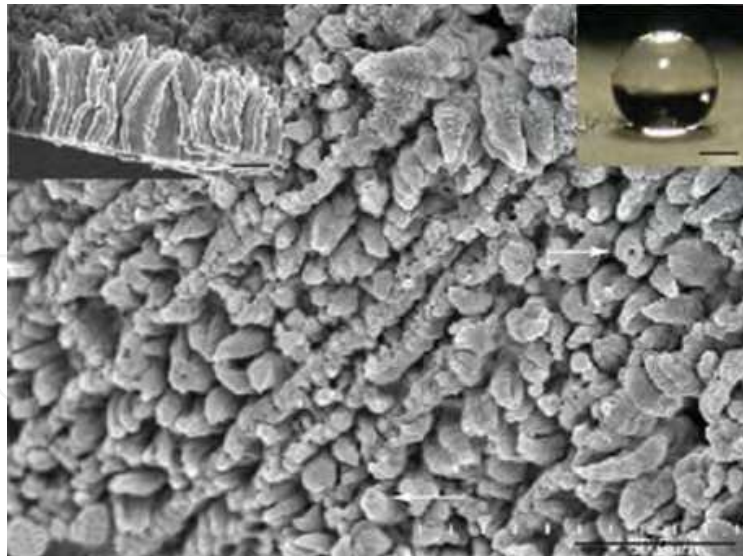


Fig. 5. Scanning electron microscopic image of the super water-repellent poly(alkylpyrrole) film (scale bar: $15\ \mu\text{m}$). Left inset: scanning electron microscopic image of the cross section of the film (bar: $15\ \mu\text{m}$). Right inset: image of a water droplet on the film (bar: $500\ \mu\text{m}$) (Yan et al., 2005). (Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Copyright 2005.)

Our group reported a Pt nanowire array superhydrophobic surface on a Ti/Si substrate by utilizing electrodeposition of Pt into the pores of anodic aluminium oxide templates and surface fluorination. The method can be extended to other metals to which the recently developed chemical etching method is not applicable (Qu et al., 2008). Zhou and coworkers reported a fabrication of superhydrophobic materials with a water contact angle of 178° using a perpendicular brucite-type cobalt hydroxide nanopin film fabricated with a bottom-up process (Fig. 6) (Hosono et al., 2005).

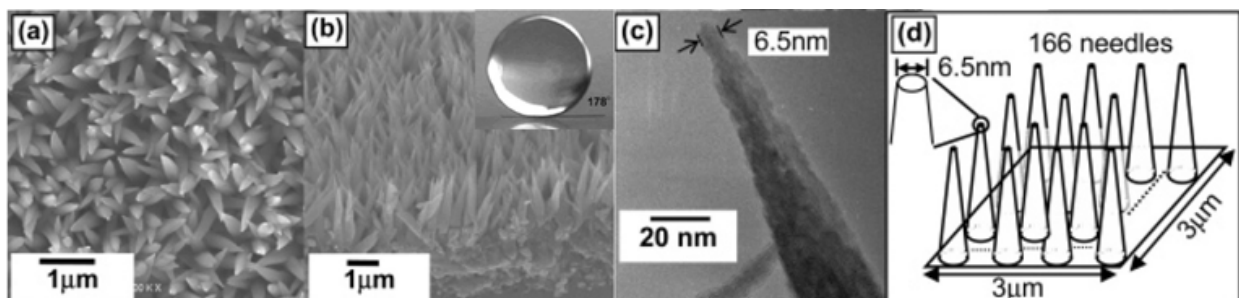


Fig. 6. (a,b) Field-emission scanning electron microscopic images of the brucite-type cobalt hydroxide films observed from the top and side, respectively. (c) Transmission electron microscope images of the films. (d) A simple model of the film with the fractal structure. Inset: image of a water droplet on the film with a contact angle of 178° (Hosono et al., 2005). (Reproduced with permission from the American Chemical Society, Copyright 2005.)

