

## Superhydrophobicity from microstructured surface

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**Abstract** Superhydrophobicity is referred to the wettability of a solid surface which has a water apparent contact angle greater than  $150^\circ$ . It has attracted great interest in both fundamental researches and practical applications. This paper discusses two models: Wenzel model and Cassie model, to describe the superhydrophobic states of surface. The effects of surface morphology and microstructure on superhydrophobicity are discussed, and the internal relationship between Wenzel and Cassie states is presented. These two superhydrophobic states can coexist and they present different properties on contact angle hysteresis. It is reported that the irreversible transition can be realized from Cassie state to Wenzel state under some certain conditions. This paper also gives a review of recent progresses in the strategies of fabricating superhydrophobic surfaces by designing microstructured or microtextured surfaces. Finally, the fundamental research and applications of superhydrophobic surfaces are prospected.

**Keywords:** microstructured surface, self-cleaning, contact angle, superhydrophobicity, roughness.

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Surface wettability, as one of the most essential properties of solid surface, is a very common interface phenomenon in our daily life and nature. It takes place in a variety of activities of all creatures in nature, and also plays a key role in our daily life and industrial and agricultural applications. Surface wettability can be measured by contact angle (CA). Basically, surface with a CA of water lower than  $90^\circ$  can be called a hydrophilic surface, while the CA of a hydrophobic surface is greater than  $90^\circ$ . Recently, with the continuous developments of micro/nano-technologies, people learned much about state-of-the-art microstructures from natural materials, and are trying to find out approaches to mimic these natural mate-

rials<sup>[1,2]</sup>. Moreover, the demands of surface functional materials are also motivation to explore the physical and chemical mechanisms of materials properties at micro-or nano-scale. In this paper, we will review the recent progresses in superhydrophobic surfaces and fabricating strategies of artificial superhydrophobic surfaces on the basis of controlled surface microstructures.

The key advances in the understanding and fabrication of surfaces with controlled wetting properties are about to make the dream of a contamination-free (or self-cleaning) surface come true<sup>[3]</sup>. Self-cleaning surface usually can be gained by two routes: super-hydrophilic surface and super-hydrophobic surface. Wang et al.<sup>[4]</sup> utilize ultraviolet irradiation for inducement to obtain a superhydrophilic  $\text{TiO}_2$  surface with contact angle approaching  $0^\circ$ . This material has already been used successfully for anti-fogging and self-cleaning transparent coating<sup>[5]</sup>. The mechanism lies in liquid drops can spread to form liquid film on the high-energy surface, and then the flowing liquid film carries the contaminants along. Meanwhile, when scientists observed the surfaces of some animals and plants in the nature<sup>[6]</sup>, they found that it is more prevalent to gain self-cleaning function by forming superhydrophobic surfaces. The representative surfaces are some plant leaves, (e.g. lotus leaves<sup>[7]</sup>) the wings of many Lepidoptera insects (e.g. butterfly), and many waterfowls' feathers. That is the hint from the nature! The researches revealed that the microscale roughness of these surfaces is more important rather than their hydrophobic chemical components. A double structured surface on the lotus leaves can be observed under the electron microscope: cells (microstructure) and wax crystals (nanostructure) (Fig. 1). Powders on the butterfly wings are composed of about 100 micrometers flat saccular particles, which are made up of several symmetric chitins and are not smooth. That is why the butterflies have charming color (structural color) and good hydrophobicity<sup>[8]</sup>. Feathers of waterfowls also have regular compact arrayed structures in microscale or sub-microscale, which can make them porous and superhydrophobic. ♦

Wettability of solid surface is governed by the chemical properties and the microstructures of the surface. It is well known that wettability is mainly determined by its interfacial free energy ( $\sigma_{\text{SG}}$ ). The greater, the free energy of surface, the easier, the liquid can spread upon, and

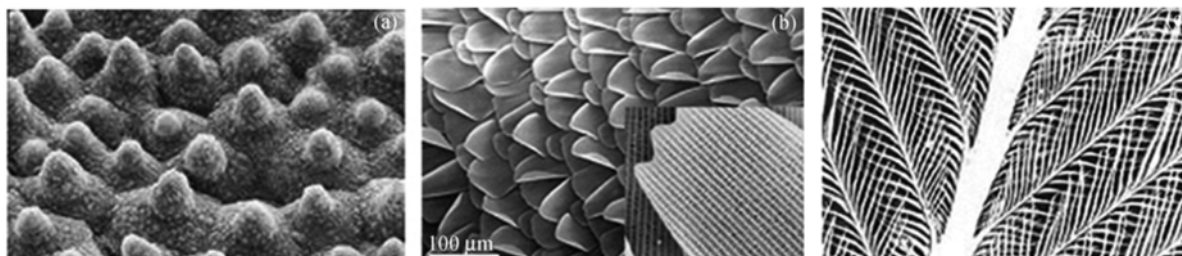


Fig. 1. Microstructures of several biologic surfaces. (a) Lotus leaf, (b) butterfly's wing, (c) waterfowls' feather.

