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FEATURE ARTICLE

Recent progress of double-structural and functional materials with special wettability

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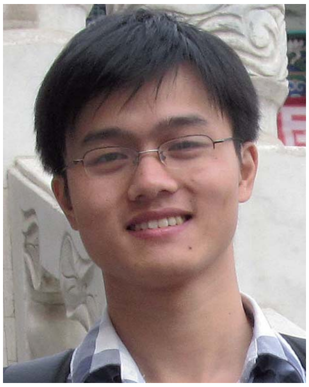
It is well known that properties of materials are largely determined by their structures. Here we introduce the special double-structural materials, which are composed of micrometre and nanometre building blocks and commonly exist in nature. This review mainly focuses on recent developments of double-structural and functional materials with special wettability. We highlight excellent properties possessed by micro- and nanostructures which initially originated from the organisms with special functions in the biological world. The excellent properties shown by such structures are discussed in three parts: special wettability, mechanical properties, and optical properties, primarily including superhydrophobicity, superhydrophilicity, superoleophobicity, low and high adhesion, low friction, structural color, antireflection and so on. We will also briefly address the research prospects and directions of micro- and nano-structures. Further study on the relationship between structures and properties will be conducive to better transfer micro- and nanostructures to the engineering materials so as to obtain desired performances and a wide range of applications.

1. Introduction

Since surfaces with special wettability have been found in plant surfaces in nature, the structures of these surfaces have attracted more and more interest[1] due to their unique properties. With the detailed investigation of these structures, scientists firstly found hierarchical structures in the plant surfaces with special wettability.[2] Based on the established theoretical models and experimental results, researchers found that micro- and nanostructures play a key role in the wetting of surface, regardless of chemical composition. These micro- and nanostructures are made up of building blocks in micrometre and nanometre scales, thus they have large specific surface areas and high surface free energies, endowing materials with a wealth of optimized properties. Apart from special wettability[3–9] found initially, a good wealth of outstanding properties increasingly found among biological organisms in nature are proved to be all related to unique micro- and nanostructures on surfaces, such as the self-cleaning effect of lotus leaves,[2,10–12] the anisotropic de-wetting


Yabin Zhang

Mr Yabin Zhang joined Prof. Guo's group at University of Hubei in 2011 in pursuing his PhD degree. His current scientific interests are devoted to fabricating surfaces with micro- and nanostructure by learning from nature, exploring the various interface effect of micro- and nano-structuring surfaces and understanding the relationship between such structures and special properties possessed by them to develop novel functional materials.


Yu Chen

Mr Yu Chen joined Prof. Guo's biomimetic materials of tribology (BMT) group at Lanzhou Institute of Chemical Physics (LICP) in April 2011, as a joint master student from Wuhan Institute of Technology (WIT). His current focus is the fabrication of biomimetic superhydrophobic surfaces, and their corresponding surface properties, especially on anti-icing.

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behavior of rice leaves and butterfly wings,[2,13,14] the superhydrophobic forces exerted by a water strider's leg,[15,16] the attachment mechanism of geckos,[17,18] the charming colors of peacock feathers, butterfly wings, and some beetles,[19] and the structure color of rose petals.[20]

Consequently, transferring this structure to technical biomimetic materials has received intense attention because of their great advantages in many real-world applications, as has been successfully done for the special properties of lotus leaves in self-cleaning textiles.[21] On the one hand, many efforts have been devoted to explore the relationship of materials with micro- and nanostructures between structure and function. Many methods to prepare micro- and nanostructures are continually developed by researchers. On the other hand, practical application presented by making artificial materials with micro- and nanostructures provides a direct impetus to push the field forward rationally. In other words, constructing novel materials with micro- and nanostructures has become an increasingly hot research topic.

In this review, we mainly focus on the recent developments (from the last three years) of properties of functional materials with micro- and nanostructures, particularly wettability, mechanical, and optical properties. The major part of this review is organized into four sections. In section 2 we will review some special phenomena in nature related to micro- and nanostructures so as to introduce the origin of micro- and nanostructures and stress the importance of micro- and nanostructures. In the following sections, special properties of functional materials with micro- and nanostructures, such as wettability, mechanical, and optical properties, will be summarized and the relationship among them will be simply illustrated. Finally, personal prospects and research directions about the properties of materials with micro- and nanostructures are briefly addressed.

Lei Shi

Associate Professor Lei Shi received her PhD with major of metal-matrix nanocomposite coatings from Lanzhou Institute of Chemical Physics (LICP) in March 2006 and worked in state key laboratory of solid lubrication, LICP. She worked in Chemnitz University of Technology, Germany, in a post-doctoral position from September 2008 to June 2010. At present, her research is dedicated to preparation and characterization of biomimetic materials, with particular interest in super-hydrophobic, tribological and mechanical properties.

Jing Li

Associate Professor Jing Li received his PhD in Materials Physics and Chemistry in 2009 from the Huazhong University of Science and Technology in China under the guidance of Prof. Heqing Tang and Prof. Lihua Zhu. Following his graduate studies, he moved to Belgium and joined Prof. Bao-Lian Su's group as a post-doctoral research fellow at the University of Namur. He is currently an associate professor at Lanzhou Insitute of Chemical Physics. His current research interests are conductive polymers, carbon materials, and surface wetting combined with energy and environmental applications.

2. Special phenomena in nature related to micro- and nanostructures

After four and a half billion years of stringent evolution, some creatures in nature possess almost perfect structures and properties, exhibiting the harmonization and unification between structure and function, and showing a wide range of fascinating properties.[22] These special functionalities of creatures are usually not governed by the intrinsic properties of the materials but are more likely related to the unique micro- or nanostructures. We will name a few phenomena in nature such as the lotus effect,[10] salvinia effect,[23] gecko effect,[17] petal effect,[24,25] and give a concise summary about these features first.

2.1 Lotus effect

The lotus is well known for the self-cleaning effect on its leaf (Fig. 1A), which shows a large contact angle above 160° and a sliding angle below 3°. According to Barthlott's and Neinhuis's opinions,[10] this property primarily originates from the cooperative effect of micrometre-scale papillae on the rough surfaces and hydrophobic epicuticular wax. However, through further investigating the lotus surface, Jiang's group revealed a novel finding of nanometre structure on micrometre-scale papillae.[2] The

Zhiguang Guo

Professor Zhiguang Guo received his PhD from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences in 2007. After that, he joined Hubei University. From October 2007 to August 2008, he worked in University of Namur (FUNDP), Belgium, as a post-doctoral researcher. From September 2008 to March 2011 he worked in Funds of National Research Science (FNRS), Belgium, as a "Charge de Researcher". During February 2009 to February 2010, he worked in Department of Physics, University of Oxford, UK, as a visiting scholar. Now he is a full professor in LICP financed by "Top Hundred Talents" program of CAS.

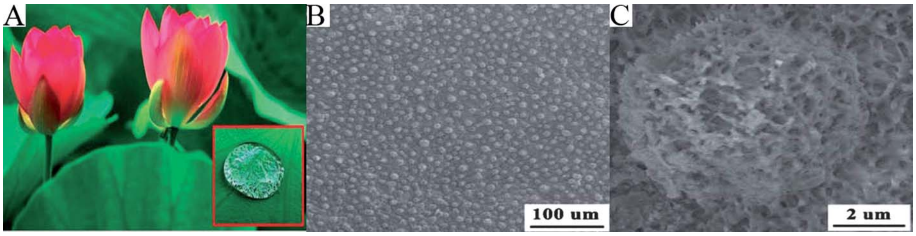

Fig. 1 (A) Typical digital photographs of superhydrophobic lotus leaf and a water droplet on the lotus leaf. (B) Low magnification scanning electron microscope (SEM) image of the surface structure on the lotus leaf. (C) High-resolution SEM image of a single papilla consisting of cilium-like nanostructures[26] (reproduced by permission of AIP).

randomly distributed papillae (Fig. 1B) with diameters ranging from 5 to 9 μm were found to consist of further branch-like nanostructures (Fig. 1C) with average diameters of 124.3 ± 3.2 nm. This complex hierarchical micro- and nanostructure is considered as the main cause of the lotus effect. Furthermore, water repellent properties and self-cleaning are also observed on other plant surfaces in nature.[3b]

2.2 Salvinia effect

As mentioned previously, plant surfaces with special micro- and nanostructures show super-hydrophobicity and self-cleaning properties. But there are exceptions in the biological world. Floating plants of the genera *Salvinia* and *Pistia* possess super-hydrophobicity, but do not have a self-cleaning ability because of the large dimensions of their surface structures.[27] The floating water fern *Salvinia molesta* is well known for its incredible rapid dispersal power and the ecological problems it causes.[28] When they are submerged under water, their surfaces can trap air to retain a layer of air around them for a long time (days to months) so that their surfaces show a silvery reflection. It is found that the upper side of the floating leaves of *Salvinia molesta* is densely covered with complex multi-cellular hairs (Fig. 2). Such structures effectively reduce the water–solid contact area, minimizing the shear stress and the frictional drag between water and the surface.[29] This phenomenon should be attributed to the specific area on the solid surface originated from micro- and nanostructures, enabling the solid surface to easily absorb air so as to lower the surface free energy. The unique combination of hydrophilic patches on superhydrophobic surfaces ("salvinia effect") provides a promising concept for the development of a coating with long-term air-retention properties.

2.3 Structure color

Flowers attract people for their dazzling iridescence colors. However, why they are so fascinating still fails to attract people's interest. Traditionally, people believe that the color of the flowers is caused by pigments, so-called chemical color. Glover *et al.* revealed the floral iridescence in *Hibiscus Trionum* and *Tulipa* species, produced by diffractive optics, which is identified to be important in pollinator attraction.[31,32] This study opened a new look on structured color in flowers and its function. Jiang's group further studied the structural color of flower petals, presenting the petal effect: there is a close array of micropapillae on the surface of the petals of red roses (*Rosa* 'Rehd.'), and many nanofolds exist on each papilla top (Fig. 3).

