# Chapter 1
# Antifouling Self-Cleaning Surfaces

**Xiangyu Yin and Bo Yu**

**Abstract** Wettability is closely related to self-cleaning surfaces, which provides many important hints for antifouling. In nature, there exist many self-cleaning surfaces from land to the ocean after hundreds of millions of years' evolution. These surfaces possess the properties of self-cleaning by minimizing the water and contaminant adhesion, or pinning spherical water droplets, collecting water droplets by integrating water vapor collection and droplet transportation, which have increasingly attracted attention of material scientists. In this chapter, we review many typical self-cleaning surfaces not only on land but also in the sea. We also conclude the principle of the self-cleaning mechanism and the hints for antifouling. On land, many self-cleaning surfaces are due to the superhydrophobicity which is related to the surface microstructures and the chemical constitution. The contamination and dust on the superhydrophobic surfaces can be readily washed away only with the flowing water. However, the superhydrophobic surfaces have a less self-cleaning effect under water, especially in the field of marine antifouling. While, the aquatic organisms also have the underwater self-cleaning capability. But different from the terrestrial organisms, they provide another self-cleaning approach to overcome the problems of fouling underwater, and also afford many hints in the anti-fouling field. The study and mimicking of the self-cleaning surfaces in nature should inspire the development of intelligent antifouling materials for applications in relative fields.

## 1.1 Introduction

Many creatures are able to repel contaminants, including dust, organic liquids, and bio-contaminants. The phenomenon exists in nature widely which implies that contamination and dust can readily be washed away only with the flow of water. In

B. Yu (✉) · X. Yin
State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
e-mail: yubo@licp.cas.cn

X. Yin
e-mail: yinxiangyu1234@163.com

 
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just a few years, this phenomenon has aroused wide concern and been given many important hints for the fabrication of antibiofouling self-cleaning materials. Several typical examples as well as various surfaces in imitation of this phenomenon have been considered in detail in this chapter.

For most terrestrial creatures, superhydrophobicity is the core property that leads to the self-cleaning, which is shaped by the surface morphology and chemical composition, providing important reference to the area of antibiofouling from the land to the sea. On land, the superhydrophobic surface can repel droplets of water which has the potential for antifouling. But in many areas of antifouling applications, such as water pipes, the hulls of ship and drainage systems have to operate underwater in permanent water flow. In this case, not all of the superhydrophobic self-cleaning surfaces existing on land are suitable for underwater antifouling. Fortunately, in the marine environment, a large number of aquatic organisms have different types of self-cleaning properties, which are more useful for antifouling. In a sense, the applications of underwater antifouling self-cleaning surfaces are more meaningful and more difficult than those on land, but this does not indicate that we should deny that the self-cleaning terrestrial organisms can be used as references for marine antifouling.

In this chapter, we mainly discuss the self-cleaning surfaces from the land to the sea. After that, the hints for antibiofouling are also discussed, as well as many materials and technology, which can be used to create antibiofouling self-cleaning surfaces.

## 1.2 Superhydrophobic Surfaces in Nature

Self-cleaning surfaces have been frequently observed in nature, which is closely related to the surface wettability. Wettability is a fundamental property of solid surface which plays an important role in daily life, industry, and agriculture. Generally, the special functionalities of organisms are not governed by the intrinsic properties of materials but are more likely related to the unique micro- or nanostructures. It is also the case for the special wettability mentioned above. The leaves of many plants, such as the lotus flower, utilize superhydrophobicity as the basis of the self-cleaning mechanism: Water drops completely roll off the leaf that carrying undesirable particulates (dust or contaminant), which also is an antifouling process.

Recently, the phenomenon of superhydrophobicity or roughness-induced non-wetting has been studied deeply and serves as the main approach to design and fabricate self-cleaning surfaces. In order to create a superhydrophobic surface, two criteria are required. First, the surface should be at least slightly hydrophobic with low surface energy. Second, a certain surface roughness is essential. Among the aforementioned two criteria, the roughness plays a crucial role in the superhydrophobicity which directly affects wettability of a solid surface. In

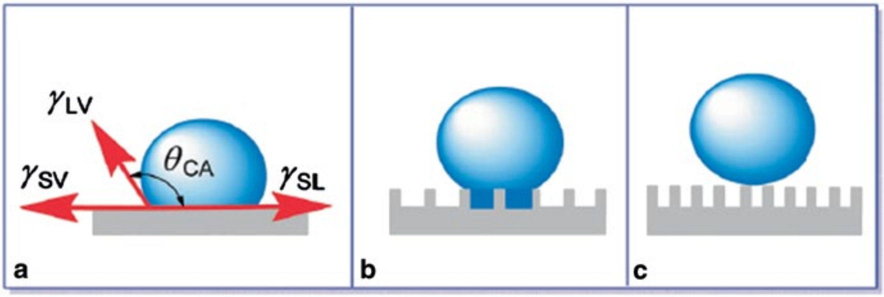


**Fig. 1.1** A droplet placed onto a flat substrate (**a**) and rough substrates (**b**) and (**c**). (Reproduced from Ref. [2] with permission from The Royal Society of Chemistry)

some cases, even hydrophilic materials can become superhydrophobic if proper roughness is applied. With regard to the superhydrophobic phenomenon, Thomas Young was the first one who described the forces acting on a liquid drop more than 200 years ago, considering the balance of "surface tension." In fact, the Young equation applies to only an ideal (chemically inert towards the test liquid), smooth, and homogeneous surface (Fig. 1.1a). However, when a droplet is placed on a rough or chemically heterogeneous surface, the contact angle (CA) can attain a different value. In this case, in 1936, Wenzel proposed an equation, which was mainly derived based on the surface force balance and empirical considerations. Essentially, the Wenzel equation deals with the effective surface energy per unit area, which predicts that if surface is already hydrophobic, roughness will further enhance the hydrophobicity, while if surface is hydrophilic, the roughness will increase its hydrophilicity (Fig. 1.1b). However, in practice, this does not happen because air pockets tend to form under the droplet, due to the effects of the gas bubbles trapped in the cavities and other reasons. For the case of a composite interface, consisting of the solid–liquid fraction and liquid–vapor fraction, yields the Cassie–Baxter equation (sometimes it is called the Cassie–Wenzel or Cassie–Baxter–Wenzel equation, since it involves the Wenzel roughness factor). This is used sometimes for the homogeneous interface instead of Wenzel equation, if the rough surface is covered by holes filled with water. The adhesion of water to the solid is reduced significantly if a composite interface with air pockets sitting between the solid and liquid can form (Fig. 1.1c). With this, two situations in wetting of rough surface should be distinguished: the homogeneous interface without any air pockets (Wenzel state) and the composite interface with air pockets trapped between the rough details (Cassie or Cassie–Baxter state) interface [1, 2].

As mentioned above, we simply summarize the related theory of superhydrophobicity, which is the basis of self-cleaning. The following sections display typical self-cleaning surfaces in nature in more detail.

### *1.2.1 Lotus Effect*

Self-cleaning is the ability of many superhydrophobic surfaces to remain clean, since rolling water droplets wash out contamination particles, such as dust or dirt. A typical example of a natural superhydrophobic self-cleaning surface is the lotus leaf as well as leaves of many similar water-repellent plants, insect and bird wings, etc. [2–7]. To date, the most successful and famous sample in the area of bionics is the lotus, because their leaves have the ability of self-cleaning. The lotus is usually considered as sacred and pure in many Asian cultures. This self-cleaning and water repellency ability of lotus was called the "lotus effect," which was coined by German botanist W. Barthlott in the 1990s [2, 8–10]. Similar to the leaves of lotus, a large number of flora and fauna found in nature have a similar water repellency ability (Fig. 1.2), which is collectively called superhydrophobicity, and it is the core property that leads to the "lotus effect"-based self-cleaning. The self-cleaning surface is one special kind of hydrophobic surface which is widely studied. To our knowledge, the word hydrophobic can be traced into antiquity (in Greek, "hydro-" means "water"), which is used to describe the contact of solid surface with any liquid. Hydrophobic surfaces have wide applications in the coating industry, textile industry, packaging, electronic devices, bioengineering, and drug delivery [11]. The most important factor to determine the superhydrophobic materials is the static CA, which is defined as the angle that a liquid makes with a solid. The CA mainly depends on the interfacial energies of the solid–liquid, solid–air, as well as liquid–air interface. When the value of the water static CA is $0° < \theta < 90°$, it means the water can wet the surface, and this surface is called hydrophilic; if the liquid does not wet the surface, the value of the CA is $90° < \theta < 150°$; only the surfaces with very high CA (more than 150°) are called "superhydrophobic" (of course, many scientists argue that certain additional properties besides the high CA, such as low CA hysteresis, are required for surface to be called truly superhydrophobic) [12–16]. Generally, surfaces with high energy, formed by polar molecules, tend to be hydrophilic, whereas those with low energy and built of nonpolar molecules exhibit the hydrophobicity. This also means that two main requirements for a superhydrophobic surface are that the surface should be rough and that it should have a low surface energy coating. The lotus leaves simultaneously meet the two requirements mentioned above. The well-known self-cleaning effect of lotus leaves shows that it has a water CA as large as $161° \pm 2.7°$ (and slide angle (SA) as small as only about 2°). This special effect is usually not governed by the intrinsic property of materials but is more likely related to the unique micro- or nanostructures. According to Barthlott and Neinhuis, the large CA is based on the epicuticula wax and the micrometer-scale papillae structure on the leaf (Fig. 1.2) [8, 9]. The epicuticula wax provides the low surface energy and the micrometer-scale papillae structure brings a large extent of air trapping when in contact with water, which is essential for superhydrophobicity. Interest in superhydrophobicity has increased since the 1990s as a result of two factors: (1) investigations of the microstructure of plant leaves with scanning probe microscopy revealing the importance of surface roughness for the

