

## 1

## Introduction of Nature-Inspired Functional Structural Surface

### 1.1 Advanced Materials Boosted by Bionics

Learning from the all-encompassing nature and drawing inspiration from natural creatures has been always an effective way for people to invent and create new things since ancient times. It is also a wise way for human beings to get rid of survival predicaments and to develop sustainably. After nearly four billion years of evolution and optimization, natural creatures have possessed many excellent properties that are far beyond human beings. The study of typical biometric organs and structures in the nature can not only help us understand nature better but also provide useful references and inspiration to solve current scientific puzzles and technical dilemmas [1–8]. As a new and comprehensive interdisciplinary subject, bionics has maintained strong vitality since its birth in the 1960s. In fact, the ideology of bionics has been existing in the world for thousands of years. The origin of bionics could be derived that nature has been the source of all kinds of technological ideas, engineering principles and major inventions since ancient times. In other words, bionics acts a bridge to link biology in the nature with technologies developed by human beings. As known to all, a wide variety of natural creatures can adapt to harsh environments through a long period of evolutionary processes, so that they can get survival and development. Surprisingly, some typical natural creatures possess outstanding properties that even precede humanmade delicate products in the fields of optics, mechanics, dynamics, and so on. Thus, taking inspiration from biology in the nature to develop new materials and technologies is a wise choice for scientists and engineers. It has flourished to this day and has gradually integrated into biology, materials science, mechanics, optics, and many other disciplines including electronics and electromagnetism. In recent years, with the rapid development of micro-/nanomanufacturing technologies, related instruments and equipment, scientists and engineers have turned to high-performance organisms in nature. They have been trying to reproduce the organisms by artificially copying the complex micro-/nanostructures with excellent performance. With the performance of traditional materials gradually entering the plateau stage, a breakthrough is needed for the flourishing research of new functional materials. The introduction of bionics ideas will provide a new pathway to break the deadlock of functional materials research.

In fact, research on bioinspired structural surfaces is in full swing at home and abroad. The relevant achievements have sprung up. Bioinspired functional surfaces are becoming new research hotspots in bionic engineering and are showing fire-new developments. At present, from the imitation of biological prototypes, the imitation objects range from biomolecules [9–11] (DNA molecules, RNA molecules, etc.), microorganisms [12–16] (viruses, bacteria, fungi, and algae) to plants [17, 18] (wood, leaves, etc.), animals [19–44] (beetles, butterfly wings, moth eyes, bird feathers, shells, teeth, marine life, gecko feet, mosquito, leeches, polar bear fur, etc.), and even the entire biological system [45–48], as shown in Table 1.1. Most of the imitation objects are concentrated on the creature's body surface, and the corresponding artificial replicas are the bioinspired structural surfaces. From the material point of view, the material types of bioinspired structural surfaces have gradually evolved from simple organic materials and inorganic materials to broad

**Table 1.1** Typical examples of structure–function correspondence in biological systems.

	<b>Biology</b>	<b>Feature structures</b>	<b>Functions</b>
Biomolecules	DNA	Nanostructures	Miniaturization
Microorganisms	Virus, bacteria, fungi, yeast	Various nanostructures	Self-assembly, miniaturization
	Algae (diatom, coccolithophore)	Periodic porous structures/hierarchical microstructures	Chemical energy conversion, particular optical functions
Plants	Wood	Periodic porous structures	High mechanical strength
	Leaves	Hierarchical structures	Chemical energy conversion, superhydrophobicity, self-cleaning
Animals	Insects (beetles, butterfly wings, etc.)	Periodic porous structures/hierarchical structures	Structural color, superhydrophobicity
	Compound eyes	Periodic structures	Antireflection
	Feathers	Periodic structures	Structural color, superhydrophobicity
	Seashells, teeth	Periodic structures	Structural color, high mechanical strength
	Marine animals (sea urchin exoskeleton)	Periodic structures	Particular optical functions
	Gecko feet	Hierarchical structures	Strong adhesive force
	Mosquito's legs	Hierarchical structures	Water-supporting ability
	Fur and skin of polar bear	Hollow structures	Thermal insulation
Biological systems			Self-repair, self-heating, sensory-aid devices

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material systems such as hybrid materials and composite materials. Nature-inspired functional structural surfaces (NIFSS) are present in a variety of different material states and structural forms. As expected, they also show remarkable functional characteristics.