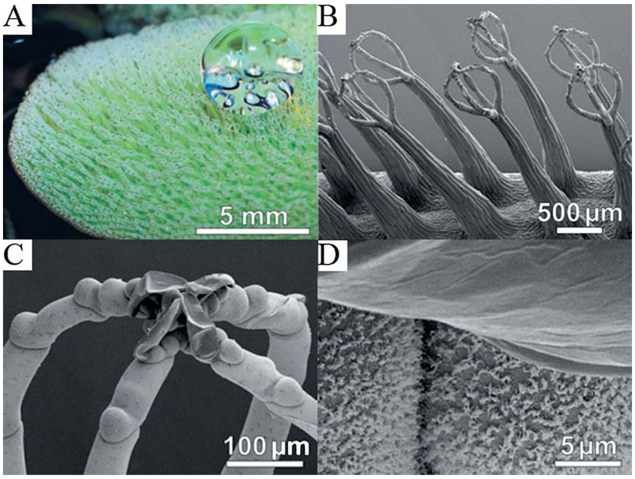

Fig. 2 (A) Upper side of *Salvinia molesta* floating leaf surface densely covered with hairs. The spherical shape of the water drop on the leaf indicates its superhydrophobic character. (B–D) SEM images of the complex hair structures. (B) Four multicellular hairs grouped on top of an emergence and connected at the terminal end leading to an eggbeater-shaped structure. (C) The terminal cell of each hair is collapsed forming a patch of four dead cells. (D) The whole leaf surface is covered with nanoscale wax crystals (below) with the exception of the terminal cells (above)[30] (reproduced by permission of Wiley-VCH).

In the flower petal surfaces, micro- and nanostructures play an essential role in the surface wettabilities. These hierarchical micro- and nanostructures not only provide super-hydrophobicity with water contact angles higher than 150 °C and a high adhesive force with water, but also induce a modulation of the optical reflectivity and a filtering effect in specific wavelength ranges. These results lead to the dazzling iridescence seen in flower petal and specific parts of other animals.[34–37] Besides, the insight into natural petal surfaces can supply us with examples to understand the relationship between surface structures and surface properties, which in turn give us a direction for biomimetic study in both theoretical and practical aspects.

2.4 Gecko effect

In nature, several creatures, including insects, spiders, and lizards, have a unique ability to cling to and detach from walls using their attachment systems. For instance, geckos are known for their excellent ability to climb walls and run on ceilings (highly adhesive "gecko" feet), because the feet of geckos have

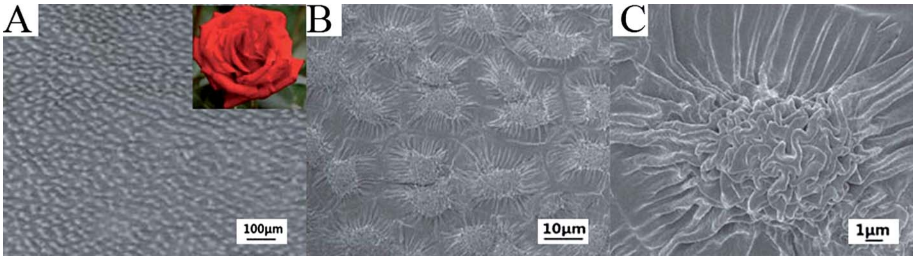

Fig. 3 (A–C) SEM images of the surface of a *Rosa sinensis* petal under various magnifications, showing a periodic array of micropapillae and nanofolds on each papilla top[33] (reproduced by permission of RSC).

the ability to easily attach to or detach from walls. This phenomenon is attributed to the highly adhesive force originating from the hierarchical micro- and nanostructures on their feet. The gecko foot is made up of well-aligned microscopic keratinous hairs called setae (30 to 130 mm in length and 5 mm in diameter), which are split into hundreds of smaller nanoscale ends (0.2–0.5 mm in diameter) called spatulae (Fig. 4).[36,37] Contact between the gecko spatulae and an opposing solid surface generates van der Waals forces that are sufficient to allow the gecko to climb vertical walls or across ceilings.[38]

Besides the remarkable adhesion property, gecko feet also exhibit superhydrophobicity and self-cleaning properties.[40,41] In summary, many unique properties found in nature can be attributed to hierarchical structures (micro- and nanostructures). Therefore, learning from nature will guide us to optimize the structural design of functional materials, to prepare novel smart materials for industrial applications.

3. Special properties of micro- and nanostructured functional materials

As discussed in the previous sections, special phenomena in nature are closely related to micro- and nanostructures possessed by creatures. Successfully transferring these functions or structures to technical materials will provide opportunities for the design and synthesis of novel functional materials. In the past years, papers about mimicking the structures and functions of organisms increasingly emerged. Materials with special functions are obtained by various methods, constructing similar architectures to organisms. According to the foundational principles of materials science, the structures and compositions of materials mainly determine the properties. Consequently, micro- and nanostructures found in nature offer a model for us to prepare excellent materials because this structure in nature shows a large number of outstanding functions, such as special wettability,

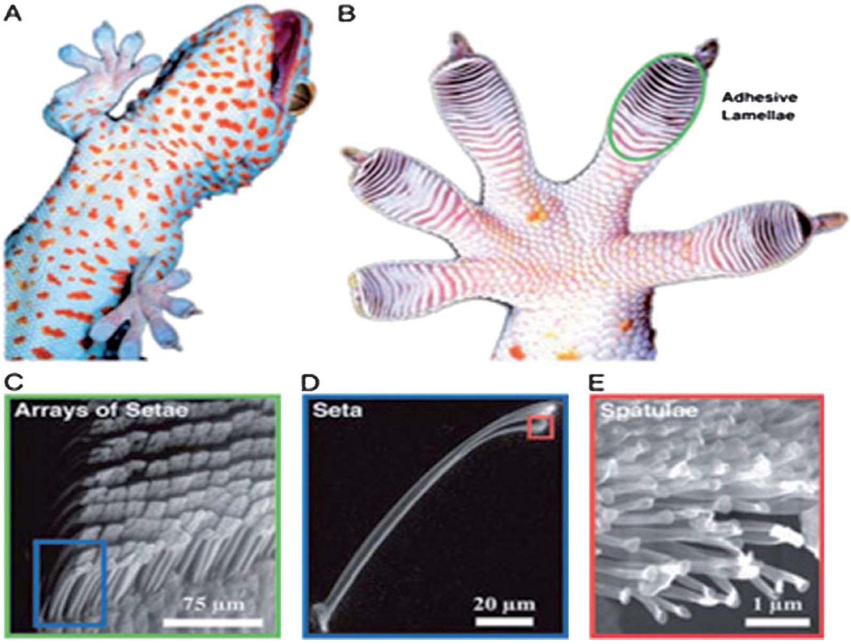

Fig. 4 Structural hierarchy of the gecko adhesive system. (A) Macrostructure: ventral view of a tokay gecko (*G. gecko*) climbing vertical glass. (B) Mesostructure: ventral view of the foot, with adhesive lamellae (scansors) visible as overlapping pads. Note the clean appearance of the adhesive surface. (C) Microstructure: proximal portion of a single lamella, with individual setae in an array visible. (D–E) Nanostructure: single seta with branched structure at upper right, terminating in hundreds of spatular tips[39] (reproduced by permission of PNAS).

high adhesive forces, low friction under water, structural color, anti-reflectivity and so on. We mainly introduce these properties from the viewpoint of artificial bio-mimetic materials obtained by researchers in recent years.

3.1 Special wettability

Wettability is an important property of a solid surface, which plays a significant role in daily life, industry, and agriculture. Functional surfaces with special wettability have aroused much interest because of their great advantages in applications. For example, a superhydrophilic surface with a water contact angle of almost 0 °C has been successfully used as a transparent coating with antifogging and self-cleaning properties, while a superhydrophobic surface can avoid contamination, the sticking of snow, and erosion. Researchers found through the investigation of plant surfaces that special wettability is dependent on the structure, morphology and chemical composition of plant surfaces.[17b] Thus, mimicking the structure of plant surfaces to prepare materials with special wettability is crucial for the study and application of wettability. During the investigation of surface structures related to wettability, micro- and nanostructures attract much attention from researchers because of the many unique properties shown by organisms with these structures. These complex multiscale structures in which there are nanostructures on the top of microstructures effectively increase the surface area and roughness and amplify the solid–liquid contact area.

Until now, two models are commonly employed to correlate the surface structures with the wetting behavior (measured by the apparent contact angle): the Wenzel and Cassie models.[42,43] According to the Wenzel model, as illustrated in Fig. 5A, the liquids completely fill the valleys of this surface where they come into contact. The apparent contact angle on this surface, θ_w, can be described as:

$$\cos\theta_W = \gamma\cos\theta_Y$$

From the equation above, it can be found that a hydrophobic surface ($\theta_Y > 90°$) will become more hydrophobic with micro- and nano-structuring of the surface, while a hydrophilic surface ($\theta_Y < 90°$)will become more hydrophilic if the same type of surface structure is introduced.[6] That is, micro- and nanostructuring surface leads to an amplification of the wetting properties of the smooth material. However, for some surfaces, such as high roughness or porous structures, the Wenzel model is not valid. Thus, the Cassie model is proposed. In the Cassie model, liquids are assumed to only contact the solid through the top of the asperities, and air pockets are assumed to be trapped underneath the liquid, which brings about three phase contact (air–liquid–solid) and leads to a composite state[6] (Fig. 5B).When the liquid–gas contact area is larger than the liquid–solid contact area, droplets only contact the points of protrusions, which allows the liquid to roll off easily if tilted slightly.