3.3 Sol-Gel Processing

For many materials, the sol-gel processing can also bestow the surface superhydrophobicity. Many research results showed that the surfaces can be made superhydrophobic while it

needs not the surface hydrophobic process after the sol-gel processing because that the low surface energy materials already exist in the sol-gel process. Shirtcliffe and coworkers reported superhydrophobic foams with contact angles greater than 150° which were prepared using a sol-gel phase-separation process. A rapid hydrophobic to hydrophilic transition was presented in the surface at around 400°C , generating a material that absorbed water rapidly (Shirtcliffe et al., 2003). Cho and coworkers reported a fabrication of superhydrophobic surface from a supramolecular organosilane with quadruple hydrogen bonding by a simple sol-gel processing at room temperature. Compared with other template syntheses, this approach to fabricating a phase-separated continuous material is a very simple way of producing a superhydrophobic coating and is made possible by the supramolecular characteristics of the novel organosilane (Han et al., 2004). Wu and coworkers prepared the ZnO surface with micro- and nanostructure via a wet chemical route. The surface showed superhydrophobic after the surface chemical modification with the moderate-length alkanic acids (Wu et al., 2005).

3.4 Etching and Lithography

Etching is the most efficient way for the construction of rough surface. The detailed methods are plasma etching, laser etching, chemical etching et al. These methods have been greatly applied for the biomimic fabrication of the superhydrophobic surface. Teshima and coworkers formed a ultra water-repellent polymer sheets on a poly(ethylene terephthalate) substrate. Its nanotexture was formed on a poly(ethylene terephthalate) substrate surface via selective oxygen plasma etching and subsequent hydrophobic coating by means of low temperature chemical vapor deposition or plasma-enhanced chemical vapour deposition (Teshima et al., 2005). The as-prepared polymer sheets are transparent and ultra water-repellent, showing a water contact angle greater than 150° . Shen and coworkers reported fabrication of superhydrophobic surfaces by a dislocation-selective chemical etching on aluminium, copper, and zinc substrates (Qian & Shen, 2005). Our group developed a solution-immersion process to fabricate of superhydrophobic surfaces on engineering materials, such as steel, copper alloy and titanium alloy by wet chemical etching and surface coating with fluoroalkylsilane (Qu et al., 2007). The synergistic effect of the two-lengthscale surface microstructures and the low surface energy of the fluorinated surface are considered to be responsible for this superhydrophobicity. Compared with the other methods, it is convenient, time-saving, and inexpensive. The as-fabricated superhydrophobic surfaces show long-term stability and are able to withstand salt solutions in a wide range of concentrations.

For the fabrication of large proportion and periodic micro- and nanopatterns, lithography, such as the electronic beam lithography, light lithography, X-ray lithography and nanospheres lithography, are fairly good methods. Riehle and coworkers fabricated ordered arrays of nanopits and nanopillars by an electronic beam writer with the desired pattern and investigated their dynamic wettability before and after chemical hydrophobization (Martines et al., 2007). These ordered patterns showed superhydrophobic after the surfaces were coated with octadecyltrichlorosilane. Tatsuma and coworkers reported superhydrophobic and superhydrophilic gold surfaces which were prepared by modifying microstructured gold surfaces with thiols (Notsu et al., 2005). The patterns required by the superhydrophobic surface were obtained by photocatalytic lithography using a TiO_2 -coated

photomask. The perfluorodecanethiol modified rough gold surface can be converted from superhydrophobic to superhydrophilic by photocatalytic remote oxidation using the TiO₂ film. On the basis of this technique, enzymes and algal cells can be patterned on the gold surfaces to fabricate biochips.