Here are some typical examples. A series of multidimensional biomimetic silicon-based nanocomposites were prepared by DNA origami [49]. Bioinspired photo-controlled nanochannels based on DNA molecules can be used for drug sustained release, optical information storage, and logic networks [50]. The shell-like ordered layered structure material exhibits ultra-high mechanical properties [51]. By mimicking the unique topology of plant viruses, nano-optical antennas can be prepared for molecular fingerprinting [52]. The membrane of bacteria *Bacillus subtilis* exhibits durability against liquid wetting and gas permeation and is expected to provide an example for the study of antibacterial and biomimetic drainage surfaces [53]. The natural photonic crystals with opal-like structures of algae *Cystoseira tamariscifolia* cells can produce vivid structural colors by reversibly changing the stacking state of the internal structure in response to external environmental conditions, thereby exhibiting light manipulation ability in addition to visual signals [54]. By using the natural structure of wood anisotropy and the cellulose component therein, material scientists design and manufacture low-cost, lightweight, and high-performance structured “super wood,” all-wood supercapacitors, “transparent timber” with mechanical and transparent properties [55–57]. A series of hydrophobic, oleophobic, and amphiphobic “lotus effect” inspired self-cleaning surfaces [58–61] and so on. It can be seen that the surface structures of organisms and their excellent performance interdependent to form an integration of structure and function. It should be noted that structures lay the foundation for superior performance. Performance also reflects the extension of the structures. Therefore, excellent functional properties of biological surfaces are revealed. On this basis, the design and manufacture of the NIFSS that meet the requirements have become a hotspot and a challenge in bionic engineering.

Many unique functional properties of biology in nature are inextricably linked to ultrafine 3D micro-/nanostructures. Taking the most common species of plants and animals as examples, studies have shown that the self-cleaning effect of the lotus leaf, also known as the “leaf effect,” benefits from the convex-packed structures densely distributed on leaf surfaces [62]. The magical phenomenon of continuous directed transport of liquid film on the surface of the *Nepenthes alata* rim is related to the multistage groove structures of the lip and the blind-hole structures with a one-way wedge angle in some grooves [63]. The gecko can freely climb on the vertical wall, which mainly relies on the rich microvilli structures of the sole to provide strong adhesion [64, 65]. Another similar case is the adhesion phenomenon of the sacral bristles of the ladybug *Coccinella septempunctata* to the rough surfaces [66]. The antireflective effect of the moth eye is closely related to the conical array of the outer surface of the eyes [64]. The directional water-collecting effect of the spider silk is realized by its unique periodic spindle knots [63]. The single scale of the chafer *Cyphochilus* wings can be dazzling white, and the optical performance is closely related to the filamentous network microstructure of the wing scale surface [67, 68].

## 1.2 Definition and Classification of NIFSS

Bioinspired structured surfaces are referred to as NIFSS in this book. Due to the excellent functional properties of biological surfaces in many respects, materials scientists and engineers have long focused on biomimetic structures of biological surfaces and artificial reproduction of their excellent functions. The so-called NIFSS is a general term for all kinds of artificial structural surfaces with various materials at different scale levels inspired by biological surfaces.

In this book, according to the different sources of the original micro-/nanostructures of the biological surfaces, the NIFSS can be divided into two categories. One is biology-based structure surfaces with similar or enhanced functional properties, which are designed and developed using the biological surface itself as a raw material or by chemical modification and physical evaporation. The other one is biology-inspired structural surfaces with similar or enhanced functional properties, which are designed and developed in combination with existing micro-/nanomanufacturing processes. The two types of NIFSS are explained one by one in the following text.

The NIFSS can be further subdivided into two subclasses: (i) the biological surface itself is an original structural material to get the desired functional surface with the natural functional characteristics. Various types of biological surfaces with excellent functional characteristics, previously reported, can be regarded as natural structural surfaces. Since the biological surfaces have been separated from the biological body, the excised biological surfaces themselves can be considered a special kind of NIFSS; (ii) denatured biomimetic structural surfaces based on biological surfaces are obtained by chemical modification. Since the main component of the biological surfaces itself is organic, it is still difficult to meet the stringent requirements for practical applications. Therefore, it has become a kind of modification and enhancement treatment of the natural structure surfaces.

NIFSS mainly refer to artificial biomimetic materials or devices that mimic the excellent functional properties of the biological surface or the internal mechanism, and the final realized functions can be similar to or different from original biological surfaces. The biology itself is only used as a source of inspiration and imitation, and it is not used as the original material to participate in the design and manufacture of the NIFSS.

## 1.3 Typical Prototypes with Structural Surfaces

### 1.3.1 Butterfly Wings

Among these outstanding research examples, butterfly is undoubtedly one of the most diverse and well-known biological prototypes. A variety of butterflies is biologically and geographically diverse (Figure 1.1). The collection channel of butterfly samples is convenient, providing a stable sample source and a huge database of biological structures for in-depth study of typical butterfly wings.



