1

Wetting-Controlled Systems of Biological Surfaces

1.1 Introduction

Creatures and animals have achieved the unique wetting-controlled system through the evolvement of biological surfaces over thousands of years in a natural environment. These natural biological properties have taken much attention: for instance, plant leaves and duck feathers for superhydrophobic property, butterfly wings for directional water repellency, spider silks for capturing tiny water droplets from air, and so on. In recent years, more biological surfaces with wetting-controlled abilities have been discovered, which have inspired researchers and scientists to develop novel systems of surfaces with self-cleaning, water repellency, super-slipper, water collecting, etc.

The wetting phenomenon can be easily explained. Wenzel explained the state of droplets on plants in 1936 [1]; he proposed that the leaves' roughness raised the droplet's contact angle (CA). A rule of wetting contact is regulated by Wenzel, which is named as Wenzel equation. Meanwhile, in 1944, Cassie and Box suggested another rule about the air fraction on the rough surface of plants [2], explaining why droplets slide away from the surfaces of plants' leaves and animals. The air–solid fraction plays a role in raising the contact angle of water droplets on the rough surface of lotus leaves. It is attributed that the trapped-air state appears on the surface of lotus leaves, accordingly reducing the solid interface contact with the droplets, resulting in the droplet's easy-sliding-off property. A rule can be set and named as Cassis and Box equation, having been extended into today, which is used to elucidate the properties of superhydrophobic surfaces. Following these equations and viewpoints based on surfaces, scientists and researchers have basically understood the wetting-controlled properties of biological surfaces.

Based on the first discoveries of wetting properties on biological surfaces in years, the examples can be taken as shown in Figure 1.1.

1.1.1 Duck Feather

In 1945, Cassie A. B. D. first reported the hydrophobicity of duck feather surfaces in his groundbreaking study of large CAs on animal and plant surfaces [3]. This seminal work laid the foundation for our understanding of the unique surface properties

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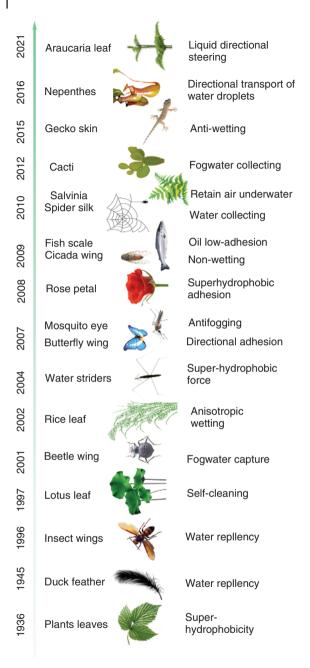


Figure 1.1 The groundbreaking findings on wetting-controlling from biological surfaces in years for promising future applications.

exhibited by various natural materials. Cassie's pioneering research revealed that duck feathers possessed an exceptional resistance to wetting by water droplets. He observed that when water droplets came into contact with the feather surfaces, they did not immediately wet the feathers but instead formed highly spherical beads that

rested atop the surface. This phenomenon was attributed to the combined effects of the microstructure of the feather surface and the intrinsic hydrophobicity of the materials involved. As a result, water droplets could maintain their spherical shape, exhibiting high CAs, and could easily roll off the surface, leaving the feathers dry.

Cassie's findings not only advanced our understanding of the physical properties of natural surfaces but also inspired the development of biomimetic materials with hydrophobic characteristics. Researchers in various fields, from materials science to engineering and beyond, have drawn inspiration from the remarkable hydrophobicity of duck feathers to design surfaces and coatings with applications ranging from self-cleaning materials to water-resistant textiles and advanced adhesives.

Over the decades since Cassie's pioneering work, our comprehension of surface wetting and the underlying principles governing the behavior of liquids on solid surfaces has deepened.

1.1.2 Insect Wings

In 1996, the research conducted by Wagner [4] provided groundbreaking insights into the relationship between insect wing surface structures, wettability, and contamination resistance. This study focused on the surface structures found on insect wings and how these structures influence wettability and contamination resistance. It highlighted the role of these structures as vital adaptations in the insect world and sparked interest in biomimicry for developing advanced materials and technologies. The study highlighted that different insect species have evolved unique surface sculptures on their wings, leading to variations in wettability and contaminability.

The research has implications beyond entomology. It inspired biomimicry in materials science and engineering, where scientists and engineers aim to replicate these hydrophobic surface structures for various applications, such as self-cleaning materials, antifouling coatings, and water-repellent textiles.

1.1.3 Lotus Leaf

In 1997, Barthlott and Neinhuis [5] published a groundbreaking paper titled "Purity of the sacred lotus, or escape from contamination in biological surfaces" in the journal Planta. This paper is notable for presenting the first scientific exploration and documentation of the lotus leaf effect, a natural phenomenon characterized by the remarkable self-cleaning and water-repellent properties of lotus leaves and certain other plant surfaces. They identified and described the specific micro- and nanoscale structures found on lotus leaves' surfaces. These structures included tiny wax-covered bumps and nanoscale wax crystals. They recognized these surface features as crucial contributors to the lotus leaf's hydrophobicity.

This work highlighted the potential applications of the lotus effect in various fields, such as materials science and engineering. It inspired scientists and engineers to mimic the lotus leaf's surface structures to create self-cleaning materials and technologies.

1.1.4 Beetle Back

In dry and hot Namib Desert, there are several beetles showing superior water collections to feed themselves. In 2001, Parker A.R., et al. found the hydrophilic smooth "bumps" were distributed on superhydrophobic wax-covered valleys [6]. The "bumps" (0.5 mm in diameter) are randomly distributed in an array with 0.5-1.5 mm apart, and the wax layer constructs the hydrophobic valley. Therefore, the integration of alternated hydrophilicity and hydrophobicity has endowed the beetles with efficient fog-harvesting abilities.

During the nighttime, the wind containing dense drops that blow from the nearby ocean brings amounts of water to the creatures in the Namib Desert. Water in a foggy atmosphere is captured by the hydrophilic regions then coalesces into a bigger one, and finally transported to the hydrophobic area till to the maximal drop weight. It can be understood that water is captured on hydrophilic areas and transported by hydrophobic regions on the dorsal back of the Namib Desert beetle to achieve fog harvesting.

1.1.5 Rice Leaf

In 2002, a significant development in the field of superhydrophobic surfaces was made by Feng et al. [7], who made an intriguing discovery regarding the unique properties of rice leaves. The research unveiled an anisotropic dewing trend on the surface of rice leaves and identified striking similarities in microstructures and nanostructures between rice leaves and the renowned superhydrophobic lotus leaves.

The insights gained from the study of rice leaves, along with the principles outlined, have been instrumental in the design of superhydrophobic coatings, surfaces, and materials with applications in self-cleaning, anti-icing, and anticorrosion technologies, as well as in the development of water-repellent textiles and countless other innovations across various industries.

1.1.6 Water Strider

Water striders, also known as pond skaters or Gerridae, are fascinating insects known for their ability to move effortlessly on the surface of the water. In 2004, a significant scientific breakthrough occurred when Gao and Jiang et al. [8] discovered and explained the underlying physics and mechanisms that allow water striders to perform this remarkable feat. This discovery enhanced our understanding of interfacial science and biomechanics.

This work not only provided a more comprehensive understanding of water strider locomotion but also offered insights into biomimicry and the design of small-scale water-walking robots. His research has continued to influence the field of fluid dynamics and the study of surface tension in biology and engineering.

Butterfly Wing 1.1.7

The existence of scales on the surface of butterflies makes their wing surfaces hydrophobic. In 2007, Zheng et al. [9] published an article revealing the influence of nanostructures on the surface wettability of butterflies. This groundbreaking research shed light on the intricate mechanisms underlying the hydrophobicity of butterfly wings.

One of the key findings of the study was the directional adhesion exhibited by butterfly wings. This directional adhesion is essential not only for repelling water but also for self-cleaning. Furthermore, the study highlighted the potential for biomimicry in engineering superhydrophobic surfaces. Researchers and engineers have since drawn inspiration from butterfly wings to develop new materials and coatings with enhanced water-repellent properties. These innovations have found applications in a wide range of industries, from self-cleaning surfaces to anti-icing coatings on aircraft and ships.

1.1.8 Mosquito Eye

In 2007, a significant breakthrough in the study of antifogging properties was made by Gao et al. [10], who discovered that the eyes of mosquitoes exhibit remarkable resistance to fogging. This discovery opened up new avenues for understanding and harnessing antifogging mechanisms in both biological and synthetic materials. This research shed light on the connection between this phenomenon and the superhydrophobic effect, which is based on the unique micro- and nanostructures found on the surfaces of superhydrophobic materials.

Today, the principles discovered by Jiang L continue to play a crucial role in the design of antifog materials for a wide range of applications, including eyewear, camera lenses, and various optical devices, where maintaining clear vision in humid or foggy conditions is essential.

1.1.9 Rose Petal

The research conducted by Feng et al. [11] in 2008 was the first to systematically investigate the surface hydrophobicity of rose petals and introduce the concept of the "petal effect." It unveiled the intricate micro- and nanoscale structures on rose petals that enable superhydrophobicity and high adhesive force, opening up opportunities for biomimetic materials design and applications in a wide range of industries.

The research highlighted the potential for biomimicry, where the surface structures of rose petals could inspire the design of advanced materials with superhydrophobic and adhesive properties. Such materials have applications in self-cleaning surfaces, antifogging coatings, and water-harvesting technologies. The study suggested that the ability to control wettability and adhesion on surfaces, as demonstrated by rose petals, could have implications for the development of functional materials in various industries, including textiles, electronics, and medical devices.

1.1.10 Fish Scale

In 2009, Liu et al. [12] made a significant contribution to the field of biomimicry and surface science by drawing inspiration from the remarkable ability of fish to maintain surface cleanliness in oil-contaminated water. Liu MJ's research focused on the wetting behavior of oil droplets on the surface of fish in water, leading to the discovery of the superhydrophobic properties of fish surfaces, primarily originating from their micro- and nanohierarchical structures in the water phase.

