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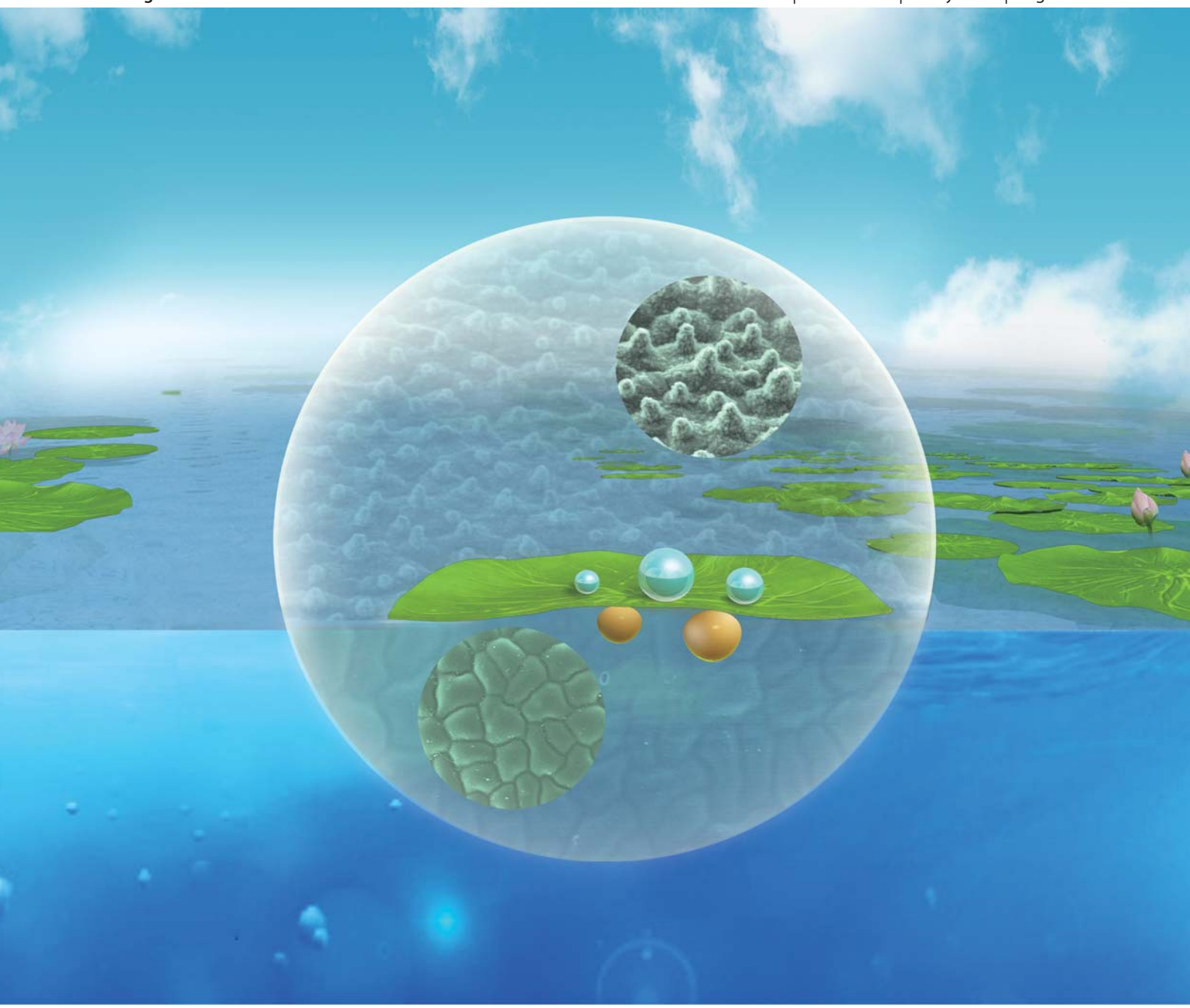

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COMMUNICATION

Janus interface materials: superhydrophobic air/solid interface and superoleophobic water/solid interface inspired by a lotus leaf†

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We discovered underwater superoleophobicity on the lower side of a lotus leaf, and fabricated Janus interface materials with in-air superhydrophobicity on one side and underwater superoleophobicity on the other side inspired by the Janus feature of the lotus leaf. The ingenious design on lotus leaf surfaces, superhydrophobicity on its upper side and underwater superoleophobicity on its lower side, not only helps us thoroughly understand the special surface wettability of the lotus leaf, but also gives a typical example of multi-functionality in biological systems. This study supplies us with an intelligent strategy to design and create bionic multi-functional interface materials.