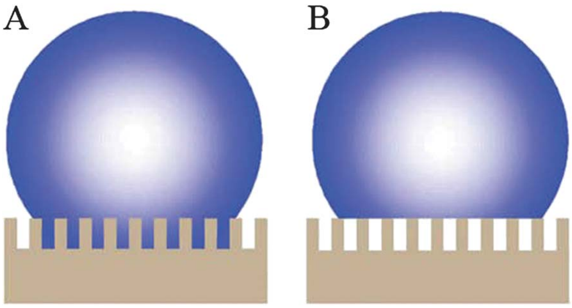

Fig. 5 Typical wetting behavior of a droplet on rough solid substrates. (A) Wenzel's mode. (B) Cassie's mode.

During the past decade, many experimental and theoretical studies have been dedicated to understanding the wettability of plant surfaces. Liu *et al.* have thermodynamically analyzed the effect of the hierarchical architecture of a superhydrophobic surface on a condensed drop state from the point of interface free energy, concluding that the micro–nano hierarchical structure is the key structural factor for the stability of a Cassie state on a superhydrophobic surface.[44] The condensation drops on the surface only with microroughness display a Wenzel state, existing at a minimum value corresponding to a Wenzel drop. By contrast, on a surface with proper hierarchical roughness, the interface energy curve of a condensed drop will continuously decrease until reaching a Cassie state. Therefore, a condensed drop on a hierarchically rough surface can spontaneously change into a Cassie state. The calculated results well-coordinated to experimental clarifications show that micro- and nano-hierarchical structure is the key structural factor for sustaining condensed drops in a Cassie state on a superhydrophobic surface. Liu *et al.* have further performed a thermodynamic analysis of wetting behavior of different scales of hierarchical structures using a 2D model, showing that a hierarchical geometrical structure can lead to a hierarchical "free energy barrier structure" so as to decrease the receding free energy barrier, which is especially helpful to improve the so-called self-cleaning property.[45] On increasing of the scale of roughness of the structure, the wetting state of droplets on the superhydrophobic surface becomes more stable and possesses good mechanical durability (Fig. 6A and B). By comparing the free energy, free energy barrier, contact angle and contact angle hysteresis of the single-, dual-, and three-scale roughness surfaces respectively, they indicate that the secondary or tertiary structure (*i.e.* nanostructure) can play a dominant role in resisting droplets into troughs of multi-scale structures. Su *et al.* have proposed that the mechanism of water-repellent of such micro- and nanometre hierarchical structures (Fig. 6C).[46] The nanostructure makes the surface sustain the highest pressure in nature so as to maintain a robust Cassie state, while the microstructure significantly reduces the contact area, thereby largely removing adhesion between solid and fluid at the macroscopic level. The selection of micro- and nano-structure might be attributed to natural evolution toward a stable Cassie state under harsh environmental conditions, since the characteristic size of the smallest structure of biological surfaces is determined by dynamic loading (rainfall pressure), while the number of hierarchical levels seems to be dependent on the static loading (static pressure of the liquid) in the natural environment of relevant plants and insects. Such principles can provide useful guidelines for engineering new materials for industrial applications. Recently, the roles of the hierarchy of surface structures were

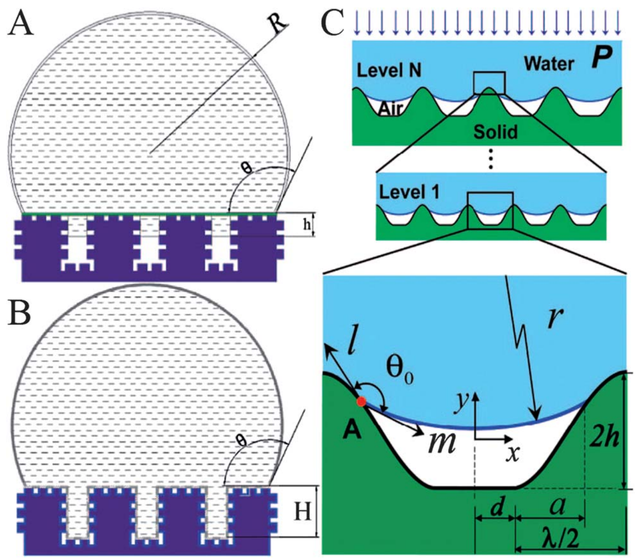

Fig. 6 Schematic of a composite or wetted drop on a superhydrophobic surface with micro–nano hierarchical textured pillars: (A) composite[46] (reproduced by permission of ACS); (B) wetted[46] (reproduced by permission of ACS); (C) a liquid drop in contact with an *N*-level hierarchical wavy surface, where air is trapped between the liquid and structure at each level. The lowest panel is for an illustration of the contact angle at the triple-line and the physical quantities involved in the problem[46] (reproduced by permission of ACS).

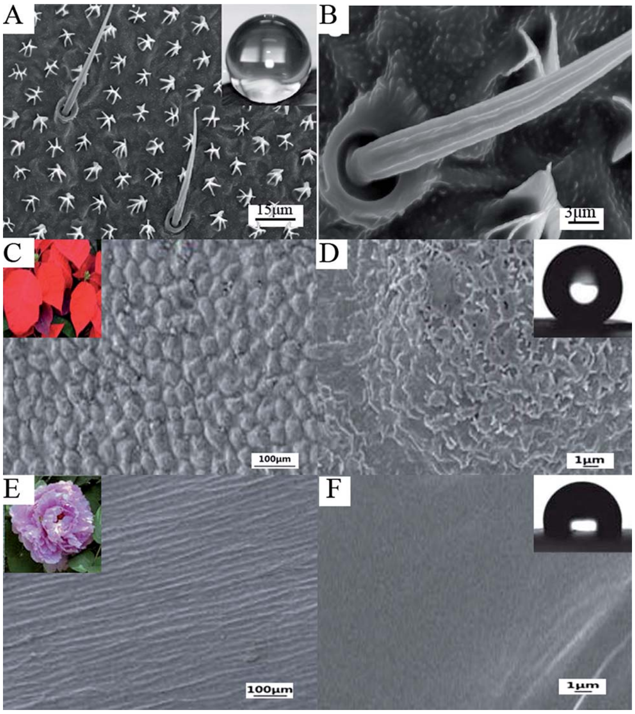

Fig. 7 (A, B) SEM images of the termite wing membrane surface *Nasutiterems walkeri*. Topographical landscape showing hairs in sockets (macrotrichia) and star-shaped structures (micrasters) evenly spaced on the surface in A. Inset showing remarkable apparent contact angles (CA) of 180° with the underlying membrane. Higher resolution image showing the hair and micraster fine structure in B[50] (reproduced by permission of ACS). (C, D) SEM images of the surface of a poinsettia petal under various magnifications, showing the microsphere and nano-sheet structures in two scales. Inset image in F is the shape of a water droplet on the petal's surface with an average CA of 135.5°[33] (reproduced by permission of RSC). (E, F) SEM images of the surface of a peony petal, showing a relatively smooth surface structure except for their own veins. Inset images are the shapes of a water droplet on each petal's surface, indicating hydrophobicity with an average CA of 105.8° (inset in F)[33] (reproduced by permission of RSC).

studied by Li and Amirfazli[47] and Yu *et al.*[48] However, few studies have been dedicated to the quantitative understanding of the questions why the biological surfaces with micro- and nanostructures possess special wetting behaviors and what are the underlying mechanisms that determine the effect of length scales on the wettability. The role of such structures with microscale and nanoscale building blocks has not been completely understood.

At present, a large number of functional materials with special wettability, in particular superhydrophobicity, have increasingly been fabricated by mimicking organisms such as plant leaves in nature. Li *et al.* have studied hierarchical structures for natural superhydrophobic surfaces.[49] On the basis of a set of criteria, it was demonstrated the dual scales of the hierarchical structure for surface geometry can guarantee not only wetting but also suitable mechanical characteristics, which can be an inspiration for the fabrication of artificial surfaces. Watson *et al.* have examined termite wings, finding that they consist of an underlying non-wetting membrane substructure comprising an array of star-shaped microstructures which minimizes interaction with micro-sized droplets of water (Fig. 7A–B).[50] This sophisticated micro- and nano-structured hierarchy on the termite wing membrane not only results in non-wetting at different length scales but also demonstrates a design for weight and material minimization while achieving this state (Fig. 7A inset). Feng *et al.* have conducted the investigation of the surfaces of various flower petals, finding that most of the flower petals possessed hierarchical micro- and nanostructures except for a few which possessed only a smooth structure, which result in different wetting behaviors from super-hydrophobic, hydrophobic to super-hydrophilic.[33] These results indicated that micro- and nanostructures played an essential role in the surface wettabilities, which can effectively enhance the surface wettability, *i.e.*, change hydrophobicity (Fig. 7E–F) to superhydrophobicity (Fig. 7C–D), and hydrophilicity to superhydrophilicity. Wu *et al.* have imparted microstructures onto silicon substrates using photolithographic techniques by adjusting pillar size and pitch to precisely control the microstructures.[51] Dual-scaled micro- and nanostructures were obtained by spin-coating a thin layer of nanoparticles. By combining the wetting behaviour at both micro- and nanoscale, a wetting model was proposed to explain the transition between preferential micro- and nano-wetting behaviors for dual-scaled surfaces.