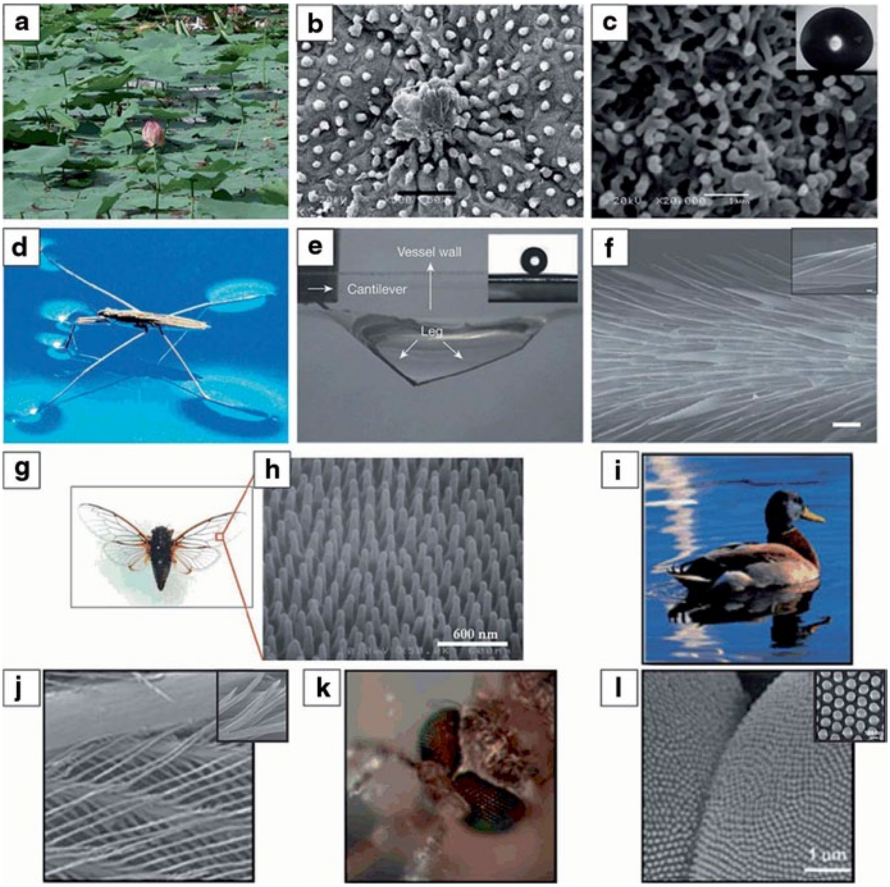


**Fig. 1.2** A series of self-cleaning phenomena in nature. **a**–**c** Photos of some lotus leaves on a pond and the corresponding SEM images of lotus leaves with different magnifications. **d**–**f** Photographs of a water strider standing on the water surface and the corresponding SEM images. **g**, **h** Digital pictures of *Cicada orni* and the FE-SEM image of its wing's surface nanostructure. **i**–**l** The digital and corresponding SEM images of duck feather and mosquito eye, respectively. *SEM* scanning electron microscope, *FE-SEM* field emission-scanning electron microscope. (Reproduced from Ref. [3] with permission from The Royal Society of Chemistry)

superhydrophobicity and (2) the ability to produce micro/nanostructured surfaces on different materials, which emerged due to advances in nanotechnology.

Figure 1.3 shows the microstructures of lotus leaves in nature; the randomly distributed papillae (Fig. 1.3a) with diameters ranging from 5 to 9 μm were found to consist of further column-like nanostructures (Fig. 1.3b) with average diameters of about 124 nm, which could also be observed on the lower part of the leaf (Fig. 1.3c). Theoretical simulation indicates that the water contact angle (WCA) may increase to about 160° after considering the contribution of the nanostructures, which is well consistent with the experimental results [4, 17, 18]. Based on the analysis above,

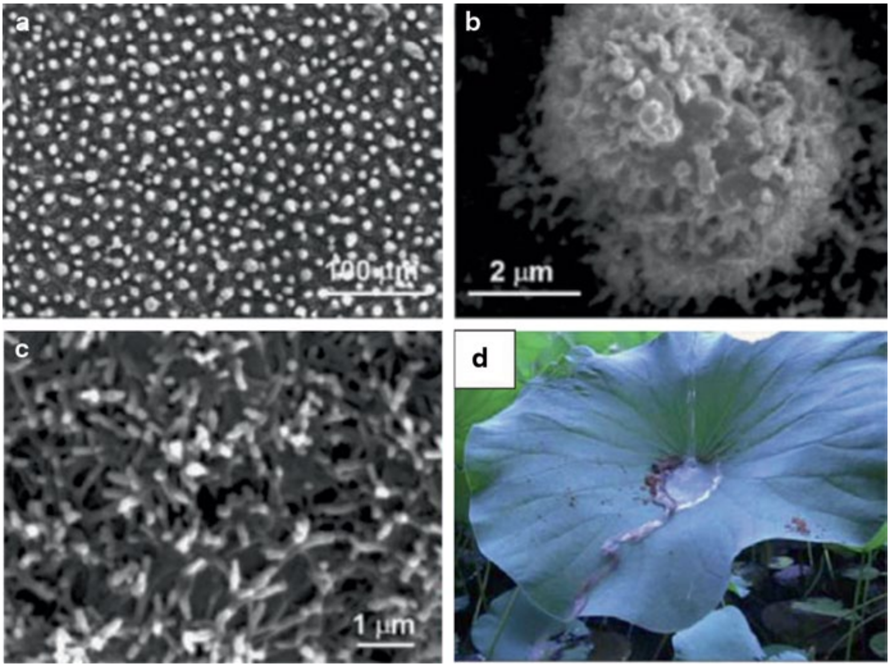


**Fig. 1.3** Micro- and nanostructures on the lotus leaf (*Nelumbo nucifera*) and their artificial simulation by ACNT film. **a** Large-scale SEM image of the lotus leaf. Every epidermal cell forms a papilla and has a dense layer of epicuticular waxes superimposed on it. **b** Magnified image on a single papilla of A. **c** SEM image on the lower surface of the lotus leaf. (Reprinted with permission from Ref. [15]. Copyright 2005, American Chemical Society) **d** Water droplets roll easily across the lotus leaf surface and pick up dirt particles, demonstrating the self-cleaning effect. *ACNT* aligned carbon nanotube, *SEM* scanning electron microscope. (Reprinted with permission from Ref. [20]. Copyright 2011, Elsevier)

we can see that the surface microstructure is an important factor and directly influences the wettability. Most of the self-cleaning plant surfaces found in nature are composed of hierarchical structures consisting of 3D wax crystallites. Surface roughness fabricated by the microstructures directly affects wetting of a solid surface and can be applied in such a manner that the surface becomes water-repellent or superhydrophobic (Fig. 1.3d).

To better understand the mechanism behind the superhydrophobic phenomenon, theoretical analysis of the wetting of rough surfaces is quite significant. The effect of roughness on wetting was first investigated in the 1930s by Wenzel (1936) who studied experimentally the wetting of textiles and concluded that roughness increases the solid–water area of contact, and as a result the CA changes. Later, Cassie and Baxter (1944) suggested that air trapped between a rough surface and a water droplet affects wetting properties of rough surface. The original studies by Wenzel (1936) of Cassie and Baxter (1944) used simple considerations of the surface tension force magnified by surface roughness, similar to those of the original paper of

Young (1805) [8]. The CA $\theta_0$ supplied by the following Young equation is the main parameter, which directly characterizes wetting of a solid surface:

$$\cos\theta_0 = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}, \tag{1.1}$$

where S, L, and A stand for solid, liquid, and air, respectively. Notably, in the term "air" we used above, the analysis does not change in the case of another gas, even a liquid vapor. Equation (1.1) was directly derived by Young using the considerations of the balance of surface tension forces, or more exactly, their horizontal components. It provides the value of the so-called static CA which is attained by a liquid droplet accurately and slowly placed on solid surface. The most stable CA corresponds to the minimum of net surface energy of the droplet [17].

However, when a droplet is placed on a very rough or a very smooth flat surface, its CA can attain a different value. Therefore, Wenzel proposed an equation concerning the CA of a rough surface. The Wenzel equation, which was derived using the surface force balance and empirical considerations, relates the CA of a water droplet to rough solid surface with that upon a smooth surface, $\theta_0$, through the nondimensional surface roughness factor, $R_f$, equal to the ratio of the surface area to its flat projection. Wenzel's equation is expressed as follows:

$$\cos\theta' = R_f \cdot \cos\theta_0, \tag{1.2}$$

where $\theta_0$ is the CA on a flat smooth solid surface, $\theta'$ is the CA on rough surface, and $R_f$ is the roughness factor, which is larger than 1. Hence, this equation means that the hydrophobic properties are obviously enhanced when the roughness of the plate surface is increased. Similarly, it also shows that the hydrophilic properties are enhanced when the roughness of the hydrophilic surface is increased. This also means that if surface is already hydrophobic ($\theta_0$>90°), roughness will further enhance the hydrophobicity, while if surface is hydrophilic ($\theta_0$<90°), roughness will increase their hydrophilicity (which is widely assumed as mentioned above). According to the Wenzel equation, for a hydrophobic surface, a further increase of the roughness factor above $R_f = -1/\cos\theta_0$ would make $\theta'$ approximately equal to 180° and endow the surface with the property of a complete rejection of the liquid. These principles above provide us an important hint for fabricating self-cleaning surfaces, and recently, on the basis of these principles, lots of studies have been made to realize superhydrophobicity via constructing surface roughness. Among them, the surface structures have also been reported to greatly influence the dynamic wetting properties of the solid surface. 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 wettability, etc., on functional surfaces.

