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# Bioinspired Surfaces with Special Wettability

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## ABSTRACT

Biomimetic research indicates that many phenomena regarding wettability in nature, such as the self-cleaning effect on a lotus leaf and cicada wing, the anisotropic dewetting behavior on a rice leaf, and striking superhydrophobic force provided by a water strider's leg, are all related to the unique micro- and nanostructures on the surfaces. It gives us much inspiration to realize special wettability on functional surfaces through the cooperation between the chemical composition and the surface micro- and nanostructures, which may bring great advantages in a wide variety of applications in daily life, industry, and agriculture. This Account reviews recent progress in these aspects.

## Introduction

Wettability is a fundamental property of a solid surface, which plays important roles in daily life, industry, and agriculture. Functional surfaces with special wettability have aroused much interest because of their great advantages in applications. For example, the superhydrophilic surface<sup>1</sup> with a water contact angle (CA) of almost 0° generated by UV irradiation has been successfully used as a transparent coating with antifogging and self-cleaning properties. On the other hand, various phenomena, such as contamination, snow sticking, erosion, and even current conduction are expected to be inhibited on superhydrophobic surfaces<sup>2–5</sup> with a CA larger than 150° and a sliding angle (SA) less than 10°.<sup>6</sup>

The chemical compositions<sup>7,8</sup> determine the surface free energy and thus have great influence on wettability.

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Lei Jiang received his B.S. degree in physics (1987), and M.S. degree in chemistry (1990) from Jilin University of China. From 1992 to 1994, he studied in Tokyo University of Japan as a China–Japan joint course Ph.D. student and received his Ph.D. degree from Jilin University of China with Tiejun Li. Then, he worked as a postdoctoral fellow in Akira Fujishima's group in Tokyo University. In 1999, he joined ICCAS as "Plan of Hundreds Scientists in CAS". Now, he is also working as a chief scientist of the National Center for Nanoscience and Technology of China.

However, it has certain limitation. For example, the  $-\text{CF}_3$ -terminated surface was reported to possess the lowest free energy and the best hydrophobicity, while on flat surfaces, the maximum CA could only reach about 120°.<sup>9</sup> The surface topographic structure is also an important factor that influences the wettability. As described by Wenzel's equation,<sup>10</sup>

$$\cos \theta' = r \cos \theta \quad (1)$$

in which  $\theta'$  is the apparent CA on a rough surface, while  $\theta$  is the intrinsic CA on a flat surface, the surface roughness ( $r$ ) can enhance both the hydrophilicity and the hydrophobicity of the surfaces. The modified Cassie's equation,<sup>11</sup>

$$\cos \theta' = f \cos \theta - (1 - f) \quad (2)$$

in which  $f$  is the fraction of the solid/water interface, while  $(1 - f)$  is that of the air/water interface, indicates that, when a rough surface comes into contact with water, air trapping in the trough area may occur, which would contribute greatly to the increase of hydrophobicity. On the basis of these principles, intensive studies have been made to realize superhydrophobicity via constructing surface roughness.<sup>12,13</sup> The topographic structures have also been reported to greatly influence the dynamic wetting or dewetting properties of the solid surface.<sup>14</sup> It has been recognized that the cooperation between the surface chemical compositions and the topographic structures is crucial to construct special wettability, such as excellent anti-adhesion property, anisotropic dewetting, etc., on functional surfaces. In this Account, our recent progress in these fields will be reviewed.

This Account is organized into five sections. First, we will review the biomimetic research of special wettability in nature to stress the importance of the micro- and nanostructures. In the following two sections, some facile methods to construct superhydrophobicity on artificial surfaces will be introduced. Then, we will show that the combination of special surface structure and the responsive materials may result in the external stimuli-driven reversible switching between superhydrophilicity and superhydrophobicity. Subsequently, some successful applications will be reviewed.