Likewise, inspired by organisms in the biological world, a large amount of artificial micro- and nanostructures also have been obtained. Zhu *et al.* have prepared a series of surfaces with large-area ordered binary structure arrays which consist of droplet rows and parallel stripes by mimicking the natural rice leaf in surface structure (Fig. 8A–B).[52] Through adjustment of the polymer solution concentration and the modified underlying

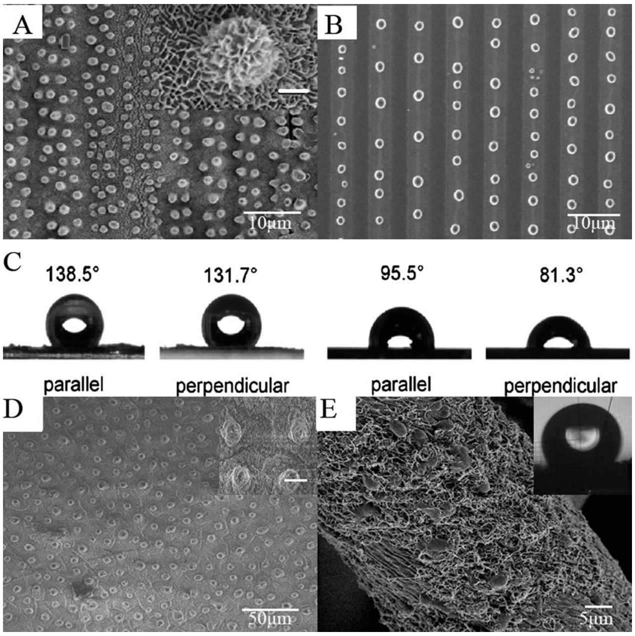

Fig. 8 (A–B) SEM images of natural rice leaf and artificial rice leaf respectively. The scale bar in the inset of (a) is 1 μm[52] (reproduced by permission of ACS). (C) Static contact angles of water droplets on a natural rice leaf seen from the direction parallel to the stripes (CA = 138.5°) and from the direction perpendicular to the stripes (CA = 131.7°); water droplets on an artificial rice leaf, as taken from the direction parallel to the stripes (CA = 95.5°) and from the direction perpendicular to the stripes (CA = 81.3°).[52] (reproduced by permission of ACS). (D) Top view of a lotus leaf. Inset showing magnified image of the lotus leaf (bar = 5 nm)[53] (reproduced by permission of RSC). (E) Carbon nanotube coated cotton fibre[53] (reproduced by permission of RSC).

pattern on the substrate, diverse surface topographies can be obtained. These as-prepared surfaces all exhibited good anisotropic wettability for water droplets like natural rice leaves, which confirmed that the anisotropy had been influenced by the periods of the patterns (Fig. 8C). This technique will offer an effective new way of designing the wettability of materials and smart controllable devices. Liu *et al.* have fabricated artificial lotus leaf structures on cotton substrates *via* the controlled assembly of carbon nanotubes onto the surface of cotton substrates (Fig. 8D–E).[53] The cotton fabrics with otherwise perfect water absorbabilities have been endowed with superhydrophobic properties. The method provides a new strategy for the fabrication of self-cleaning textiles *via* tailoring the surface microstructures of cotton fibers using nanomaterials as building blocks.

Mao *et al.* have prepared a lotus-leaf-like polystyrene micro- and nanostructure film which exhibited both superhydrophobicity and good blood compatibility (Fig. 9A–C).[54] This could be important for further understanding the non-wettability of biological surfaces with micro- and nanostructures and for application in biomedical devices. Three-dimensionally hierarchical micro/nano-oriented arrays constructed from nanometre-sized particles have been successfully synthesized through a facile biomimetic hydrothermal method by Gao *et al.*[55] The product demonstrates excellent sunlight self-cleaning performance in terms of wettability and enhanced photocatalytic activities, which provided a bright future for self-cleaning photovoltaic coatings (Fig. 9D–F).

Mozumder *et al.* have obtained polymeric superhydrophobic surfaces analogous to double-scale hierarchical (micro- and nano)structures on lotus surfaces by a solvent-free ultrafine powder coating technique.[56] The developed surfaces exhibited the lotus effect with water contact angles of over 160° and sliding angles of less than 5°,which are attributed to the appropriate surface micro- and nanoscale textures as observed in AFM and SEM images of these surfaces. Sharma *et al.* have prepared superhydrophobic polymeric and carbon surfaces by biomimicking natural leaf patterns by repeated micromolding and by nanoimprint lithography.[57] Two distinct classes of textures,

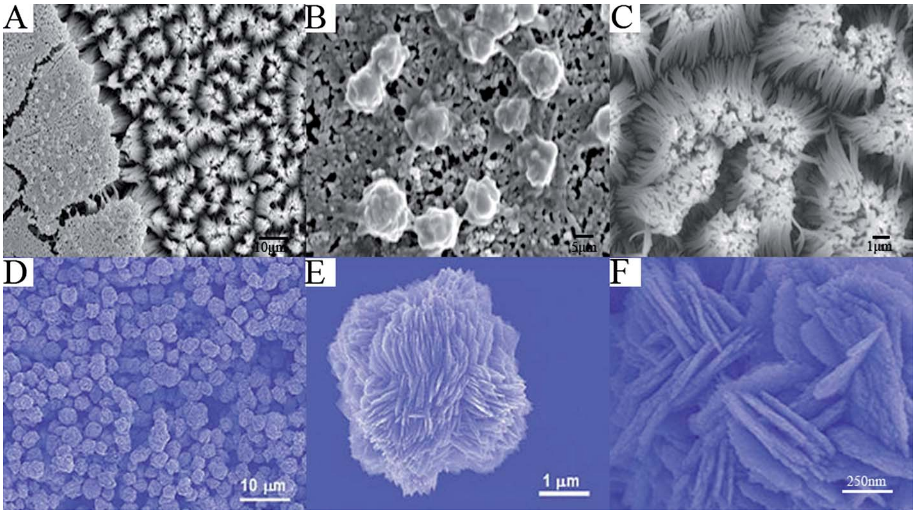

Fig. 9 (A) SEM view of dualistic PS nanotube film surface after contact with PRP for 90 min[54] (reproduced by permission of RSC). (B) Enlarged view from left region of (A)[54] (reproduced by permission of RSC). (C) Enlarged view from right region of (A)[54] (reproduced by permission of RSC). (D) Low-magnification panoramic view of the Ag/CuO micro/nanostructures with Ag content of 0.36 at.% using L-tryptophan[55] (reproduced by permission of RSC). (E) A single microflower[55] (reproduced by permission of RSC). (F) The surface of the microflower[55] (reproduced by permission of RSC).

namely, high aspect ratio hairs and lower aspect ratio microtextures which mimicked leaves of elephant creeper (*Argyreia nervosa*) and nasturtium (*Tropaeolum majus*) showed good structural superhydrophobicity. Weibel *et al.* have investigated the effect of the micro- and nanostructures on the superhydrophobicity and hysteresis using chemical etching of Al substrates followed by chemical surface functionalization and an anodic aluminum oxide template generated on the etched Al substrates followed by chemical surface functionalization.[58] The experimental results evaluated using water contact angle measurements and scanning electron microscopy showed that a superhydrophobic nanostructure superimposed on a microstructure is the main cause of the self-cleaning properties obtained in the treated Al substrates. Koch *et al.* have produced artificial lotus (*Nelumbo nucifera*) leaves with hierarchical structure by replication of the microstructure of a lotus leaf using a two-step molding process and by self-assembly of the tubule forming waxes isolated from lotus leaves (Fig. 10A–E).[59] In comparison with flat surfaces, microstructure and nanostructure surface, micro- and nanostructures have higher static contact angles and lower contact angle hysteresis which are characteristic of superhydrophobicity and lower adhesion (Fig. 10F). Besides these, Stratakis *et al.* have constructed silicon-based water-repellent surfaces possessing hierarchical micro- and nanostructures using ultrafast laser irradiation method under a reactive gas atmosphere. The as-prepared structure qualitatively and quantitatively mimicked both the structure and the water repellent characteristics of the natural lotus leaf.[60] Utilizing a coating–curing process, superhydrophobic coating surfaces with both micro/nanoscale binary structure roughness on engineering materials such as stainless steel have been created by Liu *et al.*, which showed good cohesional strength, and high- and low-temperature resistance.[61] *Via* surface oxidation and post-modification, the as-obtained copper surface with hierarchical structures not only conforms to that of the lotus leaf but also exhibits a high contact angle and a low sliding angle over a wide pH range.[62]

Based on the increasingly emergence of new fabrications and different models, Zhang *et al.* reviewed the historical and recent research on superhydrophobic surfaces, introducing the characterization of superhydrophobicity and different fabrications of rough surfaces.[63] Roach *et al.* have summarized work on the preparation of superhydrophobic surfaces, with focus on the different techniques used, in particular how techniques have progressed to form multi-scaled roughness to mimic the lotus leaf effect.[8] Kim *et al.* have made a comprehensive evaluation of wettability on micro/nano hierarchically engineered surfaces by measuring the apparent contact angles and analyzing theoretically with analytical models based on the Wenzel, Cassie, and combined wetting theories.[64] The proposed dual-scale hierarchical surfaces, which are composed of highly robust micro-post-arrayed and highly ordered nano-rippled structures, were fabricated stably using a simple and cost-effective batch process, based on the anodic aluminum oxide and micro-fabrication technologies. The experimental and theoretical observations revealed that these structures can not only improve the wetting property easily and efficiently, but also ensure the superhydrophobic robustness of high- and low-density micro-post-arrayed surfaces.