For a rough surface, this can be wetted in other modes, the Cassie–Baxter mode, for which parts of the interface under the drop is the liquid–vapor state (the vapor exists in the troughs of the rough surface beneath the drop). This superhydrophobic

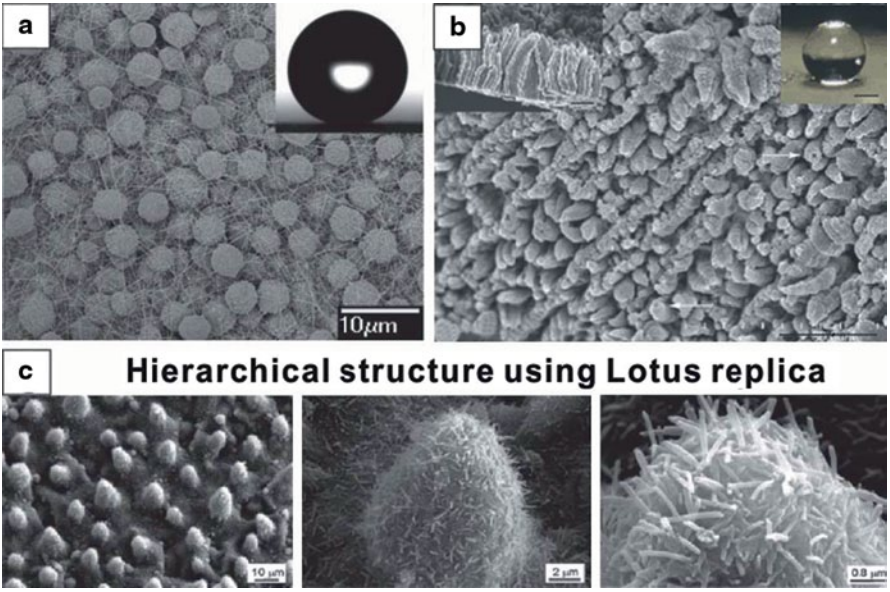


**Fig. 1.4** **a** SEM images of superhydrophobic polystyrene films with special microsphere/nanofiber composite structures prepared via the EHD method. **b** SEM image of an aligned poly(alkylpyrrole) microtube film prepared via the ECD method. The *inset* shows a water droplet on the film (scale bar: 500 mm). **c** Hierarchical structure using a lotus leaf. Nanostructures and hierarchical structures were fabricated with a mass of 0.8 mg $mm^{-2}$ of lotus wax after storage for 7 days at 50 °C with ethanol vapor. *SEM* scanning electron microscope, *EHD* electrohydrodynamics, *ECM* electron capture detection. (Reproduced from Ref. [3] with permission from The Royal Society of Chemistry)

phenomenon (the superhydrophobic surfaces are surfaces with extremely high CA and low CA hysteresis) can be explained by the equation of Cassie and Cassie/Baxter (1.3). Nowadays, the low adhesion properties of superhydrophobic surface have been commonly understood through the Cassie–Baxter wetting mode and their work has been frequently referenced in recent years:

$$\cos\theta' = f_1 \cos\theta - f_2. \tag{1.3}$$

Cassie and Baxter defined $f_1$ as the total area of solid under the drop per unit projected area under the drop, with $\theta_1$ as the CA on a smooth surface of material 1. $f_2$ is defined in an analogous way, with material 2 as air ($\theta_2 = 180°$). They thought that $\theta_1$ could be either of the advancing or receding smooth surface CA, giving advancing and receding predictions of the Cassie–Baxter CA, respectively [15].

Inspired by the lotus effect and the corresponding theory, a great variety of artificial superhydrophobic self-cleaning surfaces have been fabricated. For example, Jiang et al. reported a superhydrophobic surface resembling the surface morphology of a lotus leaf (Fig. 1.4a) [19]. So many approaches to form complex and hierarchical surface morphologies have been vastly developed depending on material types to be modified, including light irradiation, solvent evaporation, wet chemical etching, plasma polymerization, electrosynthesis (Fig. 1.4b) or electrodeposition, etc. [20–25]. To better mimic the morphology of nature's examples, replication using sample surfaces from nature as templates is the feasible way. For instance, Koch et al. replicated surface structures of the lotus leaf and afterwards assembled the natural lotus wax on the surfaces by thermal evaporation to obtain superhydrophobic surfaces with low adhesion (Fig. 1.4c) [26]. For superhydrophobic surfaces to be used in practice, both the surface structure and the modification coatings must be robust enough, and they must be suitable for mass production as well. These surfaces must resist abrasive friction and contamination, and their mechanical robustness is of primary concern. Apparently, most post-modifications, where a thin layer of perfluorinated compounds is used, might not match the requirement as the coating materials are liable to be scratched off. Bell et al. reported that the disks made from compressed metal powders premodified by alkylthiol can maintain superhydrophobicity even after surface abrasion. Another way relies on implementing complex structures into low-surface-energy bulk materials so that damage of the top surface layer will not affect the surface properties. For example, as we reported, very complex micro/nanostructures on anodized alumina can be imprinted into polymeric coatings and materials, such as silicone elastomers, polyurethane, ultrahigh molecular weight polyethylene, polytetrafluoroethylene, etc. The replicas exhibited superhydrophobicity even without further modification with low surface energy coatings [27].

### *1.2.2 Rose Petal Effect*

We can often see the dew on the leaves in early mornings, although most of them are superhydrophobic, which show very low surface adhesion to water droplets (low CA hysteresis), sticky superhydrophobicity (superhydrophobicity with a high sliding angle due to high WCA hysteresis) exists in nature, and the contact modes of sliding superhydrophobicity and sticky superhydrophobicity are different. There is an argument in the literature as to whether superhydrophobicity is adequately characterized by a high CA meanwhile water droplets rolling off easily owing to the low CA hysteresis, but another surface can have a high CA but with the same strong adhesion. It is now widely believed that a surface can be superhydrophobic and at the same time strongly adhesive to water. For example, in nature, when tiny raindrops land on rose petals, they are almost spherical but resist rolling off the flower (inset of Fig. 1.6a, b). Rose petals show not only superhydrophobicity but also high water droplet adhesion and this effect is defined as the "petal effect" [28]. The spherical water droplets that glitter in the sun are expected to attract insects for pollination, and this phenomenon also has a huge impact to antifouling and self-cleaning. The difference between lotus effect and rose petal effect also can be explained by Wenzel (2.2) and Cassie equation (2.3) [29, 30]. This phenomenon of the large CA hysteresis and high water adhesion to rose petals (and similar surfaces), as opposed to small CA hysteresis and low adhesion to lotus leaf, was observed by

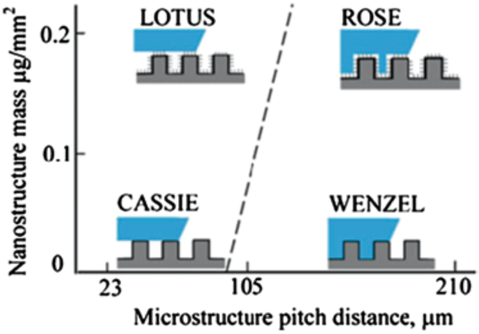


**Fig. 1.5** Schematic of a wetting regime map as a function of microstructure pitch and the mass of nanostructure material. The mass of nanostructure material equal to zero corresponds to microstructure only (with the Wenzel and Cassie regimes). Higher mass of the nanostructure material corresponds to higher values of pitch, at which the transition occurs. (Reprinted from Ref. [29], with kind permission from Springer Science+Business Media)

several research groups [31, 32]. Bormashenko et al. reported that the nanostructure is responsible for the CA hysteresis and low adhesion between water and the solid surface. The wetting regimes are shown schematically in Fig. 1.5 as a function of the pitch of the microstructure and the mass of *n*-hexatriacontane. A small mass of the nanostructure material corresponds to the Cassie and Wenzel regimes, whereas a high mass of nanostructure corresponds to the lotus and rose regimes [34]. The lotus regime is more likely for larger masses of the nanostructure material.