## I. Structural Effect on Wettability—From Natural to Artificial

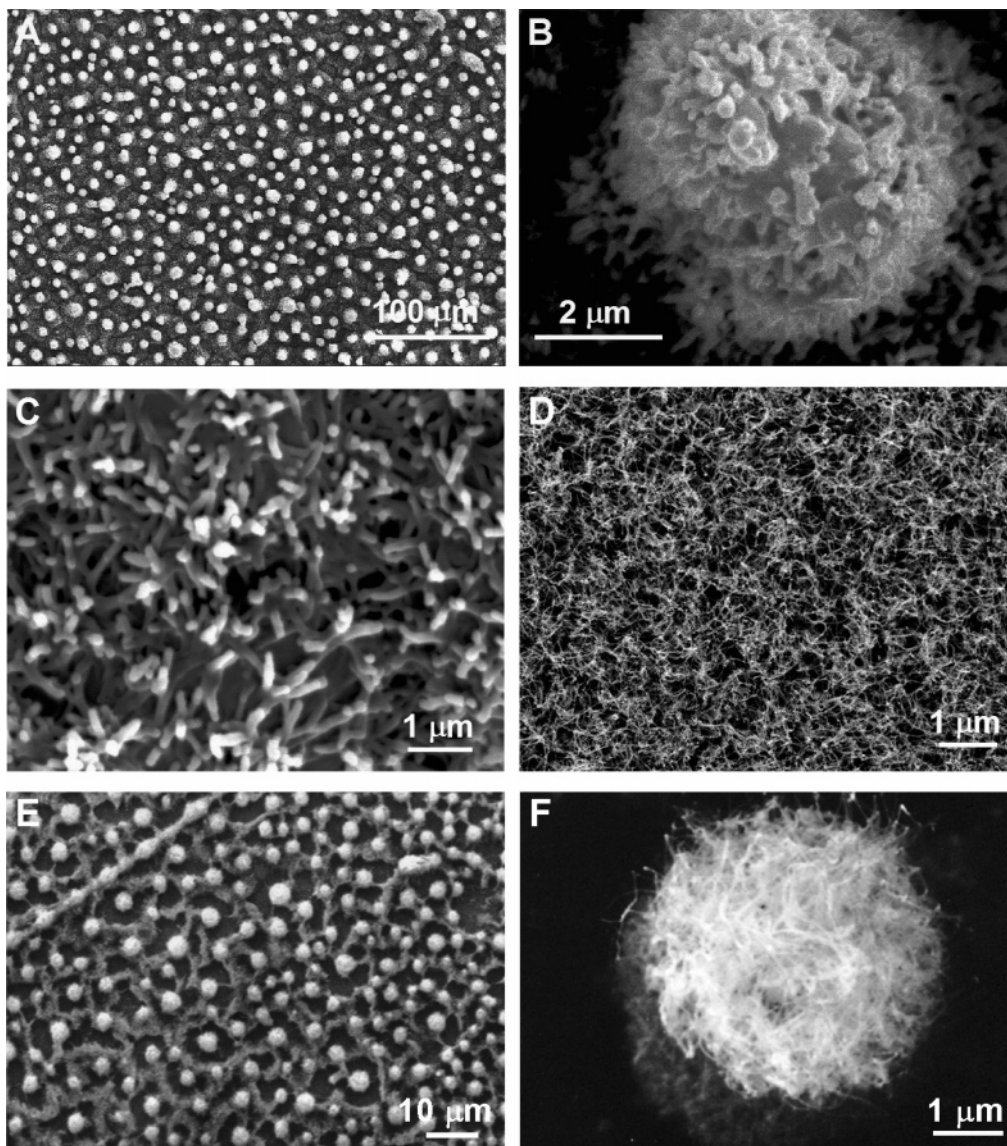
The special functionalities of organisms are usually not governed by the intrinsic property of materials but are more likely related to the unique micro- or nanostructures. It is also the case for the special wettability that has been frequently observed in nature.

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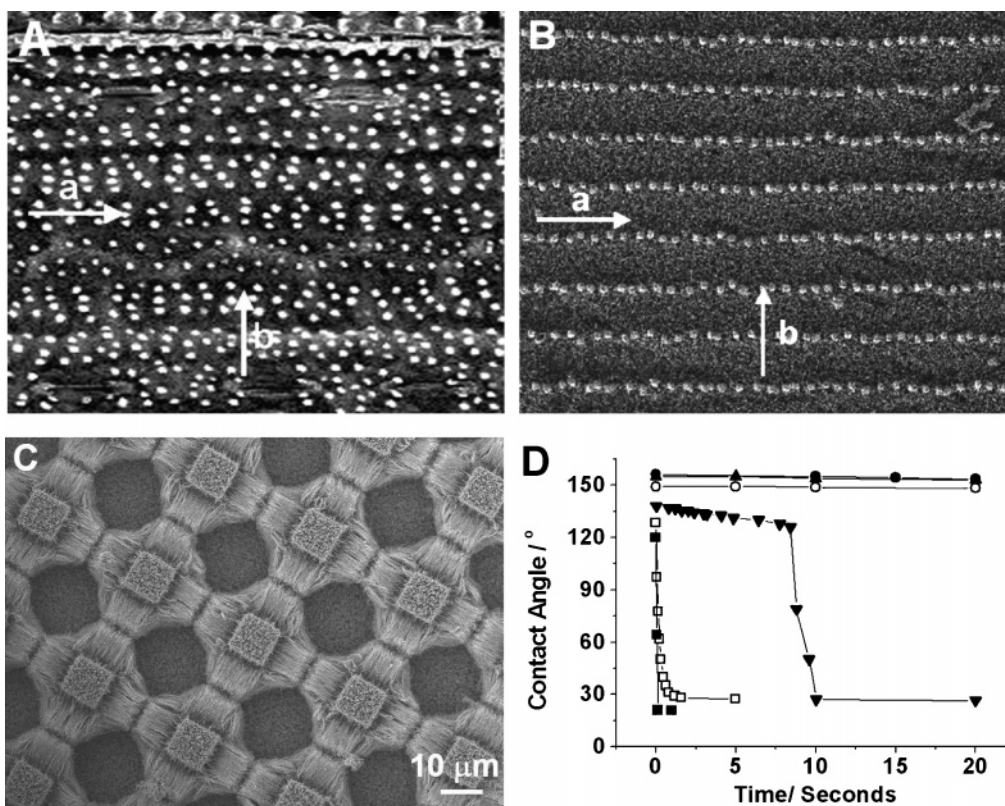
**FIGURE 1.** Micro- and nanostructures on the lotus leaf (*Nelumbo nucifera*) and their artificial simulation by ACNT film. (A) Large-scale SEM image of the lotus leaf. Every epidermal cell forms a papilla and has a dense layer of epicuticular waxes superimposed on it. (B) Magnified image on a single papilla of A. (C) SEM image on the lower surface of the lotus leaf. (D) SEM image of the densely packed ACNT film with pure nanostructure (top view). (E) Large-scale SEM image of lotus-like ACNT film. (F) Magnified image of a single papilla from E. Adapted from Feng et al.<sup>3</sup> and Li et al.<sup>17</sup>