**Figure 1.1** Different butterflies with colorful wings in the nature.

In recent decades, there have been numerous research cases based on the butterfly wings or inspired by the micro-/nanostructures of the wing scales, and the research content is rich enough. For example, in a study related to the structures of butterfly wings, the main research content includes the microscopic characterization of the micro-/nanostructures on the butterfly wing surface and the intrinsic formation mechanism of the brilliant structural colors [26, 69–82]. A quantitative study on the contribution of single wing scales to interference and diffraction in the structures of butterfly wings was also carried out [83]. A bioengineering method of butterfly wing structural colors is also an emerging hotspot [84–90]. In terms of wettability research, related studies have shown that the micro-/nanostructures of the butterfly wing scales endow the wing surface with higher roughness. They can regulate surface wettability and control the bounce behavior of droplets on the surface [91, 92]. Based on this, directional wet super-slip fibers [93] and structured water-proof surfaces [94] are developed. In the study of responsive materials, the scales of the *Morpho sulkowskyi* make it selectively optically react to different vapors. This optical response is derived from the polarity gradient of the micro-/nanostructure material itself and is superior to the performance of existing nanophotonic sensors [24, 95]. The micro-/nanostructures of the *Greta oto* butterfly wing surface have piezoelectric response characteristics, which are expected to provide a reference for the development of new optoelectronic devices. It can be applied to the field of

electro-stealth [96]. Photonic crystal-type micro-/nanostructures and pigment-type micro-/nanostructures on the butterfly *Polyommatus icarus* can exhibit differential response characteristics to cold stress [97]. Photonic crystal structures of *Papilio ulysses* wing scales can follow the change in the external refractive index to produce a reversible thermochromic reaction [98]. *Morpho* wing scales can be slightly deformed by external thermal radiation. Inspired by this, researchers have proposed a new thermal imaging technology [99]. In catalytic research, the main research work includes photocatalysis induced by structural colors of butterfly wings [90] and chemical catalysis using butterfly or its imitation as support materials [100]. In addition, in the oil/water separation research, researchers have used butterfly wings as the osmosis membrane to imitate the artificial filter membrane for oil/water separation [101].

Butterfly wings have shown great research value and the application potential in various research fields, such as micro-/nano-optics, water transportation, sensing detection, optical catalysis, and even oil/water separation. They have very broad and potential application prospects.

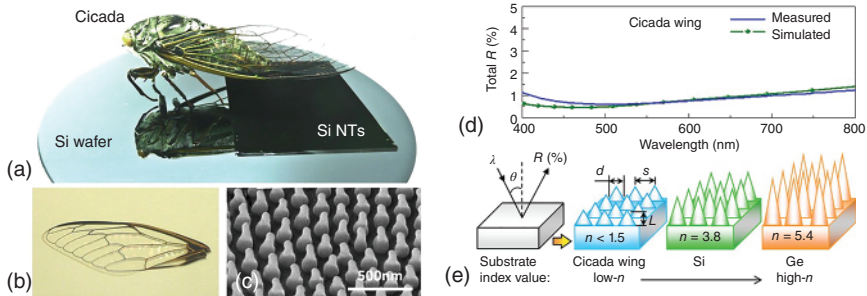
### 1.3.2 Cicada Wings

Similarly, cicada is another typical biological prototype for bionic research. Especially, its wing has attracted intensive research interest in the field of antireflective materials. Cicada wings have typical periodic micro-/nanostructure arrays. Huang et al. [102] characterized the micro-/nanostructures of cicada wings by scanning electron microscope (SEM) and measured total reflectance of cicada wings in the wavelength range of 400–800 nm, which is as low as 1%. A three-dimensional (3D) array model based on the micro-/nanostructures of its wing surface was established. The simulation results were in good agreement with the experimental results (Figure 1.2). It has been confirmed that cicada wings have ultra-low reflectivity and exhibit excellent antireflective properties.