To further illustrate the origin of this high adhesion, we studied the microstructures of the rose petal (Fig. 1.6) [2]. Figure 1.6a exhibits a periodic array of micropapillae compactly arranged on the rose petal. There exist nanoscaled cuticular folds on the top of the micropapillae (Fig. 1.6b). It is demonstrated that both the microscale and nanoscale structures are larger than that of lotus leaves; therefore, water droplets can easily penetrate into these larger grooves, leading to high capillary force and high adhesion force. A water droplet on the petal's surface is expected to penetrate into the microscale grooves, but air gaps are present in the nanoscale folds, thus forming a partial Wenzel state. It can be readily understood that water sealed in micropapillae would cling to the petal's surface, resulting in a strong adhesion between solid surface and liquid. To prove their mechanism of high adhesion, Jiang et al. designed three types of superhydrophobic structures: nanopore array models (Fig. 1.6c), nanotube array (Fig. 1.6d), and nanovesuvianite structures (Fig. 1.6e) [34]. When a water droplet contacts the solid surface, sealed air pockets could be formed in the nanopore array and nanotube array surfaces, while only open air pockets could be formed in the nanovesuvianite surface. The results show that the normal adhesive force (NAF) plays a dominant role in enhancing adhesion behavior on the nanopore array and nanotube array surfaces, while the nanovesuvianite surface showed extremely low adhesion to water. The NAF may be produced by the negative pressure induced by the volume change of the sealed air in the nanotubes.

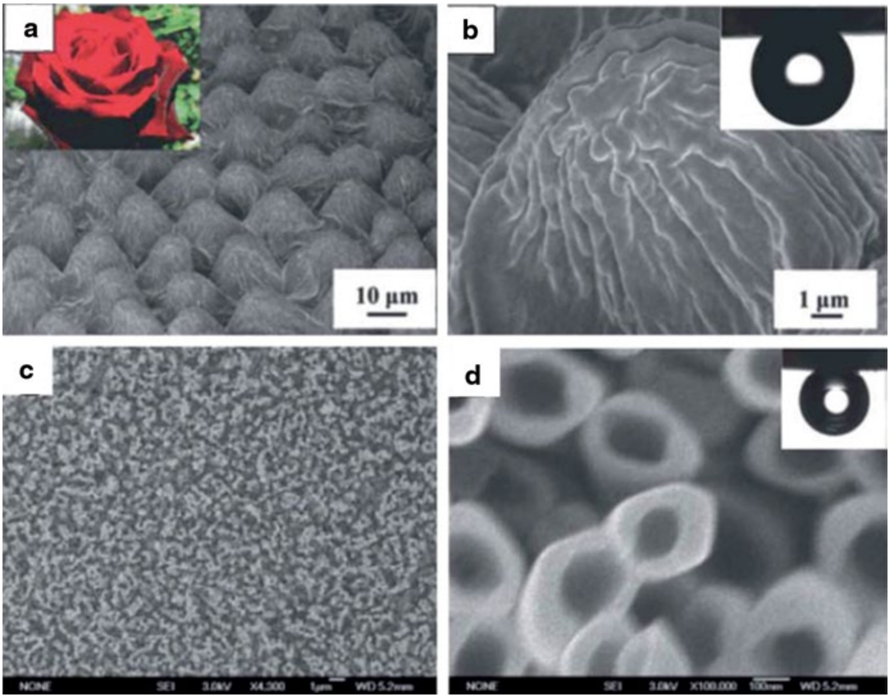


**Fig. 1.6** **a**, **b** SEM images of the surface of a red rose petal, showing a periodic array of micro-papillae and nanofolds on each papillae top; **c**–**e** top view of a superhydrophobic $TiO_2$ **c** nanopore array, **d** nanotube array. (Reproduced from Ref. [3] with permission from The Royal Society of Chemistry)

The understanding of the rose petal inspires us to fabricate biomimic polymer films that possess both superhydrophobicity and the high adhesion property. Inspired by the sticky superhydrophobicity of rose petals, Jiang et al. have prepared a densely packed and aligned polystyrene (PS) nanotube film that shows high adhesion superhydrophobicity [35]. A high adhesive superhydrophobic engineering aluminum alloy surface has been reported by Guo and Liu [36]. Lai et al. reported a superhydrophobic sponge-like nanostructured $TiO_2$ film with controllable adhesion by modulating the hydrophobic/hydrophilic components on the substrate [37]. Recently, Jiang et al. fabricated a high adhesive surface by using the concept of the petal effect. Besides the surface morphology mimicking the petal effect, the surface chemistry may also play a key role in inducing high droplet adhesion [38]. Ishii et al. fabricated a hybrid biomimetic surface having the property of "affinity-driven adhesion" [39]. Very recently, Zhou et al. reported some smart responsive superhydrophobic surfaces triggered by external condition. The superhydrophobic surface has the property of press-responsive wetting transition, and we also fabricated a surface having the ability of stick-slip switching of water droplet only by

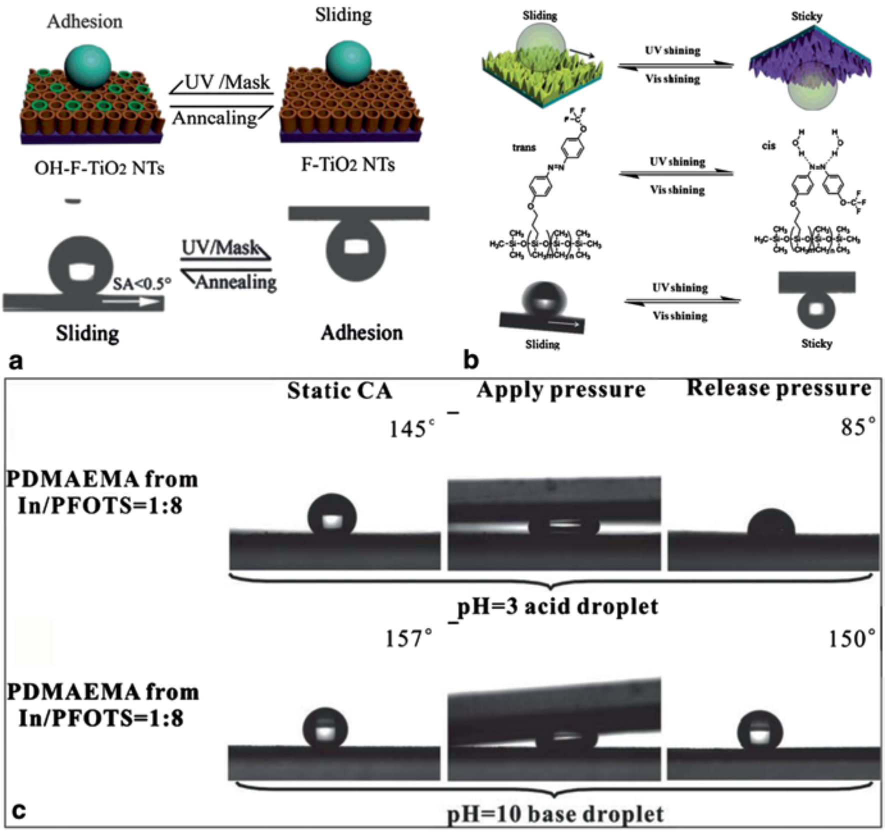


**Fig. 1.7** Schematic illustration of the mechanism of **a** producing $TiO_2$ nanotubes with switchable wettability and adhesion and the corresponding digital images (Reproduced from Ref. [3] with permission from The Royal Society of Chemistry) and **b** water droplet reversible adhesion on PDMS and azobenzene-modified anodized alumina upon UV and via irradiation and corresponding digital images. (Reproduced from Ref. [40] with permission from The Royal Society of Chemistry.) **c** The corresponding digital images of acid droplet (pH = 3) and base droplet (pH = 10) on the PDMAEMA-grafted anodized alumina (from initiator/PFOTS = 1:8) before and after application of external pressure. *PDMS* polydimethylsiloxane, *PDMAEMA* poly(dimethylaminoethyl methacrylate), *PFOTS* perfluorooctyltrichlorosilane. (Reproduced from Ref. [41] with permission from The Royal Society of Chemistry)

photo-regulation; the scheme of these surfaces can be seen in Fig. 1.7. These ideas are from nature but superior to nature organisms [2, 40, 41].

### 1.2.3 Insect

In nature, besides the self-cleaning plants, other external surfaces of animals (Fig. 1.1g–l) also have attracted more and more attention due to their various intelligent abilities [42–45]. For example, the Namib desert beetles (Fig. 1.8a) can collect