**Hierarchical Micro- and Nanostructures and the Excellent Anti-adhesion to Water.** Lotus is well-known for the self-cleaning effect on its leaf, which shows a water CA as large as  $161.0 \pm 2.7^\circ$  and a SA as small as only about  $2^\circ$ . Such a superhydrophobicity and the excellent anti-adhesion capability are the origin of the self-cleaning effect. According to Barthlott and Neinhuis,<sup>15</sup> the large CA is based on the epicuticula wax and the micrometer-scale papillae structure on the leaf. The epicuticula wax provides the low surface free energy, and the micrometer-scale papillae structure brings a large extent of air trapping when contacting with water, which is essential for superhydrophobicity. However, numerical calculation indicates that the CA could only reach a maximum of about  $147^\circ$  according to this model, much smaller than the experimental value. Our recent research<sup>3</sup> revealed a novel finding of micro- and nanoscale hierarchical structures

on the leaf. The randomly distributed papillae (Figure 1A) with diameters ranging from 5 to  $9 \mu\text{m}$  were found to consist of further branch-like nanostructures (Figure 1B) with average diameters of  $124.3 \pm 3.2 \text{ nm}$ , which could also be observed on the lower part of the leaf (Figure 1C). Theoretical simulation<sup>3</sup> indicates that the CA may increase to about  $160^\circ$  after considering the contribution of the nanostructures, which is well-consistent with the experimental result.

The SA is defined as the critical angle by which the water drop begins to slide on the tilted surface that depends on the difference between the advancing and receding angles, which is also termed as CA hysteresis.<sup>16</sup> Small SA, as well as the large CA, comprises the two important criteria of good anti-adhesion property on the surface. To find the role of the hierarchical micro- and nanostructures on this property, a comparison between





**FIGURE 2.** Anisotropic structure and special wettability. (A) Anisotropic arrangement of micropapilla on rice leaf (*Oryza sativa*). (B) Rice-like ACNT film. (C) Typical SEM image for three-dimensional anisotropic ACNT films (pillar spacing = 20  $\mu\text{m}$ ). (D) Water spreading behaviors on films of C with pillar spacings ■, 6  $\mu\text{m}$ ; □, 10  $\mu\text{m}$ ; ●, 13  $\mu\text{m}$ ; ▲, 15  $\mu\text{m}$ ; ▼, 20  $\mu\text{m}$ , and on ○, flat silicon substrate. Adapted from Feng et al.<sup>3</sup> and Sun et al.<sup>21</sup>

aligned carbon nanotube (ACNT) films with and without hierarchical structures was made. The ACNT film with pure nanostructure (Figure 1D, top view) fabricated by the chemical vapor deposition (CVD) technique on silica substrate with homogeneous catalyst distribution is composed of multiwall carbon nanotubes that aligned almost normal to the substrate, the diameters of which range from about 15 to 50 nm. The CA on this film is as large as about  $158.5 \pm 1.5^\circ$ ,<sup>17</sup> however, the SA is higher than  $30^\circ$ , indicating a relatively large CA hysteresis and strong adhesion to water. The lotus-like ACNT film<sup>3</sup> was fabricated by the same CVD technique on a silica substrate with heterogeneous catalyst distribution. In Figure 1E, the micrometer-scale papillae are composed of a further nanostructure (Figure 1F) of the carbon nanotubes. The CA on its surface is about  $166^\circ$ , and the SA is as low as about  $3^\circ$ . Another honeycomblike ACNT film<sup>18,19</sup> with hierarchical structure was also fabricated based on the capillary effect between ACNTs. It also exhibits a large CA of about  $163^\circ$  and a small SA of less than  $5^\circ$ . The comparison between these films indicates that the hierarchical structures would not only further improve the hydrophobicity of the films but also bring small SA. These results are well-consistent with the theoretical analysis proposed by Marmur<sup>20</sup> that such structures may efficiently reduce the concrete contact between water drop and the surface and the triple contact line of water, solid, and air and greatly impact its contour and continuity, which are important factors influencing the SA.<sup>2,12,20</sup>

**Effect of Anisotropic Arrangement of Microstructure on Wettability.** The anisotropic surface structure also has great influence on wettability. One example is the anisotropic dewetting phenomenon on the rice leaf.<sup>3</sup> The scanning electron microscopic (SEM) image (Figure 2A) indicates a hierarchical structure on its surface that is similar to the lotus leaf. Accordingly, the surface is superhydrophobic. However, differently, the papillae are arranged in one-dimensional order parallel to the edge of the leaf (arrow a). The water drop can roll off freely along this direction but moves much harder along the perpendicular one (arrow b). The SAs in these two directions are  $\sim 3\text{--}5^\circ$  and  $\sim 9\text{--}15^\circ$ , respectively. Such a phenomenon is also considered to be relevant to the triple contact line. For the rice leaf, it is greatly influenced by the anisotropic arrangement of the papillae, while it is the same in all direction on the lotus leaf because of the homogeneous distribution of papillae. To mimic this phenomenon, we<sup>3</sup> prepared a rice-like ACNT film (Figure 2B) by controlling the surface distribution of catalyst, on which the microscale ACNT arrays were patterned with different spacings in the mutually orthogonal directions. The anisotropic dewetting phenomenon was also observed on such a film.