3.5 Chemical Vapor Deposition and Physical Vapor Deposition

The chemical and physical vapour depositions have been also widely used for the nanostructure fabrication and the chemical modification in the surface chemistry. Lau and coworkers deposited vertically aligned carbon nanotube forest with a plasma enhanced chemical vapor deposition technique, which is a fairly good technique that produces perfectly aligned, untangled (i.e., individually standing) carbon nanotubes whose height and diameter can be conveniently controlled (Lau et al., 2003). While after the depositing a thin hydrophobic poly(tetrafluoroethylene) coating on the surface of the nanotubes through a hot filament chemical vapor deposition process, the surface showed stable superhydrophobicity with advancing and receding contact angles are 170° and 160°, respectively. Furthermore, Lau and coworkers also reported a formation of a stable superhydrophobic surface via aligned carbon nanotubes coated with a zinc oxide thin film. The carbon nanotubes template was synthesized by chemical vapor deposition on a Fe-N catalyst layer. The ZnO film, with a low surface energy, was deposited on the carbon nanotubes template by the filtered cathodic vacuum arc technique. The ZnO-coated carbon nanotubes surface shows no sign of water seepage even after a prolonged period of time. The wettability of the surface can be reversibly changed from superhydrophobicity to hydrophilicity by alternation of ultraviolet irradiation and dark storage. Contact angle measurement reveals that the surface of the ZnO-coated carbon nanotubes is superhydrophobic with water contact angle of 159° (Huang et al., 2005). Jiang and coworkers demonstrated a honeycomb-like aligned carbon nanotube films which were grown by pyrolysis of iron phthalocyanine in the Ar/H₂ atmosphere by the physical vapour deposition (Li et al., 2002). Wettability studies revealed the film surface showed a superhydrophobic property with much higher contact angle ($163.4 \pm 1.4^\circ$) and lower sliding angle (less than 5°).

3.6 Electrospinning

Electrospinning is a very good method for the fabrication of the ultra-thin fibers. Heretofore, many groups have applied this technique to the preparation of the superhydrophobic surfaces. The merit of electrospinning is that the superhydrophobic surface can be obtained within one step. Rutledge and coworkers produced a block copolymer poly(styrene-*b*-dimethylsiloxane) fibers via electrospinning from solution in tetrahydrofuran and dimethylformamide (Ma et al., 2005). The submicrometer diameters of the fibers were in the range 150–400 nm and the contact angle measurements indicate that the nonwoven fibrous mats are superhydrophobic, with a contact angle of 163°. Jiang and coworkers reported a polyaniline/polystyrene composite film which was prepared via the simple electrospinning method (Zhu et al., 2006). The as-prepared superhydrophobic surface showed stable superhydrophobicity and conductivity, even in many corrosive solutions, such as acidic or basic solutions over a wide pH range, and also in oxidizing solutions.

4. The Category of the Artificial Superhydrophobic Materials

4.1 Carbon nanotubes

Carbon nanotubes are new type of carbon structures which was discovered in 1991. Due to their excellent electrical and mechanical properties, the carbon nanotubes are widely used in both fundamental and applied research. Jiang and coworkers prepared an aligned carbon nanotubes films with micro- and nanometer structure. The aligned carbon nanotube films showed superamphiphobic properties after the surface modification with a fluoroalkylsilane coating. The surface showed high contact angles for both water and rapeseed oil on the film and the values of the contact angles were 171° and 161° , respectively (Li et al., 2001). Lau and coworkers demonstrated a creation of a stable, superhydrophobic surface using the nanoscale roughness inherent in a vertically aligned carbon nanotube forest together with a thin, conformal hydrophobic poly(tetrafluoroethylene) coating on the surface of the nanotubes (Lau et al., 2003).