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vice versa. At this point, materials with high (low) surface free energy are the candidates for the substrate to create superhydrophilic (superhydrophobic) surfaces. High surface free energy materials, such as metals and metal oxides, are generally used to make the superhydrophilic surfaces. The superhydrophobic surfaces are usually designed with low surface free energy materials, such as fluorinated or alkylated compounds. However, the chemical modification of flat surface can typically lead to a water contact angle of up to  $120^\circ$ <sup>[3]</sup>. To reach the extra values of the contact angles near  $180^\circ$ , a second strategy has to be employed: surface construction. Microstructures on the surfaces (smaller than droplet) can dramatically enhance the hydrophobicity (hydrophilicity) of hydrophobic (hydrophilic) surfaces. This observation was noticed early in the last century, and some mathematical models of various complexities were devised to explain it. Due to the complicated situations and lack of abundant experimental data, there still exist some deficiencies and inconsistency in both theoretical and experimental results. Therefore, this observation has been forgotten or ignored for several times by scientists. With the progress of technologies, the advanced surface techniques, such as laser micromachining, photolithography, and plasma etching, allow people to construct solid surface with designated microstructure or microtexture. This makes it possible to study the inherent principles between the surface morphology and wettability. Meanwhile, rough surfaces can also be applied to obtaining superhydrophilic surfaces (for CA, less than  $5^\circ$ ) with the similar mechanism superhydrophilicity works by. Normally, the CA of a well-hydrated flat silicious surface can reach less than 5 degree, at this point, the rough effect on hydrophilicity is not as significant as that of hydrophobicity. In this paper, we will only focus on the superhydrophobic surfaces enhanced by roughness.

In 1936, Wenzel<sup>[9]</sup> firstly studied the superhydrophobic surfaces. Cassie and Baxter<sup>[10]</sup> also presented the theoretical hypothesis of superhydrophobic surfaces in studying fabrics and feathers of waterfowls. In 1996, Kao Company prepared the fractal rough surface by AKD (alkylketene dimmer) on glass, yielded a contact angle of  $174^\circ$  for water<sup>[11]</sup>. This is the first experiment to produce artificial superhydrophobic surface by chemical method via creating surface topography. From then on, the study of superhydrophobic (self-cleaning) surfaces stepped into a new era. Conventionally, superhydrophobic surfaces can be produced mainly in two ways. One is to create a rough structure on a hydrophobic substrate, and the other is to modify a rough surface with low surface free energy materials. Additionally, surface microstructures also affect the adhesive properties, friction<sup>[12]</sup> and wear behavior, and lubrication capabilities. Recently, more and more studies focus on microstructured surfaces with superhydrophobic or self-cleaning properties. However, to produce superhydrophobic surfaces with required wettability, self-cleaning,

desired mechanical strength and longevity, is still a challenge for us. There is much room for research of the physical mechanism and fabrication of superhydrophobic surface.

### 1 Shape analyses of drop on a microstructured surface

The basic law governing the equilibrium of a liquid drop on a surface was formulated by Thomas Young. The drop is shaped by the resultant forces pulling at the three-phase contact line of the drop, where the solid/liquid, liquid/gas and solid/gas interfaces meet, in the plane of the solid (Fig. 2)<sup>[13]</sup>. The forces (per unit length) acting at this line are the surface tensions, and their balance yields the famous equation bearing Young's name,

$$\sigma_{SG} = \sigma_{SL} + \sigma_{LG} \cos \theta_e, \quad (1)$$

where  $\sigma_{SG}$ ,  $\sigma_{SL}$  and  $\sigma_{LG}$  are the solid/gas, solid/liquid and liquid/gas surface tensions, respectively. According to Taylor's depiction<sup>[14]</sup> about liquid droplet shape on solid surface, the droplet's height  $h = 2a \sin(\theta^*/2)$ , wherein  $a$  is the capillary length ( $a = (\sigma/\rho g)^{1/2}$ ,  $\sigma$ , the liquid surface tension and  $\rho$ , its density,  $a = 2.7$  mm for water). It shows that gravity  $g$  can affect drop shape besides the three phase forces. Only if drop is small enough that the effect of gravity is negligible, which typically is the case for drops of millimeter size down to micrometers, the drop will have the shape of spherical cap and the liquid/gas interface meets the solid surface at an angle  $\theta_e$ , which is the so-called intrinsic contact angle of a flat surface.

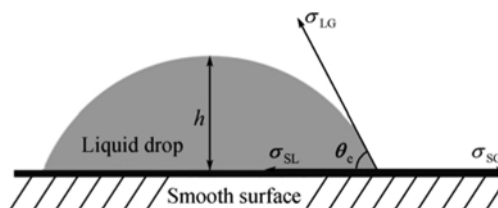


Fig. 2. Shape of droplet on the smooth surface.

(i) Wenzel model. As mentioned before, the existence of microstructure on the surface can change the wettability of a solid surface. There is a difference between the apparent contact angle and the intrinsic contact angle. For instance, surface microstructure can allow the surface with an intrinsic contact angle of  $100^\circ$ — $120^\circ$  to own an apparent contact angle of  $160^\circ$ — $175^\circ$ , or even greater. Such values of CA cannot be achieved if only utilizing chemical modification on the flat surface. To explain this phenomenon, Wenzel considered that roughness would increase the real contact area of liquid/solid more greatly than macroscale apparent contact area, which geometrically enhances hydrophobicity. He assumed that the liquid filled up the grooves on the rough surfaces (Fig. 3), and it could be referred to as the wetted contact (or wicked contact) with the rough surface, where the surface free energy is

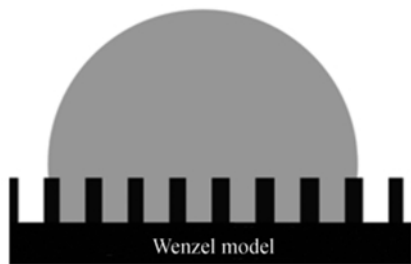


Fig. 3. Scheme of Wenzel model.