The above results show the great influence of the two-dimensional anisotropic arrangement of surface structure on wettability. It can be anticipated that the three-dimensional anisotropic structure may also exhibit an interesting effect on wettability. To verify this idea, a kind

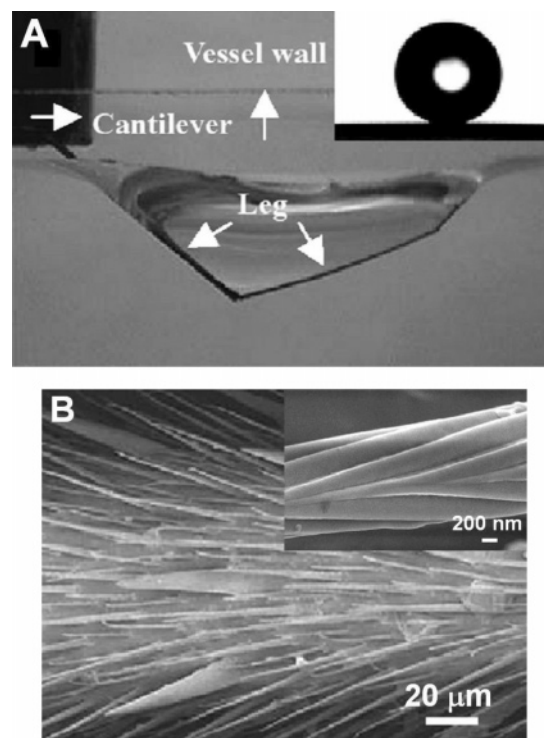
of three-dimensional anisotropic ACNT film<sup>21</sup> was prepared from a structured silicon substrate with well-defined quadrate pillar arrays. They show a periodic pattern with a mutually orthogonal microstructure composed of horizontal and vertical ACNT arrays (Figure 2C). Interestingly, the wettability and the spreading behaviors of the water drop rely very much on the spacing between the pillars of the substrate. When the spacing is small, the water drop may rapidly spread out on the film to reach a very hydrophilic state ( $CA < 30^\circ$ ) (Figure 2D). When the spacing is large, the water drop can stand on the film for several seconds before its rapid spreading. While for the medium spacing, the film is superhydrophobic. It indicates that the wettability can be switched from very hydrophilic to superhydrophobic by simply adjusting the structural parameter without alteration of the surface free energy, which is unusual according to eqs 1 and 2. Further research indicates that the horizontal ACNT arrays may act as hydrophilic components and help water to spread, while the vertical ones act as the superhydrophobic components. The different arrangement of these components is considered to be the origin of the above-mentioned effect.

The anisotropic dewetting property and the wettability switching induced by the two- and three-dimensional anisotropic structures may bring interesting insights to design novel microfluidic devices. For example, the lossless liquid transportation channels and novel microfluidic valves may be fabricated in this light.

**Striking Superhydrophobic Force on Water Strider's Leg.**<sup>22</sup> Water striders are remarkable in their nonwetting legs standing effortlessly and walking quickly on water, which is the result of the striking superhydrophobic force provided by their legs.

The force-displacement curves of the striders' legs pressing on the water surface indicate that the leg does not pierce the water surface until a dimple of  $4.38 \pm 0.02$  mm depth is formed (Figure 3A). The maximal supporting force of a single leg reaches up to 152 dynes, that is, about 15 times the total body weight of a water strider. This striking repellent force is attributed to the superhydrophobicity on the legs, which is verified by a static CA of about  $167.6 \pm 4.4^\circ$ . SEM observation indicates that there are numerous oriented micrometer-scale needle-shaped setae on the legs (Figure 3B), which are arranged at an inclined angle of about  $20^\circ$  from the surface. Interestingly, many elaborate nanoscale grooves are found on each microseta to form the unique hierarchical structure (inset of Figure 3B). Such a hierarchical structure is considered to be the origin of the superhydrophobicity and the striking repellent force on water strider's legs, which may shed light on applications of microfluidics and an aquatic robot.

In summary, biomimetic research on wettability of plant leaves and insects reveals the importance of surface micro- and nanostructures on the special wettability. Hierarchical micro- and nanostructures are essential for superhydrophobic surfaces with both large CA and small SA. The arrangement of microarrays may not only lead to



**FIGURE 3.** The nonwetting leg of water strider (*Gerris remigis*). (A) Typical side views of the maximal dimple just before the leg pierces the water surface. (Inset) Water droplet with CA of  $167.6 \pm 4.4^\circ$  on a leg. (B) SEM image of the leg with numerous oriented spindly microsetae. (Inset) Nanoscale groove structure on a seta. Adapted from Gao et al.<sup>22</sup>