The study underscored the value of biomimicry in materials science, demonstrating how nature's solutions to complex challenges could serve as a wellspring of inspiration for the design of advanced materials and technologies. Researchers have since drawn from these insights to develop a wide range of innovative solutions in both environmental and industrial contexts, all with the aim of achieving more effective and sustainable means of managing oil-contaminated water.

1.1.11 Cicada Wing

Sun et al. [13] published a study on the hydrophobic structure of cicada wings in 2009. This research represents a significant milestone in the exploration of natural adaptations and their potential applications in materials science and engineering. In their pioneering study, the researchers meticulously examined the wings of cicadas, a group of insects known for their distinctive songs and fascinating adaptations. What they uncovered were intricate nanostructures covering the wing surfaces, a discovery that would revolutionize our understanding of superhydrophobicity in the natural world.

The nanostructures on cicada wings inspired the design of materials with superhydrophobic properties, leading to the development of self-cleaning surfaces, antifog coatings, and water-repellent technologies.

1.1.12 Spider Silk

In 2010, a significant scientific breakthrough emerged when Zheng et al. [14] and her colleagues published an academic cover paper in the prestigious journal *Nature*. This groundbreaking study unveiled, for the first time, the remarkable water-harvesting effect of spider silk and proposed a multisynergistic driving mechanism for liquid droplets on these extraordinary natural fibers. This research was focused on the water-interaction properties of spider silk, which had long intrigued scientists due to its unique surface characteristics.

The research had implications for bioinspired technologies, inspiring scientists and engineers to explore the potential applications of spider-silk-inspired materials for water harvesting, moisture management, and other areas.

1.1.13 Salvinia

The floating-leaved water fern of the *Robinia* genus, commonly known as Salvinia, has long intrigued scientists due to its exceptional ability to retain air under water. In 2010, a groundbreaking study led by Barthlott et al. [15] and his colleagues revealed the precise surface design of Salvinia, shedding light on the remarkable phenomenon of air retention under water. Salvinia's ability to trap and retain air for extended periods while submerged in water is often referred to as the "Salvinia

paradox." This unique adaptation is critical for the plant's survival in aquatic environments, as it allows the fern to access atmospheric oxygen and maintain buoyancy.

The research had profound implications for biomimicry, inspiring scientists and engineers to replicate Salvinia's surface design for various applications. These applications include the development of underwater devices with enhanced buoyancy and reduced drag.

1.1.14 Cacti

Cacti are renowned survival experts in arid desert environments, characterized by their succulent inner stems and needle-like leaves, which serve as adaptations for maximizing water storage. In 2012, a groundbreaking study conducted by Ju et al. [16] brought to light the extraordinary droplet collection behavior of cacti in fog. This research not only elucidated the mechanism behind cactus cone-shaped needles and hydrophilic fluff in droplet capture and liquid transport but also proposed a novel mechanism for air-water extraction by these remarkable desert plants.

This research inspired biomimicry and sparked interest in developing technologies inspired by cacti's fog collection mechanisms. These technologies have applications in water-harvesting systems for arid and water-scarce regions.

1.1.15 Gecko Skin

Watson et al. [17] in 2015, delved into a comprehensive investigation of the lesser explored interfacial properties of gecko skin, offering a holistic perspective on the remarkable attributes of this reptile's integument. While much research has been devoted to understanding the exceptional adhesive capabilities of gecko feet, he expanded the scope of the investigation to encompass the entire gecko skin, acknowledging that geckos possess remarkable properties beyond just their adhesive abilities. It highlighted the intricate micro- and nanostructure present on gecko skin. This structure contributes to a multitude of beneficial surface properties, including low adhesion, superhydrophobicity, antiwetting characteristics, and self-cleaning capabilities. The research underscores the biocompatibility of the gecko skin surface, making it suitable for applications in the field of biomaterials.

1.1.16 Nepenthes

Nepenthes, a tropical carnivorous plant, boasts a remarkable adaptation in the form of its insect-trapping organ, often referred to as the "pitcher." This organ is cylindrical in shape, with a slight enlargement in the lower half and a lid covering the opening, which gives it a resemblance to a pig cage. The pitcher is a critical structure for the plant's nutrient absorption as it captures and digests insects. The research on the directional transport of water droplets inside the pitcher plants took a significant leap forward, thanks to the pioneering work of Chen, H.W.'s research group [18]. Their groundbreaking findings revealed a fascinating mechanism related to water transport within the pitcher of Nepenthes.

1.2 Wetting Features of Biological Surfaces

Some biological surfaces with wetting features evolved as facing the natural environment, such as spider silk, beetle back, Nepenthes pitcher plant, etc. These wetting properties can play an essential role in biological activities and their functions. The wetting features can be characterized with super-hydrophilic and hydrophilic properties, as shown in Figure 1.2. The liquid droplets on the surface take on different shells, along with an angle θ . The $\theta < 5^{\circ}$ can be termed as superhydrophilicity, and $5^{\circ} < \theta < 90^{\circ}$ can be called as hydrophilicity. In nature, such a phenomenon generally exists. Interestingly, biological creatures use such unique properties to complete their activities.

Here are some typical examples to elucidate the wetting features; for instance, spider silk for water harvesting, beetle back for fog water collecting, and cactus spines for liquid transport are of different wetting styles based on structures of surfaces and surface chemistry.

1.2.1 Wet-Rebuilt Spindle-Knot with Nanofibrils on Spider Silk

The marvel of spider silk extends far beyond its legendary strength and elasticity. One of its most intriguing characteristics is its unique interaction with water, a product of nature's meticulous design shaped by eons of evolutionary fine-tuning. Upon close inspection, spider silk reveals a mesmerizing landscape of varying structures. The silk is punctuated by spindle-knot-like formations, interspersed with slender connecting sections. This variation in diameter, coupled with its nanoscale roughness, plays a pivotal role in its interaction with water. Water droplets are instinctively drawn to these spindle-knots, congregating around them due to the interplay of surface tension and capillary forces. The result is a string adorned with water droplets at regular intervals, shimmering like jewels in the morning sun.

Adding to this complexity is the spider silk's unique chemical composition. Woven from a tapestry of proteins, the silk contains regions with distinct affinities

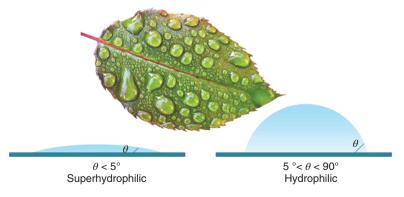


Figure 1.2 Super-hydrophilic and hydrophilic surfaces in nature.

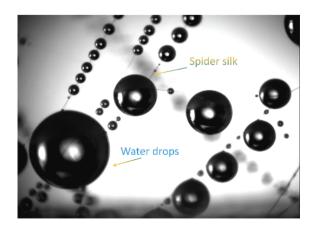
for water. Some segments are hydrophilic, drawing water toward them, while others are hydrophobic, repelling it. This intricate balance allows water droplets to not only cling to the silk but also move along its length, guided by the delicate dance of attraction and repulsion. Some spiders, especially those in regions where morning dew is a frequent visitor, harness this water-collecting prowess of their silk. They craft dense webs that trap moisture from the air, channeling it along the strands. As droplets merge and grow, the spider gains access to a crucial source of hydration, especially vital in arid environments. There is also an evolutionary angle to this story. In areas where fog or morning dew is commonplace, the water-collecting capacity of spider webs might offer a survival advantage. Not only does it provide the spider with a drink, but a moisture-laden web could also be more adept at ensnaring unsuspecting prey.

Spider silk, which is composed of humidity-sensitive hydrophilic flagelliform proteins, enjoys a high reputation as a fiber with excellent mechanical properties. A recent report reveals another intriguing feature, i.e., its ability to collect water from humid air, where the pearly droplets brighten under sunlight on the web of spider silks. This phenomenon can be observed further by an optical microscopy camera (Figure 1.3).

The environmental scanning electronic microscopy (ESEM) images of the cribellate spider silk in Figure 1.4 illustrate its structure. Puffs composed of nanofibrils are spaced along two main-axis fibers with a periodicity of ~86 µm (Figure 1.4a). The puffs' diameter is $\sim 130 \,\mu\text{m}$, and they are separated by joints with a diameter of \sim 42 µm (Figure 1.4b). The zoomed-in image in Figure 1.4c shows the puffs to be composed of random nanofibrils (~20-30 nm in diameter). These highly hydrophilic nanofibrils enhance the wettability of spider silk, which is favorable for condensing water drops.

Interestingly, when dry capture silk of spider silk is placed in fog, its structure changes as water starts to condense and form drops that move along the silk fiber (Figure 1.5). At the initial stage, tiny water drops (black dots indicated by arrows in Figure 1.5a) condense on the semitransparent puffs. As water condensation continues, the puffs shrink into opaque bumps (Figure 1.5b) and finally form periodic

Figure 1.3 Spider silk with hanging the large water drops.



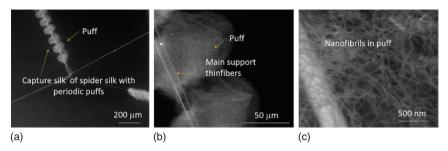


Figure 1.4 (a-c) ESEM images of capture silk of cribellate spider silk including periodic puff composed of nanofibrils.

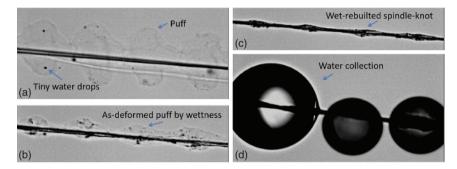


Figure 1.5 (a-d) Optical images of capture silk of cribellate spider silk change its structures after wetting.

spindle-knots (Figure 1.5c). The impact of fog on the mechanical properties of spider silk has been noted before; interestingly, the observation indicates that in the case of cribellate spider silk, the material changes its fiber structure as a result of wetting. After this "structural wet-rebuilding," directional water collection starts (Figure 1.5d), i.e., it is shown that the pearly droplets form on spider silk.