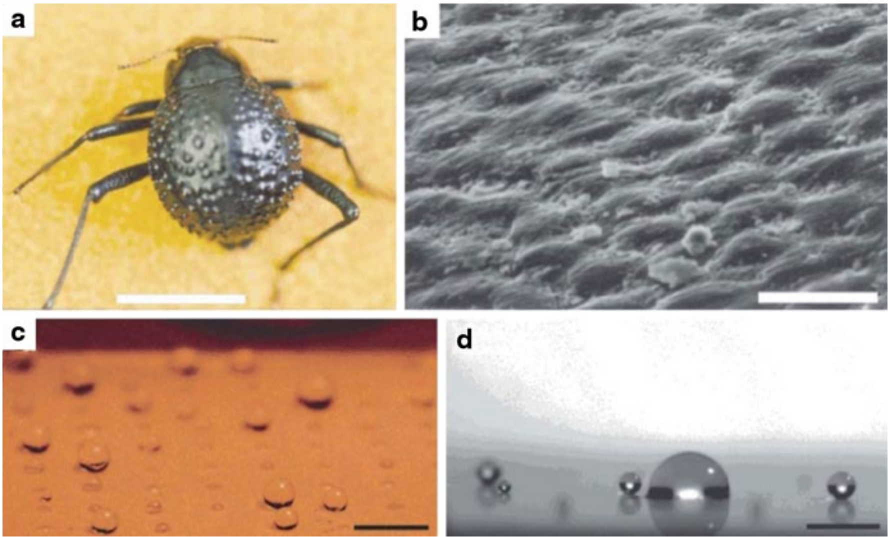


**Fig. 1.8** The water-capturing surfaces of desert beetle (**a**, scale bar = 10 mm), scanning electron micrograph of the textured surface of the depressed areas (**b**, scale bar = 10 mm). **c** Small water droplets sprayed on a (PAA/PAH/silica nanoparticle/semi-fluorosilane) superhydrophobic surface with an array of hydrophilic domains patterned with a 1 % PAA water/2-propanol solution (scale bar = 5 mm). **d** Sprayed small water droplets accumulate on the patterned hydrophilic area shown in (**c**) (scale bar = 750 mm). *PAA* polyacrylic acid, *PAH* polyallylamine hydrochloride. (Reproduced from Ref. [3] with permission from The Royal Society of Chemistry)

water from fog-laden wind on their backs, the mechanism of which is based on the alternating hydrophobic and hydrophilic regions of its bumpy surface (Fig. 1.8b) [46]. This bumpy surface provides a way to fabricate the surface thanks to the capability of harvesting water, which is very beneficial to the arid region. Inspired by Namib desert beetles, Cohen et al. fabricated hydrophilic patterns on superhydrophobic surfaces with a water harvesting property, and Badyal et al. also have mimicked this phenomenon to fabricate a surface with a superhydrophobic–hydrophilic/superhydrophilic pattern only by using plasma treated for water collection [47, 48]. Among them, insect and bird wing surfaces provide very important information for the studies of self-cleaning.

### 1.2.4 Cicada Wing

As mentioned above, various insect surfaces can provide a novel way for the studies of self-cleaning. Among them, the cicada wing is a typical example of self-cleaning. Figure 1.9 shows the microstructure of a cicada wing, which consists of hexagonally close-packed nano-columns, the height of the pillar structure is about 250 nm, diameter is about 70 nm, and the column-to-column distance is about 90 nm. Due to this microstructure and the waxy coating on it, cicada wings show

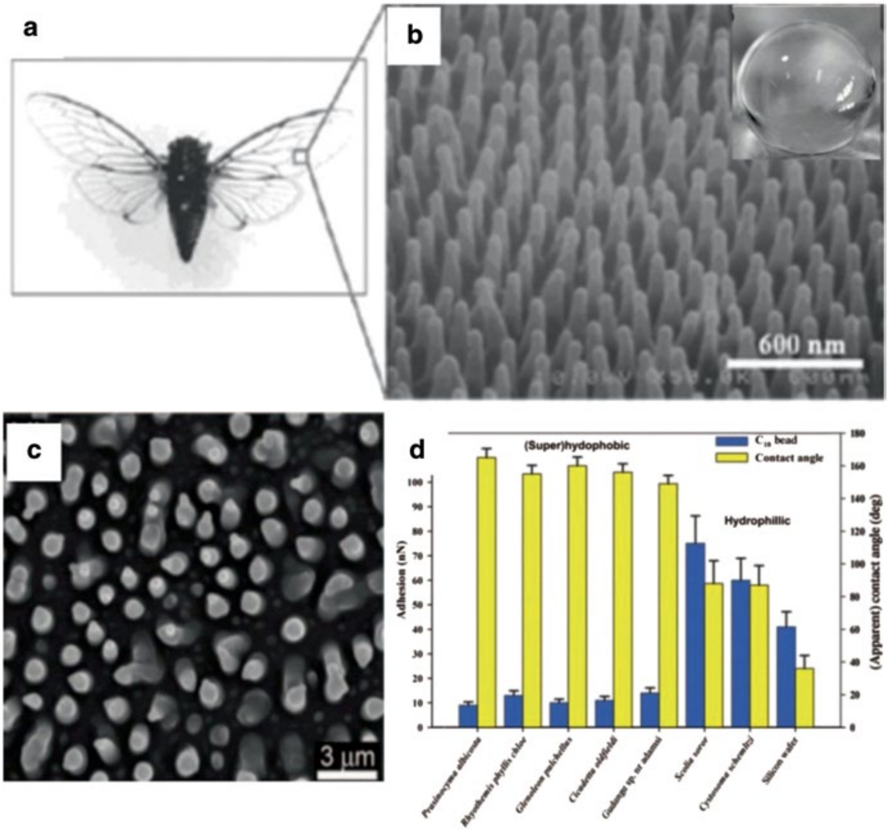


**Fig. 1.9** The morphology of **a** Cicada and its microstructure **b** (Reprinted with permission from Ref. [18] by permission of Elsevier.) **c** Hydrophobic PDMS surface and **d** graph displaying the relationship between the apparent contact angle and adhesion with the C18 particles on the hydrophilic and super/hydrophobic insect wing surfaces. (Reprinted from Ref. [50] by permission of Taylor & Francis Ltd.)

superhydrophobicity (CA≈160°). In addition to the superhydrophobicity and low adhesion, the array structure also gives them an antireflection property and excellent self-cleaning property [49, 50]. Therefore, contaminants on the surface are readily removed with the water in environment; this process is very similar to the lotus leaf (Fig. 1.9d). The difference is that the wing movement and windblast may accelerate the self-cleaning effect. Such natural structures also offer us a new insight into not only the design of artificial superhydrophobic structures but also the solar cell applications.

There are also several reports on the fabrication of surfaces by mimicking cicada wings [51–53]. Figure 1.10a shows Min et al. fabricated the nano-column array on the Si surface by the templating procedure, and after fluorination the as-prepared surface exhibited excellent superhydrophobicity (CA≈172°) [51]. Lee et al.

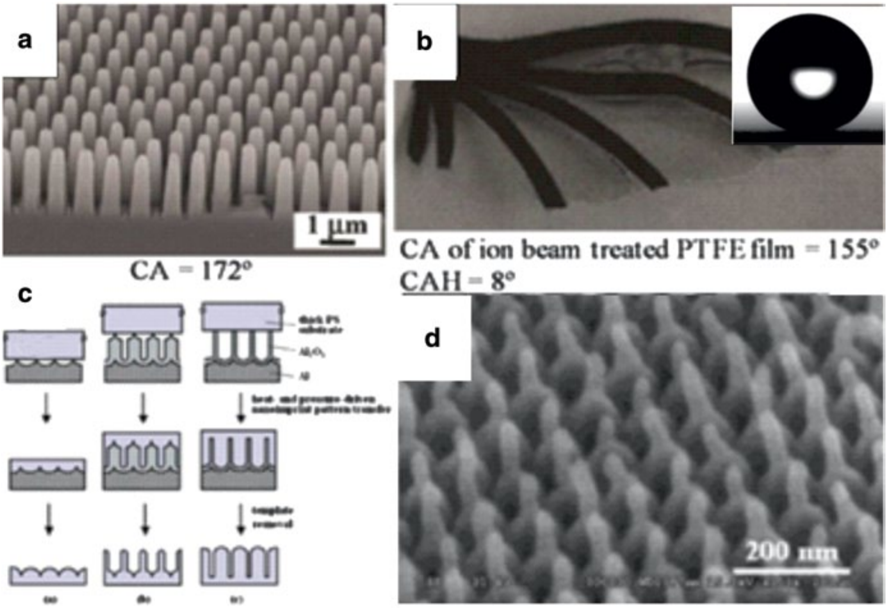


**Fig. 1.10** Artificial cicada wing surfaces by the templating procedure (**a**) and by ion beam treatment (**b**); schematicillustration and FE-SEM image of the heat and pressure-driven nanoimprint pattern transfer process (**c**) and (**d**) the *FE-SEM* image of the as-prepared surface. (Reproduced from Ref. [51] by permission of The Royal Society of Chemistry)

mimicked the structures of cicada wings to fabricate polytetrafluoroethylene films by ion beam treatment (Fig. 1.10b) [52]. The bioinspired cicada wing surface also can be fabricated by a heat-and pressure-driven nanoimprint pattern transfer process which was also reported by Lee et al. (Fig. 1.10c, d) [53].

### *1.2.5 Butterfly*

Besides isotropic wettability on natural superhydrophobic surfaces such as lotus leaves and rose petals, the patterned surfaces exist in some animals, such as the desert beetle; there also exists anisotropic wettability in nature, the typical example of which is butterfly wings. Without any doubt, we are always amazed by the gorgeous colors of several butterfly wings, which have attracted research interests of some materials researchers. So far, some studies have found that the brilliant colors of the butterfly wings arise from their multiscale photonic structures. Besides the brilliant colors, the multiscale structures also endow the butterfly wing with superhydrophobicity, anisotropic adhesion, and self-cleaning properties [54–58]. Figure 1.11 shows the morpho butterfly (found in Central and South America) and the microstructures of their wings [18].