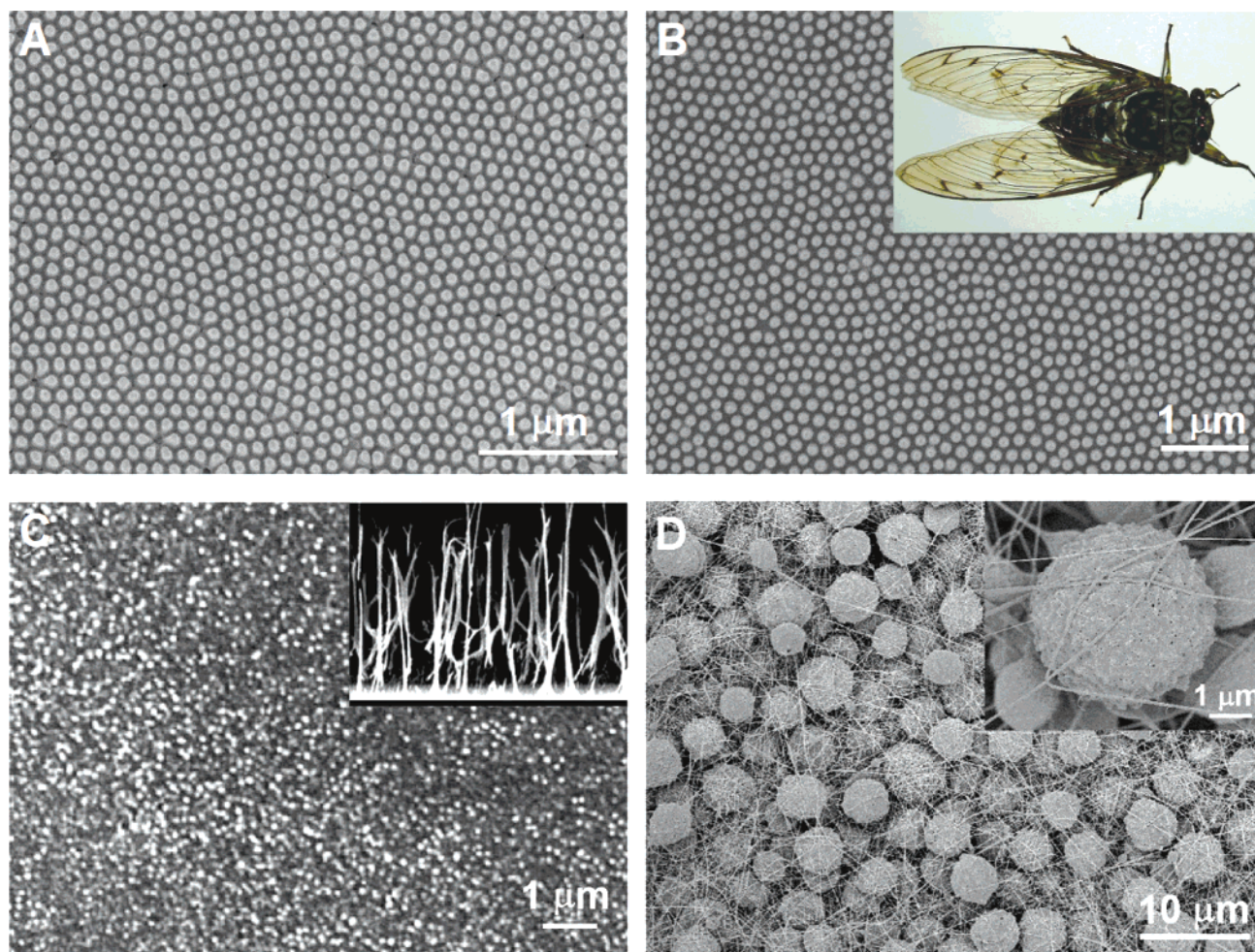
anisotropic dewetting but also bring better controllability of the wettability. Moreover, the directional arrangement of the needlelike microstructure with further nanoscale grooves can greatly influence the hydrodynamics and bring super-repellent force to water.

It indicates from the study of the lotus leaf that the superhydrophobic surfaces can be conveniently fabricated through cooperation between the micro- and nanostructures and the surface chemical compositions of low free energy. On the basis of this recognition, it can be inferred that there are two approaches to realize superhydrophobicity on artificial surfaces: one is to construct a special surface structure on hydrophobic materials, and the other is to modify a preformed structured surface by materials with low free energy, which will be further demonstrated in the following two sections.

## II. Creating Superhydrophobicity through Constructing Surface Structure

To realize superhydrophobicity from different materials, many elegant methods have been developed to construct micro- and nanostructures on them, such as laser ablation and photolithography-based microfabrication,<sup>23–25</sup> solidification of melted alkylketene dimer,<sup>12</sup> microwave plasma-enhanced CVD of trimethoxymethoxysilane,<sup>26</sup> phase separation,<sup>13</sup> domain-selective oxygen plasma treatment,<sup>27</sup> sol-gel method,<sup>28</sup> and so on. Polymers have been widely utilized in our daily life and in industrial applications. They can be easily processed and have good plasticity or





**FIGURE 4.** SEM images for superhydrophobic polymer films with special micro- and nanostructures. (A) Polymer film with well-patterned nanopillar structure. (B) Nanostructure on the superhydrophobic wings of cicada (*Cicada orni*). (Inset) Cicada (*Cicada orni*). (C) Aligned PAN nanofiber film (top view). (Inset) Side view. (D) PS film with microsphere/nanofiber composite structure. Adapted from Guo et al.,<sup>29</sup> Feng et al.,<sup>31</sup> and Jiang et al.<sup>36</sup>

fluidity after being heated or dissolved. Thus, various facile methods can be used to build micro- and nanostructures on their surfaces. In this section, we will give some examples to show that superhydrophobicity on polymer surfaces can be conveniently realized by these approaches.