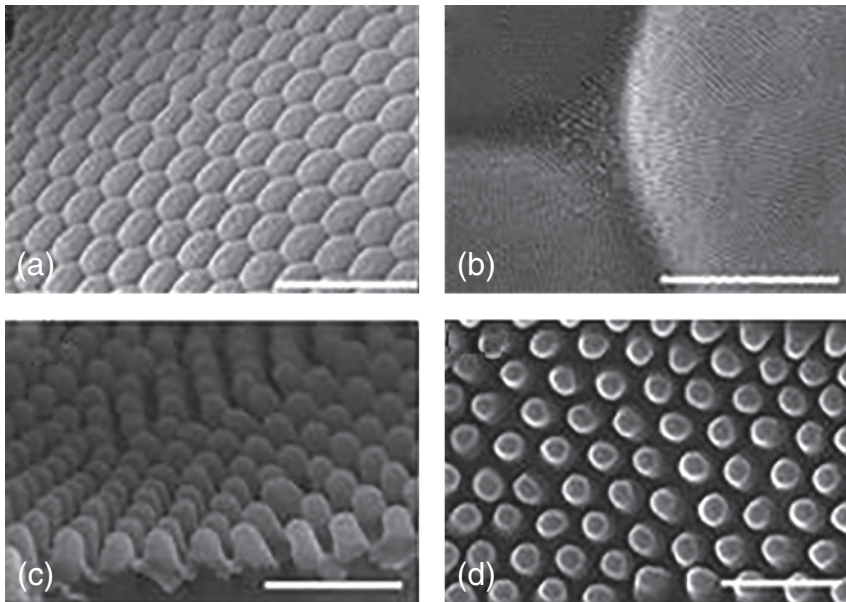
### 1.3.3 Moth Eyes

In the insect world, compound eyes present an attractive physiological optical performance in terms of optical sensitivity and antireflection [103–105]. Compound eyes usually contain thousands of small eyes (ommatidia) [106], as shown in Figure 1.3. The eyes are usually neatly distributed along a spherical or hemispherical surface in a hexagonal pattern. The surface of these small eyes is not smooth. It is tightly covered by hemispherical nanoscale bumps, forming a grating that enhances the ability of small eyes to absorb light [107]. Taking nocturnal moths as an example, the cornea of the subwavelength structures has an optical antireflective function, which can provide stealth help for its nighttime activities [108, 109]. It has been confirmed that the antireflective function of the moth eye is caused by the micro-/nanostructures, which makes a gradient change in the refractive index between the air and the cornea, achieving the inhibition of light reflection [64].

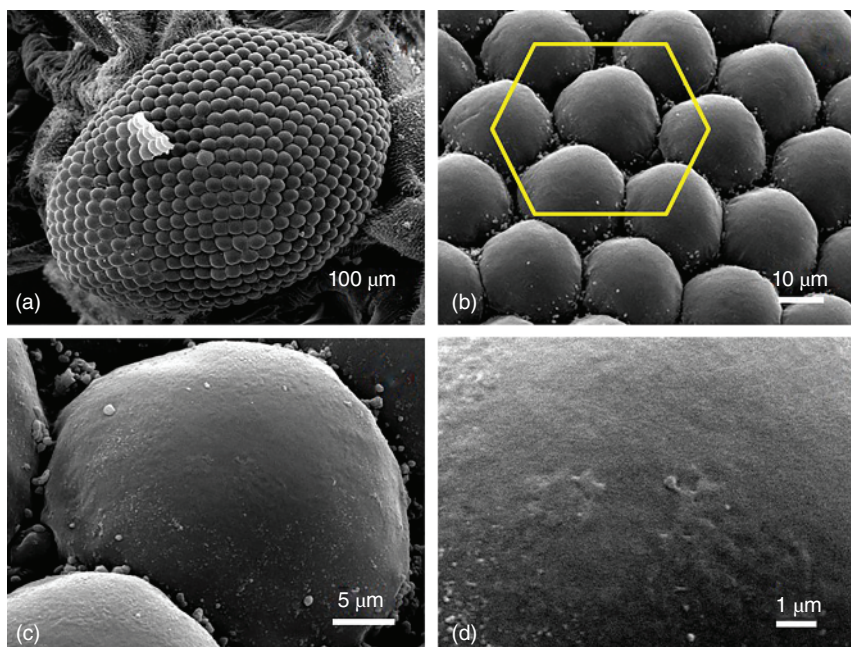




**Figure 1.2** Transparent cicada wings with antireflective nanostructure arrays. (a) A cicada specimen was placed partially on a polished silicon wafer and a piece of Si nanotips. (b) Photographic image of a singing cicada wing. (c) SEM image of the cicada wing surface. (d) Comparison of measured and simulated total reflectance (total  $R\%$ ) spectrum as a function of wavelength for the cicada wing. (e) Schematics of reflectance reduction of biomimetic nanostructures with feature parameters compared to planar surfaces. Abbreviations:  $\lambda$ , incident wavelength;  $\theta$ , angle of incidence;  $d$ , diameter;  $s$ , spacing;  $L$ , length;  $n$ , bulk refractive index; Si, silicon; Ge, germanium. Source: Reproduced with permission from Liimatainen et al. [102]. Copyright © 2015 American Chemical Society.



**Figure 1.3** SEM images of the *Attacus atlas* moth eye showing the compound eye structures. Scale bar: (a) 100  $\mu\text{m}$ , (b) 5  $\mu\text{m}$ , (c) and (d) 500 nm. Source: Reproduced with permission from Wang et al. [106]. Copyright © 2011 The Royal Society.



**Figure 1.4** SEM images of compound eyes. (a) The compound eyes are ellipsoidal, composed of hundreds of ommatidia. (b) Ommatidia are uniform and tightly arranged. (c) The upper part of ommatidia is spherical, and the lower is cylindrical, with a diameter of 20  $\mu\text{m}$  or so. (d) There is no more tiny structure on the ommatidia surface. Source: Reproduced with permission from Han et al. [110]. Copyright © 2014 Science China Press and Springer-Verlag Berlin Heidelberg.

