Multifunctional Integration: From Biological to Bio-Inspired Materials

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ABSTRACT Nature is a school for human beings. Learning from nature has long been a source of bioinspiration for scientists and engineers. Multiscale structures are characteristic for biological materials, exhibiting inherent multifunctional integration. Optimized biological solutions provide inspiration for scientists and engineers to design and to fabricate multiscale structured materials for multifunctional integration.

Over the past several decades, most biological materials have been found to possess multiscale structures constructed through programmed assembly.[1] Recent research indicates these multiscale structures of biological materials possess multifunctional integration. A good example is demonstrated in superhydrophobic biological materials.

Multifunctional Integration in Superhydrophobic Biological Material Systems. In nature, some biological surfaces, such as lotus leaves, rice leaves, butterfly wings, water strider legs, mosquito compound eyes, and red rose petals exhibit fascinating superhydrophobicity, arising from the cooperative interactions of multiscale surface structures and chemical compositions.[2−7] Multiscale structures of these biological materials not only possess mutual superhydrophobicity, but also confer other unique functionalities, demonstrating multifunctional integration (Figure 1A−F).

> In nature, some biological surfaces, such as lotus leaves, rice leaves, butterfly wings, water strider legs, mosquito compound eyes, and red rose petals exhibit fascinating superhydrophobicity, arising from the cooperative interactions of multiscale surface structures and chemical compositions.

Lotus leaves exhibit low adhesive superhydrophobicity originating from multiscale structures with randomly distributed micropapillae covered by branch-like nanostructures (Figure 1A). Micropapillae and branch-like nanostructures are about 5−9 μm in length and 120 nm in diameter, respectively. Water can roll freely in all directions, resulting in a self-cleaning effect.[2] The water contact angle and sliding angle of lotus leaves are about 160° and 2°, respectively.[8]

While maintaining lotus-like micro/nanostructures, superhydrophobic rice leaves present anisotropic wetting by adjusting the arrangement of micropapillae with one-dimensional order (Figure 1B). Water droplets flow preferentially along the direction parallel to the leaf edge.[2] Sliding angles along the direction parallel to the rice leaf edge and along the perpendicular are about 3−5° and 9−15°, respectively. Utilizing rice leaves as templates, rice-leaf-like multiscale structures were well replicated on different materials. The resulting replicas showed superhydrophobicity and anisotropic wetting.[9,10]

Superhydrophobic butterfly wings with multiscale structures exhibit directional adhesion owing to an oriented one-dimensional arrangement with periodic overlapping microsquamas covered by lamella-stacking nanostripes (Figure 1C). Water can easily roll along the radial outward direction but is tightly pinned in the opposite direction.[3] Besides superhydrophobicity and directional adhesion, butterfly wings also exhibit structural color, directional self-cleaning, acute chemical sensing capability, and directionally controlled fluorescence emission functionalities

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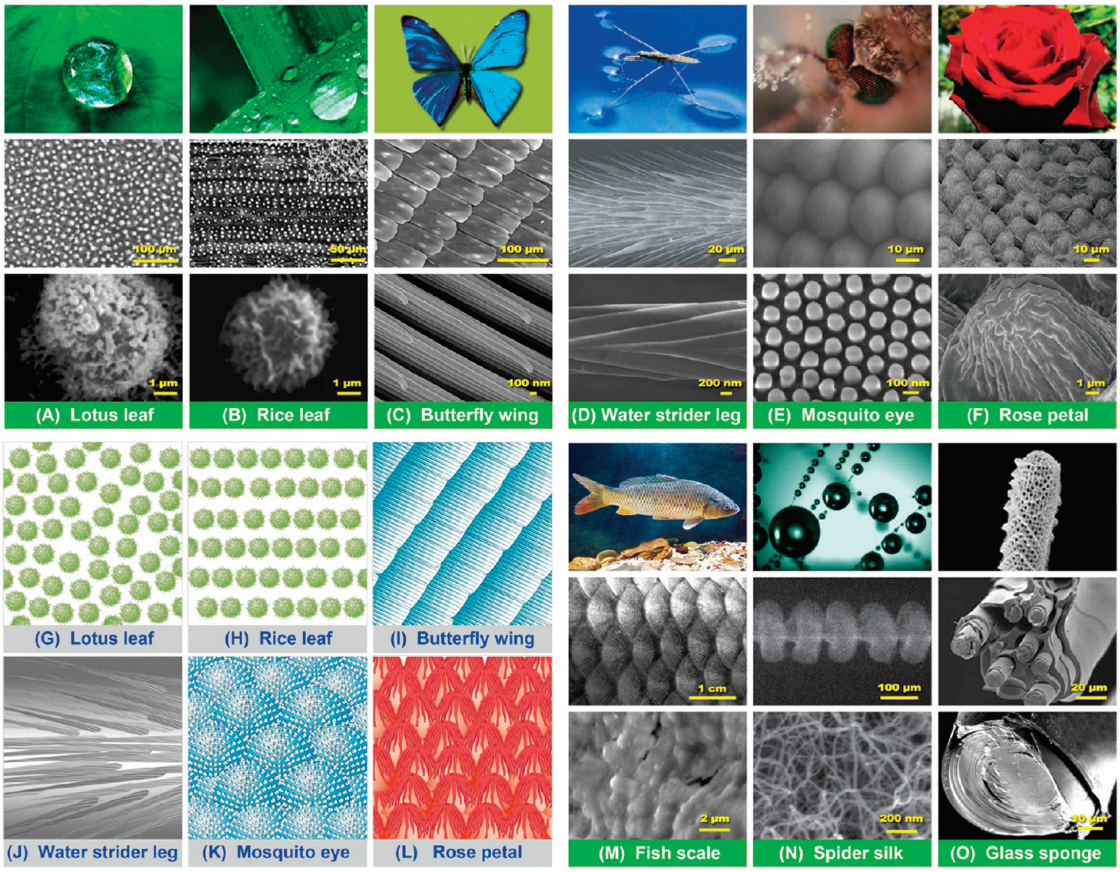