4.2 Metallic compounds nanorods and nanoparticles

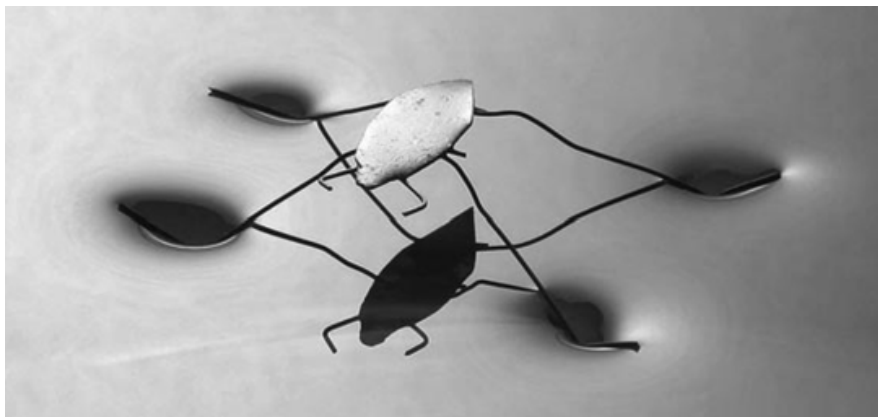


Fig. 7. A metallic model “pond skater” (body length 28 mm) standing on a water surface. Note the deformation of the water surface around the legs (Larmour et al., 2007). (Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Copyright 2007.)

With the development of the research on inorganic materials, the superhydrophobic inorganic materials were also reported numerously. For example, ZnO is a novel II - IV semiconductor material with a direct bandgap of 3.2 eV, excellent lattice, photovoltaic, pizeoelectric and dielectric properties, and it is non-toxic and low cost from cheap and abundant raw materials. Jiang and coworkers reported a controllable wettability of aligned ZnO nanorod films. This inorganic oxide films show superhydrophobicity and superhydrophilicity at different conditions, and the wettability can be reversibly switched by alternation of ultraviolet irradiation and dark storage (Feng et al., 2003). This effect is believed to be due to the cooperation of the surface photosensitivity and the aligned nanostructure of the films. Such special wettability will greatly extend the applications of ZnO films to many other important fields. Futherore, Jiang and coworkers deposited similar TiO₂ nanorod films and aligned SnO₂ nanorod films on glass substrates for the preparation of the superhydrophobic surface. The two kinds of superhydrophobic surfaces can all be switched between superhydrophobicity and superhydrophilicity by the alternation of

ultraviolet irradiation and dark storage (Feng et al., 2005; Zhu et al., 2006). Bell and coworkers reported a remarkably straightforward method for treating metals uses electroless galvanic deposition to coat a metal substrate with a textured layer of a second metal to fabricate superhydrophobic surfaces on metal surface (Larmour et al., 2007). The process is carried out under ambient conditions using readily available starting materials and laboratory equipment. The as-prepared superhydrophobic surfaces show approximately 180° contact angle. It is very striking and interesting that they have applied this preparation method to the four legs of a metallic model “pond skater” (*Gerridae*) and made this metallic model with the capacity of floating on the water (Fig. 7).