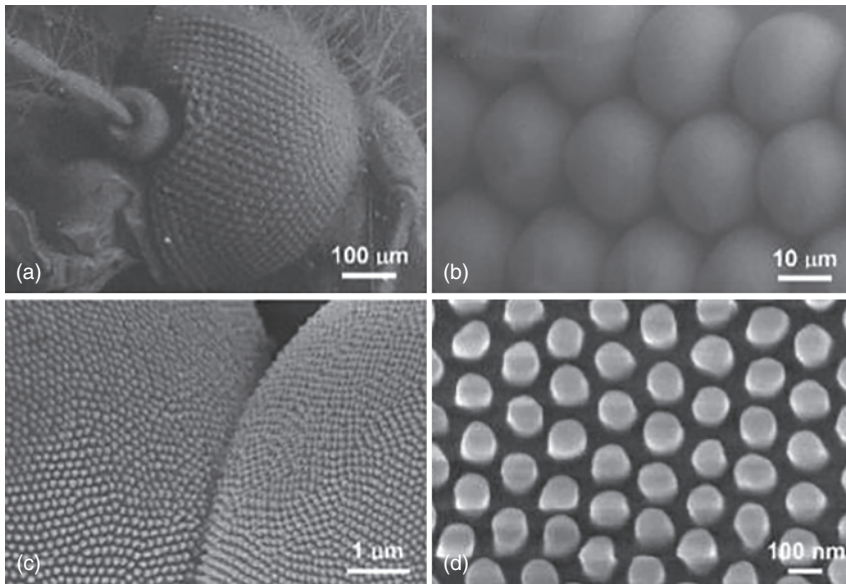
#### 1.3.4 Mayfly Eyes

Mayfly *Ephemera pictiventris* is a kind of insect that lives in the near water environment. Its compound eyes can still maintain a clear view in the environment where water vapor is concentrated [110]. The main component of the cornea of the compound eyes is chitin, whose intrinsic contact angle is about  $100^\circ$ . The eyes exhibit excellent superhydrophobic properties. The top of the small eye and the diameter of the base is not equal. The small eye can be seen as the upper and lower parts. The upper part is approximately spherical. The lower part is a truncated cone shape, which is closely arranged in a hexagonal shape. The overall height of the small eye is about 11  $\mu\text{m}$ ; the diameter of the base is about 22  $\mu\text{m}$ . The upper spherical surface is straight. The compound eye size is consistent and closely arranged. Further enlargement results show that the surface of the small eye is relatively smooth and has no tiny nanoscale structures (Figure 1.4).

#### 1.3.5 Mosquito Eyes

Other insects like mosquitoes *Culex pipiens* also exhibit excellent superhydrophobic properties [111], which keep mosquitoes live in extremely humid environments



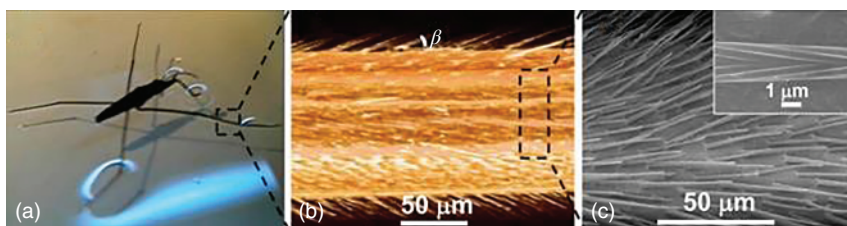


**Figure 1.5** Complex hierarchical micro-/nanostructures of the compound eyes of mosquitoes. (a) SEM image of a single mosquito eye. (b) Numerous ommatidia forming a hexagonally close-packed micro-hemisphere. (c) Two neighboring ommatidia with nanonipple arrays. (d) Hexagonally non-close-packed nanonipples covering an ommatidial surface. Source: Reproduced with permission from Tadepalli et al. [111]. Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

with clear vision. For mosquitoes, the complex hierarchical micro-/nanostructures of the compound eyes provide a structural basis for the realization of this function as shown in Figure 1.5. Similarly, this compound eye is also composed of a large number of small eyes. On the one hand, the microlevel protrusion structure of the compound eye is uniformly arranged in close-packed hexagons, which can effectively prevent larger droplets from staying in the gap of the small eyes. On the other hand, the nanosized mastoid in the small eyes plays a key role in avoiding small-scale water vapor condensation. With the synergistic effect of these two features, hydrophobicity and anti-fogging of the mosquito compound eye are finally realized.