$$dG = r(\sigma_{SL} - \sigma_{SG})dx + \sigma_{LG}dx \cos \theta^*, \quad (2)$$

where  $dG$  is the energy needed for the three-phases line move  $dx$  distance,  $dG = 0$  at equilibrium, which yields the relationship between apparent contact angle  $\theta^*$  and the intrinsic contact angle  $\theta_e$ :

$$\cos \theta^* = r \cos \theta_e, \quad (3)$$

where  $r$  is the ratio of the actual area over the apparent surface area of the substrate ( $r \geq 1$ ). From Fig. 4, which shows the variation trend of  $\cos \theta^*$  versus  $\cos \theta_e$ , we can learn that the slope of the line is  $r$ . Because  $r \geq 1$ , roughness can make hydrophobic surfaces more hydrophobic ( $\cos \theta^* < \cos \theta_e$ ), and hydrophilic surfaces more hydrophilic ( $\cos \theta^* > \cos \theta_e$ ). When the intrinsic contact angle  $\theta_e > \cos^{-1}(-1/r)$  or  $\theta_e < \cos^{-1}(1/r)$ , the apparent contact angle will be  $180^\circ$  or  $0^\circ$ , respectively, which are denoted by the leftmost and rightmost lines in Fig. 4. The experimental results of the Kao group<sup>[11]</sup> are shown in Fig. 5. Three regions can be observed. First of all, most data fit the Wenzel linear equation nicely, which implies that surface roughness has a significant impact on the apparent contact angle. Secondly, while the substrates turns highly hydrophilic, the resulting data do not locate on the line  $\cos \theta^* = 1$ , which conflicts with Wenzel's prediction. As a matter of fact, in this region,  $\cos \theta^*$  obeys a linear increasing with  $\cos \theta$  with a smaller slope than  $r$ . Complete

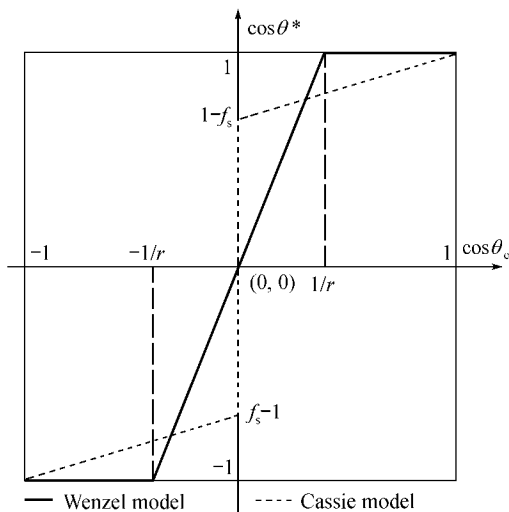


Fig. 4. Sketch of  $\cos \theta^*$  versus  $\cos \theta_e$  for two models.

wetting ( $\theta^* = 0$ ) is reached only if the substrate itself becomes completely wettable ( $\theta = 0$ ). For highly hydrophobic states, unfortunately, due to the practical difficulty of fabrication of "rough" surface at earlier time, very few data are available in the region. We complement these data obtained in recent publications, and denoted with triangle as shown in Fig. 5<sup>[11,15]</sup>.

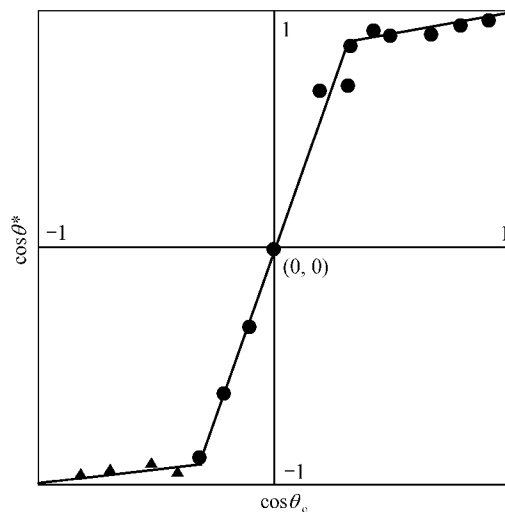


Fig. 5. Experimental results of the Kao group,  $\cos \theta^*$  is measured as a function of  $\cos \theta_e$ .

(ii) Cassie model. After Cassie and Baxter studied abundant superhydrophobicity in nature, they put forward a concept of composite contact. It is assumed that the liquid forms composite surfaces on the rough substrate (Fig. 6), i.e. if the microstructured surface is hydrophobic enough, the liquid does not fill the grooves on the rough surface and the droplet is just sitting on the air and protruded surface. In this case,

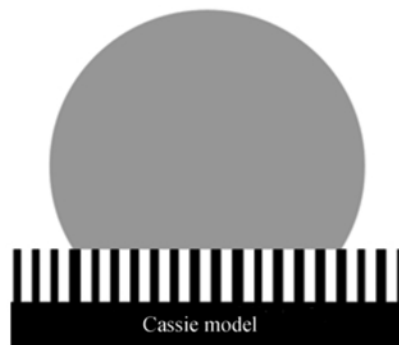


Fig. 6. Scheme of Cassie model.

$$dG = f_s(\sigma_{SL} - \sigma_{SG})dx + (1 - f_s)\sigma_{LG}dx + \sigma_{LG}dx \cos \theta^*, \quad (4)$$

at equilibrium:

$$\cos \theta^* = f_s (1 + \cos \theta_e) - 1. \quad (5)$$

Cassie and Baxter also obtained the Cassie-Baxter equation, which adapts to any composite surface contact from

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a thermodynamic point of view.

$$\cos\theta^* = f_1 \cos\theta_1 + f_2 \cos\theta_2, \quad (6)$$

where  $\theta^*$  is the apparent contact angle of the composite surfaces,  $\theta_1$  and  $\theta_2$  are the intrinsic contact angles of two materials, respectively, and  $f_1$  and  $f_2$  are the fractions of two materials of the composite surfaces. When one of these two materials is air, whose contact angle for water is  $180^\circ$ , eq. (5) also can be obtained.