4.3 Engineering Alloy Materials

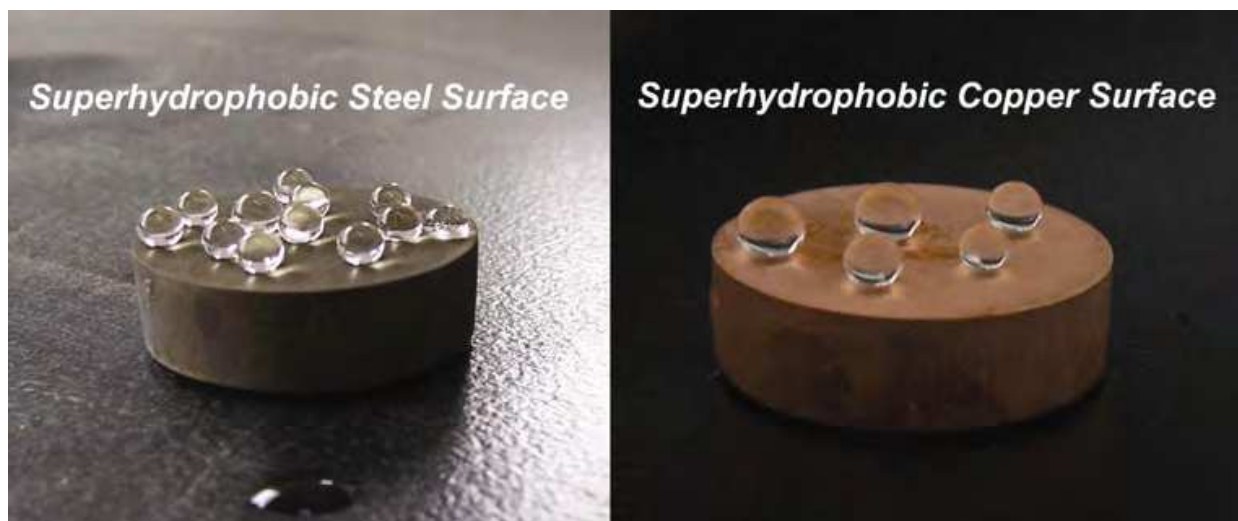


Fig. 8. Image of water droplets with different sizes on the superhydrophobic surface of steel having a contact angle of $161 \pm 1^\circ$ and on the superhydrophobic surface of copper alloy with a contact angle of $158 \pm 1^\circ$ respectively (Qu et al., 2007). (Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Copyright 2007.)

Engineering materials, such as steel, aluminium and its alloy, copper alloy and titanium alloy, have diverse technological applications in the marine, auto, aviation, and space industries. Superhydrophobicity will greatly extend their applications as engineering materials. Liu and coworkers reported a simple and inexpensive method to produce superhydrophobic surfaces on aluminium and its alloy by oxidation and chemical modification (Guo et al., 2005). The superhydrophobic surfaces show long-term stability overall wide pH range. Our group reported a novel mixed-solution system for the fabrication of superhydrophobic surfaces on steel, copper alloy and titanium alloy by a chemical etching method (Fig. 8). The superhydrophobic surfaces are able to withstand salt solutions in a wide range of concentrations, which may open a new avenue in applications especially for the marine engineering materials where salt resistance is required. We expect that this technique will accelerate the large-scale production of superhydrophobic engineering materials with new industrial applications (Qu et al., 2007).

4.4 Polymer Materials

Jiang and coworkers synthesized superhydrophobic needle-like polyacrylonitrile nanofibers via extrusion of the polyacrylonitrile precursor solution into the solidifying solution under pressure. The aligned nanofibers with different diameters and densities can be easily obtained by using anodic aluminium oxide membrane with different pore diameters, and the alignment process can be applied to different polymer precursors such as poly(vinyl alcohol), polystyrene, polyesters, and polyamides (Feng et al., 2002). The superhydrophobicity is believed that not only the nanostructure of the nanofibers but also their lower density contributes to the very large fraction of air in the surface. McCarthy and coworkers fabricated superhydrophobic polypropylene surfaces by the simultaneous etching of polypropylene and etching/sputtering of poly(tetrafluoroethylene) using inductively coupled radio frequency argon plasma. The as-prepared surfaces showed superhydrophobicity with a water contact angle of 172° (Youngblood & McCarthy, 1999). Shimomura and coworkers fabricated a honeycomb patterned fluorinated polymer films by casting of the polymer solution under humid conditions. Such honeycomb patterned films have application as transparent and superhydrophobic polymer films and it films can be formed from a large variety of materials and on a wide variety of substrates (Yabu & Shimomura, 2005). Our group prepared a polymer superhydrophobic surface on Ti/Si substrates via the fabrication of conductive polyaniline nanowire film. The polyaniline nanowire film was synthesized by electrodeposition of aniline into the pores of an anodic aluminum oxide template on Ti/Si substrate followed by the removal of the template (Qu et al., 2008). The surface showed conductivity and superhydrophobicity, even in many corrosive solutions, such as acidic or basic solutions over a wide pH range. Compared with the electrospinning method, the method in this paper is cheap and time-saving and avoided high-voltage power, and the method can be easily applied to other conducting polymers.