### 1.3.6 Water Striders' Legs

It is well known that water striders can float on water surface and they can be propelled rapidly with their superhydrophobic hairy legs by transporting the momentum [112, 113] waves to propel themselves across the water surface [112, 114–116]. Water strider *Gerris remigis* (Figure 1.6a) living at the water surface in a highly humid environment. Without any external force, tiny, condensed droplets in the range of femtoliters (fL) to microliters ( $\mu\text{L}$ ) are removed from the strider's legs, owing to the presence of oriented conical setae. The leg of *Gerris* is a centimeter-sized cylinder (of typical diameter  $150\ \mu\text{m}$ ) decorated by an array



**Figure 1.6** (a) *Gerris remigis* lives at the water surface in a highly humid environment. (b, c) Micro-XCT and SEM images of a water strider's leg showing typical hierarchical structures. Source: Reproduced with permission from Wang et al. [112]. Copyright © 2015 National Academy of Sciences.

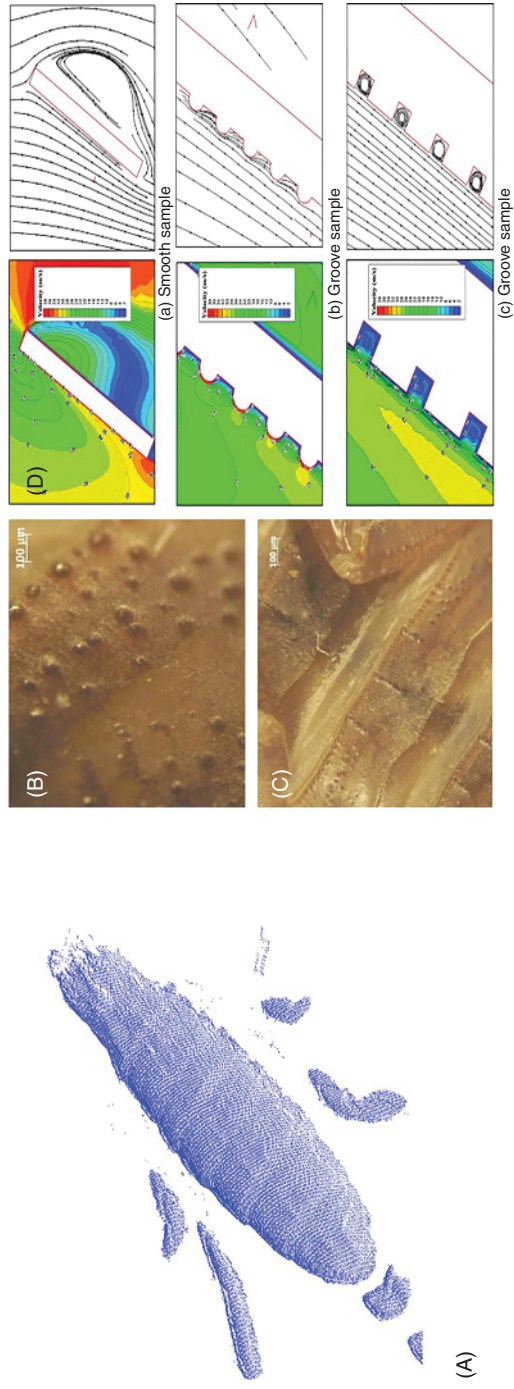
of inclined tapered hairs (Figure 1.6b,c) characterized by micro X-ray computed tomography (XCT) and SEM. Individual setae have a length  $L = 40\text{--}50\text{ }\mu\text{m}$ , a maximum diameter of  $\sim 3\text{ }\mu\text{m}$ , and an apex angle of  $\sim 5^\circ$ . They make regular arrays with a mutual distance of  $5\text{--}10\text{ }\mu\text{m}$  and are tilted by an angle  $\beta = 25\text{--}35^\circ$  to the base of the leg (Figure 1.6b,c). In addition, longitudinal or quasi-helicoidal nanogrooves are found on the setae surface, as shown in Figure 1.6c (*inset*).