Figure 1. Typical biological materials with functional integration and corresponding multiscale structures and models. (A) Lotus leaves are famous for their superhydrophobic, low adhesive, and self-cleaning properties, originating from randomly distributed micro-papillae covered by branch-like nanostructures. Reproduced with permission from ref 2. Copyright 2002 Wiley. (B) Anisotropic wettability can be observed on superhydrophobic rice leaf surfaces owing to the arrangement of lotus-like micro-papillae in one-dimensional order. Reproduced with permission from ref 2. Copyright 2002 Wiley. (C) Butterfly wings present superhydrophobicity, directional adhesion, structural color, self-cleaning, chemical sensing capability, and fluorescence emission functions depending on the multiscale structures. Reproduced with permission from ref 3. Copyright 2007 Royal Society of Chemistry. (D) Water strider legs exhibit durable and robust superhydrophobicity due to directional arrangements of needlelike micro-setae with helical nanogrooves. Reproduced with permission from ref 4. Copyright 2004 Nature Publishing Group. (E) Superhydrophobic, antifogging, and antireflection functions can be found on mosquito compound eyes arising from HCP micro-ommatidia covered by HNCP nanonipples. Reproduced with permission from ref 5. Copyright 2007 Wiley. (F) Red rose petals possess superhydrophobicity with high adhesion and structural color originating from periodic arrays of micro-papillae covered by nanofolds. Reproduced from ref 6. Copyright 2008 American Chemical Society. Schematic multiscale structure models of (G) lotus leaf, (H) rice leaf, (I) butterfly wing, (J) water strider leg, (K) mosquito compound eye, and (L) red rose petal. (M) Fish scales possess drag reduction, superoleophilicity in air, and superoleophobicity in water owing to oriented micro-papillae covered by nanostructures. Reproduced with permission from ref 20. Copyright 2009 Wiley. (N) Spider capture silks have superior water collection ability, mechanical property, elasticity, and adhesiveness due to hierarchical fiber structures. Reproduced with permission from ref 28. Copyright 2010 Nature Publishing Group. (O) Spicules exhibit amazing mechanical and fiber-optical properties arising from concentric lamellar structures separated by organic interlayers. Reproduced with permission from refs 30 and 31. Copyright 2005 American Association for the Advancement of Science and copyright 2003 Nature Publishing Group, respectively.

depending on their multiscale structures.[11−13] For instance, upon interaction with different vapors (such as water, methanol, ethanol, and isomers of dichloroethylene), photonic structures of the *Morpho sulkowskyi* butterfly can produce diverse differential reflectance spectra, achieving a highly selective optical response to individual vapors with a single photonic structure. The optical response dramatically outperforms that of existing nanoengineered photonic sensors.[13] Utilizing *Euploea mulciber* butterfly wings as templates, multiscale SnO_2 structures were prepared *via* a sol−gel process. The resultant biomimetic analogue showed high sensitivity and fast response/recovery time for ethanol.[14] Mimicking *Morpho* butterfly wings, multifunctional inverse opal films have been fabricated through the self-assembly of polystyrene spheres and silica nanoparticles, exhibiting both superhydrophobicity and structural color.[15]

In the case of water striders' legs, multiscale structures confer durable and robust superhydrophobicity by modulating their surface structures in the form of oriented, needle-shaped microsetae with helical nanogrooves (Figure 1D). The maximal supporting force of a single leg reaches up to 152 dyn, that is, about

15 times the total body weight of a water strider. Therefore, water striders can stand effortlessly and move quickly on water.[4] Mimicking the setae of water strider legs, robust water-repellent materials possessing ribbed, conical nanoneedle arrays have been fabricated on copper surfaces.[16] Lotus leaves, in contrast, do not possess such durable and robust superhydrophobicity and become highly hysteretic and even hydrophilic-like when soaked in water.[17]

Apart from superhydrophobicity, mosquito compound eyes possess antifogging and antireflection functionalities arising from their surface multiscale structures, consisting of hexagonally close-packed (HCP) micro-ommatidia covered by hexagonally nonclose-packed (HNCP) nanonipples (Figure 1E). Tiny fog drops cannot stay on compound eye surfaces, thus inducing a dry, clear state even in foggy and moist environments.[5] Inspired by mosquito compound eyes, multifunctional artificial compound eyes with superhydrophobic and antifogging properties have been prepared using a soft lithography method followed by low-surface-energy fluoroalkylsilane modification.[5]