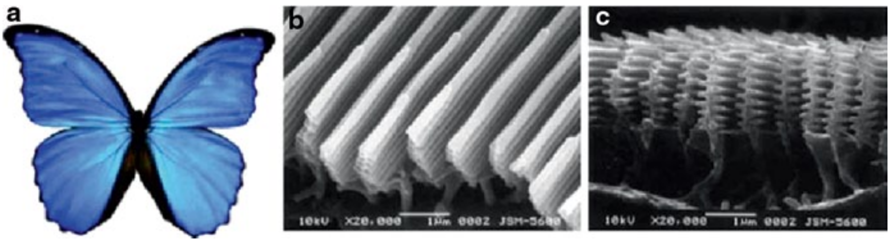


**Fig. 1.11** Photograph of the morpho butterfly (**a**) and the microstructures of their wing (**b** and **c**). (Reprinted from Ref. [18]. Copyright 2011, with permission from Elsevier)

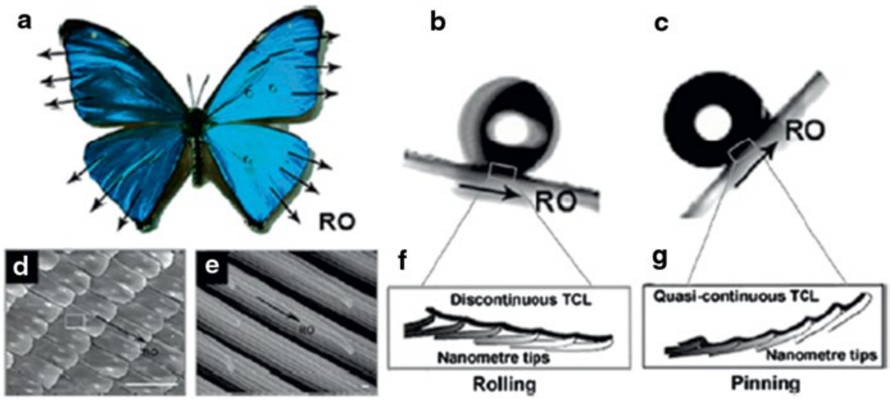


**Fig. 1.12** **a** The morpho butterfly and their radial outward (RO) direction, **b** the motions of a water droplet along (**b**) and opposite (**c**) the RO direction (**d**, **e**) SEM images of the wings. **f**, **g** Two schematic diagrams of the potential mechanism of rolling state (**f**) and pinning state (**g**). When the wing is tilted down, the oriented nanotips on the nanostrips and microscales separate from each other. *SEM* scanning electron microscope. (Reprinted with permission from Ref. [28]. Copyright 2010, American Chemical Society)

Besides superhydrophobicity, directional wettability was also observed on the butterfly wings; a water droplet can readily roll off the surface of the wings along the radial outward (RO) direction, but it is tightly pinned at the opposite direction (Fig. 1.12b, c), this phenomenon is similar to that of rice leaves. The difference is that on the butterfly wing, the two distinct wetting states can be tuned by changing the posture of the wings and influenced by the direction of airflow across the surface (Fig. 1.12f, g). It is demonstrated that this unique ability is ascribed to the one-dimensional oriented arrangement of flexible nanotips and microscales overlapped on the wings at the one-dimensional level (Fig. 1.12d, e) [59].

To thoroughly understand this high selective directional liquid–solid adhesion resulting from the oriented micro- and nanostructures on the butterfly wings, Jiang et al. mimic the microstructures of the butterfly's wing by fabricating a microscale ratchet structure on the aluminum alloy surfaces [60]. With the help of the external alternative magnetic field, a magnetic water droplet could exhibit anisotropic behav-

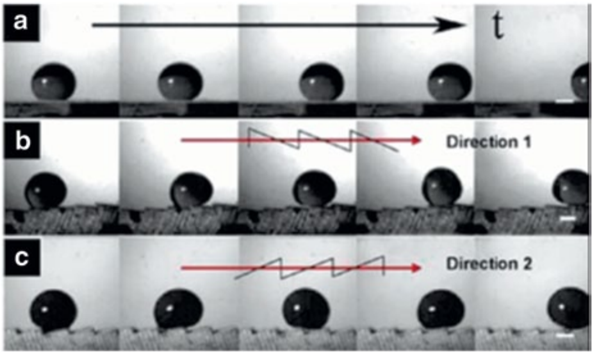


**Fig. 1.13** Optical images of a magnetic water droplet moving on the flat surface (**a**) and a microscale ratchet superhydrophobic surfaces along different directions 1 (**b** and **c**). (Reprinted with permission from Ref. [60]. Copyright 2009, AIP Publishing LLC)

ior on surface with this unique structure (Fig. 1.13). In their study, the morphology of the magnetic water droplet exhibits obvious differences when the droplet slides on the flat surface (Fig. 1.13a), and on the ratchet structured surface (Fig. 1.13b deform distinctly). Meanwhile, the magnetic water droplet also exhibits differences when it moves along different directions of the ratchet structured surface, and direction 2 displays a far higher adhesion than direction 1 (Fig. 1.13b, c). The reason for this is attributed to a relatively lower solid–liquid contact area along direction 1, while this case is opposite along direction 2. This phenomenon mentioned above implies a distinct directional adhesion by means of the ratchet structure. This highly selective mechanism response of wettability is superior to that of existing artificial response superhydrophobic surfaces. Moreover, the findings offer a promising route to the design of rapid mechanical-chemical response wetting of biomimetic surface for diverse applications. The natural butterfly wings were utilized as the templates, their intricate micrometer- and nanometer-scale hierarchical structures can be completely replicated by the alumina coating through a low-temperature atomic layer deposition technology [61].

### *1.2.6 Water Striders*

Another typical example of the superhydrophobic surface in nature is the water strider; the water strider is an insect that lives on the surface of ponds, slow streams, and other quiet waters, which are remarkable in their nonwetting legs standing easily and walking quickly on water surface (Figs. 1.2 and 1.14). Explaining the physical mechanism behind its ability to float on the water and mimicking its ability has attracted more and more attention and becomes an interesting research area in material science [5, 62–65]. Among the relative researches, Hu et al. have demonstrated that the curvature force and the buoyancy force jointly support the water strider's weight, and concluded that the curvature force produced by the insect's legs is much larger than the buoyancy force [66]. Jiang et al. studied the structures and the motion state of the water strider's leg [5]; their finding is that the force–displacement

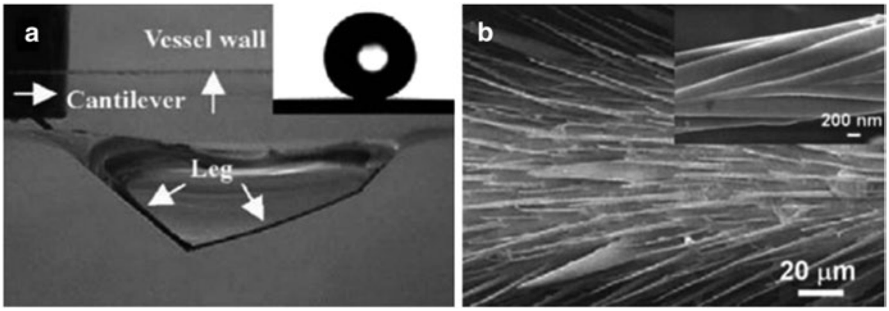


**Fig. 1.14** The nonwetting leg of water strider. **a** Typical side views of the maximal dimple just before the leg pierces the water surface. **b** SEM image of the leg with numerous oriented spindly microsetae. *SEM* scanning electron microscope. (Reprinted by permission from Macmillan Publishers Ltd: Ref. [5], copyright 2004)

curves of the striders' legs pressing on the water surface, indicating that the leg does not pierce the water surface until 0.02 mm depth is formed (Fig. 1.14a). Through theoretical and microstructure analysis, they found that the superhydrophobicity of the legs plays an important role in their striking repellent force, and it can be seen in Fig. 1.14b that there are numerous oriented micrometer-scale needle-shaped setae on the legs which are arranged on the surface, and the maximal supporting force produced by this structure is about 15 times the total body weight of a water strider. 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 the applications of microfluidics and aquatic robot.

In summary, biomimetic research on wettability of the plant leaves and insects mentioned above reveals the importance of the microstructures on their special wettability and self-cleaning ability. So far, the relative reports of the self-cleaning surfaces are all conveniently fabricated through cooperation between the micro- and nanostructures and the surface chemical compositions of low free energy, and this principle is also provided by natural creatures. From the analysis and study, we found that the hierarchical and complex microstructures are essential for superhydrophobic surfaces. For some natural creatures, their arrangement of microarrays may not only lead to anisotropic dewetting but also bring better controllability of the wettability. In addition, the directional arrangement of the microstructure can greatly influence the hydrodynamics and bring super-repellent force to water, which is contributed to better autogenous regulation of the wettability.