Recently, there has been growing interest in oleophobic and superoleophobic surfaces,[65,66] since the non-sticky behavior of super-repellent surfaces is important for oils and inks in applications such as inkjet printing, xerography,[67] and so forth. Although little information about whether multi-scale structure (micro/nano usually) may be beneficial for oleophobicity has been reported, multi-scale topography is preferred for organisms in nature to achieve both mechanically robust and energetically favorable superhydrophobic states.[68] Learning from natural surfaces with special wettability, we know that surface roughness at a dual or multilength scale plays a critical role in generating surprising nonwetting solid surfaces.[69] Inspired by the natural design principle, a variety of biomimetic artificial superoleophobic surfaces have been produced *via* hierarchical micro/nanostructures. Ellinas *et al.* have produced amphiphobic and amphiphilic surfaces with ordered, hierarchical (triple-scale) structures (Fig. 11A) on poly(methylmethacrylate) (PMMA) polymer substrates by combining polystyrene microparticle colloidal lithography, oxygen plasma etching–nanotexturing and fluorocarbon plasma deposition.[70] Diverse topographies with pillar arrays of different heights and diameters were fabricated through the control of the etching process and exhibited different wetting behaviors, which demonstrated hierarchical micro- and nanostructures are beneficial also for oils. Zhao *et al.* have designed and fabricated a model superoleophobic surface on silicon wafer by a simple photolithography and surface fluorination procedure.[71] This superoleophobic structure consist of arrays of ~3 μm diameter and ~7 μm height pillars, the side wall of which actually consist of a wavy structure made up of repeating "loops" ~300 nm in dimension (Fig. 11B). These authors discussed the mechanism of superoleophobicity, concluding that the geometry of the micro- and nano-structures in the surfaces is critical to achieving superoleophobicity. Leng *et al.* have successfully obtained superlyophobic surfaces on the basis of cotton textiles by introducing a micro/nanoparticle dual-size structure to the woven fiber network followed by surface perfluorination (Fig. 11C).[72] The modified textiles were completely nonwettable by both water and hexadecane, which both showed high contact angles and low roll-off angles. It proved to be essential to increase the surface roughness to achieve superoleophobicity. It was obvious that micro- and nanostructures are very important for achieving superoleophobicity, especially in terms of low roll-off angles for hexadecane. Liu *et al.* have used liquid-based metal-assisted etching and various silane treatments to create superoleophobic surfaces on a Si(111) surface (Fig. 11D).[73] The as-prepared different re-entrant structures formed using diverse etch conditions exhibited oleophobicity/superoleophobicity. It is noted that oleophobicity/superoleophobicity can be achieved by controlling the surface structure shape to form re-entrant structures, which indicated that the geometry of micro-/nanostructures generated played a critical role in achieving oleophobicity and superoleophobicity. Liu *et al.* have studied the wetting/antiwetting behavior of oil droplets on the surfaces of fish in water, creating a low-adhesive superoleophobic interface on solid substrates.[74] The obtained micro- and nanostructured surfaces showed enhanced superoleophobicity and lower adhesion with the increase of surface roughness. A qualitative model was proposed to interpret the mechanism of superoleophobic phenomena in water. Although

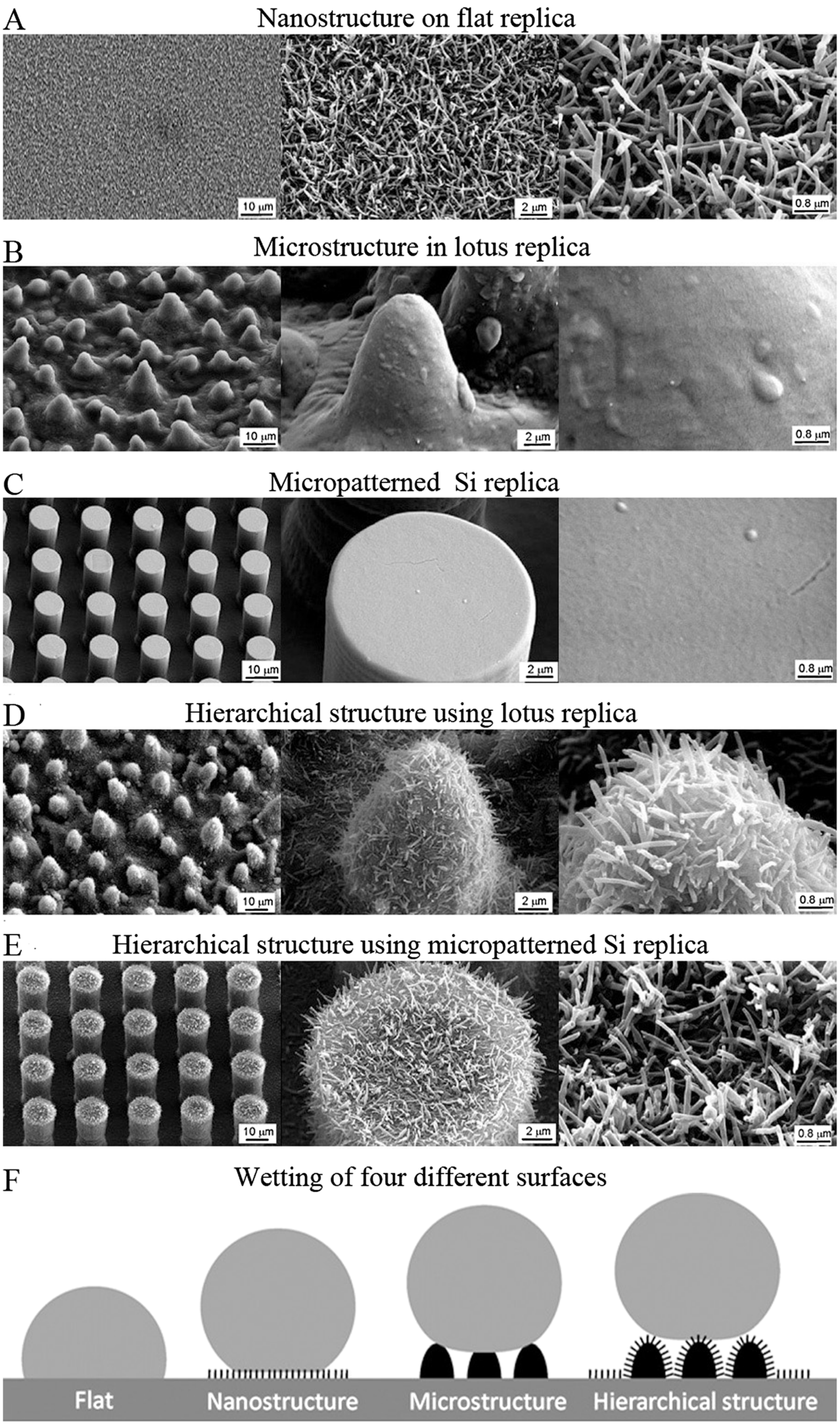

Fig. 10 (A–E) SEM micrographs taken at 45° tilt angle (shown using three magnifications) of (A) nanostructure on flat replica, (B,C) microstructures in lotus replica and micropatterned Si replica, and (D,E) hierarchical structure using lotus and micropatterned Si replicas. Nano- and hierarchical structures were fabricated with mass of 0.8 μg mm^{-2} of lotus wax after storage for seven days at 50 °C with ethanol vapor[59] (reproduced by permission of RSC). (F) Schematic and wetting of the four different surfaces fabricated. The largest contact area between the droplet and the surface is given in flat and microstructured surfaces, but is reduced in nanostructured surfaces and is minimized in hierarchical structured surfaces[59] (reproduced by permission of RSC).

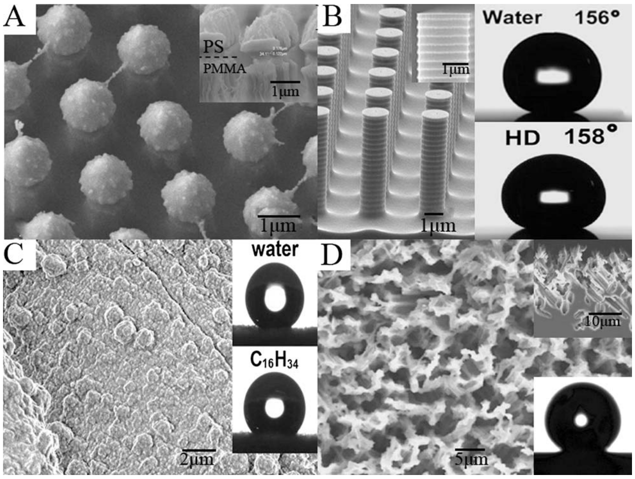

Fig. 11 (A) Undercut, re-entrant topography of a PMMA surface after 3 μm PS colloidal microparticle lithography followed by a two-step etching process in oxygen plasma. Notice the top nanotexture on the top half PS hemisphere. Inset is the side view[70] (reproduced by permission of ACS). (B) SEM micrograph of the textured surface on Si wafer with water CA of 156° and hexadecane CA of 158° (inset: higher magnification micrograph showing details of the pillar structure)[71] (reproduced by permission of ACS). (C) Morphology of cotton textiles observed by SEM. Insets are profiles of water and hexadecane ($C_{16}H_{34}$) on the corresponding sample[72] (reproduced by permission of ACS). (D) SEM images of the surface morphologies from Au-assisted $HF/H_2O_2/H_2O$ etching on Si (111) surfaces; SEM image of the cross section and the contact angle image of hexadecane are shown in the insets[73] (reproduced by permission of ACS).

many different synthesis strategies of micro- and nanostructures mentioned previously have been developed to fabricate functional surfaces with special wettability, most of them are limited to laboratory research and not suitable for industrial scale production. In addition, properties and preparation of micro- and nanostructures have been reported in many literatures, but the wetting mechanisms of these structures have seldom been studied. Therefore, a lot of efforts should be made to investigate further such structures theoretically and experimentally.

So far, it is found that the special wettability of micro- and nanostructures should be mainly attributed to their specific structures according to present theories. The quantitative relationships between the properties and structures are still unclear. The theoretical models have been proposed by some researchers in the previous sections, but we must still optimize them to better exactly illustrate the mechanism of such structures. Therefore, establishing typical theoretical models and finding the novel properties on the basis of wettability are current tasks. The insight of living organisms in nature can supply us with examples to understand the relationship between surface structures and surface properties, which in turn give us a direction for biomimetic study in both theoretical and practical aspects.