A template-based “rolling press” technique<sup>29</sup> was developed to create well-patterned nanopillars on polymer surface. A tubular porous alumina was used as the template and rolled on the polymer surface applying a pressure of several hundred thousand Pa and a temperature above the glass transition point of the polymer. In this process, the polymer will become intercalated and enter the nanopores on the template because of the pressure. Thus, a well-aligned and hexagonally arranged nanopillar array (Figure 4A) will be generated on the polymer surface. It is worthy to note that the as-prepared surface shows remarkable structural similarity with the wings of cicada (Figure 4B), which makes them superhydrophobic and nonwetted by dew and rains and uncontaminated by the dust.<sup>30</sup> As a result, the hydrophobicity of the polymers is greatly enhanced and increases with decreasing size of the nanopillars. For a weakly hydrophilic polymer, polycarbonate (PC), the CA on the as-

prepared film can reach about  $145.6 \pm 1.6^\circ$  when the size of the nanopillars is as small as  $28.3 \pm 2.1$  nm, although it is only about  $85.7 \pm 0.8^\circ$  on a flat surface. However, it is hard to obtain a larger CA by this method when the nanopillar size decreases further, because the height of the nanopillars is relatively low (50–200 nm), which is insufficient to bring a large proportion of air.

To solve this problem, we developed another template-based extrusion technique to fabricate aligned polyacrylonitrile (PAN) nanofiber film, in which only extrusion of the PAN precursor solution into the solidifying solution under pressure is necessary.<sup>31</sup> The nanostructure (Figure 4C) of the as-prepared film is similar to that of the densely packed multiwall ACNT film (Figure 1D) but has much lower density, and their height is relatively very large (higher than  $10 \mu\text{m}$ ), which may bring a very large proportion of air trapping in the surface. As a result, although the intrinsic CA on the flat PAN surface is only about  $100.8 \pm 0.6^\circ$ , the CA on the as-prepared film is as high as  $173.8 \pm 1.8^\circ$ . On the basis of this technique, we have also reported a nanostructured carbon fiber film,<sup>32</sup> which may exhibit superhydrophobicity for not only pure water but also corrosive liquids, such as strong acidic (pH

$\sim 1$ ) and basic solutions (pH  $\sim 14$ ), and a superhydrophobic aligned poly(vinyl alcohol) (PVA) film,<sup>33</sup> although the bulk PVA is very hydrophilic (CA on flat surface =  $72.1 \pm 1.1^\circ$ ), which validates the theoretical anticipation proposed by Herminghaus<sup>34</sup> that a super water-repellent surface can be constructed from a hydrophilic material.

The porous structure on polymer surface can be conveniently fabricated utilizing the difference in solubility<sup>13</sup> of different polymers. On the basis of this idea, we prepared a composite porous polymer film by a one-step cast-coating process.<sup>35</sup> SEM images indicate a lotus-like hierarchical structure, that is, every micropapilla (300–700 nm) is covered by nanopapilla ranging from 30 to 40 nm. As a result, the film shows superhydrophobicity with a large CA of about  $166^\circ$  and a small SA of about  $3.4 \pm 2.0^\circ$ .

The electrohydrodynamic technique has proven to be a versatile and effective method for manufacturing micro- to nanoscale fibers or particles from a wide variety of materials. We have reported a porous microsphere/nanofiber composite polystyrene film (Figure 4D) by using this technique.<sup>36</sup> It also shows superhydrophobicity with a large CA of about  $160.5^\circ$ .

### III. Surface Modification<sup>37</sup> Induced Superhydrophobicity

The self-assembly technique provides a promising approach to modify the solid surfaces chemically, which can be conveniently used to adjust the surface free energy. In this section, we show that we can not only obtain superhydrophobicity but also adjust the wettability from superhydrophilic to superhydrophobic through the modification of organic molecules on the preformed structured surfaces by this technique.

We used an electrochemical deposition method to deposit Au clusters on conductive ITO glass substrate modified with polyelectrolyte multilayer.<sup>38</sup> The clusters exhibit an interesting dendritic structure with nanoscale protuberances, which is a typical hierarchical lotus-like structure. Although the as-prepared film is very hydrophilic, it exhibits superhydrophobicity after being immersed in an ethanol solution of *n*-dodecanethiol. The reason is that the self-assembly of *n*-dodecanethiol on Au clusters may largely decrease their surface free energy. The CA on such a surface is about  $156^\circ$ . It changes to a larger value of  $\sim 173^\circ$  after a 40 min exposure to ambient atmosphere, indicating a good stability of the superhydrophobicity. Similar to the lotus leaf, such surface also shows a small SA of about  $1.5^\circ$ . Such a good anti-adhesion to water is of great significance in metal surface protection.

This method has also been applied on metal oxide and other materials. For example, we<sup>39</sup> prepared a porous conductive ZnO film through a typical cathodic electrodeposition process. The as-prepared film is hydrophobic with a water CA of about  $128^\circ$ . While interestingly, after modification with fluoroalkylsilane, a compound with low

free energy, by the self-assembly technique, the film shows superhydrophobicity with a CA of about  $152^\circ$ .

To gain better control over the wettability on metal surfaces, we<sup>40</sup> used a series of *n*-alkanoic acids with different chain length to modify the copper films to adjust their surface free energy. On flat films, the CA may change from about  $68^\circ$  to  $113^\circ$  with the increase of chain length for the *n*-alkanoic acids, while on rough ones, it may change from about  $0^\circ$  to  $157^\circ$ , indicating that the wettability on copper films can be well-controlled from superhydrophilic to superhydrophobic through the cooperation of surface roughness and the different chemical modification.