### 1.3.7 Scorpion Back

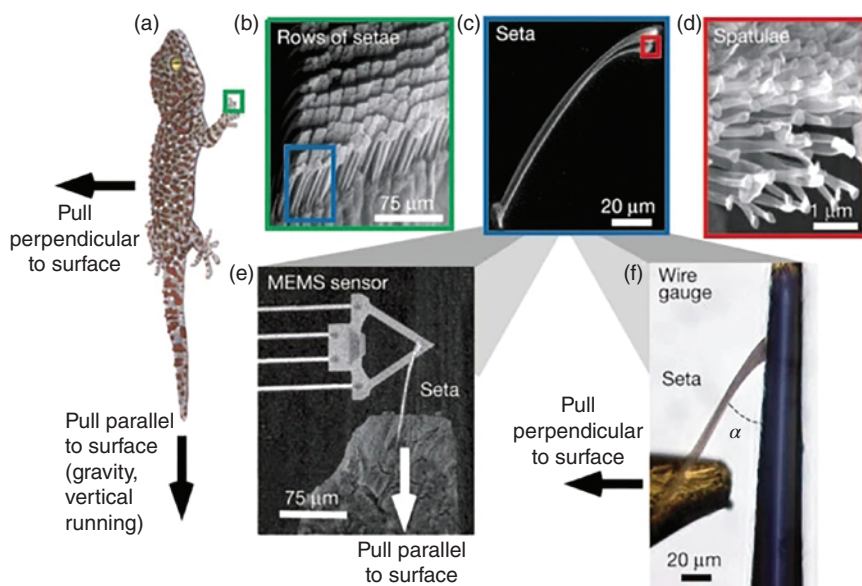
For creatures surviving in deserts, the abrasion of the body surface by wind and sand is main challenge. Abrasion is also undesirable, which can cause catastrophic failures in most industrial applications [117]. In nature, some animals such as desert lizards and scorpions live in a gas–solid mixed medium environment such as sand. They perform in this environment through the synergy of special surface morphology, internal microstructure, and biological flexibility. The back of the scorpion can resist abrasion and protect it from damage (Figure 1.7). Han and Zhang et al. [118–120] showed the erosion resistance mechanism of scorpion back, which is the result of multiple coupling effects. The surface morphology, material, and elasticity of the back of the desert scorpion are important biological coupling elements to resist the erosion. According to their analysis, the scorpion can form special protrusions and grooves on the back through adaptation to the living environment and its evolution, thereby changing the flow state of the surface boundary layer and reducing surface erosion. On the other hand, the elastic internodal membranes and side membranes play the role of energy release and help reduce erosion.

### 1.3.8 Gecko's Feet

Gecko is the largest animal known to support its weight by producing high (dry) adhesion [121]. The ability of geckos (Figure 1.8a) to climb on vertical walls has been noticed in ancient times. However, it was not until the invention of the electron microscope in the 1950s that it was possible to observe the skin on the gecko's feet (Figure 1.8b) and toes (Figure 1.8c). The observed skin has a complex fibrous structure composed of lamellae, setae, branches, and spatula (Figure 1.8d) [64, 122–129].



**Figure 1.7** The dorsal surface of the scorpion. (a) Scanned data using a laser scanner. (b) The convex hull of scorpion back. (c) The groove of scorpion back. (d) Mechanism of the anti-wear surface of the scorpion: the air is rotating in the groove channel, forming a stable low-speed reverse flow zone. Source: Adapted from Han et al. [118] with permission from the American Chemical Society.

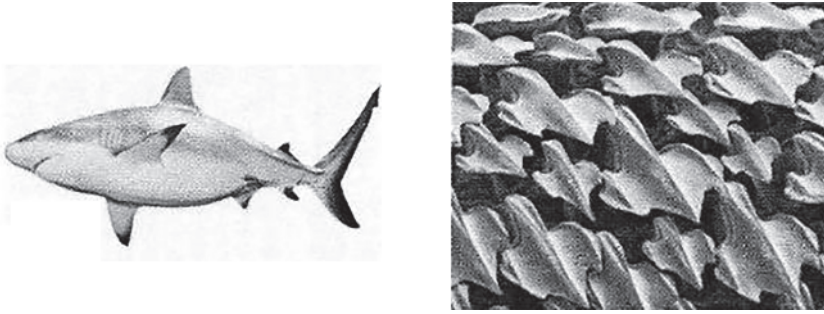


**Figure 1.8** Gecko setae and apparatus for force measurement. (a) Photo of the Tokay gecko (*Gekko gekko*). (b) SEM image of arrays of setae from a toe. (c) A single seta. (d) The finest terminal spatula of a seta. (e) Single seta attached to a microelectromechanical system (MEMS) cantilever capable of measuring force production during attachment parallel and perpendicular to the surface. (f) Single seta attached to an aluminum bonding wire capable of measuring force production during detachment perpendicular to the surface. Source: Reproduced from Autumn et al. [64] with permission from Nature Publishing Group.

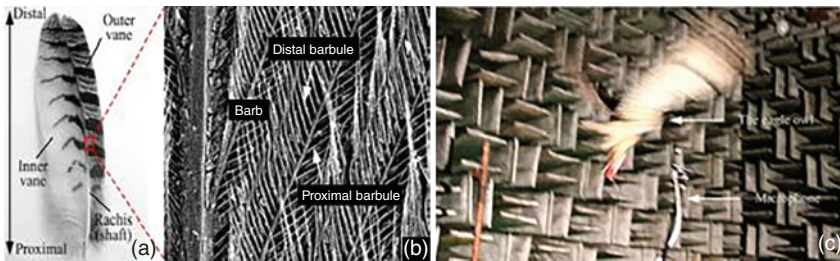
This hierarchical structure allows the gecko to attach to or detach from the surfaces at will. One explanation for the gecko's ability to control adhesion is that it can adapt to surface roughness and achieve a very large actual contact area between its feet and the surface [64, 125–130]. Also, compliance and adaptability of the setae contribute to high adhesion. This could inspire the innovative design of high-sensitive sensors for force measurement (Figure 1.8e and f).