## 1.3 Underwater Self-Cleaning

In nature, excluding the self-cleaning mechanisms that involve the self-cleaning ability (superhydrophobicity) of creatures on land, all of them require the three-phase system involving solid, water, and air. There also exist many creatures in

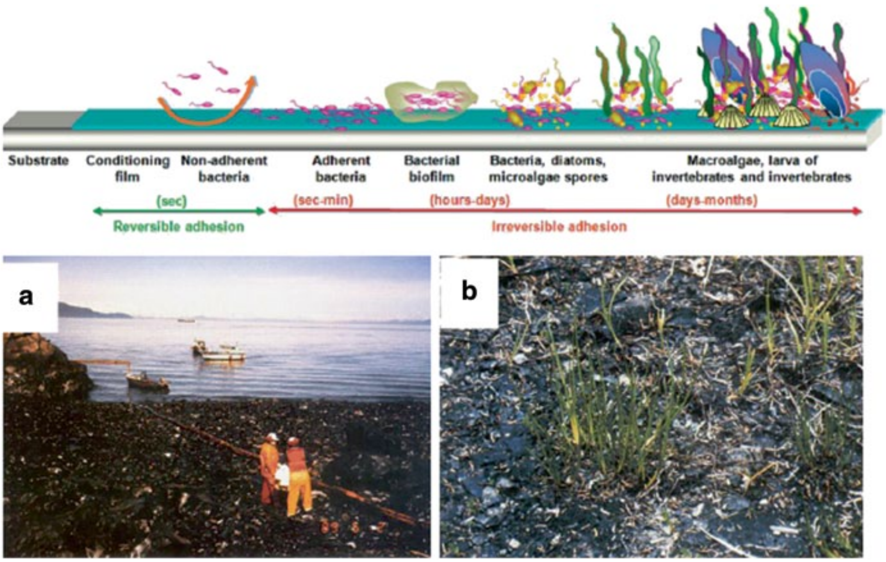


**Fig. 1.15** **a** Development processes of marine fouling. (Reprinted with the permission from Ref. [68]. Copyright 2012 American Chemical Society). **b**, **c** Oil leak in Smith Island, Prince William Sound Residual oil. (Reprinted with the permission from Ref. [69]. Copyright 1991, American Chemical Society)

sea that have self-cleaning abilities (hydrophilicity) different from the abilities possessed by creatures on land. After billions of years of evolution, nature provides us valuable guidance, and there are many aquatic organisms that also have similar self-cleaning capabilities. The self-cleaning ability of aquatic organisms provides great significance for marine equipment, such as marine pipeline, ship hulls and drainage systems. For this case, the self-cleaning ability of most terrestrial organisms will be useless. Therefore, a similar and related approach of self-cleaning in water can be used instead, with the three-phase system of solid, water, or any organic liquid. In this system, the organic liquid plays a similar role as water in the solid–water–air system, but water takes the place of the role of air.

Any surface immersed in seawater is subjected to the settlement of marine organisms (bacteria, algae, mollusks), known as fouling or biofouling. On the other hand, the growing oil leak in the gulf and numerous of industrial spills that have damaged water environment and in some cases harmed aquatic organisms (Fig. 1.15) [67–69]. Besides the pollution mentioned above, biofouling is gradually becoming a worldwide and serious problem for many man-made underwater structures, such as drilling platforms, vessels, and oceanographic stations, costing billions of dollars per year in transportation [68]. In order to solve the above problems, a number of methods have been reported, but current antifouling agents or coatings usually have a negative impact on the environment [70, 71]. Because the design and manufacture of universal, environmentally friendly coatings with both antifouling and

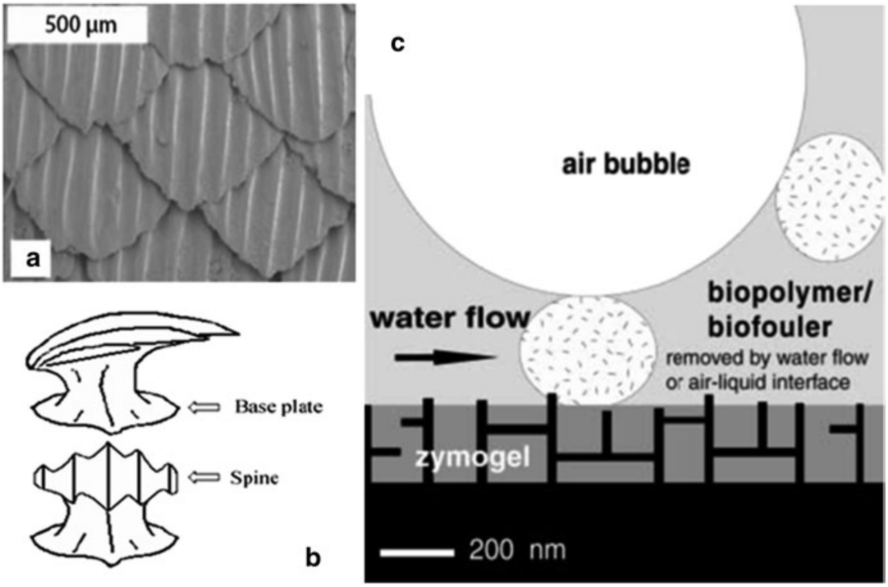


**Fig. 1.16** The microstructures of skin (**a**) (Reprinted from Ref. [74], with kind permission from Springer Science+Business Media), the illustration of a single shark scale (**b**), and **c** the model of self-cleaning abilities of *Globicephala melas*. (Reprinted from Ref. [75], with kind permission from Springer Science+Business Media)

fouling-release properties are still an enormous challenge, it is important to learn from nature. There are so many marine organisms such as sharkskin, whale skin and carp scales, mollusks, all possessing natural self-cleaning properties. The fish body is well protected from plankton and has the self-cleaning properties even though the sea can be polluted by oil [72].

### *1.3.1 Sharkskin*

Sharkskin can effectively prevent marine microorganisms from adhering to its surface, exhibiting the self-cleaning and self-lubrication ability. Recently, sharkskin has attracted more and more attention for biomimetic antifouling self-cleaning research and drag reduction properties in aircraft design, which has been investigated initially for its drag reduction properties in mechanic design [73]. Similarly, the microstructure of their surface determines their excellent self-cleaning property, as shown in Fig. 1.16, there are amount of diamond-arranged scales covering the sharkskins, and on which there are fine longitudinal grooves. Furthermore, their scales are made of enamel, and related research found that the scales consist of sharp spines and a rectangular base plate which is deeply embedded in the skin, so the spines and the base plate commonly build a firm cantilever beam structure [74, 75].

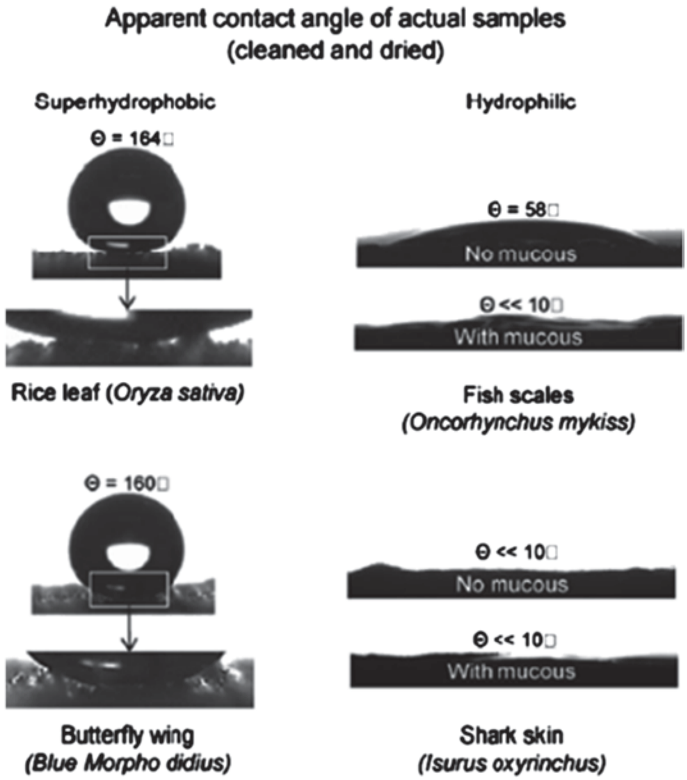


**Fig. 1.17** Wettability of actual rice leaves, butterfly wings, fish scales, and shark skin. (Reprinted with permission from ref. [79]. Copyright 2012, Royal Society of Chemistry)

The mucosal coating secreted by epidermal cells not only endows the shark with the self-cleaning ability but also enables the shark to swim faster. Bhushan studied the differences of the self-cleaning mechanisms between terrestrial organism and the fish skin (Fig. 1.17). Different from the superhydrophobic surfaces of terrestrial organism, the fish skin exhibits hydrophilicity in air, while it exhibits superoleophobicity (Oil CA of 156 ± 3°) in water [76]. The self-cleaning mechanism of sharkskin is that these unique microstructures of the sharkskin help to accelerate water flow at a shark's surface and reduce the contact time of fouling organisms. Meanwhile, the rough structure reduces the available surface area for contaminant and the dermal scales will flex in response to the changes in internal and external pressure, controlling the release of the slime and creating a moving for fouling organisms [77, 78]. The microstructures of a shark provided the inspiration for the design of multifunctional coatings with self-cleaning functions.