The above work shows that the wettability on the rough surfaces can be controlled in a large extent by adjusting their surface free energy. In this way, the surfaces can be not only superhydrophobic but also superhydrophilic depending on the chemical compositions on them.

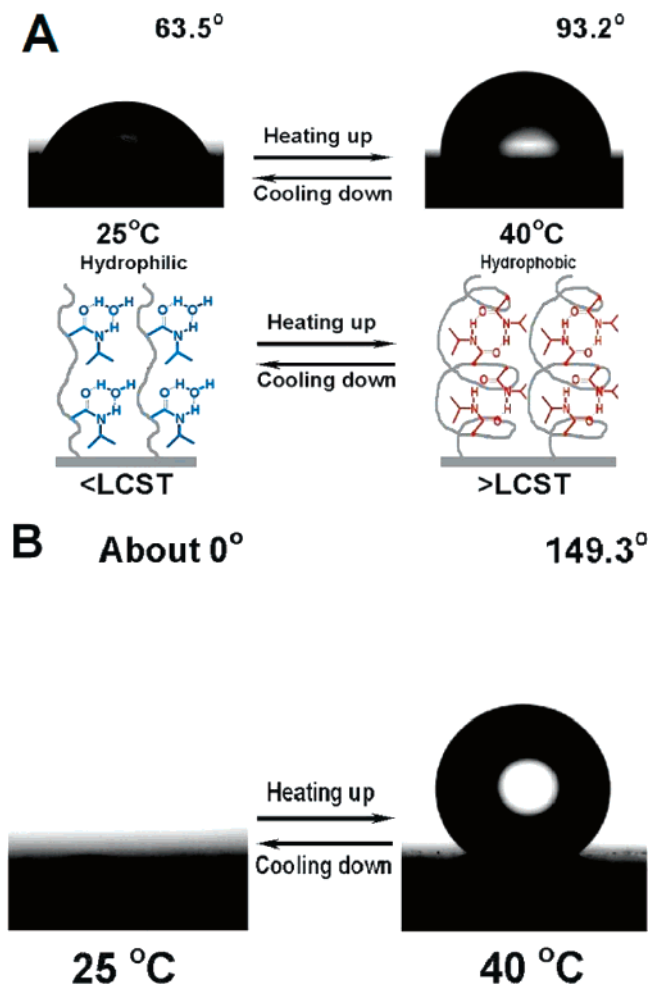
### IV. Responsive Switching between Superhydrophilicity and Superhydrophobicity

Stimuli-responsive materials<sup>41</sup> make it possible to alter the surface chemical property and control the wettability reversibly, which has been realized by various methods including light irradiation,<sup>42,43</sup> electric field,<sup>44</sup> thermal treatment,<sup>45</sup> solvent treatment,<sup>46</sup> and so on. However, the responsive wettability is usually very limited. For example, the photosensitive wettability transition can be obtained on the azobenzene polymer-coated surfaces, while the reported maximum CA change is only about  $11 \pm 1^\circ$ .<sup>43</sup>

As anticipated by Wenzel's (eq 1) and Cassie's equations (eq 2), both the hydrophilicity on hydrophilic surfaces and the hydrophobicity on hydrophobic surfaces can be greatly enhanced by the surface roughness. Therefore, for a stimuli-responsive surface, the responsive wettability may be amplified by introducing surface roughness, which provides an opportunity to realize reversible switching between superhydrophilicity and superhydrophobicity.

We<sup>47</sup> selected the poly(*N*-isopropylacrylamide) (PNIPAAm),<sup>48</sup> an excellent thermal responsive polymer, modified surface to verify this idea. On the flat substrate, the CA can change from about  $63^\circ$  to  $93^\circ$  (upper part in Figure 5A) when the temperature is elevated from 25 to 40 °C, which is the result of the competition between the intra- and intermolecular hydrogen bonding below and above the lower critical solution temperature (LCST) of about 32–33 °C (lower part in Figure 6A). However interestingly, on the rough substrate, both the hydrophilicity under low temperatures and hydrophobicity under high temperatures increase with the increase of the roughness. When the roughness is large enough, the CA can reach a value of about  $149.3^\circ$  at high temperatures, while at low temperatures, the CA becomes about  $0^\circ$ , indicating that the temperature-triggered switching between superhydrophilicity and superhydrophobicity (Figure 5B) has been realized. Such a kind of amplified temperature-responsive

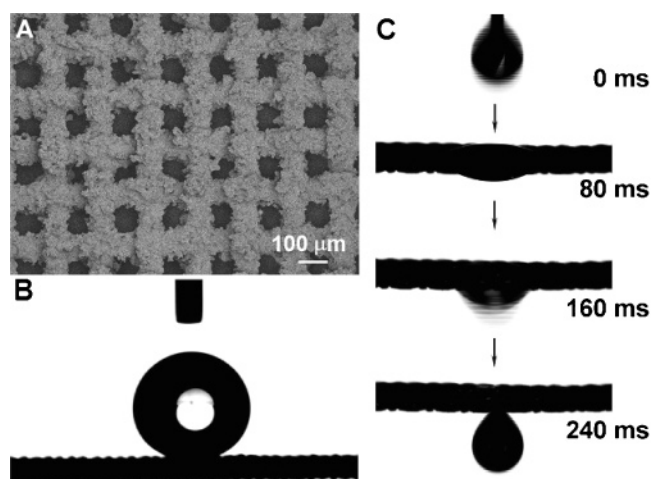




**FIGURE 5.** Responsive switching between superhydrophilicity and superhydrophobicity. (A) Schematic diagram of reversible competition between inter- and intramolecular hydrogen bonding in PNIPAAm chains (lower part), which is the molecular mechanism of the temperature responsive switching on PNIPAAm film. The upper part is the corresponding water drop profiles on a flat surface. (B) Water drop profiles for thermally responsive switching between superhydrophilicity and superhydrophobicity on a rough surface. Adapted from Sun et al.<sup>47</sup>

wettability has also been reported on a PNIPAAm-modified nanostructured substrate of anodic alumina.<sup>49</sup>