3.2 Mechanical properties

Besides special wetting behavior, living organisms with micro- and nano-structures also exhibit other properties such as high and low adhesive force, antireflection, structural color and so on. With the deep investigation of wetting surfaces, mechanical properties existing in plants and animals are found. Superhydrophobic surfaces with special liquid–solid adhesion have recently raised broad scientific interest, which are normally divided into two classes: low adhesion to water and high adhesion to water. Lower adhesion surfaces exist commonly in nature, on which water droplets can easily roll off at any tilt angles. Recent studies revealed the low adhesion of lotus leaves originates from the composite contact mode due to the hierarchical micro/nanostructures.[75,76] On the other hand, when a water droplet is placed on the petal of a red rose, it does not readily slide off.[77] The rose petal shows superhydrophobicity with a high adhesive force to water, where water droplets can stick to the rose petal even when upside down. This is because the micro- and nanostructures of rose petals are both larger than those of the lotus leaf, which provides larger scale grooves that water droplets can enter into, wetting out and clinging to the petal surface. Likewise, such high adhesion occurs in solid–solid interfaces. For example, geckos can attach to and easily detach from almost any kind of surface with varying roughness and orientation. Researchers have revealed that the ability of geckos to firmly attach their feet to and easily detach from varied types of surfaces was also attributed to the unique hierarchical micro/nanostructures on the gecko's feet.

As stated previously, two basic models: Wenzel's model and Cassie's model are proposed to be responsible for special wetting behavior. In fact, the liquid–solid adhesion property should be considered as the fundamental difference between the two models and the main cause of structure induced superhydrophobicity.[78,79] In Wenzel's model, the liquid completely fills the grooves of the rough surface at the contact area (Fig. 5A). This results in the continuous three-phase contact line and the enlargement of the liquid–solid contact area, thus the adhesion on the liquid/solid interface is strongly increased, while in Cassie's case, air pockets are formed beneath the liquid droplet leading to a composite surface (Fig. 5B). In such case, the three-phase contact line is usually discrete and the liquid–solid contact area is smaller than that in Wenzel's regime. The adhesion on the liquid/solid interface will dramatically decrease. Consequently, it can be found that the liquid–solid adhesion can be controlled between Wenzel's model with high adhesion and Cassie's model with low adhesion by tuning surface geometrical structures to obtain certain solid–liquid contact modes.[80–82] Accordingly, many methods for the artificial synthesis of special adhesive wettable surfaces have been developed in the past years, including template synthesis,[83–85] phase separation,[86,87] electrochemical deposition,[88,89] or electrohydrodynamics[90] and so forth.

However, in the case of solid–solid adhesion, the structures of gecko's feet have been depicted in detail in previous sections and some mechanisms are proposed, but the underlying mechanisms have not been fully clarified. In 2000 Full's group put forward in *Nature* that the special adhesion of gecko's feet originates from the accumulation of van der Waals interactions between the many setae and molecules on the solid surfaces.[91,92] Autumn *et al.* have provided the first direct experimental evidence for dry adhesion of gecko setae by van der Waals forces, and reject the use of mechanisms relying on high surface polarity, including capillary adhesion.[39] Estimates using a standard adhesion model and measured forces were performed to predicting the tip size of gecko seta which was consistent with the experimental value. It is verified that the dependence is on size and not surface type in this system by using physical models of setal tips nanofabricated from two different materials. Hansen *et al.* have further studied the properties and structure of gecko's feet, verifying the self-cleaning adhesion of gecko's feet by analyzing the microstructures on their feet and establishing the self-cleaning model, which were consistent with adhesion models.[93] Kamperman *et al.* have critically examines the principles behind gecko-inspired adhesion from a contact mechanics perspective, providing the mechanics of gecko-inspired adhesion which is called the effects of contact splitting.[17] Contact splitting into finer contact elements resulted in stronger adhesion for several independent reasons. This was observed in different natural species and corroborated by a large amount of experimental data. It is noted that adhesive test results showed hierarchical micro- and nanostructures played a important role in increasing adhesion *via* size effect and hierarchy effect. Zeng *et al.* have theoretically analyzed the correlated adhesion and friction (frictional adhesion) of patterned surfaces against smooth (unstructured) surfaces by applying well-established theories of van der Waals forces, together with the classic Johnson–Kendall–Roberts theory of contact (or adhesion) mechanics, to recent theories of adhesion-controlled friction.[94] By calculating theoretically both the van der Waals adhesion and the friction forces of flexible, tilted, and vertical pillars, results showed that these adhesion was high enough to support not only a large gecko on rough surfaces of ceilings and walls but also a human being if the foot or toe pads have a total area estimated at $\sim$230 cm^2. Previous studies about gecko feet have shown that structural hierarchy plays essential roles in mechanical properties of biological systems. There are interesting analogies between the roles of the hierarchical structures in wetting behaviors and those in the adhesion ability of geckos. Recently, a large number of studies have been focused on the fabrication and characterization of special adhesive surfaces inspired by plants and animals, and the relationship between structure and property is still the concern, which will provide opportunities for the design of novel smart materials in application for liquid transportation, biochemical separation, and microfluid systems.[95,96,97]

Xi *et al.* have created superhydrophobic polydimethylsiloxane surfaces that contained micro- and nanostructures by duplicating the microstructures of a rose petal. The resulting surface has the same microstructures and high adhesive property as a rose petal with a water contact angle of >150° and very strong adhesive forces close to 63.8 μN (Fig. 12A).[98] This provided the practical application of micro- and nanostructures in the fabrication of chemical engineering materials and microfluidic devices. Zhao *et al.* have produced large-area positive and negative lotus and rice leaf topographies on Au surfaces based on PDMS using a simple, efficient, and highly reproducible method.[99] The as-prepared surfaces with dual-scale micro- and nanostructures exhibited improved hydrophobic ability after chemical modification and showed nearly opposite adhesion properties between water droplet and Au surfaces with positive and negative dual-scale micro- and nanostructures (Fig. 12B). The authors proposed an understandable model to interpret the mechanism which causes the different adhesion performance between Au surfaces with positive and negative biomimetic structures. They ascribed the strong adhesion to van der Waals and the capillary force interactions between the biomimetic Au surfaces with negative plant topographies and water droplet. Ho *et al.* have successfully fabricated a gecko-inspired hierarchical topography of branched nanopillars on a stiff polymer by the nanoimprinting technique using specifically prepared multitiered branched porous anodic alumina templates.[100] These hierarchically branched pillar structures also showed a marked increase in hydrophobicity which is a salient property required in practical applications of these structures for good self-cleaning in dry adhesive conditions (Fig. 12C). Compared to the linear structures, such hierarchical structures improved the shear adhesion force by 150%. The artificial materials with high adhesion have not only been fabricated as elaborated above, but also lower adhesive surfaces have been obtained for the practical applications. Zhao *et al.* have prepared Au surfaces with micro/nano-hierarchical structures by replication of micropatterened silicon surfaces using PDMS and self-assembly of alkanethiol.[101] The as-obtained Au surfaces exhibited lower adhesion and improved nano-tribological properties, which confirmed that the adhesive force and friction force are regulated greatly by tailoring the surface topography and surface chemistry. Sugihara *et al.* have developed cutting tools with micro- and nanostructures surfaces formed using femtosecond laser technology.[102] The textured surface showed significantly improved lubricity and anti-adhesive properties by the evaluation of face-milling experiments on aluminum alloys. Sheparovych *et al.* have designed a composite responsive surface that demonstrates low adhesion to various

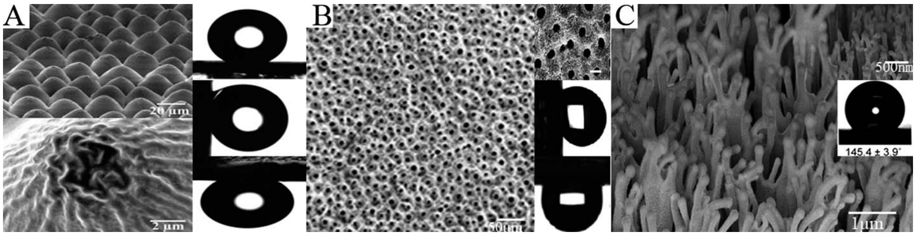

Fig. 12 (A) SEM images of the surface of the obtained replica [low magnification (lower) and high magnification (upper), respectively], insets show shapes of water droplets on the as-prepared replica surface with different tilt angles: (top) 0°, (middle) 90°, and (bottom) 180° [98] (reproduced by permission of ACS). (B) SEM images of the Au surface with negative biomimetic lotus topography at low and high magnification. Top right inset: magnified image of (B), other inset show shapes of water droplets on the as-prepared Au surfaces with negative biomimetic structures under tilt angles of 90 and 180° [99] (reproduced by permission of ACS). (C) SEM images of the topography for branched polycarbonate pillar structure. Top right inset is magnified image, and the other shows water CA of 145.4° [100] (reproduced by permission of ACS).

materials in air as well as in an aqueous environment.[103] Three major factors contributing to the adaptive low-adhesiveness of the designed surface in both humid air and liquid water are summarized, in particular the low contact area due to micro- and nanostructure according to the Cassie model.

In this regard, the studies of special adhesive surfaces have attracted more and more attention, the fabrication of these materials becomes more simple and efficient. But the relationships between adhesive force and microstructures still remains unclear even if several mechanisms are proposed, which show that a large amount of work should be performed to understand the structures and properties.