In eq. (5),  $f_s$  is the solid fraction of substrate. The smaller the  $f_s$  is, the greater the apparent contact angle will become. It also can explain the existence of the broken line in Fig. 4, which cannot match Wenzel model well. In the highly hydrophobic region, the surface microstructure can prevent the liquid drop from invading in and can pocket to form air film, and the liquid drop seems to sit above the rough surface. For “very rough” surface, for which  $f_s$  tends to zero,  $\theta^*$  will thus tend to  $180^\circ$ , and the drop will “lift off” the solid surface. The ruling criterion in calculation is the fraction of solid  $f_s$ , but not  $r$ , thus the Wenzel model is inapplicable to the case in this area. Wenzel model is only applicable to the region between moderate hydrophobicity to moderate hydrophilicity as shown in Fig. 7.

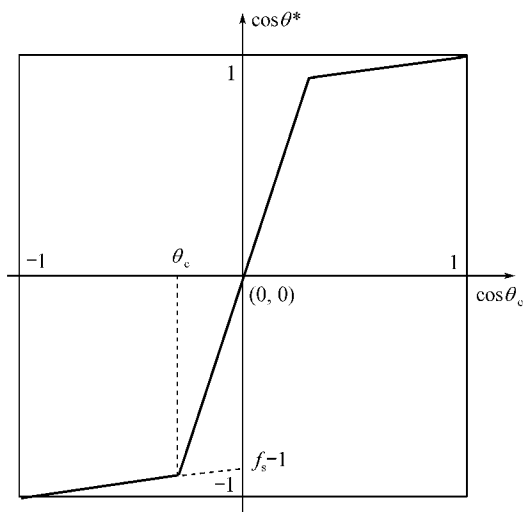


Fig. 7. The application scopes of two models.

Furthermore, the linear relationship in the highly hydrophilic region can also be interpreted well by the composite contact theory. The rough surface can be considered as a kind of 2-dimension porous materials, in which the liquid can be absorbed. Consequently, a liquid/air interface must develop during the imbibition: following a suggestion of Steven Garoff, we could call this hemi-wicking<sup>[16,17]</sup>, since it is intermediate between spreading ( $\theta = 0$ ) and imbibition ( $\theta < 90^\circ$ ). If a film propagates from a deposited drop, a small amount of liquid is easily sucked into the texture of the surface with good hydrophilicity, and the remaining drop sets on a patchwork of solid and

liquid—a case very similar to the superhydrophobic one, except that here vapor phase below the drop is replaced by the liquid phase. According to eq. (6) or from the thermodynamic point of view:

$$dG = f_s(\sigma_{SL} - \sigma_{SL})dx - \sigma_{LG}(1 - f_s)dx + \sigma_{LG} \cos\theta^* dx, \quad (7)$$

and

$$\cos\theta^* = f_s \cos\theta_e + (1 - f_s) \cos 0^\circ = f_s \cos\theta_e + 1 - f_s, \quad (8)$$

where  $f_s$  is the emerged fraction of solid, corresponding to islands above the film level. It is obvious that the smaller  $f_s$  will result in smaller apparent contact angle.

(iii) The relationship between two models. To some extent, the increasing of contact angle indicates more work needed to spread the liquid on the surface. In Wenzel model, the extra interfacial free energy is a resultant of extra liquid/solid interface. While in Cassie state, it is caused by the extra gas/solid interface (Fig. 8). That is why roughness can enhance the hydrophobicity on hydrophobic substrate. Eqs. (3) and (5) should therefore be successively obeyed as the contact angle increases, and the threshold value  $\theta_c$  is called contact angle between the two regimes given by equating the two. This yields  $\cos\theta_c = (f_s - 1)/(1 - f_s)$ , where  $\theta_c$  is denoted as the critical contact angle (Fig. 7). Only if  $\theta_c$  is larger than  $\theta_c$ , air pockets would be favorably trapped below the drop and form the composite contact (Cassie model). However, it is noticeable that a dotted line matches Cassie model in the moderate and slightly hydrophobicity region ( $90^\circ < \theta < \theta_c$ , dotted line in Fig. 7). This suggests that two superhydrophobic states might coexist. It is evident that the drop need not necessarily form a shape having global minimum energy. The hydrophobic state is related to the history of drop forming. Usually, the Wenzel state can be gotten through condensing or spraying of oversaturated vapor on the rough surface, while the Cassie state can be achieved by surface deposition. Furthermore, an irreversible transition can occur from Cassie to Wenzel in the region of  $90^\circ < \theta < \theta_c$ . It was reported that the contact angle would be permanently changed if certain work is applied upon the liquid drop. In the region of  $90^\circ < \theta < \theta_c$ , the apparent contact angle will be reduced from the Cassie states to the Wenzel states (i.e. from composite contact to wetted contact) in order to minimize the system energy when the drop is subjected to pressure. As seen before, the liquid must start filling the valleys or grooves of the substrate as the transition occurs, the physical details of the transition are not well understood, but it is likely that some intermediate states will have higher energy than those corresponding to a composite or a wetted contact. The transition



Fig. 8. Scheme of Cassie model (hemi-wicking).

from Cassie to Wenzel state is irreversible, and the global energy in Wenzel is lower than Cassie state in this region (see energy analysis). Actually, in these two states, both systems energy is in stable or metastable state. Moreover, although these two contact angles are comparable, their hysteresis behavior of the contact angle is physically different, which leads to a substantial difference in adhesion properties and self-cleaning properties. Compared with that of Cassie state, the adhesive force and hysteresis of contact angle are dramatically increased in the Wenzel state, which should be avoided in the preparation of self-cleaning surfaces. Therefore, at this point, Cassie state is demanded in fabricating the self-cleaning surfaces.