Lotus leaves have attracted immense scientific interest in recent years due to their superior self-cleaning properties.[1–6] The upper side has a typical micro-/nanoscale hierarchical papillae and epicuticular wax, which makes the water freely roll along the leaves resulting in the "lotus effect". The lotus leaf margin with high energy barrier can keep the upper side dry when the lotus leaf floats on water.[7] Thus the upper side of a lotus leaf can keep itself clean from dirty particles which can be brought away when a water droplets roll off. So far, only the self-cleaning on its upper side has been studied. The properties of the lower side of a lotus leaf are often neglected. In this communication, we reveal the underwater superoleophobicity on its lower side, indicating biological multi-functionality of lotus leaves. Inspired by this, we successfully fabricated Janus interface materials with superhydrophobicity on one side in air and superoleophobicity on the other side in water. This ingenious design on lotus leaf surfaces, superhydrophobicity on the upper side and underwater superoleophobicity on the lower side, not only helps us thoroughly understand the special surface wettability of lotus leaves, but also gives a typical example of multi-functionality in biological systems. This study supplies us with an intelligent strategy to design and create bionic multi-functional interface materials and enrich the community of Janus materials.[8–14]

In-air superoleophobic surfaces are very useful in daily life and in industry. The design and creation of superoleophobic surfaces is very difficult due to the low surface tension of oils. The traditional method for fabricating superoleophobic surfaces is modifying a rough surface with fluorinated compounds.[15] Recently, the concept of surface curvature[16,17] was successfully introduced to construct re-entrant structures by Tuteja and co-workers,[18] which shows superoleophobicity with low surface tension oils such as decane, octane and pentane in air. However, these in-air superoleophobic surfaces modified with fluorinated materials will become superoleophilic in water.[19] The design of underwater superoleophobic surfaces has attracted increasing attention for potential in anti-bioadhesion,[20] microfluidics,[21] and marine anti-biofouling coatings.[22] Inspired by fish scales, hydrogen-based underwater superoleophobic fluoride-free surfaces were successfully fabricated.[23,24]

Fig. 1a shows the representative digital photograph of a lotus leaf floating on the water surface. The water droplets retain a spherical shape on its upper side (Fig. 1b). The oil droplets (n-hexane dyed red) can stay on its lower side in water in the shape of spheres (Fig. 1b). This Janus feature of the lotus leaf works together and keeps the purity of the lotus leaf floating on the water.

We further tested underwater contact angles of apolar and amphiphilic oils, including 1,2-dichloroethane, n-hexane, rapeseed oil, sunflower oil, and octanol, on the lower side of a lotus leaf as shown in Fig. S1.† Take 1,2-dichloroethane as an example: the oil contact angle (OCA) reaches up to $155.0 \pm 1.5°$ (Fig. 2a). Meanwhile, the oil droplets can roll off on its lower side (Fig. 2b). The tilt angle with oil is about $12.1 \pm 2.4°$. In air the lower side of the lotus leaf can be completely wetted with water (Fig. S2†). This is because its lower side has no three-dimensional wax crystals,[5] like other species grown completely in water or partially floating on the water surface.[25] The environment scanning electron microscope (ESEM) image shows that its lower side consists of numerous tabular and slightly convex papillae with 30–50 μm length and 10–30 μm width (Fig. 2c). A single papilla was further tested by atomic force microscope (AFM). Every single papilla is covered with nanogroove structures with size of 200–500 nm and the height of a single papilla is around 4 μm (Fig. 2d). Moreover, the epidermal glands of its lower side may secrete some hydrophilic compounds, like ferns.[26] The stability of oil droplets on its lower side in water was also tested. The OCAs of different oils keep