In addition, water strider legs possess superior water repellency so that they can stand effortlessly and walk quickly on water. Jiang's group found the water repellency mechanism of water strider legs.[104] It is revealed in the SEM images that the uniquely hierarchical structure on the legs consist of numerous oriented needle-shaped microsetae with elaborate nanogrooves (Fig. 13A–C). Such a structure plays a crucial role in inducing the superhydrophobicity of legs with a higher contact angle, which ensures that the legs can make tremendous dimples that are as deep as possible without piercing the water surface. Calculations through the Young–Laplace equation and three-dimensional model shows the maximal supporting force of a single leg against water surprisingly reaches up to 152 dynes, about 15 times the total body weight of this insect (Fig. 13D–E). On the other hand, it is noted that the superhydrophobic nanopatterned surfaces may dramatically reduce flow resistance[105] and fluidic drag.[106] Su *et al.* have studied the effect of the hierarchical surface structures on the low adhesion and water-repellent properties of water striders' legs from the point of view of the mechanics of adhesion.[107] Based on the 2D model established, they analyzed the nanoscale to microscale hierarchical surface structure on striders' legs and the processes of the legs pressing on and detaching from the water. The results indicated that the structural hierarchy and the length of the legs not only reduced the adhesion between biological surfaces and water in several ways but also decreased the energy dissipation in the quasi-static pressing and pulling

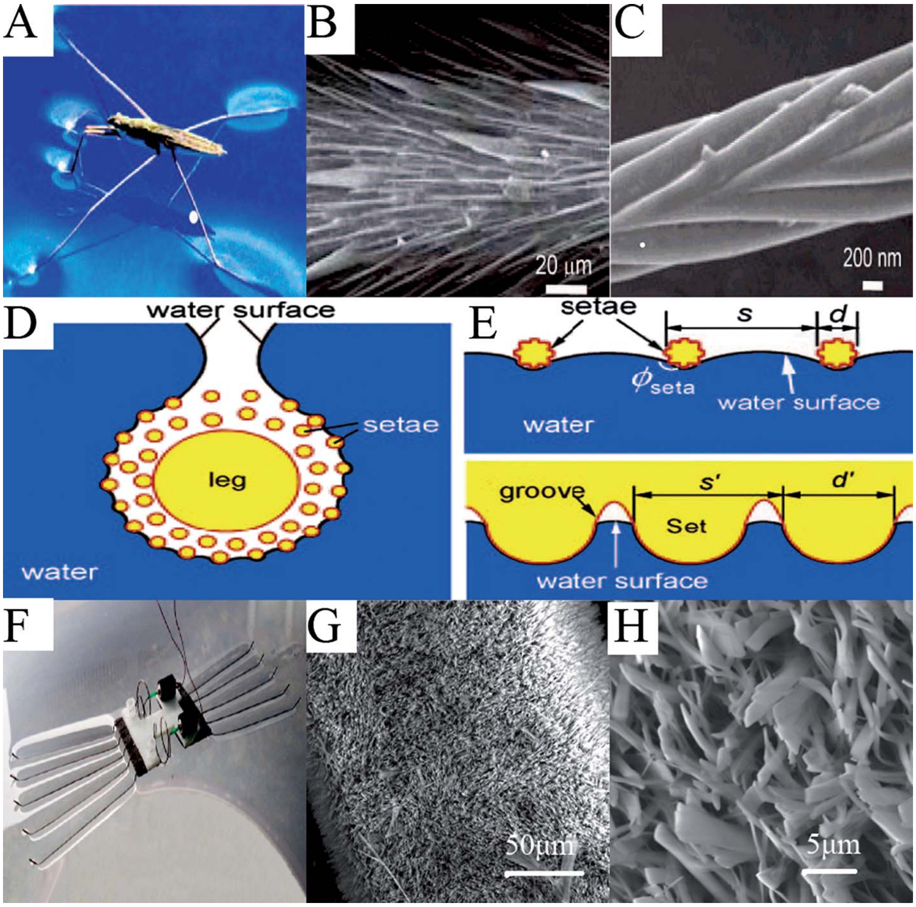

Fig. 13 (A) Water strider resting on water[104] (reproduced by permission of ACS). (B) SEM images of a water strider leg covered by numerous oriented needle-shaped microsetae[104] (reproduced by permission of ACS). (C) SEM image of grooved nanostructure on the seta surface. Transect models of oriented microsetae and nanogrooves on the strider leg used to predict its apparent contact angle[104] (reproduced by permission of ACS). (D) Illustrative transect of a leg in contact with water, where small circles represent transects of setae[104] (reproduced by permission of ACS). (E) Model of the oriented arrangement of microsetae in the upper view, with d and s being the mean diameter and spacing of setae, respectively, while model of oriented nanogrooves in the lower view, with $d'/2$ and s' denoting the radius of curvature and spacing of grooves, respectively[104] (reproduced by permission of ACS). (F) Top view of the water strider-like microrobot on the surface of water[108] (reproduced by permission of ACS). (G–H) SEM images of nanoribbon formed on the surfaces of artificial legs in low and high magnifications, respectively[108] (reproduced by permission of ACS).

processes and enhanced the efficiency of energy transfer from bioenergy to kinetic energy in the dynamic process during the locomotion of the water striders, which may provide useful guidelines for the design of superior water-repellent surfaces and novel aquatic robots. Zhang *et al.* have fabricated a novel water strider-like robot composed of ten superhydrophobic supporting legs, two miniature DC motors, and two actuating legs (Fig. 13F).[108] The bioinspired aquatic microrobot could not only stand effortlessly but also walk and turn freely on the water surface, exhibiting an interesting motion characteristic. A numerical model established showed the mechanism for the large supporting force of the leg lay in super-hydrophobicity due to the micro-and nanostructures of the legs (Fig. 13G–H). Thus, the special micro- and nanostructures endow the legs with higher hydrophobicity and lower drag, which ensures that they may walk rapidly on the water surface. In view of this, we can tune the flow drag by designing the micro- and nanostructures.

However, even though high drag reduction of up to 50% was measured using micro- and nanostructured technical superhydrophobic surfaces, an effect recently called “giant liquid slip”, the practicality is tempered by the short time (few minutes) that the air films persisted.[109,110] Thus, we must learn continually from nature because creatures in nature provide us with a large natural lab, their special, excellent structures and properties are worthwhile for studying and mimicking further. In particular, the micro- and nanostructures originating from nature exhibit some good performance as discussed in detail above. Based on making the mechanisms clear, the design and fabrication of functional materials with these properties will become a focus in the future. Although we have introduced the mechanical properties about micro- and nanostructures, other properties which exist in nature need to be explored.

3.3 Optical properties

It is well known that various optical phenomena exist commonly among creatures in nature. The investigations of their structures and mechanisms reveal that these phenomena should be attributed to the interactions between light and structures of these organisms. In the previous sections, we have referred to micro- and nanostructures which originated from living organisms, and summarized a few properties of these structures. However, with the progress of scientific testing methods and the further studies on nature, together with the need for optical devices for practical application of solar cells,[111] communication, optical properties of these structures receive much attention due to the multifunctionality exhibited by such structures, which open up avenues for novel multifunctional materials.

Brilliant, iridescent colors found on the bodies and wings of many birds and butterflies have been the subject of study for centuries. Generally, it is believed that color production in nature takes advantage of dyes, which is called chemical color, such as pigments in beautiful petals. However, scientist found that some colors are produced by structural variations, which are called structural colors. Newton was the first to suggest that such brilliant iridescent colors in birds and insects might perhaps be due to the presence of thin-film structures, as he had observed the color producing properties of such thin films.[112] Recently, structural colors have attracted great interest because their applications have been rapidly progressing in many fields related to vision, such as the paint, automobile, cosmetics, and textile industries. As the research progresses, it has become clear that these colors are due to the presence of surprisingly minute microstructures, which are hardly attainable even by ultramodern nanotechnology. Fundamentally, the structural color originating from microstructures has been proved to provide some insects and birds with charming colors, *e.g.*, some tropical butterflies, peacock feathers and some beetles.[113–115] The studies on structures of these species show that the dazzling iridescence arises from natural optical phenomena, the brightest of which originate in nano-scale structures that produce ultrahigh reflectivity and narrow-band spectral purity.

As early as 1999, Srinivasarao made a summary of nano-optics in the biological world, focusing on the color production in nature purely by physical means such as diffraction, interference, and scattering, and then analyzed the cause of color production on butterfly wings and bird feathers from the perspective of the interaction between light and architecture.[19] It is indicated that the structures responsible for these phenomena led to renewed interest in creating such intricate structures and to an understanding of their optical properties in much greater detail. Yoshioka *et al.* have explained the fundamental optical properties underlying the structural colors, and then surveyed these mysteries of nature from the viewpoint of regularity and irregularity of the structure, and finally proposed a general principle of structural colors based on structural hierarchy and showed their up-to-date applications.[116] Although the explanations of structural colors from the viewpoint of regularity and irregularity considering the hierarchy of the structure are just beginning, it will offer important information on developmental and ethological studies. Sato *et al.* have reviewed a structural color film with lotus effect, superhydrophobicity and tunable stop-bands inspired by using the original structure of the wings of a Morpho butterfly as a template (Fig. 14A–C).[117] Because the mechanism that causes the coloration of the wing was consistent with that of the coloration of colloidal crystals, the as-prepared films prepared by using colloidal crystals also displayed both blue color and superhydrophobic property due to the micro- and nanostructures on the surface. Feng *et al.* have observed the surface of a red rose petal, finding that there are micropapillae on the surface and many nanofolds exist on each papilla (Fig. 14D–E). Then biomimic polymer films are fabricated by duplicating the petal’s hierarchical micro- and nanostructures, which exhibit only structural color by UV-vis spectra (Fig. 14F).[118] The results showed that the flower’s bright color and special functions for human and animal visual systems originated from the combination of structural color driven by the micro- and nanostructures, and chemical color driven by pigments.[119] Later Üpping *et al.* have fabricated PDMS replicas analogous to the micro- and nanosized structural hierarchy on the petal surface with a biotemplated two-step replication approach.[120] The optical reflectance measurement of the native rose petal and its positive replica indicated that the micro- and nanosized structural hierarchy on the petal surface could induce a modulation of the optical reflectivity and a filtering effect in specific wavelength ranges. It is noted that a variation in the size of the micro- and nanostructures on the petal surface would lead to an effective modulation of the reflectance. These could