### 2 Energy analysis

Consider an experimental setup where a liquid is dispensed from a narrow tube to form a drop on the substrate. Assume that the diameter of the dispensing tube is negligible compared to the drop size, which implies the initial energy of the droplet can be neglected. And assuming that the effective energy per unit area of liquid-substrate contact with respect to the dry substrate is  $(\sigma_{SL}-\sigma_{SG})^{eff}$ ,  $(\sigma_{SL}-\sigma_{SG})^{eff}/\sigma_{LG}$  equals  $\cos\theta^*$ , the change in energy from the initial state (no drop) to the final state (drop formed) is given by

$$G = S\sigma_{LG} - (\sigma_{SL} - \sigma_{SG})^{eff} A, \quad (9)$$

where

$$\cos\theta^* = (\sigma_{SL}-\sigma_{SG})^{eff}/\sigma_{LG}$$

then

$$G/\sigma_{LG} = S - \cos\theta^*A.$$

The droplet can be regarded as a shape of ideal spherical cap, when the gravity is neglected. Then the area of drop surface (liquid-gas)  $S = 2\pi a^2(1 - \cos\theta^*)$  (wherein  $a$  is the radius of the drop), and the area of contact with the substrate projected on the horizontal plane  $A = \pi a^2 \sin^2\theta^*$ , and the energy equation can be described as below:

$$G/\sigma_{LG} = 2\pi a^2(1 - \cos\theta^*) - \pi a^2 \sin^2\theta^* \cos\theta^* \quad (10)$$

Being subject to the volume constraint,

$$g = V - \frac{1}{3}\pi a^3(1 - \cos\theta^*)^2(2 + \cos\theta^*) = 0,$$

when  $a$  is substituted by eq. (7) and the energy of a drop of given volume in equilibrium on a substrate is given by<sup>[18]</sup>

$$\frac{G}{\sqrt[3]{9\pi V^{2/3}}\sigma_{LG}} = (1 - \cos\theta^*)^{2/3}(2 + \cos\theta^*)^{1/3}. \quad (11)$$

It can be easily verified that the right-hand side is a monotonically increasing function of  $\theta^*$  for  $0^\circ < \theta^* < 180^\circ$ . As a result, on the same substrate, an equilibrium drop shaped with lower value of the apparent contact angle  $\theta^*$  will have lower energy. Compared with the  $\theta^*$  in Fig. 4, the conclusion in Fig. 7 is confirmed. The existence of the broken line in Fig. 7 reveals that the drop is at metastable state, and there is an energy barrier from this me-

tastable state to the stable one (Wenzel model). External work is required to overcome this barrier although the transition is thermodynamically favored.

### 3 Contact angle hysteresis

Generally, surface hydrophobicity is characterized by contact angle, and the higher angle indicates higher hydrophobicity. Outwardly, almost everyone would agree that the left one in Fig. 9<sup>[19]</sup> is more hydrophobic than the other two, because it has the highest contact angle. However, the real situation maybe is much more complicated. What will happen if the rightmost surface is tilted a bit from the horizontal, the droplet slides off, and the leftmost is tilted to any angle even upside down and the droplet stays pinned to the surface? With the facts known we can learn the intrinsic difference between static CA and dynamic CA. To fabricate or to research the applications of water-repellent surfaces or self-cleaning surfaces, the dynamic movement of the liquid drops with very little applied force must be taken into account. Thus, dynamic wettability, which is a function of contact angle hysteresis, is a very important issue<sup>[20,21]</sup>.

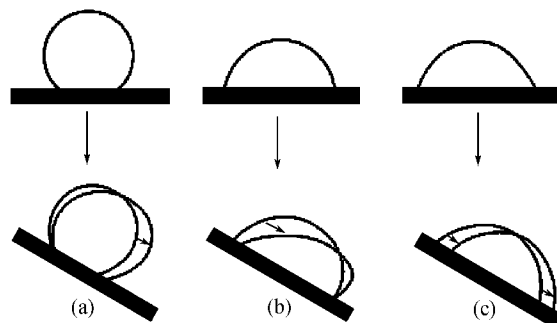


Fig. 9. Three drop states on different surfaces (CA and CA hysteresis).

The importance of contact angle hysteresis was first addressed by Furmidge et al.<sup>[22]</sup> in the research of hydrophobicity 40 ago. But it is apparently necessary as indicated by numerous subsequent reports of surfaces described as “super water repellent”, “ultrahydrophobic” and “ultra water repellent” that report only one contact angle for a long period<sup>[23]</sup>. Only recently more attention has focused on the CA hysteresis and the importance of the three-phase line. For only the CA is not enough to describe the surface hydrophobicity, and the CA hysteresis is more important than the greatest angle it can reach. The relationship shown in eq. (12) also was derived and reported by Furmidge.

$$F = mg(\sin\alpha) / w = \sigma_{LG}(\cos\theta_R - \cos\theta_A), \quad (12)$$

The equation predicts the minimum angle of tilt ( $\alpha$ ) at which a droplet (with surface tension  $\sigma_{LG}$ ) will spontaneously move, where  $F$  is the minimum force that can make the droplet move on the horizontal surface,  $m$  and  $w$  are the mass and width (horizontal to the direction of drop movement) of the droplet,  $\theta_A$  and  $\theta_R$  are the advancing