These exciting features open the inspiration of scientists and researchers to design materials for water collecting and water capture for promisingly practical applications in arid places.

1.2.2 Slippery in Multiorder Ridges on Peristome Surface of Nepenthes

Nepenthes, commonly known as the pitcher plant, is an astonishing testament to the ingenuity of nature's designs. This carnivorous plant has perfected an elegant trap over millions of years, ensuring its survival in nutrient-poor soils by luring, capturing, and digesting unsuspecting prey. Central to this mechanism is the sophisticated wetting feature of the pitcher's lip, also known as the peristome.

The peristome's wetting characteristics are an intricate dance between structure and function. On a microscopic level, the surface of this lip reveals a dense network of ridges and grooves. These structural intricacies, combined with the plant's natural secretions, result in a surface that is strikingly hydrophilic, meaning it

readily attracts and spreads water. When the pitcher plant is exposed to the ambient humidity or after a bout of rain, the peristome becomes slick with a thin layer of water. This watery film drastically reduces the friction between the surface and any creature that happens to tread upon it. Insects, attracted by the plant's vibrant colors and enticing nectar, often find themselves on this treacherously slippery slope. The unique hydrophilic properties ensure that their feet cannot find purchase, causing them to slide uncontrollably into the pitcher's deep cavity. Once inside, escape becomes a near impossibility. The inner walls of the pitcher are equally crafty, with hydrophobic properties that prevent climbing. Moreover, the digestive enzymes waiting at the bottom of the pitcher ensure that the entrapped prey meets its demise, providing the plant with essential nutrients.

Beyond its role in prey capture, the wetting properties of the pitcher plant have another subtle yet crucial function. By maintaining a consistent layer of water on the peristome, the plant ensures that the inner walls of the pitcher remain humid. This humidity is vital, as it aids in the digestion of prey and prevents the trapped insects from dehydrating too quickly, which would make them less nutritionally valuable. The Nepenthes provides a vivid illustration of how nature, through the crucible of evolution, devises intricate solutions to life's challenges. Its wetting features underscore the elegance with which nature can intertwine form and function, turning a simple leaf into a sophisticated trap that ensures the plant's survival in some of the world's most challenging habits.

The peristome surface of the Nepenthes pitcher plant is featured with a relatively regular microstructure, where straight rows of epidermal cells constructed firstand second-order radial ridges. When rainwater wetted peristome in a slippery state, a glossy surface is obtained without any individual droplets. The intermediary liquid is locked in microtextures on the pitcher, forming a repellent layer. The surface energies between liquid and solid are well matched, which cooperated with microtextural roughness to create a highly stable state and a continuous overlying film is obtained. So, amounts of ants are quickly captured and moved down to digestive fluid. Recently, it is found that the continuous, directional water transport happens [18] on the surface of the "peristome" – the rim of the pitcher (Figure 1.6a-c) - because of its multiscale structure (Figure 1.6d), which optimizes and enhances capillary rise [20, 21] in the transport direction, and

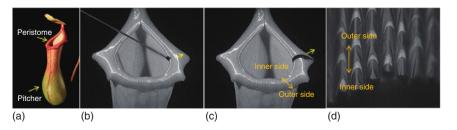


Figure 1.6 (a-d) The directional water transport on the surface of the "peristome" along the rim of the pitcher with multiorder ridges. Source: Li et al. [19]/National Academy of Sciences.

prevents backflow by pinning in place any waterfront that is moving in the reverse direction (from inner side to outer side). This feature inspires researchers to design structured surfaces that control liquid transport in different directions [19].

1.2.3 Selectively Directional Ratchet Transport

Recently, there is an unexpected liquid transport behavior that happens on the Araucaria leaf, which consists of three-dimensional (3D) ratchets with transverse and longitudinal reentrant curvatures that are characterized by the low surface-tension liquids selecting a pathway along the ratchet-tilting direction, whereas high surface-tension liquids select an opposite.

As shown in Figure 1.7, the Araucaria leaf consists of periodically arranged ratchets tilting toward the leaf tip (Figure 1.7a). Such ratchets exhibit dual-reentrant topography with a transverse curvature (radius R1, Figure 1.7b, the top) and a longitudinal curvature (radius R2, Figure 1.7b, the bottom) [22]. There are water and ethanol CAs of \sim 59° and \sim 21° on the Araucaria leaf, respectively, along with a typical hydrophilic property. When continuously infusing water and ethanol (flow rate of 3 ml s⁻¹) on the Araucaria leaf, the ethanol spreads along the ratchet-tilting direction (Figure 1.7c), whereas water propagates in the opposite direction (Figure 1.7d).

The spreading direction of liquids with different surface tensions can be tailored by designing 3D capillary ratchets that create an asymmetric and 3D spreading profile both in and out of the surface plane direction. Different from the conventional microstructures with directional liquid transport in the two-dimensional (2D) domain [23–27], the Araucaria leaves have 3D ratchets that enable liquid wicking both in and out of the surface plane. Moreover, the transverse and longitudinal

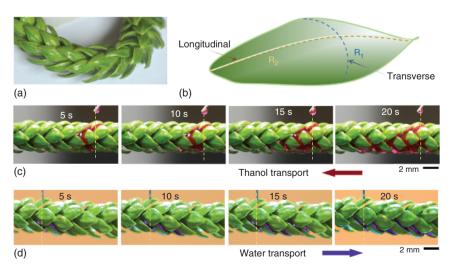


Figure 1.7 (a-d) The ratchet capillary structures of Araucaria leaf for liquid directional steering. Source: Feng et al. [22]/American Association for the Advancement of Science - AAAS.

reentrant curvatures impart asymmetric contact line pinning, which enables the directional steering and rapid transport of liquids with different surface tensions in a well-controlled manner. This feature inspires researchers to design novel surface structures for selective fluid-controlling [22].

Multilevel Structured System of Cacti

In the harshest sun-drenched deserts, cacti emerge as nature's marvels, having perfected the art of water collection and conservation. Every aspect of their design serves the singular mission of capturing, directing, and preserving every possible droplet in their arid homes.

The surface of cacti, upon closer examination, reveals a complex network of grooves and channels. These are not merely decorative quirks; they are nature's aqueducts, guiding water from the sparse rain or morning dew down toward the plant's base. Even the spines, which may seem like mere defensive structures at first glance, have a dual role. They cast shadows, reducing evaporation from the plant's surface and guiding water droplets toward the plant, acting like mini catchment systems. Adding to this is the skin of the cacti, which leans toward being hydrophilic, meaning it attracts water. In a world where every drop counts, ensuring that water clings to you rather than evaporating or being whisked away by the breeze is invaluable. This affinity for moisture comes into particular play during the cool desert nights. As humidity rises, cacti capitalize on it, capturing and condensing moisture on their surfaces, which is then absorbed.

However, the magic is not just on the outside. Within their green walls, cacti have evolved a unique method of photosynthesis. Cacti predominantly do so at night, unlike most plants that open their stomata during the day. This strategy, called CAM photosynthesis, is a masterstroke to prevent water loss from the intense daytime heat. Further aiding in their water retention efforts is a thick waxy coating that many cacti sport. This is not just about giving them a unique sheen. The wax acts as a shield, reflecting some of the sun's intense rays and forming a barrier that locks moisture in, keeping the internal tissues hydrated. Finally, beneath the sand and pebbles, the cacti extend their reach with an impressive root system. These roots, both wide-spreading and deep-penetrating, are always ready to absorb any available moisture, be it from a rare shower or hidden underground reserves.

Consider the example [16] as shown in Figure 1.8. The optical image shows a plant of Opuntia microdasys stem covered with well-distributed clusters of spines and trichomes (Figure 1.8a). Magnified optical images reveal a single cluster with spines growing from the trichomes (Figure 1.8b, c). Scanning electron microscopy (SEM) reveals that a single spine can be divided into three regions: the tip with an apex angle (2α) and oriented barbs (Figure 1.8e), the middle with gradient grooves, and the base with belt-structured trichomes (Figure 1.8f, g). The microgrooves near the base are wider and sparser than those near the tip. There are barbs with an apex angle (2β) covering the tip of the spine (Figure 1.8h). Such a spine system achieves the directional collection of the water drops, as shown in Figure 1.8i, where the deposited drop (1) and the coalesced drops (2-4) combine together, moving

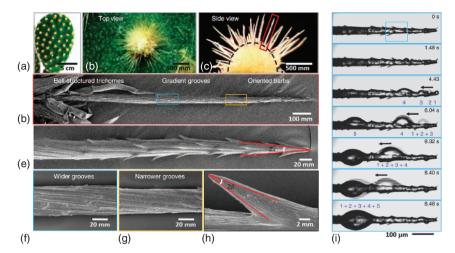


Figure 1.8 (a–i) Appearance and surface structures of the cactus and fogdrop harvesting. Source: Ju et al. [16]/Springer Nature.

directionally along the spine (black arrows) to form a large drop (1+2+3+4+5). Finally, the as-combined drops were absorbed immediately through the trichomes for the water-harvesting task.

In the world of plants, cacti are the ultimate survivalists. [28] In addition, there is also a spine of plant similar to cacti for water harvesting [29]. Their entire being, from the spiny tip to the deepest root, is a testament to evolution's power to innovate, turning challenges into opportunities. Through their many adaptations, cacti offer lessons in resilience, efficiency, and the elegance of nature's engineering, which inspire scientists to design novel materials.

1.2.5 Overlapping Arrangement of Fish Scale

Fish scales are a marvel of nature's design, seamlessly integrating protection with fluid dynamics to help these aquatic creatures glide effortlessly through the water. While, at first, they might appear as simple protective elements, a closer look reveals the multifaceted roles they play.

The texture and topography of fish scales are meticulously designed. Their overlapping arrangement, reminiscent of roof shingles, ensures that water flows smoothly over the fish's body. This overlapping design channels water in a laminar flow, minimizing turbulent wake behind the fish and consequently reducing drag. Essentially, each scale serves as a tiny deflector, guiding water along the contours of the fish. Beyond the physical architecture, fish scales have a unique relationship with water due to their protective mucus layer. This slimy coating might be off-putting to us, but it is a crucial component of a fish's hydrodynamic toolkit. Being hydrophilic or water-attracting, this mucus ensures that the interaction between the fish and its environment remains smooth and frictionless. The lubrication it provides allows fish to swim with reduced resistance, conserving energy and increasing agility.