Similar effects can be observed in the amplified electrowetting phenomenon on the nanostructured surface, which can be tunable from nearly superhydrophilic to superhydrophobic.<sup>50</sup> On the basis of this effect, we have also reported an aligned<sup>51</sup> ZnO nanorod and a porous<sup>52</sup> ZnO film, on which reversible switching between superhydrophilicity and superhydrophobicity can be obtained by UV irradiation and dark storage or heat treatment. The films are originally superhydrophobic, while after a period of UV irradiation, the water can spread over the surfaces to show a CA of about 0°, and after being stored in darkness for some days or heated for several minutes, the superhydrophobicity may be restored. In this case, the reversible generation and annihilation of the photogenerated surface oxygen vacancies<sup>53</sup> bring the change of the surface free energy, which may result in the alteration of



**FIGURE 6.** PTFE-coated copper mesh and its extreme wettability responses for water and oil. (A) SEM image of the coated mesh. (B) Shape of a water drop on the mesh. (C) Quick penetrating process of oil drop. Adapted from Feng et al.<sup>52</sup>

wettability, and the surface topographic structures enhance this effect.

## V. Successful Applications of Special Wettability

The potential application value of the special wettability is vast. A successful example is the application of the superhydrophobic technique in the field of oil/water separation.<sup>54</sup> We prepared a novel poly(tetrafluoroethylene)-coated mesh (Figure 6A) by a facile and inexpensive spray-and-dry method. The film shows extremely contrary wettability to water and oil. Figure 6B shows the shape of the water droplet on the as-prepared mesh film. The CA in this case is  $156.2 \pm 2.8^\circ$ , indicating that it is superhydrophobic. Moreover, the water SA on this film is only about 4°, showing a good anti-adhesion to water. However, when an oil droplet is dropped onto the film, it spreads out rapidly to reach a CA of about 0° and then penetrates thoroughly in about 240 ms (Figure 6C). These extremely contrary wettabilities enable the possibility to separate water and oil efficiently. When a mixture of oil and water is put on the mesh film, the water will remain on the upper part of the film, while the oil will gather together and penetrate through the film, which can be collected in the container below it.

The superhydrophilicity has been applied in polymer filter films. For example, the filtration efficiency of the original polypropylene (PP) filter is poor because of the hydrophobic nature of the material. We realized superhydrophilicity and the rapid wetting properties on this film through surface chemical modification and constructing a further nanosized topographic structure without changing the average pore size. In this way, the filtration efficiency has been largely improved, and the filter may serve as an ultrafilter.

The rapid spreading of water is very important in various applications. It can also be realized by controlling a special topographic structure. For example, on a microfiber/nanoparticle composite nonwoven mat, we have



obtained the ultrafast wetting property, in which the water drop might rapidly spread to show superhydrophobicity within even 15 ms. This technique may be utilized in some special applications, such as papers in ink-jet printing. In addition, the highly water-adsorbent materials that may be applied in diapers and napkins may also be fabricated in this light.

In textile applications, amphiphilicity may bring good comfortableness, perspiration property, and permeability, and the hydrophilic treatment may improve the coloration property and the color fastness of fabrics. It has been successfully utilized in woolen, PP fiber textiles and so on. The nanostructure has also been combined onto some cloths to realize superhydrophobic fabrics, such as a self-cleaning necktie<sup>55</sup> and shirt, which possess super water-repellent and self-cleaning effects that may make them wash-free. These new functionalities may bring great convenience in daily life and provide a high additional value to the products.

## Conclusion and Outlook

Learning from nature gives us inspirations to construct special wettability on functional surfaces through generating topographic structures. Hierarchical micro- and nanostructures are necessary for superhydrophobic surfaces with both large CA and small SA, which are the origin of the self-cleaning effect. The special arrangement of the micro- and nanostructures may not only result in anisotropic wetting or dewetting properties but also bring better control over the wettability. The directional arrangement of needlelike microstructure with further nanoscale grooves may greatly influence the hydrodynamics and bring a super-repellent force to water. Artificial superhydrophobic surfaces can be conveniently fabricated through the cooperation of the surface structures and chemical compositions, which can be realized in two approaches: constructing micro- or nanostructures on hydrophobic materials and modifying the preformed structured surfaces with molecules of low free energy. Combining special topographic structures onto functional surfaces with responsive wettability may result in a remarkably amplified responsive wettability and give an opportunity to realize responsive switching between superhydrophilicity and superhydrophobicity.

The structural effects on wettability may not be restricted in the aspects as described above. The biomimetic research of special wettability in nature may give us more inspirations, which is one of the goals in our future work. On the other hand, the application of the special wettability is also very important. In the future, we will further our research work in this aspect and mainly focus on microfluidics<sup>56</sup> and biological and biomedical domains.<sup>57</sup>

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