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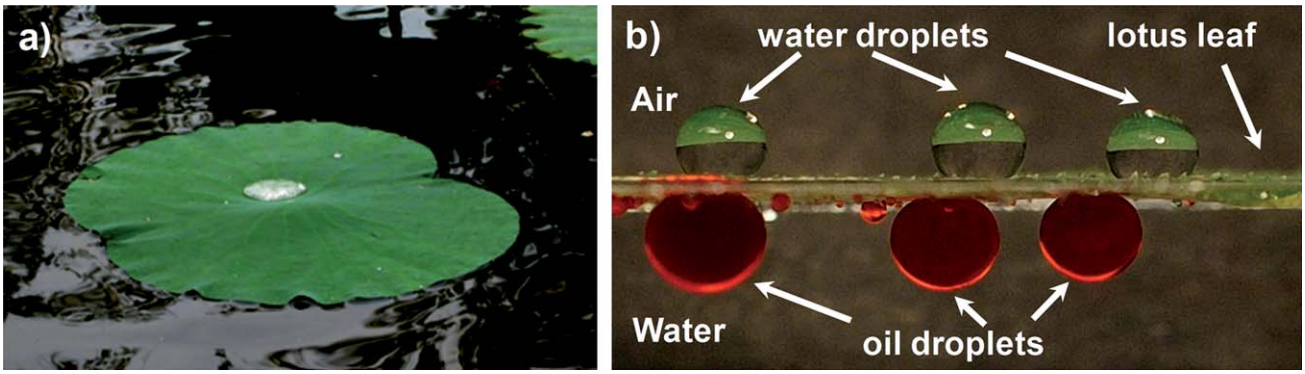


Fig. 1 Digital photographs of alotus leaf floating on the water surface showing different wettabilities for water and oil droplets. a) The floating lotus leaf on the water surface with some water droplets on the upper side. b) Three water droplets form spheres on its upper side. The oil (n-hexane dyed red) droplets stay as perfect spheres in water on its lower side.

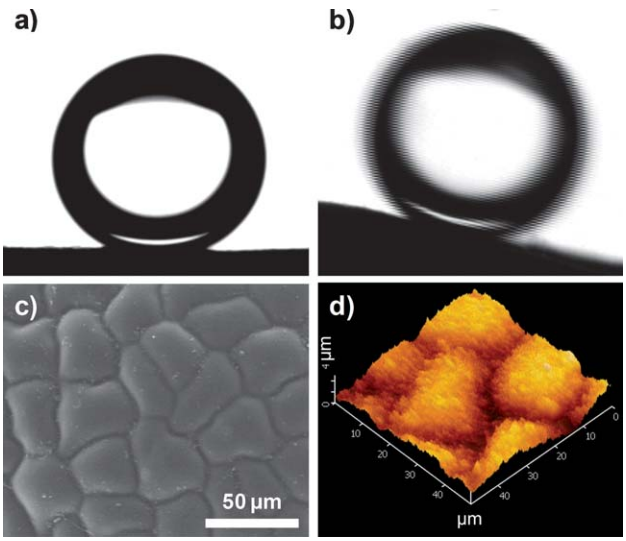
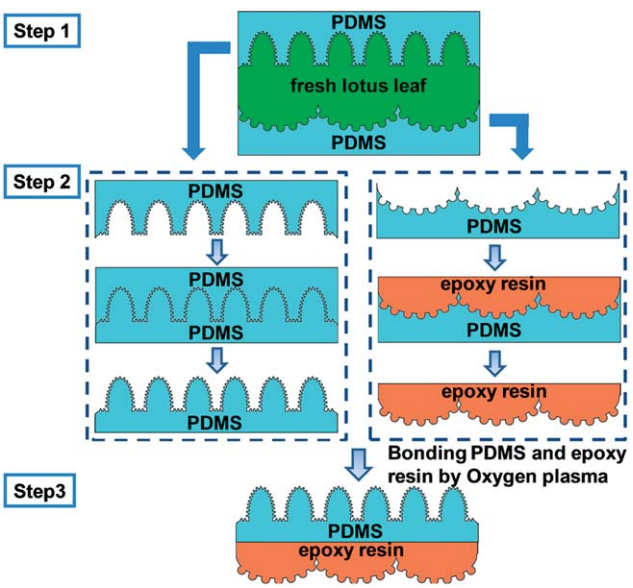


Fig. 2 Wettability of the lower side of a lotus leaf with an oil droplet in water. a) Shape of an oil droplet (*e.g.*, 1,2-dichloroethane) on its lower side in water, showing superoleophobicity with a contact angle of 155.0 ± 1.5°. b) The oil droplet can roll off when the tilt angle reaches up to 12.1 ± 2.4°. c) Environment scanning electron microscope (ESEM) image shows its lower side consists of numerous tabular and slightly convex papillae with 30–50 μm length and 10–30 μm width. d) Atomic force microscope (AFM) image further shows the tabular papillae are covered with nanogroove structures with size of 200–500 nm and the height of a 3single papilla is around 4 μm.

larger than 150°, even after 24 h in water (Fig. S1). It indicates good stability of the underwater superoleophobicity of its lower side. Therefore, the lower side of a lotus leaf shows stable underwater superoleophobicity for apolar and amphiphilic oils.