This mucus layer has implications beyond just reducing friction. It plays a vital role in the dynamics of the boundary layer, which is the thin layer of water directly in contact with the moving fish. By keeping this layer stable and smooth, the scales and their mucus coat help diminish drag forces acting on the fish, allowing it to move faster and more efficiently. Protection is another feather in the cap of the mucus-coated scales. They form the first line of defense against potential pathogens, ensuring harmful microorganisms find it challenging to take hold. The mucus can even contain compounds that aid in wound healing, showcasing its multifunctional nature.

Interestingly, the wetting properties of fish scales can also impact their appearance. In some species, the combination of the mucus, the inherent structure of the scales, and the way they interact with light can produce stunning visual effects, such as iridescence. This is not just about esthetics; these optical properties can be essential for camouflage, communication, or mate attraction. In essence, fish scales epitomize the elegance of nature's solutions through their wetting features and design. They harmoniously balance protection with hydrodynamic efficiency, demonstrating how evolution has fine-tuned organisms for optimal survival. For us, they offer a window into understanding fluid dynamics in nature and inspire innovations in areas as diverse as swimwear technology and naval engineering.

Sharks, known for their swift swimming capabilities and resistance to fouling organisms, owe much of these abilities to the microsized dermal denticles on their skin. These denticles have riblet geometries, tiny grooves that reduce friction by encouraging the flow of water to slide in the direction of the shark's movement, thus resulting in reduced drag and a surface less likely to be fouled by marine life.

Figure 1.9 shows the environmental scanning electron microscope (ESEM) images of the bonnethead shark (Sphyrna tiburo) skin surface at different body locations,

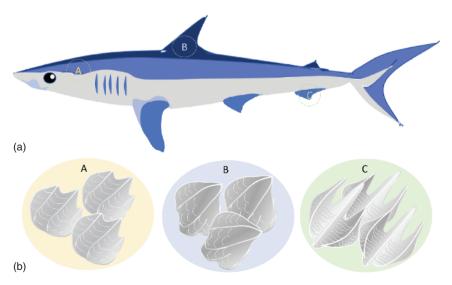


Figure 1.9 The illustration of (a) shark and (b) microstructures of shark skin. Source: Wen et al. [30]/The Company of Biologists Ltd.

including an illustration of the shark (Figure 1.9a). The different positions can be marked with letters A (the head), B (the leading edge dorsal fin), and C (the anal fin). As observed by ESEM (Figure 1.9b), the head position has the normal oriented structure array, the leading edge fin has the irregular structures, and the anal fin has the sharp oriented structure array, where the overlapping scales are shaped with normal, complex, and distinct ridges, respectively. These structured features can play a role. When the shark is swimming, the natural flow direction across the denticle surface is from lower left to upper right, from denticle base to tip [30]. The structured feature has inspired researchers to develop a method for the fabrication of biomimetic surfaces for applications [31, 32].

1.3 **Antiwetting Features of Biological Surfaces**

Antiwetting features (Figure 1.10) of biological surfaces can be taken with some examples, such as duck feathers, cicada wings, lotus leaves, strider legs, butterfly wing, etc., which is significant to develop the materials of anti-icing, waterproof, water repellency, superhydrophobicity that would have application in the building construction and electron devices manufacturing industries. By understanding the biological features, the bioinspired researches are opened with a new angle for the design of new materials.

1.3.1 Multilevel Wetting-Controlling on Duck Feather

Duck feathers, nature's marvel of water repellency, showcase a blend of intricate structures and biological processes that collectively deter water absorption. When you look closely at a duck feather, you do not see a simple, flat surface. Instead,

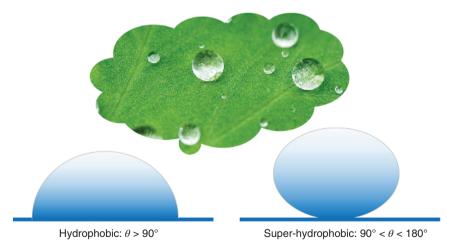


Figure 1.10 Antiwetting features of biological surfaces. Source: moccabunny/Adobe Stock Photos.

there's a central shaft with myriad barbs branching out. These barbs further break down into tinier structures called barbules. This complex design does more than just add beauty; it amplifies the feather's surface area, creating a multitude of air pockets that actively repel water.

Zooming in even further, these barbs and barbules reveal minuscule nanostructures. These tiny formations serve as air traps, bolstering the feather's inherent ability to fend off water. Think of it as nature's version of a high-tech water-repellent fabric on a microscopic scale. However, it is not just about structure. Nature equips ducks with a fascinating adaptation - a specialized gland located near their tail base, known as the uropygial gland. This gland secretes a waterproofing oil. If you have ever observed a duck closely, you might have noticed it frequently running its beak over its feathers. It is not merely grooming; the duck is meticulously spreading this oil, thereby enhancing its feathers' resistance to water. This natural oil ensures that water does not soak in but rather forms beads that gracefully roll off. Consider the layered armor ducks possess: on the exterior, contour feathers lay closely packed, forming the first line of defense against water. Right beneath, the down feathers act as insulating agents, trapping warmth. This layered defense means that the inner sanctum remains untouched and dry even if a droplet trespasses the outer layer. Additionally, the tight arrangement of the barbs coupled with the preen oil disrupts the capillary action. This phenomenon, in most contexts, would pull water into narrow spaces. Here, it is effectively neutralized, ensuring moisture does not seep deep into the feather.

All these water-resistant features are not just about ducks wanting to stay dry for comfort. Evolution has crafted them as vital survival tools. A soaked duck would grapple with buoyancy issues in water and face difficulty taking to the skies due to the added weight. In essence, duck feathers are a masterclass in nature's design - melding structure, function, and adaptation to create an almost poetic resistance to water. Ducks have a remarkable ability to repel water due to the hydrophobic nature of their feathers. What's particularly fascinating about these feathers is that they are multilayered.

As shown in Figure 1.11 [33], Figure 1.11a shows the environmental scanning electron micrograph of a wing feather of a mallard. There are nanostructured

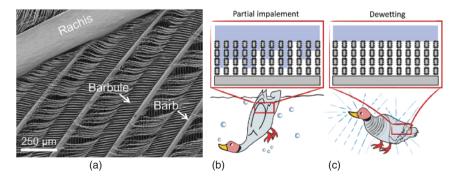


Figure 1.11 (a-c) The microstructures of duck and switching wetting/dewetting behaviors. Source: Ahmadi et al. [33]/American Chemical Society.

microbarbules extending from an array of barbs, which, in turn, extend from the central rachis. Such structures take on flexible wetting features. The feathers of water-dwelling birds exhibit multiple degrees of hierarchy, with several layers of feathers, all exhibiting nanostructured microbarbules. It is hypothesized that this facilitates partial wetting transitions during diving/submersion, where both the nanostructure and the bottom-most layers are able to retain air pockets (Figure 1.11b). This is supported by the corresponding photograph of a gannet, deceased and frozen, being dropped into water, where there is the partial presence of air pockets. In contrast, it exists a partial Wenzel state can easily dewet to the Cassie state upon forcing, as illustrated in Figure 1.11c; there is a switch between wetting behaviors [34]; it happens when a duck dewets via shaking its feathers.

For engineers and material scientists, it is more than just fascinating; it is a blueprint for crafting next-generation water-repellent solutions. This study opens doors to various potential applications. The synthetic feathers could be used in the design of advanced water-resistant materials or clothing, buoyancy devices, and even in creating surfaces where it is essential to prevent water accumulation.

1.3.2 Gradient Micro- and Nanostructures for Droplet Suspending-up

The lotus leaf is a captivating emblem of nature's ingenuity, often evoking wonder for its pristine ability to repel water. This inherent quality is not merely an esthetic trait but a sophisticated interplay of structure and chemistry that has enthralled scientists, engineers, and nature enthusiasts for years.

Figure 1.12a shows the nonwetting feature on the surface of the lotus leaf [35], where the water droplet can be suspended on the surface of the leaf, and the light part reflects the air layer between the droplet and the surface of the leaf. Figure 1.11b, c shows the micropapillae (Figure 1.12b) and nanohair on papilla (Figure 1.12c) that were observed by ESEM, respectively.

When we delve into the intimate details of the lotus leaf, we discover that its surface is far from the smooth expanse it might appear to the naked eye. Instead, it is a complex landscape of minuscule bumps or protrusions known as papillae. These papillae are not just architectural marvels; they are cloaked in a layer of waxy, hydrophobic compounds that play a pivotal role in the leaf's water-repelling saga.

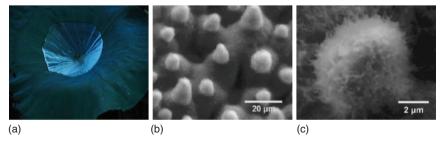


Figure 1.12 (a-c) Photograph of leaf surface with air-layer and topography of leaf surface with micropapillae and nanohairs. Source: Zheng et al. [35]/AIP Publishing LLC.

Upon gracing the surface of the lotus leaf, water droplets find themselves in an environment that is somewhat alien. Rather than spreading out, they bead up, mimicking perfect little pearls. This bead-like behavior arises from two primary mechanisms. Firstly, the micro- and nanostructures of the papillae ensure that the water droplet touches only a minuscule fraction of the actual leaf surface. This structural design minimizes contact, allowing the droplets to maintain their spherical elegance. Secondly, the hydrophobic compounds adorning the papillae deter the water from sprawling, bolstering the leaf's innate ability to repulse water.