Multiscale structured red rose petals with a periodic array of micropapillae covered by nanofolds exhibit both superhydrophobicity with high water adhesion and structural color (Figure 1F).[6,18] Water droplets on petal surfaces cannot roll off even when the petal is turned upside down. Utilizing red rose petals as templates, poly(vinyl alcohol) films with negative petal structures and polystyrene films with positive petal structures have been fabricated. These biomimetic materials presented superhydrophobicity with high adhesive force to water and structural color.[6,18]

Representative multiscale structure models of the lotus leaf, rice leaf, butterfly wing, water strider leg, mosquito compound eye, and red rose petal are shown in Figure 1G–L, respectively. These models clarify that these biological materials all possess multiscale structures while exhibiting different arrangements, orientations, and morphologies. Inherent multiscale structures not only result in universal superhydrophobic functionality, but also add other special functionalities. Multiscale structures of biological materials play important roles in achieving functional integration.

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Multifunctional Integration in Other Biological Materials Systems. Special biological solutions are not restricted to the above superhydrophobic biological materials systems, which can also be found in other biological material systems (such as fish skin, spider silks, spicules, brittlestars, and nacre). Some biological materials possessing functional integration and their corresponding multiscale structures are presented in Figure 1M–O.

Besides its drag-reducing function,[19] fish skin with multiscale structures presents superoleophilicity in air and superoleophobicity in water (Figure 1M).[20] Recently, inspired by the oil-repellent nature of fish scales, multiscale macromolecule-nanoclay hydrogels with robust underwater superoleophobicity were constructed through photoinitiated polymerization.[21] Ribbed textures of shark scales provided the inspiration for the design of multifunctional coatings with drag-reducing and self-cleaning functionalities, resulting in trials on an aircraft.[19]

Apart from classical mechanical properties, spider dragline silks with multiscale structures exhibit wetting-induced supercontraction and torsional shape memory.[22−24] Spider dragline silks provide important inspiration for human beings for the design of multifunctional materials for high-technology applications.[25] For spider capture silks, in addition to extraordinary strength, elasticity, and adhesiveness, they possess directional water-collection ability owing to their special multiscale fiber structures (Figure 1N).[26−28] In these silks, wet-rebuilt fibers with periodic spindle-knots composed of random nanofibrils separate joints made of aligned nanofibrils. Forces generated by a gradient of surface energy on the fibrils and by the spindle shape of the knots act together to direct water droplets toward the knots. Mimicking the directional water-collecting ability of spider capture silks, a series of artificial fibers with spindle-knots were fabricated recently.[28,29]

Spicules of glass sponge possess both remarkable fiber-optical and mechanical properties originating from concentric lamellar multiscale structures (Figure 1O).[30−32] Brittlestar is also a multifunctional biomaterial that fulfills both mechanical and optical functionalities.[33] Nacre with layered brick-and-mortar multiscale structures has not only superior mechanical properties but structural colors.[34−36] Inspired by nacre, nacre-like multifunctional materials with brick-and-mortar structures have been fabricated *via* layer-by-layer assembly.[36−38]

What Else Can We Learn from Nature? Creating composite functional materials is an eternal goal for human beings. Bioinspired approaches are expected to be particularly effective.[39] Inspired by biological materials, a great variety of multifunctional materials with multiscale structures have been prepared by using different synthesis strategies.[39−41] In the near future, the following research directions should be addressed.

(i) Further investigate biological materials, discover new functionalities, and provide design principles for novel functional materials. For example, recently, it was found that termite wings with multiscale structures possess nonwetting functionalities at different length scales. Intricate hierarchical arrays of termite wings demonstrate an elegant design for weight and material minimization, which could contribute to the next generation of bioinspired materials and devices.[42] Recent research revealed that floating leaves of the water fern *Salvinia* are covered with complex hydrophobic hairs that retain a layer of air when submerged under water. These hydrophilic patches stabilize the air layer by pinning the air—water interface. The unique "*Salvinia* Effect" provides an innovative strategy to construct biomimetic surfaces with long-term air-retention capabilities for underwater applications.[43]

(ii) Design new multifunctional materials inspired by two or more biological materials. The fusion of two or more seemingly distinct ideas found in biological materials into composites with novel function remains an exciting research direction. For example, inspired by both mussels and geckos, a reversible wet/dry adhesive consisting of an array of gecko-mimetic nanoscale polymer pillars coated with a thin mussel-mimetic polymer film was prepared, exhibiting high adhesive performance for over a thousand contact cycles in both dry and wet environments.[44], Self-cleaning antireflection coatings were fabricated using a colloidal templating technique and by mimicking functionalities of both antireflective moth eyes and superhydrophobic cicada wings.[45]

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Nature has evolved different solutions to achieve efficient multifunctional structures, that is, functional integration. Optimized biological solutions continue to inspire and to provide design principles for the rational design and reproducible construction of multiscale structures for multifunctional integration.

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