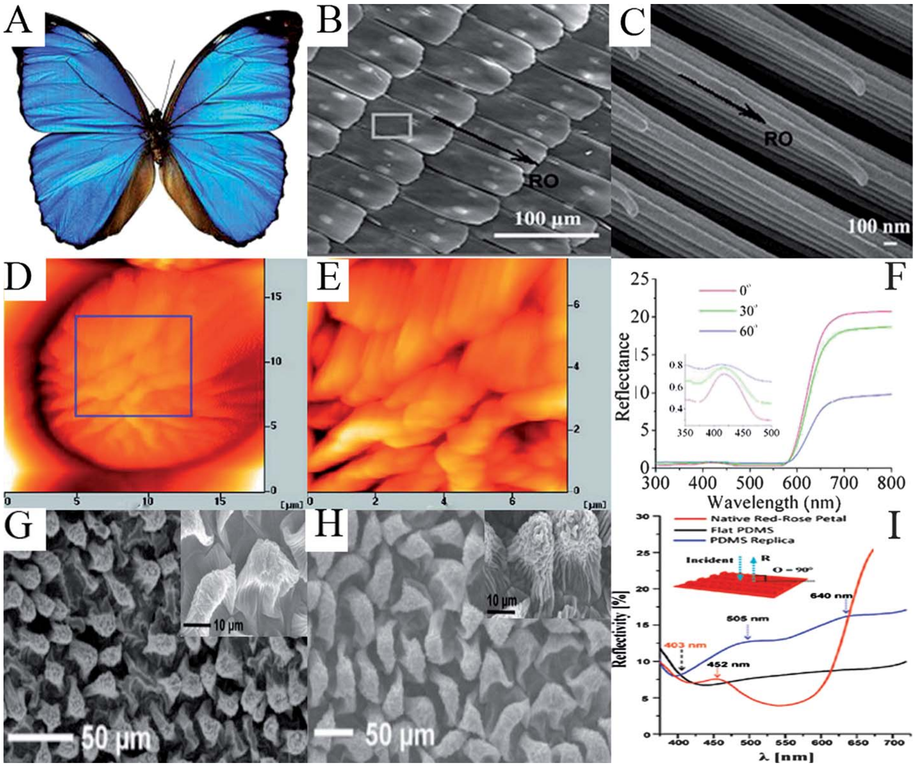

Fig. 14 (A) Typical digital photographs of the butterfly wings[117] (reproduced by permission of ACS). (B–C) SEM images of the periodic arrangement of overlapping micro-scales on the wings and fine lamella-stacking nano-stripes on the scales[117] (reproduced by permission of ACS). (D) AFM images of a red rose petal's surface, showing the hierarchical micropapillae and nanofold structure. (E) Enlarged image of the square area in D, showing the nanorods periodically patterned on the nanofolders[118] (reproduced by permission of ACS). (F) UV-vis reflectance spectra of a red rose petal at different incident angles, showing two peaks of both pigment and structural colors. The inset shows an enlarged plot of the region between 350 and 500 nm to illustrate the change in stop-band[118] (reproduced by permission of ACS). (G) SEM images of an air-dried native red-rose petal surface. Inset: magnified SEM imag.[120] (reproduced by permission of ACS). (H) Low magnifications of the positive PDMS replica. Inset: magnified SEM image[120] (reproduced by permission of ACS). (I) Reflectivity of a petal and its replica for normal angle of incidence[120] (reproduced by permission of ACS).

provide useful tips for the design of bioinspired optical devices (Fig. 14G–I).

Interestingly, insects' compound eyes and wings exhibit unique functions due to nipple arrays on the surface, which result in antireflective, water-repellent properties and so on. Xu *et al.* have fabricated biomimetic antireflective hierarchical structures based on the combination of self-assembled polymer spheres and nanoimprint lithography.[121] The hierarchical structures were constructed by creating nanopillars on microscale round protrusion arrays, which were analogous to natural mosquito eyes consisting of combined micro- and nanostructures (Fig. 15A). Such structures dramatically reduced the surface reflection from visible to near-infrared regions with an angle of incidence of up to 70° (Fig. 15B), and the more lower reflection could be realized by further increasing the height of the primary arrays. Qi *et al.* have obtained pyramidal hierarchical structured silicon surfaces by employing KOH etching and silver catalytic etching (Fig. 15C).[122] The as-prepared surfaces exhibited strong antireflection property (Fig. 15D) and the reflectivity was strongly reduced with the fabricated hierarchical structures. After fluorination these surfaces also exhibited superhydrophobic properties. These may have applications in optical and optoelectronic fields, such as prolonging the life of devices by self-cleaning and improving the performance of photon sensitive devices. Xiu *et al.* have prepared superhydrophobic surfaces with reduced hysteresis by Au-assisted etching of pyramid-structured silicon surfaces to generate hierarchical surfaces (Fig. 15E).[123] The obtained silicon surfaces showed low light reflection (Fig. 15F) because the presence of surface nanostructures makes the surfaces absorb most of the incident light, which offers significant advantages for high efficiency solar cells with self-cleaning properties. Nayak *et al.* have created self-assembled micro/nanostructures on a silicon surface for efficient light trapping using an ultrafast-laser micro/nanostructuring technique. Light reflection (including scattering) of the Si surface could be reduced to less than 3% for the entire solar spectrum and the material appears completely black to the naked eye.[124]

Although micro- and nanostructures exhibiting some optical phenomena on biological surfaces have been successfully transferred to engineering materials,[125–127] and desired properties also have been obtained, the specific mechanisms of structure-inducing optical phenomena still remain unknown even if some researchers ascribed it to the effects of interference, scattering, diffraction. Thus, making clear the principles of these properties based on further investigating new performance is our current focus.

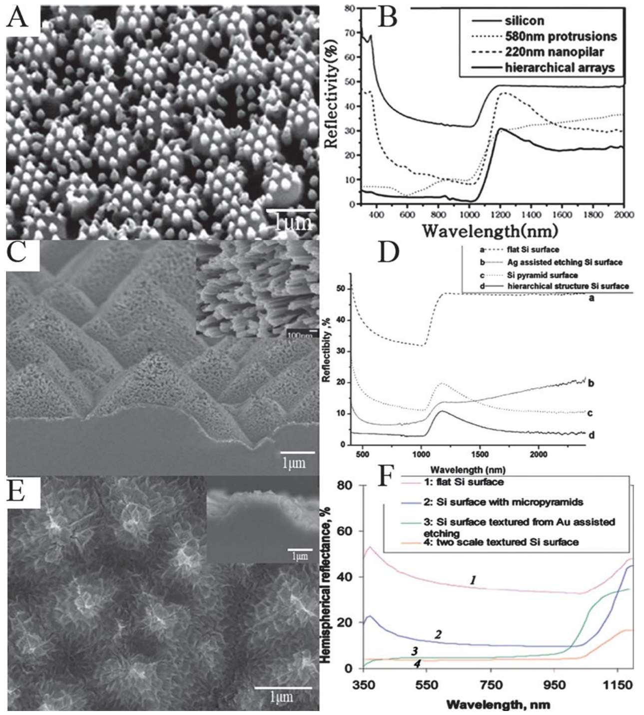

Fig. 15 (A) SEM image of the silicon hierarchical arrays created by etching on 1 μm protrusions with 220 nm spheres as the mask[121] (reproduced by permission of ACS). (B) Hemispherical reflection at the angle of normal incidence[121] (reproduced by permission of ACS). (C) Hierarchical structures generated with Ag-assisted etching. Inset: magnified SEM image[122] (reproduced by permission of ACS). (D) Hemispherical reflectance spectra of flat silicon (a), nanohole textured silicon surface (b), pyramid textured silicon surface (c), and hierarchically structured silicon (d)[122] (reproduced by permission of ACS). (E) Si hierarchical pyramid surface etched by Au-assisted etching, the inset is cross sections of Si pyramid surfaces etched by Au-assisted etching. (F) Light reflection of flat Si surface (1), Si surface with micropyramids (2), Si surface textured from Au assisted (3) and two scale textured Si surface (4)[123] (reproduced by permission of ACS).

Conclusion and outlook

In summary, we review briefly the recent developments of micro- and nano-structural functional materials with special wettability. Particular attention is devoted to summarizing the properties exhibited by such structures from the aspect of wetting behavior, mechanics and optics, which include superhydrophobicity, superhydrophilicity, superoleophobicity, low and high adhesion, reducing drag underwater, antireflection, structural color and so forth. Most of these properties are desired pursuits of scientists due to the unique functions shown by living organisms in nature and their potential applications. Research on micro- and nanostructures has not only fundamental interest but also promising practical applications in the realm of industry, which has become an increasingly hot research topic. Theoretical models about these structures have been improved continually through new experimental results. Many different synthesis strategies have been developed to fabricate functional materials with micro- and nanostructures.

However, it should be pointed out that the investigations in this field are still facing many challenges, and some of the problems still need to be solved for further study. First and foremost, the mechanisms of the features of micro- and nanostructures are still unclear. Relationships between structures and properties are only described qualitatively, while the exact quantitative descriptions still need to be investigated in depth. What's more, the stability of artificial micro- and nanostructures is worth considering. The stability of these structures against external damage including mechanical stress and chemical contamination should be addressed as they can largely affect the properties and restrict the material's application. Finally, whether other behaviours such as electricity, magnetic, acoustics are shown by micro- and nanostructures, and how to tune structural parameters to fabricate multi-performance materials, are still necessary to make further fundamental investigations. These will be beneficial for the practical applications of micro- and nano-structural functional materials in real life. As discussed in section 2, micro- and nanostructures were firstly found on plant surfaces in nature, thus learning from nature gives us inspiration to construct micro- and nanostructures on functional materials surfaces. Our future works will mainly concentrate on two aspects as follows: on one hand, by combining theoretical simulation with modern analytical technologies and tools, we will further explore and explain special functions related to micro- and nano-structures in the biological world so as to reveal the relationships between structures and properties to establish quantitative theoretical models. On the other hand, we will prepare multifunctional materials with micro- and nanostructures by regulating the nanometre structure superimposed on or constituted the micrometre structure.

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