The story of the lotus leaf is not confined to mere water repulsion. As these water droplets meander across the leaf, they act as miniature janitors, picking up dirt particles and contaminants in their path. By the time they roll off the edge, the droplets have cleansed the leaf's surface. This self-cleaning phenomenon, often revered as the "Lotus Effect," not only maintains the leaf's esthetic purity but also ensures its biological efficiency by facilitating unhindered photosynthesis. From an ecological perspective, this is not just a marvel to behold but a testament to evolutionary finesse. Maintaining a clean leaf surface is paramount in the watery realms where the lotus thrives. It ensures optimal photosynthesis, wards off potential pathogens, and prevents the leaf from being burdened by the weight of stagnant water or debris.

Figure 1.13a-c shows the nonwetting feature observed in ESEM (Figure 1.13a), where the droplets are condensed on the surface of the leaf (Figure 1.13b), the droplets are suspended up by micropapillae and nanohairs (Figure 1.13c). Further observation by ESEM shows the covering of liquid (Figure 1.13d). It implies the gradient of wetting along the curvature of micropapillae, i.e., the top of papillae is a high surface energy region, while the bottom of papillae is low surface energy. Figure 1.13e illustrates the effect of the wetting gradient for the suspending-up of

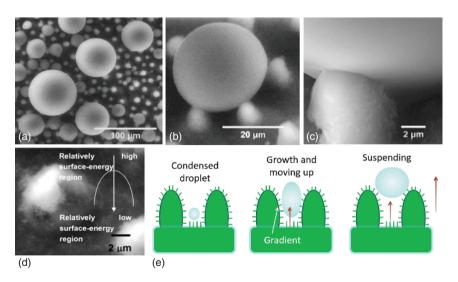


Figure 1.13 (a-e) The ESEM images of the nonwetting feature on the surface of the leaf with micro- and nanostructures and illustration of the wetting gradient effect. Source: Zheng et al. [35]/AIP Publishing LLC.

droplets on the lotus leaf [35]. The genius of the lotus leaf has not merely remained a spectacle of nature, it has ignited human imagination. Its design principles have been mirrored in our quest to craft self-cleaning materials, paints, and coatings. The ripple effects of understanding and replicating this natural phenomenon can be seen across myriad industries, reshaping how we conceive materials and surfaces. The lotus leaf stands as a poetic blend of form and function, weaving a narrative that underscores the brilliance of evolution and the endless possibilities it holds for human inspiration and innovation.

1.3.3 Oriented Microhair with Nanogroove for Superhdyrophobic **Floating**

The water strider, with its captivating ability to glide effortlessly across water surfaces, provides a stunning example of nature's problem-solving prowess. This intriguing dance on the water is not a mere spectacle but a culmination of several evolutionary adaptations, mainly manifested in the design of the insect's legs. One of the foundational features of the water strider's legs is their intricate adornment of tiny hairs or setae. These hairs are not just simple projections but branch out into even finer nanoscale structures, amplifying the leg's surface area considerably. This dense network of hairs serves a dual purpose. Firstly, they create countless grooves and pockets, which act as reservoirs to trap air. This entrapped air gives the legs a cushioning effect, making them buoyant and ensuring that the water strider remains delicately perched on the water's surface without breaking through.

Complementing this structural marvel is the insect's innate chemistry. The legs of water striders are known to secrete or accumulate certain waxy, hydrophobic compounds [36]. These chemicals, in synergy with the micro- and nanostructured hairs, supercharge the leg's water-repelling capabilities. Instead of getting wet or sinking, the legs, thanks to this combination of structure and chemistry, repel water, aiding the insect in its signature water-walking act. Beyond these features, the mechanics of the water strider's movement also play an essential role in its ability to tread on water. With a lightweight body and an even distribution of weight across its legs, the insect ensures it does not exert too much pressure on any single point, preserving the water's surface tension. When they move, water striders push down and quickly retract their legs, creating minuscule ripples. They then harness these ripples, effectively "rowing" on them, allowing for their graceful, gliding motion.

This exquisite interplay of physical structures, inherent chemistry, and biomechanics not only allows the water strider to master its watery domain but has also sparked human imagination and curiosity. Researchers and innovators have drawn inspiration from this insect, seeking to emulate its adaptations in materials science, design, and even robotics. In the grand tapestry of evolution, the water strider stands as a testament to the art of the possible, demonstrating how, through a series of nuanced adjustments and refinements, nature can craft solutions that seem to defy the very laws of physics. Water striders, with their ability to move gracefully on water surfaces, do so primarily due to the specialized design of their legs. The middle leg of the water strider moves backward, resulting in asymmetrical CAs between the

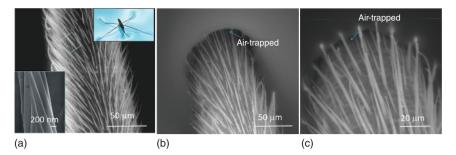


Figure 1.14 (a-c) Water strider leg with multilevel structures that can trap air to favor water walking.

water and the front and back of the leg. This asymmetry creates a curvature force that propels the insect forward, serving as the primary driving force for its surface motion.

The leg of the strider has unique multilevel structures that enable it to stand on the surface of the water (Figure 1.14a, the right top inset), which can be observed by SEM and ESEM. The left bottom inset in Figure 1.14a is a SEM image that indicates the second-level structure of conical hair with groove. Figure 1.14b, c shows the ESEM images observed on the live leg when the leg contacts the surface of the water, where the conical hair and groove trap together air for the suspension of the leg. Therefore, a unique superhydrophobic behavior generates a stronger supporting force due to the multilevel-oriented structures of the strider's leg. Such cooperative effect inspires researchers to design materials for the device of water walker [37-39].

1.3.4 **Butterfly Wing with Multilevel-oriented Structures**

Butterflies, with their mesmerizing hues and patterns, have always enthralled observers. However, beyond their visual splendor, there lies a world of intricate design and functionality, particularly evident in their wings' ability to repel water. This hydrophobicity is both a marvel of evolution and an essential adaptation for their survival.

A closer look at the butterfly wing reveals it is not a smooth surface, as one might assume. Instead, it is a complex mosaic of minute scales, each a meticulously crafted piece of nature. These scales, upon even closer inspection, are labyrinths of ridges, cross-ribs, and laminae. Such a configuration elevates the wing's surface, ensuring that when a droplet of water lands, it barely grazes these microscopic structures. As a result, the water, instead of spreading, retains a near-spherical shape, much like a bead. This shape facilitates the droplet's easy-rolling-off property, ensuring the wing remains predominantly dry. Yet, the structural intricacies are not the sole contributors to this water-repelling prowess. Nature, in its wisdom, has imparted a chemical dimension to this defense. Many butterfly wings are imbued with a layer of lipids, fatty molecules known for their aversion to water. This lipidic veneer accentuates the wing's hydrophobicity, ensuring that water not only forms beads but is also deterred from wetting the wing in the first place. The implications of such a

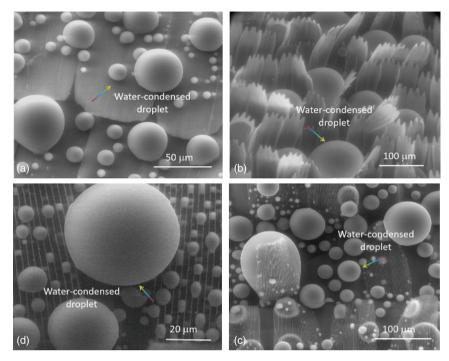


Figure 1.15 Superhydrophobic properties of butterfly wings ((a) *M. agea*; (b) Small white; (c) and (d) *M. menelaus*) can be observed in ESEM.

design are manifold and crucial. For a butterfly, a wet wing is a liability. The added weight and dampness could impede flight, reducing agility and making evasion from predators a daunting task. Moreover, a consistently wet wing could become a breeding ground for molds and other pathogens, jeopardizing the butterfly's health. The hydrophobic design, therefore, is a safeguard, a mechanism that ensures the butterfly remains airborne and healthy even after unexpected encounters with rain.

As shown in Figure 1.15, superhydrophobic properties of butterfly wings (Figure 1.15a, *Morpho agea*; Figure 1.15b, small white; Figure 1.15c, d, *Morpho menelaus*) can be observed in ESEM; the water is condensed into droplet like the balls in different sizes, indicating water repellency of butterfly wings strongly.

Beyond just repelling water, this design also bestows upon the wings a self-cleaning ability. As the water droplets roll off, they sweep away dirt, dust, and even potential pathogens, akin to a natural cleaning service ensuring the wings remain pristine. While hydrophobicity plays a pivotal role, the microstructure of the scales also serves other functions. They contribute to the vivid display of colors resulting from intricate light interactions and play a part in thermoregulation. By repelling water, the structural integrity and vibrancy of these colors remain intact, enabling butterflies to communicate, attract mates, and deter potential threats effectively.

In essence, the butterfly wing is a masterclass in nature's design philosophy, where esthetics and functionality coexist in sublime harmony. It is not just a canvas

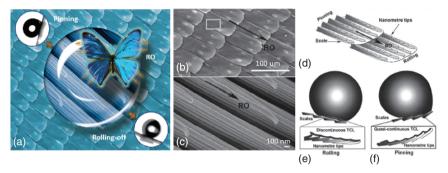


Figure 1.16 (a–c) The anisotropic water repellency property on *M. agea* butterfly wing along two superhydrophobic states. (d–f) The illustration of directional adhesion on butterfly wing, with discontinuous TCL for droplet-easy-rolling-off and continuous TCL for droplet pinning. Source: Zheng et al. [9]/Royal Society of Chemistry.

of colors but a testament to evolution's ability to craft solutions that are both enchanting and pragmatically essential. Such designs continue to inspire the realms of science and engineering, emphasizing once again that nature remains one of our most profound teachers. Butterflies have a remarkable capability with their wings. Despite being delicate, these wings can efficiently repel water, a property known as superhydrophobicity. This trait allows butterflies to fly even in rainy conditions without being hampered by water droplets clinging to their wings.