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and receding contact angles, and  $g$  is the force due to gravity. It is clear from this equation that the difference between advancing and receding contact angles (hysteresis), but not the absolute value of the contact angle, is important for the drop moving on the surface. The advancing contact angle is the value measured at the moment when adding the drop volume and the three-phase line is just about to expand, i.e. the minimum downhill side angle needed for a drop sliding on the tilted surface. While the receding contact angle is the value measured at the moment the three-phase line is about to move in reducing the drop volume, i.e. the minimum uphill side contact angle needed for sliding. And  $\theta_A$  is always larger than  $\theta_R$ , the difference between these angles can be called hysteresis of contact angle. In Fig. 9, the surfaces (a) and (b) exhibit water contact angles of  $\theta_A/\theta_R = 120^\circ/80^\circ$ , and the surface in case (c) exhibits  $\theta_A/\theta_R = 70^\circ/70^\circ$ . When the surfaces are tilted, different events happen with each droplet. On surface (a), the downhill side of the droplet can advance, but the uphill side stays pinned until the receding angle is reached. On surface (b), the uphill side of the droplet can recede, but the downhill side stays pinned until the advancing angle is reached. There are barriers to receding due to the change in shape of the droplet. On surface (c), the droplet can advance and recede simultaneously without change in the droplet shape, and a little tilt can lead the droplet to slide off the surface.

From the above analysis, the following conclusion can be drawn. The influence of contact angle hysteresis must be taken into account in defining the superhydrophobic surface, i.e. an ideal superhydrophobic surface should have a minimum hysteresis of contact angle ( $\theta_A = \theta_R$ ). For the hydrophobic surfaces, especially the surfaces with higher contact angle by microstructures, liquid cannot invade into the surface structures easily and air can be trapped under the drop to form air film to reduce the hysteresis of contact angle. The smaller distance of the surface structure and deeper grooves can prevent liquid invasion well. As discussed before, the Cassie state is favorable in fabricating the superhydrophobic surfaces for its larger contact angle and small hysteresis of contact angle.

For self-cleaning surface, the study of the equilibrium shapes of droplets or films on surfaces are not enough. What is more important is how these surface contaminants are transported along the surface, and off the surface. For the superhydrophilic route to self-cleaning, the flow of the liquid film is essential. The usefulness of this concept thus depends on the rapidity with which a liquid film runs off a surface, and without producing a beading front or pinning of contact lines. For sufficiently thick films (over several hundred nanometers), flow is hydrodynamic, and beading of the film can be avoided<sup>[24]</sup>. For thinner films, however, the flow of the film will consist of a rapid equilibration by surface diffusion. But not all liquid will move. There will also be stagnant layers on

microscopic scales. Therefore, although these surfaces can carry the materials off by the flow-film, the bottom stagnant layer remaining on the surface will bring some problems to the self-cleaning properties.

For the superhydrophobic surfaces, the dynamic behavior of droplets on these surfaces was systematically studied by Quere et al.<sup>[25,26]</sup>. The first important effect of these surfaces on liquid drops concerns the contact line of the drop, that is, the one-dimensional line of intersection of the three interfaces. Because the contact area of the drop shrinks with the increase in contact angle, the contact line can be deformed less easily, and hence the hysteresis in contact angle is drastically reduced. The small contact angle hysteresis benefits the movement of droplet. Otherwise, the droplet will vanish from the surface only by vaporizing, and leave the contamination materials, which are frequently found on the car surfaces and the glass of door or window. So the application research on self-cleaning substrate with tiny hysteresis in contact angle is highly desired. Undoubtedly, the contribution of surface microstructure cannot be ignored; in fact, it plays a key role in self-cleaning properties. For example,  $r$  is just about 2%—3% on the lotus leaves, and a little tilt can lead the droplet roll off the surface with mud particles to get the effect of self-cleaning. By comparison, on the flat surfaces, droplet only can be removed by sliding, and the ability of carrying off the dirt is much less efficient than the above one, as shown in Fig. 10. The capability of carrying dirt by rolling is more powerful than by sliding. When the contact angle of the surface reaches over  $170^\circ$ , even more sticky droplet can roll off the surface easily, but cannot slide, which was confirmed by Richard et al.<sup>[27,28]</sup> through monitoring the movement of the sticky droplet with bubble on the surface.

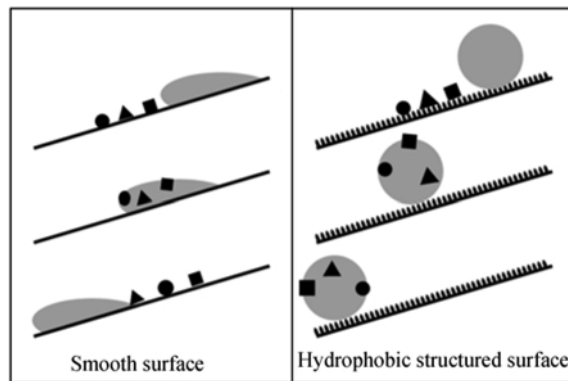


Fig. 10. Scheme of carrying dirt on different hydrophobic surfaces.

#### 4 Strategies in making rough surfaces

In terms of the topography of rough surfaces, these superhydrophobic surfaces can be classified into three types<sup>[3]</sup>: regular surface, random surface, and hierarchically structured surface. Basically, regular surface refers to the surface with periodical and ordered surface microtex-

ture, which is normally introduced by lithography or micromachining techniques with good repeatability. Highly regular surfaces are very useful for quantitative studies, especially for the equilibrium configuration and three-phase contact line dynamics of a droplet on a rough surface. For random surface, the roughness is resultant from a spontaneous process, such as freezing, deposition, precipitation, and self-aggregation. Differing from the topography of regular surface, that of random surface is arbitrary or irregular. It is not easy to control the size or shape of microstructures owing to the lack of basic understanding of these processes. Hierarchical surface is an intermediate case, and as a matter of fact, it is also of interest in biology. Hierarchical rough surfaces have periodical structures on two or more scales. Typical cases are fractal and self-affined surfaces, the latter refers to a fractal one in which its lateral and vertical scaling behavior is not identical but is submitted to a scaling law.