### 1.3.9 Underwater Animals

Underwater animals, such as carp and shark, can swim freely owing to their special surface structures. For carp, the fan-shaped scales are covered by oriented nanostructured micropapillae (Figure 1.9), which not only has a drag reduction function but also has super lipophilicity in air and super oleophobicity in water [131, 132]. The surface of super-oleophobic fish originates from the micro–nano hierarchical structure of the water phase. Sharkskin is a natural low-resistance surface model. It is covered by very small individual tooth-like scales called dermal denticles (little skin teeth), with prismatic longitudinal grooves (parallel to the direction of local water flow). These grooved scales reduce the formation of vortices present on a smooth surface, resulting in water moving efficiently over their surface [133, 134].



**Figure 1.9** Scale structure on a shark. Source: Bechert et al. [133].



**Figure 1.10** The wing feather of the eagle owl. (a) The rachis of the feather. (b) The barbs grow in different directions. (c) The eagle owl flight noise measurement. Source: Adapted from Chen et al. [135] with permission from Springer Nature.

### 1.3.10 Eagle Owl

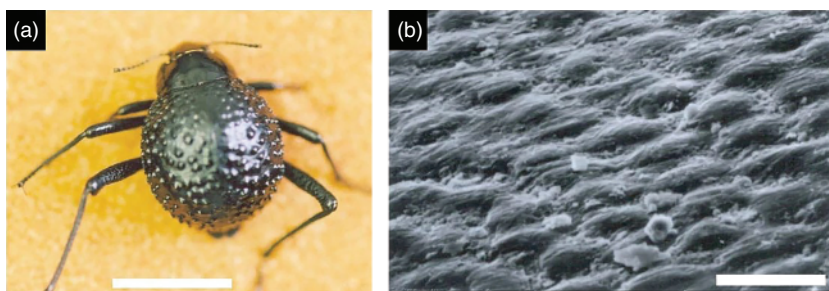
Many species of owls can fly quietly. Acoustic measurements and microscopic observations on owls (*Bubo bubo*) [135] show that owls produce lower sound intensity and low-frequency flight noise, and owls' wing feathers have greater sound absorption characteristics. The microscopic structures of three special characteristics of feathers help to improve the pressure fluctuation of turbulence boundary and suppress the generation of vortex noise (Figure 1.10).

### 1.3.11 Desert *Stenocara* Beetle

In areas with limited water resources, such as the Namib Desert, nature has developed elegant solutions to collect water from the atmosphere. The superhydrophobic pattern on the back of the *Stenocara* beetle in the Namib Desert is a good example of micro-condensation of water [136]. The *Stenocara* beetle in the Namib Desert uses the hydrophilic/superhydrophobic patterned surface on its wings (Figure 1.11) to collect drinking water from the fog-filled wind.

The back of this beetle is composed of hydrophilic hills and super-hydrophobic channels. The former can collect water from the fog in the desert atmosphere, and the latter can help the collected water droplets flow into the beetle's mouth. After these small droplets converge into larger droplets, they roll into the beetle's





**Figure 1.11** The water-capturing surface of the fused-over wings (elytra) of the desert beetle *Stenocara* sp. (a) Adult female, dorsal view, peaks and valleys are evident on the surface of the elytra. (b) SEM image of the textured surface of the depressed areas. Scale bars: (a) 10 mm and (b) 10  $\mu$ m. Source: Adapted from Parker and Lawrence [136] with permission from Nature Publishing Group.

mouth and provide a fresh breakfast drink for the beetle [136, 137]. Research has shown that the formation of these large droplets is due to the uneven surface of the insect, which is composed of alternating hydrophobic, wax-coated and hydrophilic, non-wax areas. This fog-collecting structure design can be cheaply replicated on a commercial scale and can be applied to water-collecting tents and building coverings [136]. Inspired by this wonderful natural design, Rubner and coworkers produced a superhydrophobic/hydrophilic patterned surface to mimic the structure of the beetle's back [137]. The water sprayed on the superhydrophobic pattern only forms small spherical water droplets, which are mainly concentrated on the hydrophilic pattern. Later, Garrod et al. also demonstrated the preparation of superhydrophobic/hydrophilic patterned surfaces to collect water [138]. The water collection capacity of different superhydrophobic/hydrophilic ratios on the surface has been studied in detail. Through the above examples, the application prospect of superhydrophobic/hydrophilic pattern coatings in actual water collection devices can be predicted.

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