As shown in Figure 1.16a, there is anisotropic water repellency property on butterfly wing [9], e.g., *M. agea*, the overlapping scales on wings generate the distinct direction of water repellency, i.e., two superhydrophic states: roll-off along radial-outside (RO) direction, pining against RO. It is attributed to the oriented overlapping structures and oriented tips of nanostripe structures (Figure 1.16b, c), which induce the directional adhesion along the orientation of RO, i.e., along RO direction (Figure 1.16d), there are discontinuous three-phase contact lines (TCL) to favor the droplet's easy-rolling-off property (Figure 1.16e), but against RO direction, there is continuous TCL to pin the droplet (Figure 1.16f).

Such multilevel structures can be extended into water repellency at low temperatures [40]; the flexible wing also induces the static and dynamic modes for condensed-droplet transport in direction [26]. These properties can inspire researchers to design some applied surfaces, e.g., anti-icing surfaces [41] and droplet transport in directions for heat transfer [42].

1.4 Biological Patterns on Micro- and Nanoscale Structures

Biological surfaces can be arranged into micro- and nanostructures in the form of patterns, e.g., isotropic, anisotropic, alternative wettability, etc., which usually is observed on insect compound eyes, rectangular-shaped plant leaf, beetle back, etc., playing different roles in their living activities.

1.4.1 Isotropic Micro- and Nanostructured Pattern

The mosquito, while commonly maligned for its role as a disease vector, possesses evolutionary marvels that enable it to adeptly navigate its surroundings. A notable feature lies in the design of its eyes, which have adapted over eons to thrive in environments abundant with water bodies.

The eye of a mosquito is composed of myriad tiny individual units known as ommatidia, which together give it a bulging, hemispherical appearance. This configuration grants the mosquito a panoramic field of vision, aiding it as it flits about in search of sustenance and breeding grounds. At the heart of the eye's adaptability is its superhydrophobicity, an intrinsic quality that causes it to repel water fervently. This feature is indispensable because mosquitoes lay their eggs in stagnant water and are often near to water bodies. A wet eye would obstruct vision, compromising their ability to find food, evade predators, or seek mates.

This resistance to wetting is not just a matter of chemistry but also of intricate physical design. A closer examination of the mosquito's eye reveals a plethora of nanoscale bristles. These bristles minimize the contact points between the water droplets and the eve's surface. Consequently, instead of spreading, water that comes into contact with the eye forms near-perfect beads and promptly rolls off. This phenomenon, reminiscent of the self-cleaning properties observed in lotus leaves, ensures the mosquito's gaze remains consistently clear, even when surrounded by moisture.

Furthermore, these microstructures offer another boon: they diminish reflections. As creatures of the crepuscular hours - dawn and dusk - mosquitoes encounter variable light conditions. The design of their eyes, courtesy of the tiny bristles and the layout of the ommatidia, helps to scatter light, reducing glare and optimizing visual clarity during their peak periods of activity. An additional advantage of the eye's superhydrophobic nature is its ability to self-clean. As the beaded water droplets cascade off the eye, they ensnare and carry away dust, debris, and potential microorganisms. This ensures the mosquito's vision remains sharp and unclouded, even in particulate-rich environments.

In the grand tapestry of evolution, the mosquito's eye is a testament to nature's capacity for intricate design, balancing esthetics with function. Although mosquitoes might be a nuisance to many, their eyes are a marvel of adaptation, reflecting the nuanced ways in which organisms evolve to flourish in their chosen habitats. For the keen observer and researcher, such features offer a wellspring of inspiration, highlighting the myriad ways in which nature, through trial and error, crafts perfection. Mosquitoes, despite being nuisances, have eyes that present an intriguing marvel of nature. Their compound eyes exhibit remarkable water-repellent capabilities, largely due to their unique micro- and nanohierarchical structure and the presence of chitin - a low-surface-energy material commonly found on the insect's body surface.

This design ensures that water droplets effortlessly roll off the surface of the eye (Figure 1.17a), keeping the mosquito's vision clear and unobstructed. As shown in Figure 1.17b, c, SEM images show the mosquito's compound eyes with

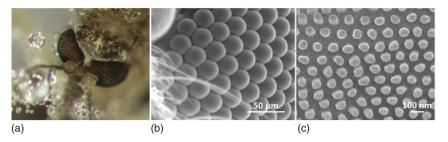


Figure 1.17 (a-c) The mosquito's compound eyes with micro- and nanostructures.

micro- and nanostructures. Every larger eye (~3-5 mm) includes thousands of small eyes ($\sim 20-30 \,\mu m$ in diameter) (Figure 1.17b), and every small eye includes thousands of nanopapillae (~80-90 nm) (Figure 1.17c). The bioinspired structures have been investigated to design for some applications [10, 43, 44], e.g., antifogging performance can be applied to microdevices used in cold, high-humidity environments [45].

1.4.2 **Anisotropic Pattern for Wetting Direction**

The rice leaf, though perhaps not as celebrated in popular culture as the lotus leaf, holds its own marvel in the realm of botanical water repellence. It stands as another testament to nature's boundless creativity, reflecting a distinctive approach to combating the challenges posed by its environment. When you observe water on a rice leaf, it behaves somewhat similarly to that on a lotus leaf: it beads up and rolls off. However, the reasons behind this behavior are uniquely adapted to the rice plant's needs and habitat.

The surface of a rice leaf is an intricate tapestry of microstructures. Microscopic hairs, known as trichomes, are interspersed across its surface. These trichomes, along with other microscopic surface features, play a pivotal role in water repellence. By increasing the roughness of the leaf surface, they reduce the contact area between the leaf and water droplets. This makes the water droplets less likely to spread out, promoting their bead-like form. Another key player in the rice leaf's hydrophobic narrative is the cuticle, a waxy layer that covers the surface of many plants. In rice, this cuticle is particularly prominent, adding an additional layer of water resistance. The waxy nature of the cuticle inherently repels water, and when combined with the physical microstructures of the leaf, the effect is magnified. Now, one might wonder: why has nature endowed rice leaves with such hydrophobic prowess? Rice plants, native to wetlands and often grown in flooded fields, are constantly surrounded by water. Keeping the leaf surface free from a film of stagnant water ensures that the leaf can effectively perform photosynthesis. Moreover, a wet leaf surface can be a breeding ground for fungal pathogens, which can devastate crops. The rice leaf minimizes the risk of fungal infections by ensuring that water rolls off easily.

Additionally, as water droplets roll off, they can carry away dirt and spores, lending a self-cleaning characteristic to the rice leaf, albeit not as pronounced as the famed

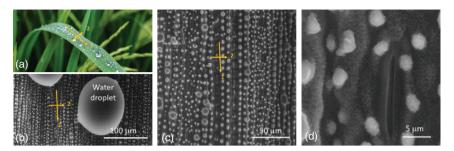


Figure 1.18 (a-d) The rice leaf with an anisotropic structured surface.

"Lotus Effect." This further helps in ensuring optimal health and productivity of the plant. The nuanced design of the rice leaf's hydrophobic surface has also caught the attention of researchers and innovators. Similar to the lotus leaf, understanding and mimicking the mechanisms behind the rice leaf's water repellence can pave the way for new materials, coatings, and agricultural innovations. The rice leaf tells a tale of evolutionary adaptation, where a plant has refined its features over millennia to thrive in its watery world. It gracefully repels water through a combination of microstructural design and chemical protection, ensuring its survival and productivity. This blend of form and function is yet another reminder of nature's infinite wisdom and the lessons it holds for us.

Rice leaves exhibit a unique behavior called anisotropic wetting, where water droplets move in a specific direction on the leaf's surface due to specialized microand nanoscale structures. This directed movement does not occur randomly but is somewhat influenced by the physical attributes of the leaf's surface.

Figure 1.18 shows the rice leaf with an anisotropic structured surface, including a photograph (Figure 1.18a), ESEM image with water-condensed droplets on the rice leaf (Figure 1.18b), and micro-papillae arrays like stripes (Figure 1.18c, d). There are distinct anisotropic structures composed of micropapillae array stripes (the arrows indicate direction 1 along the stripe and direction 2 along the vertical to stripe). Along direction 1, the droplet is easy to roll off, and along direction 2, the droplet is hard to roll off [46–48], which the features can be used to inspire the design of surfaces for droplet controlling for de-wetting [49].

1.4.3 Alternative Hydrophilic-Hydrophobic Patterns

The hydrophilic humps of beetle wings can play a role in capturing fog water because beetles live in the dry and hot Namib Desert. To develop superior water collections to feed themselves, its wing evolves into the hydrophilic smooth bumps that are distributed on superhydrophobic wax-covered valleys. The bumps are in an array, and the wax layer constructs the hydrophobic valley. An integration of alternated hydrophilicity and hydrophobicity achieves efficient fog-harvesting abilities. Water in a foggy atmosphere is captured by the hydrophobic regions and then coalesces into a bigger one and is transported by hydrophobic regions on the dorsal back of the Namib Desert beetle to achieve fog harvesting.

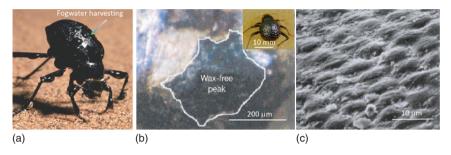


Figure 1.19 (a-c) Beetle captures fog water by means of alternative hydrophilic-hydrophobic regions of back surfaces. Source: Parker and Lawrence [6]/Springer Nature.

The Namib Desert beetle, an insect residing in one of the world's most arid environments, has evolved remarkable adaptations to survive. The Namib Desert beetle, specifically the Stenocara gracilipes, has evolved a fascinating method to survive in one of the driest environments on Earth: the Namib Desert. On its elytra (the rigid wing covers), the beetle has a unique surface topography that consists of superhydrophilic (water-attracting) bumps interspersed with superhydrophobic (water-repelling) regions. As fog rolls in from the ocean, the beetle positions itself to capture the moisture. The superhydrophilic bumps on its back capture and accumulate tiny water droplets from the fog. As these droplets grow in size and coalesce, they become too large to be held by the bumps. Due to the surrounding water-repellent regions and the pull of gravity, these droplets then roll down toward the beetle's mouthparts, allowing it to drink. This ability to harvest water from fog is a critical survival adaptation for the beetle. The combination of hydrophilic and hydrophobic regions is not solely a result of chemical properties but also due to the beetle's physical microstructure. The specific shapes, sizes, and arrangements of the bumps and surrounding areas enhance their wetting characteristics. Notably, it can harvest water from fog. The beetle's back has bumps that are superhydrophilic (they attract water) and channels that are superhydrophobic (they repel water). This ingenious combination enables the beetle to gather tiny droplets from the morning mist, which then coalesce and get directed to its mouth (Figure 1.19a). The optical image shows the wax-free peak (Figure 1.19b), which is called a hydrophilic hump for fog droplet harvesting, whereas the other part is waxy (hydrophobic) for fog droplet transport. The SEM image shows the rough surface (Figure 1.19c). Such an alternative hydrophilic-hydrophobic pattern is biologically designed for effectively capturing drinking water [6]. Inspired by this natural design, scientists and engineers are developing materials and surfaces to harvest water from fog [50–54], offering potential solutions to water scarcity challenges in arid regions.