Assorted surfaces were used to study the effect of surface topology on wettability, as shown in Fig. 11<sup>[29]</sup>. All surfaces are supposed to be chemically homogeneous with an intrinsic contact angle of 110°. However, their relationships between roughness and apparent contact angle significantly differ from each other. Curve 1 represents the full wetting in all cases. Curves 2, 3 and 4 are corresponding to composite contact of 1-D sinusoidal, 2-D sinusoidal and vertical columns ( $f_1 = 0.5$ ). It can be concluded that the surface topology strongly influences the apparent contact angle of the composite configuration in striking contrast to the case of full wetting, but this angle is much less sensitive to roughness than that of the full wetting solution. Moreover, the apparent contact angle and the critical contact angle both increase with increasing dimension of the surface topology. It can be inferred that larger apparent contact angles can be achieved when adopting more complex topology such as double sinusoidal surfaces (Hierarchical roughness), which have sinusoidal structures on large and small scales.

From the point of surface fabrication, roughness can be obtained via several approaches as below: (i) The random rough surfaces can be made by electrochemical

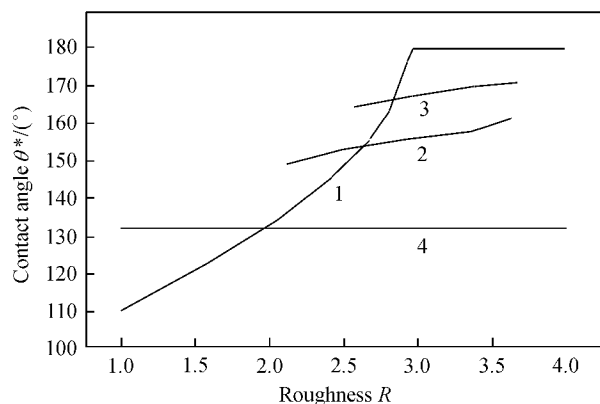


Fig. 11. The effect of surface topology on wettability.

deposition<sup>[30]</sup> and etching technologies. The solidification of the low energy materials can also be used, for instance, the earliest man-made superhydrophobic surface with fractal roughness is formed by solidification of the molten AKD<sup>[11,15,31]</sup>. (ii) Using the template-based extrusion method, Jiang et al.<sup>[2,32,33]</sup> prepared the PVA nanofibered superhydrophobic surface with a water contact angle greater than 170° without any fluorinated modification of the surface. (iii) The regular rough surfaces can be conventionally made by surface micromachining technologies, such as lithography, dry- and wet-etching. The microstructured and ordered inorganic substrates may be constructed firstly, and the required surface chemistry is then imposed by molecular self-assembling. Each method discussed above has its advantages. Here, we emphasize the micromachining technology for its advantages of controllability, repeatability, scaling-up and integration.

Highly regular microstructured surfaces are used to study the effect of the geometrical parameters of surface microstructure on the configurations of droplet. Fig. 12 shows a 3-dimensional view of a unit of surface geometry with square pillars, the pillar cross-sectional is  $a \times a$ , height is  $H$ , and the spacing between two neighbor pillars is  $b$ . According to the definition of roughness and the frac-

$$\text{tion of solid, } r = \frac{(a+b)^2 + 4aH}{(a+b)^2} \text{ and } f_s = \frac{a^2}{(a+b)^2}.$$

Here we define two geometrical parameters:  $\beta = b/a$  and  $\gamma = H/a$  (aspect ratio), and according to eqs. (3) and (5), Wenzel:

$$\cos \theta^* = \frac{(a+b)^2 + 4aH}{(a+b)^2} \cos \theta_e = \left(1 + \frac{4\gamma}{(1+\beta)^2}\right) \cos \theta_e, \quad (13)$$

Cassie:

$$\cos \theta^* = -1 + \frac{a^2}{(a+b)^2} (1 + \cos \theta_e) = -1 + \frac{1 + \cos \theta_e}{(1+\beta)^2}. \quad (14)$$

From the above two equations, we can learn that the apparent contact angles are relevant to the  $\beta$  (resolution factor). In the Cassie model  $\theta^*$  is the monotonically increasing function of  $\beta$ . It seems more complicated in the Wenzel model, and the trend is opposite compared with the Cassie model (Fig. 13). The lower energy and higher energy segments of the Wenzel and Cassie curves are marked in Fig. 13<sup>[18,34]</sup> combined with the energy analysis. The intersection point between the Wenzel and Cassie curves represents the maximum value of the apparent contact angle (for a given value of  $\gamma$ ) among all the possible lower energy states, and its abscissa is  $\beta_c$ . The Cassie state is more stable if  $\beta$  is less than  $\beta_c$ , because the small spacing of structure can prevent the liquid from invading into the microstructure and go to the composite contact. It should be born in mind that small value of  $\beta$  would lead to low apparent contact angle  $\theta^*$  even though it was enhanced by roughness. It also can be revealed from Fig. 13

## REVIEW

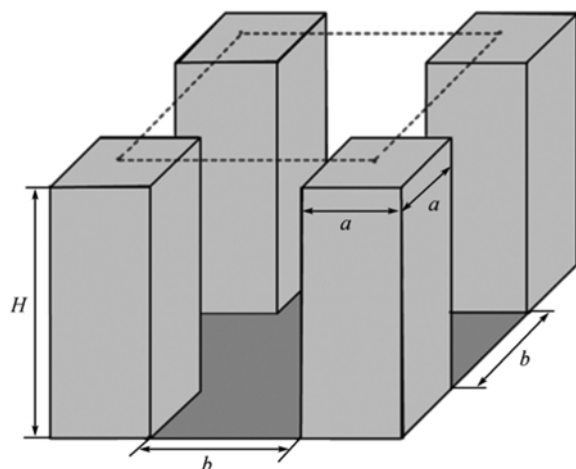


Fig. 12. A unit of surface geometry with square pillars.