5. The Superhydrophobic Surfaces Related Properties and Application

With more and more in-depth study on the preparation of the superhydrophobic surfaces, the materials researchers are not only satisfy with the preparation and the contact model of the superhydrophobic surface, but the application and the related properties of the superhydrophobic surfaces. With the increase of the surface roughness, however, the surface will lost some important properties, such as the optical transparence and the mechanics property. These unfavorable factors will limit the widespread application of superhydrophobic surface greatly. Thus more and more groups have devoted to the preparation of the multi-functional superhydrophobic surfaces.

5.1 The Superhydrophobic Surfaces with the Anticorrosive Property

The pure water (pH value is 7) was commonly used for the contact angle measurements. Recently, the measurements for contact angel in whole pH range have aroused considerable interest from many researchers because of the wide application environments of this kind of superhydrophobic materials. For the engineering materials, undoubtedly, the resistance to the water or corrosive liquid will greatly enhance their anticorrosive ability, broaden its application environment and extend their service life. The superhydrophobic surfaces are able to withstand salt solutions in a wide range of concentrations, which may open a new avenue in applications especially for the marine engineering materials where salt resistance

is required. Liu's group and our group reported the superhydrophobic engineering materials such as the, steel, copper, alloy aluminium and its alloy et al (Guo et al., 2005; Qu et al., 2007). These superhydrophobic engineering materials showed superhydrophobicity in nearly the entire pH range, so they can be used in strongly corrosive environments. Furthermore, graphite carbon has intrinsic thermal and chemical resistance. Jiang and coworkers reported a nanostructured carbon films by pyrolyzing nanostructured polyacrylonitrile films (Feng et al., 2003). The films also showed superhydrophobicity in nearly the entire pH range.

5.2 The Superhydrophobic surfaces with the Optical Property



Fig. 9. Image of a glass slide coated with a transparent, superhydrophobic multilayer with antireflection properties (Bravo et al. 2007). (Reproduced with permission from the American Chemical Society, Copyright 2007.)

For many devices, such as the car windscreen and the glasses, the optical transparency is a very special and important property. Preparing the transparent superhydrophobic surface has aroused considerable interest for many materials researchers. Hydrophobicity and transparency, however, are two contradictory properties of the surface. Increasing the surface roughness is beneficial for the hydrophobicity, while the transparency decreases due to the light-scattering losses. Therefore, controlling of surface roughness to an appropriate position is to meet the requirements for both the two key factor. Watanabe and coworkers reported a sol-gel method for producing transparent boehmite films on glass substrates. The surface roughness could be precisely controlled in the range between 20 and 50 nm (Nakajima et al. 1999). This method, however, requires as high as 500 °C heating process (500 °C), which is incompatible with many optical devices. To solve this problem, a microwave plasma-enhanced chemical vapour deposition process was adapted to prepare transparent superhydrophobic films at temperatures as low as 100 °C (Hozumi & Takai, 1998; Wu et al. 2002). Jiang and coworkers prepared multifunctional ZnO nanorod films with visible-light transparency and superhydrophobic properties through controlling the diameter and length of nanorods using a low-temperature solution approach. The diameter and the spacing between the nanorods are both less than 100 nm. Such surface nanostructures are small enough not to give rise to visible light scattering. Cohen, Rubner and coworkers demonstrate a Layer-by-Layer processing scheme that can be utilized to

create transparent superhydrophobic films from SiO₂ nanoparticles of various sizes (Fig. 9). By controlling the placement and level of aggregation of differently sized nanoparticles within the resultant multilayer thin film, it is possible to optimize the level of surface roughness to achieve superhydrophobic behaviour with limited light scattering (Bravo et al. 2007).