1.5 Wetting-Controlled Effects

We have taken some examples of biological surfaces with wetting/nonwetting properties for biological functions such as fog water harvesting, droplet transport,

water repellency, and directional adhesion. These properties are attributed to the surface structure (geometry, roughness, curvature, ratchet, conical, and stripes) and chemistry (high or low surface tension or surface energy), which play roles in wetting-controlled effects. The wetting-controlled effects can be generated by the nature-designed unique structures and surface chemistry as discussed in the following subsections.

1.5.1 Spider Silk Effect: Cooperative Effect of Roughness and Curvature

As known, the cribellate spider silk captures water by means of the wet-rebuilt micro- and nanostructures on capture silk, i.e., form the new structures with periodic spindle-knot and joint. The spindle-knot can be composed of random nanofibrils for a rough surface. The joint is composed of aligned nanofibrils for a smooth striped surface. The joint is between two spindle knots; thus, the roughness and curvature can be formed due to the gradient from the center of the spindle knot to the side near the joint.

The unique micro- and nanostructures on wetted spider silk are observed by ESEM, as shown in Figure 1.20a-e. Figure 1.20a shows a SEM image of wetted spider silk, including four spindle-knots and three joints with periodic alternative arrays [9]. There are different microstructures on spindle-knots, including random nanofibrils and joints including aligned nanofibrils, as shown in Figure 1.20b,c and Figure 1.20d, e, respectively.

In the details, spindle-knots are of more significant silk-axial roughness than joints. Meanwhile, the random surface topography of spindle-knots forms discontinuous TCL, while aligned surface topography of joints forms continuous TCL for water drops (Figure 1.20f), which is helpful for water drops' movement along joints. Surface structural anisotropy generates a surface energy gradient so that spindle-knots possess higher apparent surface energy than joints. At the same time, the conical shape of the spindle-knot generates a difference in Laplace pressure

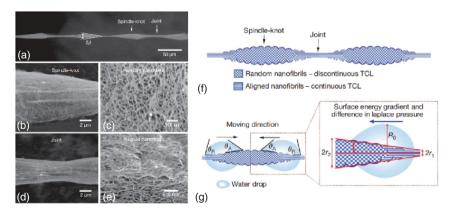


Figure 1.20 (a–g) The rough-curvature microstructure on wetted spider silk and the cooperative effect. Source: Zheng et al. [9]/Royal Society of Chemistry.

from the high-curvature region (joint) to the low-curvature region (spindle-knot). The cooperation of these two factors drives water drops from the joint to the spindle knot (Figure 1.20g). Such a cooperative effect is induced by roughness and curvature on wetted spider silk, which has inspired the design of materials for water-collecting applications [55-58].

1.5.2 Cactus Effect: Cooperative Effect of Multilevel Conical Geometries

Cactus O. microdasys has an efficient fog collection system and is composed of well-distributed clusters of conical spines and trichomes on the cactus stem. Each spine contains three integrated parts that have different roles in the fog collection process according to their surface structural features. The multilevel gradients exist, i.e., the gradient of the Laplace pressure and the gradient of the surface-free energy, which endow the cactus with an efficient fog collection ability. As shown in Figure 1.21a, an illustration indicates the efficient fog collection system of O. microdasys cactus. The conical barbs and tip of the conical spine can capture tiny water-condensed droplets, and then coalesce the tiny droplets into larger droplets due to conical geometries with Laplace pressure differences. The transport processing from "1 Deposition" on the barbs and the spine to "2 Collection" on the

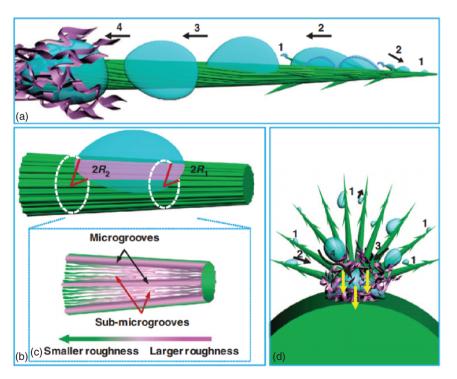


Figure 1.21 (a-d) Multilevel structures of cactus and cooperative effects. Source: Ju et al. [16]/with permission of Springer Nature.

tip of the spine, "3 Transportation" on the gradient grooves, and "4 Absorption" upon contact with the trichomes. The driving forces are generated by the gradient of the Laplace pressure and the gradient of the surface-free energy. A water drop on a conical spine should move toward the base side with the larger radius (R_2) due to the relatively smaller Laplace pressure (Figure 1.21b). In addition to the conical shape, the surface of the spine was covered with multilevel grooves. The gradient of the microgrooves is sparser near the base than near the tip of the spine (as indicated by the black arrows). The aligned submicrogrooves are similar along the spine, as indicated by the red arrows (Figure 1.21c). This gradient of the microgrooves produced a gradient of roughness, contributing to a gradient of the surface-free energy along the spine, driving the water drops toward the base side. Thus, the cooperation among the multiple spines, the multiple trichomes, and the spines' trichomes make the water drops progress through the completed processes, finally being quickly absorbed into the cactus stem upon contact with the trichomes (Figure 1.21d)

Araucaria Leaf Effect: Steering Effect of Asymmetric Capillary Ratchet Geometries

A wetting-controlled effect can be generated by asymmetric capillary ratchet geometries in directions. As reported, an unexpected liquid transport behavior on the Araucaria leaf, which consists of 3D ratchets with transverse and longitudinal reentrant curvatures that are characterized by the low surface tension liquids selecting a pathway along the ratchet-tilting direction, whereas high surface tension liquids select an opposite direction.

The Araucaria leaf is found to consist of periodically arranged ratchets tilting toward the leaf tip. Such ratchets exhibit dual-reentrant topography with a transverse curvature of radius and a longitudinal curvature of radius, which can be indicated with R_1 and R_2 , respectively, as shown in Figure 1.22a. Critical states for liquid spreading on 3D ratchet arrays can be illustrated in Figure 1.22b, where the symbols b+, b-, t+, and t- represent bottom-forward, bottom-backward, top-forward, and top-backward pinning sites, respectively. $\theta 1+$ and $\theta 1-$ are critical angles at which the liquid front reaches the b+ site and b- site, respectively.

The liquid-controlling effect is related to the curvature of R_1 and R_2 , respectively. As for the curvature of R_1 (Figure 1.22c), there is a force in the bottom-to-top wicking scenario with the transverse reentrant effect. The top-view schematics manifest the driving force at the bottom surface (D_1) and the resistance force along the ratchets (D_2) at the b+ site (left) and b- site (right), respectively. As for the curvature of R_2 (Figure 1.22d), there is a force in the top-to-bottom wicking scenario with the longitudinal reentrant effect. In this scenario, the liquid is pinned at both the b+ and b- sites and subjected to asymmetric capillary forces at the t+ and t- sites [27]. Thus, the liquid directional steering achieves, e.g., there are two distinct spreading dynamics of liquids on ratchet arrays, where liquid with $\theta = 32^{\circ}$ (i.e., in relatively low surface tension) wets the ratchet from bottom to top for forward spreading, whereas liquid with $\theta = 60^{\circ}$ (i.e., in relatively high surface tension) wets the ratchet from top

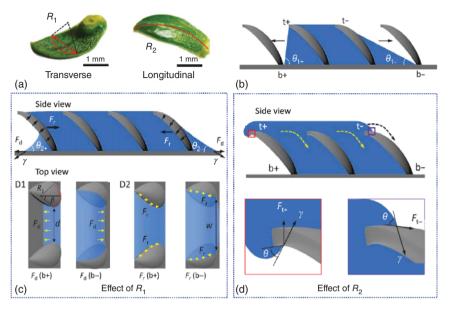


Figure 1.22 (a-d) Liquid directional steering of Araucaria leaf. Source: Feng et al. [27]/American Association for the Advancement of Science - AAAS.

to bottom for backward spreading [27]. It is significant to design novel surfaces for fluid-controlling in microdevices, etc.

1.5.4 Beetle Back Effect: Hydrophilic-Hydrophobic Heterogeneous Pattern

The wetting controlling can be achieved on a surface with a hydrophilic-hydrophobic heterogeneous pattern, e.g., Stenocara beetle back, including the hydrophilic humps and hydrophobic valleys through billion years of evolution and natural selection, which capture fog droplets and transport droplets by means of wetting heterogeneous pattern, becoming beetle get water drinking in activities. On a foggy dawn, the Stenocara beetle tilts its body forward into the wind in humid fog to capture tiny water droplets from the atmosphere. In the hydrophilic region of the beetle back, tiny droplets coalesce into a larger water droplet; when a more extensive water droplet contacts the hydrophobic region of the beetle back, it is transported onto another hydrophilic region and continuous to capture-coalescence-transport process, then roll down into the beetle's mouth, providing it with a fresh morning drink [59].