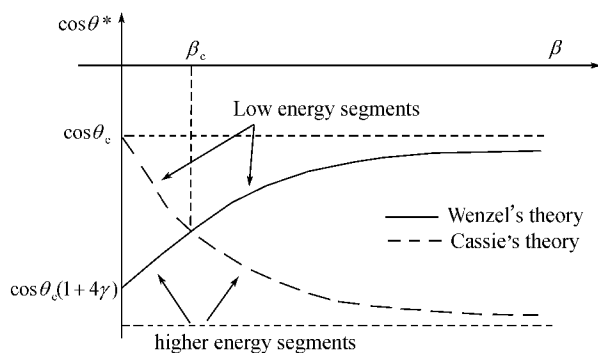


Fig. 13. Apparent CA as a function of geometric parameters for a given value of  $\theta_c$ .

that  $\beta_c$  will shift to the right with the increasing of  $\gamma$ , then the Cassie state with higher apparent contact angle  $\theta^*$  can be obtained at high value of  $\beta$ . Furthermore, the apparent contact angle in the Cassie state is independent of  $\gamma$ , because the liquid is not filled into the grooves in the composite contact. Although  $H$  does not appear in eq. (14), the influence of  $\gamma$  must be taken into account when designing the surface matching up to the Cassie model. In general, the high aspect ratio structure can prevent the liquid from invading into, though it arises the difficulties in microfabrication. For a given intrinsic contact angle,  $\beta$  and  $\gamma$  become conditioned to each other, shown as follows:

$$(15)$$

For a given value of  $\beta$ , the value of  $\gamma$  needed varies greatly with different intrinsic contact angles. The substrate with lower intrinsic CA calls for higher value of  $\gamma$ , especially, the value of  $\gamma$  will dramatically increase when the intrinsic contact angle of substrate is close to  $90^\circ$ . In conclusion, the strategy for making superhydrophobic surface: for

substrate, to utilize these materials with low surface free energy, such as fluorinated or alkylated compounds, which have high intrinsic contact angle. For surface roughness, to decrease the feature size and to increase the aspect ratio of the surface microstructure will lead to an efficient enhancement and entrance into the Cassie regime. Unfortunately, both small feature size and high aspect ratio are the embarrassment for current microfabrication techniques.

## 5 Summary and outlook

With the progresses in both basic research and practical applications of tailored surfaces, a variety of functional surfaces have been developed on the basis of characteristics of surface structures in nature. This evolution process is becoming a highlighted topic in the fields from nature to bionics. Currently, much interest has been cast on superhydrophobic surface, not only on the possibility of making this functional surface, but also on the strategy and methodology for designing, integration, and application in various scientific fields.

Superhydrophobic surfaces are very useful in commodity application, such as self-cleaning roof tiles, glass windows, house walls and waterproof coating. Meanwhile, as a functional surface, it shows promising potentials in technological fields such as clean-keep surface of satellite antennas and radar apparatus, friction reducing coating for submarine, inner-jacket decoration in petrochemical industry, and so on. Recently, tremendous efforts have been invested in microfluidic system, of which the advantages lie in the small consumption of sample and reagents, fast processing time, and high throughput compared to macroscopic systems. A crucial issue in microfluidics is the manipulation of fluids in the microchannel<sup>[35–38]</sup>. With the miniaturization of devices, it is verified that surface properties of the channel, especially the wetting property, have significant effects on the fluid behavior. It can be predicted that the microfluidics tatonics will be promoted if superhydrophobic surface can be applied in the microchannel. Jiang et al.<sup>[39]</sup> prepared nanorods arrays on a solid surface through directed growing of ZnO, and under the UV exposing it could switch reversibly between superhydrophobic and superhydrophilic states. That means the surface free energy can be switched in response to external stimuli. Superhydrophobic surface also has a variety of applications potential in biology<sup>[3]</sup>, for example, to minimize the contamination of DNA and protein containing droplet, to provide special dewetting substrates for cDNA microarrays via spotting techniques, and to solve the nuisances as “doughnut-effect” and “coffee-stain effect” in biological fields<sup>[40]</sup>.

Herminghaus<sup>[41]</sup> brought up a viewpoint that a hierarchical roughness might enable any kind of surface non-wetting, i.e. even if the surface is wettable for a liquid, the microgrooves on surface can suspend the liquid droplet. As a matter of fact, it is in the metastable Cassie state,



as mentioned before. This metastable state will remain until some external work is imposed on the system. This suggests that a hydrophobic surface might be obtained on a hydrophilic surface if the barrier from the metastable state to most stable state is high enough or scaling-up. More interestingly, it makes sense that we might make the superoleophobic surface via this approach, which has never been reported. This presumption may lead to the bloom of many promising applications.

There are many studies on the theoretical research of the superhydrophobic surfaces, and related products are stepping into in our daily life. However, because the special wettabilities of these surfaces are dependent on the surface microstructures, the mechanical strength and the out-of-door life must be taken into account besides the high contact angle and the small contact angle hysteresis. It is still a challenging task in optimizing and simplifying the fabrication process to reduce cost and enhance the properties of self-cleaning.

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