5.3 The Superhydrophobic Surfaces with Highly Adhesive Forces

It is easy and acknowledged to image that a surface with a high water contact angle and small contact area should be associated with a low adhesive force. However, some research results on superhydrophobic surfaces indicate that it is not true in any situation. Feng, Jiang and coworkers reported a superhydrophobic aligned polystyrene nanotube layer via a simple template-wetting method. The surface shows superhydrophobicity, while it can hold a spherical water droplet even when it is turned upside down (Jin et al., 2005). They hold that the large contact area (the as-prepared polystyrene films are composed of about 6.76×10^6 nanotubes mm⁻²) induces a strong interacting force between the water droplet and the polystyrene nanotube films. The mechanism described here is similar to the one geckos use in nature while the difference is that the latter interactions are between two solids. Liu and coworkers also reported sticky superhydrophobic surface which were fabricated on aluminium alloy by suitable aqueous solution to control the surface roughness (Guo & Liu, 2007). These superhydrophobic surfaces with high adhesive force to liquid are expected to be used as a “mechanical hand” to transfer mini liquid droplets for microsample analyses in the future.

5.4 The Superhydrophobic Surfaces with High Electrical Conductivity

Electrical conductivity is a very important property required for many kinds of microelectrical devices, such as field-effect transistors, light-emitting diodes, and thin-film transistors. In some applications, such as biotechnology, corrosion protection, antistatics, conductive textiles and antifouling coatings, the superhydrophobic surfaces prepared with conducting material would be very useful and vital. Our group prepared conductive superhydrophobic surfaces with polyaniline by means of an anodic deposition technique on Ti/Si substrate. The method was also general to other conductive polymers, such as polythiophenes and polypyrroles. The as-prepared surface showed conductivity and superhydrophobicity, even in many corrosive solutions, such as acidic or basic solutions over a wide pH range (Qu et al., 2008). Jiang and coworkers prepared conductive hydrophobic zinc oxide thin films by means of electrochemical deposition (Li et al., 2003). They expected that the superhydrophobic conductive thin films materials have potential use, such as microfluidic devices, in the future. In fact, many reported superhydrophobic surfaces based on the metal and metallic nanomaterials are conductive naturally, while their intrinsic nature and the potential uses were ignored at the time.

6. Outlook and Summary

In this chapter, we have presented the origin model of the superhydrophobicity in nature, the lotus leaf. In the following text, the mechanism of the surface resisting water, the recent

studies on the biomimetic preparation and the properties of the superhydrophobic surface were elaborated.

The superhydrophobic surface, because of the novel aspects of surface physics and important applications ranging from selfcleaning materials, marine coatings, antiadhesive coatings, and nanobattery to microfluidic devices, has aroused considerable interest and resulted in a growing number of reports in the recent years. In addition to the superhydrophobic research, many and many researcher focused on the other wetting properties of solid surface, that is, superhydrophilicity, superoleophobicity, and superoleophilicity. For example, when superhydrophobicity/superoleophobicity or superhydrophilicity/superoleophobicity coexist, separation of water from oil (or oil from water) can be realized. Moreover, the smart surfaces whose wettability can be modulated reversibly between superhydrophobicity and superhydrophilicity or superoleophobicity and superoleophilicity are attracting more and more researchers devoted to them. Although it is very difficult that to achieve the superoleophobic surface which resists the oil, such as the chloroform or hexane, just like the superhydrophobic surfaces resists water, the preparation of the superoleophobic materials must be a research focus in the near future.

With millions of years of evolution, creatures in nature possess amazing and mysterious properties that we do not yet know. Therefore, further exploration and explanation of surfaces with special wetting behavior in nature is also necessary. Learning from nature will give us inspiration to develop simple and cheap methods to construct biomimetic multi-functional surfaces and materials.

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Nature's evolution has led to the introduction of highly efficient biological mechanisms. Imitating these mechanisms offers an enormous potential for the improvement of our day to day life. Ideally, by bio-inspiration we can get a better view of nature's capability while studying its models and adapting it for our benefit. This book takes us into the interesting world of biomimetics and describes various arenas where the technology is applied. The 25 chapters covered in this book disclose recent advances and new ideas in promoting the mechanism and applications of biomimetics.

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