As shown in Figure 1.23, the beetle back effect can be illustrated by the dynamic process of fog droplet capture and transport. The hydrophilic region of the beetle back makes a water-condensed droplet like a ball with a high CA (indicated by a blue arrow in Figure 1.23a), but the hydrophobic region makes a water-condensed droplet-like film with nearly zero CA (indicated by a yellow arrow in Figure 1.23a). The dynamic process can be captured firstly by hydrophilic region, e.g., droplets 1, 2, and 3 on sites of hydrophilic region (indicated with red lines, the

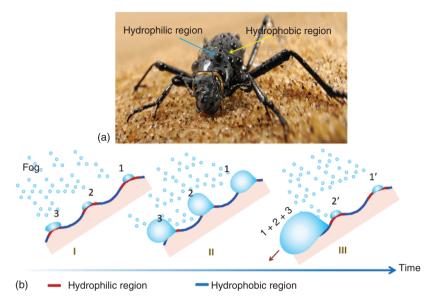


Figure 1.23 (a, b) Illustration of the beetle back effect via the dynamic process of fog droplet capture and transport. Source: Jianq et al. [53]/Elsevier.

frame I in Figure 1.23b), and then droplet growth due to the coalescence of tiny water-condensed fogdroplets (frame II in Figure 1.23b), finally, a larger coalesced droplet (1+2+3) rolls off from hydrophilic region, which remains the hydrophilic sites for subsequent fog capture (e.g. droplets 1', 2'; frame III in Figure 1.23b).

Such effect has been inspired to design various wetting patterns that are used to investigate fog water collection. With the understanding of the fog-collection principle of the patterned hydrophilic-hydrophobic surface of desert beetles, the wetting patterns can be regulated by structures, e.g., circle [60], star-angle [50], pillar [61], asymmetric hump [62] as a hydrophilic region for water capture, along with that the fabricated-techniques also have developed further in recent years.

1.5.5 Self-Propelling Effect: Ultrasuperhydrophobic Microand Nanostructures

The self-propelling effect often occur on many natural biological surfaces, e.g., lotus leaf [63], butterfly wing [26], gecko skin [64], cicada wing [63], kingfisher feather [65], strider leg [66], etc., has raised researchers to be up inspirations for the design of novel functional materials in applications. The self-propelling effect of water induces the self-cleaning of biological surfaces for biological happy activities.

Considering the example of gecko skin [64], as shown in Figure 1.24, indicates the gecko and the multilevel micro- and nanostructuring on its body and self-propelling effect and mechanism. Figure 1.24a is a photo of a gecko (*Lucasium steindachneri*, from the Mingela Ranges, Queensland, Australia) with a box pattern. Figure 1.24b is a topographical SEM image of the epidermal fold (scales) and areas between scales

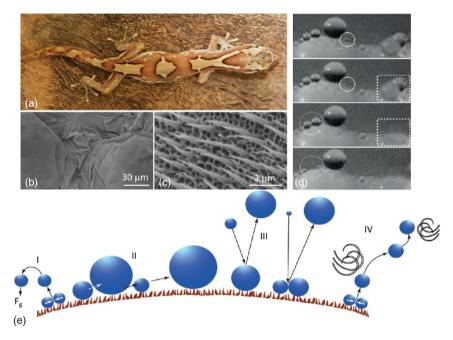


Figure 1.24 (a–e) Gecko skin with multilevel micro- and nanostructuring for self-propelling effect. Source: Watson et al. [64]/The Royal Society.

on the dorsal region. Figure 1.24c indicates the micro- and nanostructuring consisting of spinules and a base layer patterning on the dorsum. Such micro- and nanostructured surfaces generate the self-propelling effect of dew droplets, as shown in Figure 1.24d, where droplets coalesce and jump off surfaces.

The mechanism can be illustrated in Figure 1.24e. As for tiny droplets of the same size, it has direct self-propulsion of droplets off the skin surface (near vertical projection), where the droplets jump off (frame I). With the condensation of water droplets in growth, the droplet generates multiple coalescence. The coalesced droplets would sweep along the plane of the surface, along with the droplet scavenging laterally along the surface (frame II). Meanwhile, some fog droplets impact the grown droplets or other falling droplets, facilitating self-propulsion off the skin surface. The impacting droplet and coalesced droplet would all generate the energy to drive the droplet to jump off (frame III). If the surface is in nature, wind-assisted removal of droplets will happen due to the superhydrophobic microand nanostructures.

Another example is the strider leg with directional self-propelling effect due to oriented hairs. Figure 1.25a shows a water strider (named *Gerris remigis*) lives at the surface of the water in a highly humid environment. The legs suspend up the surface of the water, which is attributed to the oriented tilted-angle hairs (Figure 1.25b), which was observed by X-ray computed micro-tomography (micro-XCT). SEM observed the topological structures of a strider's leg, along with the conical tilted-angle hairs in outside-radiation orientations (Figure 1.25c). Such unique

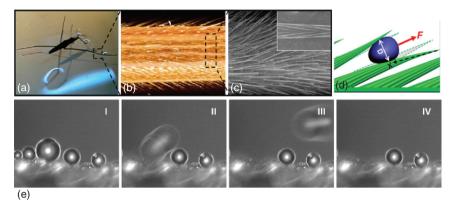


Figure 1.25 (a-e) Self-propelling effect for water droplets condensing on the leg of a water strider. Source: Wang et al. [66]/National Academy of Sciences.

structures generate the driving force (F) when droplets condense and coalesce in hairs; the droplets are driven by the F, for the removal and jump off (Figure 1.25e, from frame I to frame IV).

Benefit from the self-propelling effect on biological surfaces, except for the self-cleaning properties, the self-propelling impact is important to achieve water repellency or droplet transport in efficiency for heat transfer, nonwetting, anti-icing, etc., that can be extended into the design of surfaces and materials for engineering applications.

1.5.6 Janus Effect of Antifreeze Proteins: Controlling Ice Formation

Janus effect comes from ancient resources. The ancient Roman god Janus has two faces, one facing the past and the other facing the future, which fully systematizes the dialectical unity of philosophy, which is highly consistent with the idea of "yin and yang unity" of ancient Chinese philosophy, and its typical structural characteristics give people endless space for reverie. In 1991, Nobel Laureate de Gennes predicted in his acceptance speech that Janus particles are similar to amphiphilic molecules, which can efficiently stabilize the interface and have clear orientation characteristics, and the gap between particles provides a channel for the transport of matter between the two phases, which set off a research boom in Janus materials.

Consider an example of biological anti-icing. Nature endows antifreeze proteins (AFPs) with the unique capability of controlling ice formation. This Janus effect of AFPs is general because it is observed on three representative AFPs, i.e., a hyperactive insect AFP from the beetle *Microdera punctipennis* dzungarica (MpdAFP), a bacterial AFP from *Marinomonas primoryensis* (MpAFP), and a moderate active fish AFP (type III AFP). Both depression and promotion effects of AFPs on ice nucleation are observed via selectively binding the ice-binding face (IBF) and the nonice-binding face (NIBF) of AFPs to solid substrates. Freezing temperature and delay time assays show that ice nucleation is depressed with the NIBF exposed

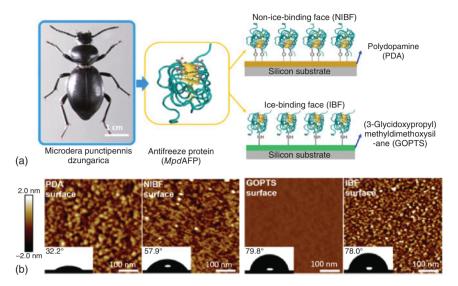


Figure 1.26 (a, b) Wetting features of tethered MpdAFPs on PDA and GOPTS surfaces. Source: Liu et al. [67]/National Academy of Sciences.

to liquid water, whereas ice nucleation is facilitated with the IBF exposed to liquid water. An AFP from M. p. dzungarica (MpdAFP) (Figure 1.26a), a beetle inhabiting Xinjiang, an autonomous region of China, along with the characterization of tethered MpdAFPs on polydopamine (PDA) and (3-glycidoxypropyl) methyldimethoxysilane (GOPTS) surfaces. Figure 1.26a illustrates AFP from an insect (M. p. dzungarica) and selectively tethered MpdAFPs on the PDA and GOPTS surfaces. Atomic force microscopy is used to further observe the PDA surface, NIBF surface, GOPTS surface, and IBF surface. The NIBF surface and the IBF surface show almost the same roughness. The static CAs on PDA surface, NIBF surface, GOPTS surface, and IBF surface indicate the differences, i.e., 32.3°, 57.9°, 79.8°, and 78°, respectively, due to the selective immobilization of MpdAFPs. The difference between the values of the CAs on the NIBF and IBF surfaces could be reconciled when one considers the fact that the IBF is more hydrophobic than the NIBF of AFPs.

The icing delay time consolidates the Janus effect of AFPs in tuning ice nucleation [67]. The icing delay time for supercooled droplets is shown in Figure 1.27. At low temperatures below zero of -28 °C (Figure 1.27a), there is little icing on the NIBF surface in comparison with that on the PDA surface (at time of 25 seconds); the completed icing is at 2254 seconds. At a low temperature below zero of -24 °C (Figure 1.27b), there is more icing on the IBF surface in comparison with that on the GOPTS surface (at a time of 8 seconds); the completed icing is at 1185 seconds. The cooling rate is 5 °C/min.

Since understanding the Janus effect by scientists and researchers, the Janus concept has been developed. In China, the research on Janus materials began around 2000. In the past 10 years (2012~2021), as a unique multicomponent multifunctional

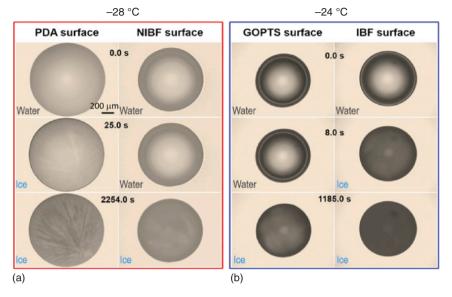


Figure 1.27 Observation of the icing delay time for supercooled droplets on NIBF, PDA, IBF and GOPTS surfaces. Source: Liu et al. [67]/with permission of National Academy of Sciences.

composite material, Janus material provided a key material means for the intersection of chemistry, physics, materials, life, and other disciplines.

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