Inspired by sharkskin, a variety of antifouling self-cleaning surfaces have been developed [73, 76, 78–84]. For example, Jiang et al. have reported an artificial underwater self-cleaning surface (the fish scale replica has been achieved by using a hydrogel) which is bio-inspired by fish scales [81]. Similarly, Jung and Bhushan

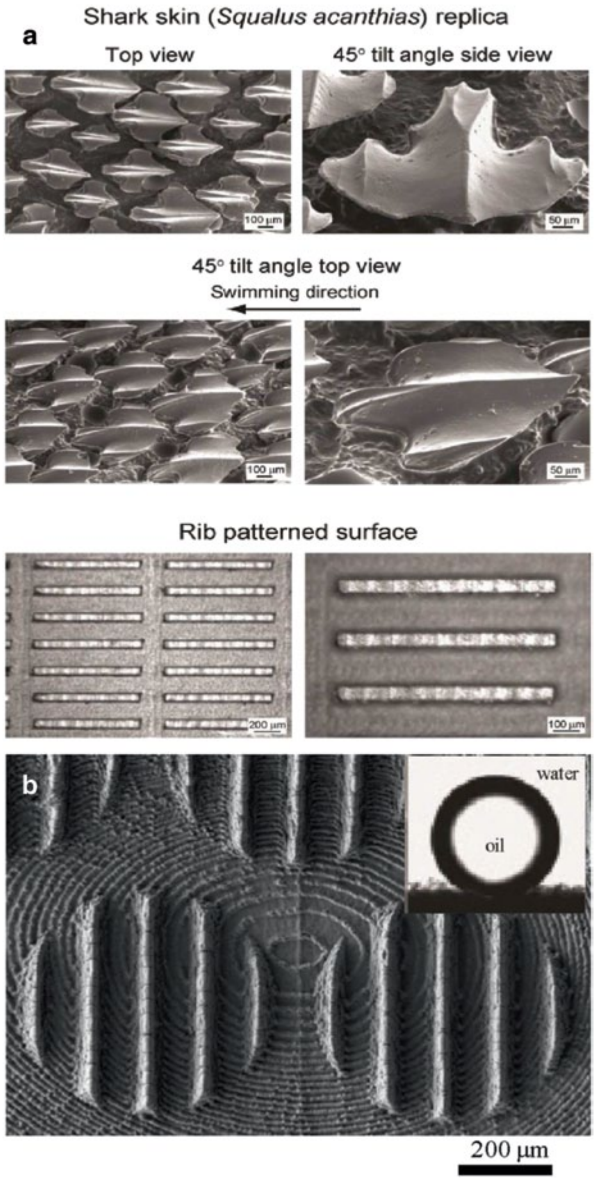


**Fig. 1.18** SEM images of sharkskin replica prepared by using polymer (**a**) and by picosecond laser mold (**b**). *SEM scanning electron microscope.* (Reproduced from Ref. [51] by permission of The Royal Society of Chemistry)

also fabricated the sharkskin replica and its microstructures as shown in Fig. 1.18 [82]. Besides, Brennan reported a method to fabricate the sharkskin-like surface structures on injection molding by picosecond laser ablation method [85]. In the self-cleaning area, Schumacher et al. analyzed the antibiofouling property of fish scale replica in detail, and they found that the topographies can significantly reduce spore settlement compared to a smooth surface.

### 1.3.2 Whale and Carp Skin

In addition to sharkskin, pilot whale (*Globicephala melas*) skin also demonstrates a very clean surface free of biomimetic antifouling and oil pollution [81, 82], and the mechanism of it is shown in Fig. 1.16c. Baum et al. suggested that the self-cleaning mechanism for oil pollution and the biofouling is that the whale skin surface and the intercellular gel contain both polar and nonpolar functional groups, which effectively reduce the fouling in the short term and long term [86]. Furthermore, the water flow along with the movement and jumping of whale may contribute to removing weakly adhered epibionts. Similarly, grass carp can swim and resist oil pollution or biofouling in water, and their self-cleaning mechanism and superoleophobicity in water is the combined action of hydrophilic mucus and hierarchical microstructures [87]. On this basis, Cao et al. recently fabricated a surface using layer-by-layer spray-coated technology, which has the self-cleaning property similar to whale skin [88]. Lin et al. prepared a hierarchical hybrid hydrogel surface having the robust underwater superoleophobicity inspired by carp scales [89]. With the rigid nano-clays and flexible macromolecules, the surface could steadily trap water in its hierarchical structure, resulting in robust underwater superoleophobicity.

### 1.3.3 Nacre

After hundreds of millions years of evolution, biological organisms produced mineralized tissues (shells, diatoms, corals, teeth, and bones) to better survive in the harsh environment [90–92]. In the sea, several marine organisms such as abalone, nacre, and some other shelled mollusks are equipped with a hard shell for protection. Among them, nacre (a typical organic–inorganic nano-composite material, consisting of predominately brittle inorganic calcium carbonate and a few percent of biomacromolecules in a layered brick-and-mortar architecture, Fig. 1.19a, b) has received a great deal of attention because of the superior mechanical strength and toughness conferred by their well-defined multiscale structures (this unique structures also endow the nacre with the iridescent colors) [93–97].

In addition to the microstructure-induced extraordinary mechanical properties and the iridescent colors, it also possesses self-cleaning properties. Such a remarkable and unique layered nanostructure of the nacre has attracted significant attention of scientists and engineers because it may give them some enlightenment in fabricating novel functional materials. Inspired by the nacre, a variety of synthesis methods have been developed to construct materials with the similar property. For example, Kotov's group utilized layer-by-layer assembly technology to fabricate a series of nacre-like artificial films (Fig. 1.19c, d) [98–100]. A nanostructured analogue of nacre fabricated by chitosan–montmorillonite clay exhibits high performance in mechanical, light transmittance, and fire-resistant properties was reported by Yu et al. Utilizing poly(N-isopropylacrylamide) (PNIPAM) and mithramycin (MTM) to fabricate a film, which exhibits not only strong mechanical properties

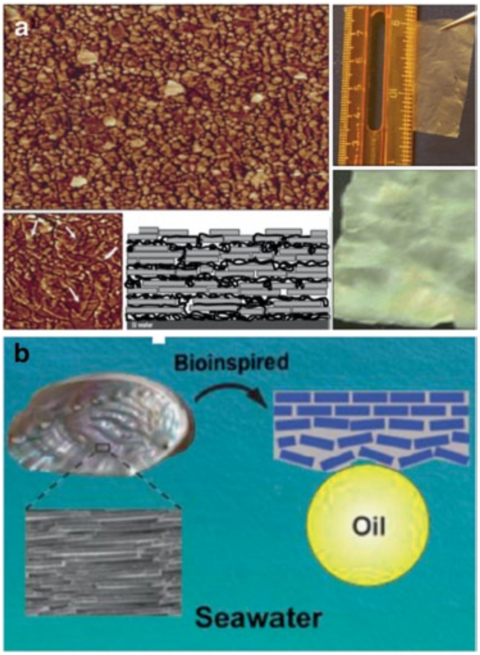


**Fig. 1.19** **a** and **b** The artificial nacre-like film [98,102]. **a** (Reprinted by permission from Macmillan Publishers Ltd: Ref. [98], copyright 2003.) **b** (Reprinted with the permission from Ref. [102]. Copyright 2013 American Chemical Society)

but also responsive properties, was reported by Lin et al. (Fig. 1.20a). Jiang et al. utilized the mechanism of underwater superoleophobicity, which is inspired by nacre, to fabricate several materials having the underwater self-cleaning property (Fig. 1.20b) [89, 103].

## 1.4 Conclusion

In this chapter, we reviewed the superhydrophobicity of various natural creatures from terrestrial to aquatic organisms, which is the basis of self-cleaning. For terrestrial organisms, self-cleaning surfaces repel water, which washes away dirt, and, under certain circumstances, they can also repel liquid organic contaminants. The unique structure of the self-cleaning organism surface is inherent to the design, exhibiting function integration. In the past few decades, inspired by natural material, a great number of self-cleaning materials have been fabricated. The results and findings discussed in this chapter provide a novel and permanent way for marine antifouling. Especially, in the existence of the water flow, aquatic organisms have a different and novel self-cleaning mechanism, which has also attracted significant attention of scientists as fine blueprints to guide the design of new materials applied in the marine antifouling.

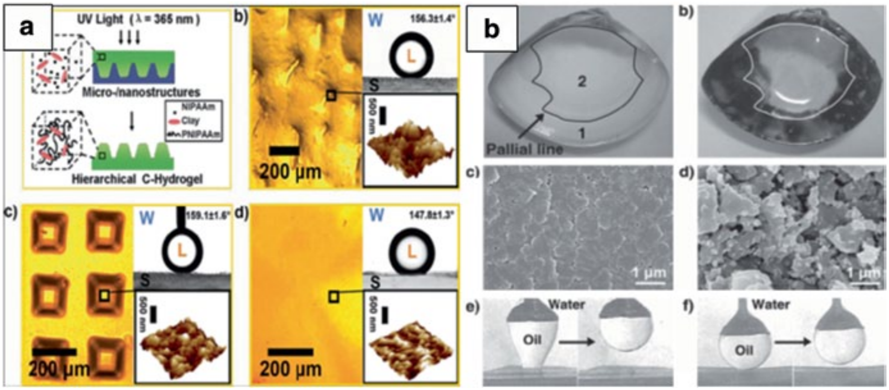


**Fig. 1.20** Bio-inspired strategy of constructing hierarchical *PNIPAAm*–nano-clay hydrogels (**a**) and **b** the oleophobic capability of the pallium-covered region of a short clam's shell. *PNIPAAm* poly(N-isopropylacrylamide), **a** (Reproduced from Ref. [89] by permission of Wiley.) **b** (Reproduced from Ref. 103 by permission of Wiley)

There are many typical self-cleaning surfaces in Nature for everybody to learn. Terrestrial organisms should inspire us and encourage design principles for the construction of self-cleaning artificial materials with multiscale structures. And the aquatic organism provides us important hints for how to fabricate self-cleaning surface underwater. Marine antifouling is a growing and vigorous field with the following research directions: (1) To develop bio-inspired self-cleaning structures through modifications with functional molecules to attain smart antifouling. (2) To fabricate novel surfaces having the properties similar to self-cleaning creatures to attain green antifouling. (3) To design and prepare surfaces which are learned from nature but superior to nature by a variety of novel methods to realize the self-cleaning.

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