As shown above, the lotus leaf shows features of a Janus interface including superhydrophobicity on the upper side and underwater superoleophobicity on the lower side. Inspired by the Janus feature of the lotus leaf, we fabricated Janus interface materials by replicating a lotus leaf using a template method,[27] which is a simple, effective and fast technique in the field of biomimetic research to obtain functional interface materials by replicating surface structures of biological surfaces. For instance, epoxy resin,[28] PDMS,[29] PMMA,[30] and photopolymer,[31] have been used to replicate the upper side of a lotus leaf. Here, PDMS and epoxy resin are chosen to replicate the upper side and lower side of a lotus leaf through two steps. An epoxy resin system contains two standard epoxy resins, glycidyl ester, and resorcinol diglycidyl ethers, and hexahydrophthalic anhydride as the curing agent.[32] At a temperature of 60 °C, the viscosity of this epoxy resin can be kept at as low as 50 cPa s for more than 12 h. The viscosity of the epoxy resin is low enough to completely replicate the nanoscale structure. The duplicated processing steps of the lotus leaf surface structure are shown in Scheme 1. More details of the fabrication process are shown in ESI.† A fresh natural lotus leaf floating on water surface was used as the original bio-template in the replication of step 1. The mixture of liquid PDMS and its curing agent (10 : 1, mass proportion) was cast onto the upper side and lower side of the lotus leaf.

After solidification at room temperature for 24 h, a flexible PDMS negative replica was obtained, as shown on the left of step 2. Then the liquid PDMS was cast on the upper side of the PDMS negative template in the same manner. After PDMS solidification, the artificial



Scheme 1 Schematic illustrating the procedure of fabricating the Janus interface materials.

upper side of the lotus leaf based on PDMS was peeled off from the PDMS negative template. The liquid epoxy resin was infiltrated into the lower side of the PDMS negative replica at 60 °C, as shown on the right of step 2. Samples were immediately transferred to a vacuum chamber for 10 min to remove trapped air and to increase the resin infiltration through the structures. After curing at 80 °C for 2 h plus 120 °C for 12 h, the artificial lower side of the lotus leaf based on epoxy resin was released from the PDMS negative replica. An AFM image shows the hierarchical micro/nanoscale structure of the lower side of the lotus leaf was well replicated by epoxy resin (Fig. S3†). The artificial PDMS upper side and epoxy lower side of the lotus leaf were bonded together using oxygen plasma,[33] as shown in step 3. This replicating method is more facile and fast for constructing Janus interface materials, especially for underwater superoleophobic interface materials, compared with silicon wafer,[23] micropatterned surface,[19] and the hybrid nanoclay hydrogels.[24] Generally, the epoxy resin is applied in many fields including coatings, adhesives and composite materials due to its excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties.[34] Selecting the epoxy resin to replicate the lower side of the lotus leaf offers the artificial underwater superoleophobic materials excellent mechanical properties. Compared with the lower side of the lotus leaf, these artificial superoleophobic interface materials have more excellent mechanical strength and good resistance to chemicals in water.

The fabricated Janus interface material floating on the water surface is shown in Fig. 3a. Its upper side shows superhydrophobicity with a contact angle of 156.0 ± 1.0° in air and its lower side shows superoleophobicity with oil (n-hexane dyed red) contact angle of 153.5 ± 1.5° in water. The morphology of this Janus interface material is shown in Fig. 3b and c, indicating the papillae on the upper side and the lower side of the lotus leaf were completely replicated by PDMS and epoxy resin, respectively.

ESEM and *in situ* AFM images have revealed that only the tops of the papillae of the lotus leaf are in contact with the water droplet and that a large volume of air between the papillae results in superhydrophobicity in air,[35] as shown in Fig. 4. To better understand the wetting behavior of oil on the lower side of the lotus leaf in water, the equations deduced from typical Young's equation[36] and Cassie model[23] were applied.

In previous reports,[23,24] the high content of water trapped by the micro-/nanoscale hierarchical structure reducing the contact area

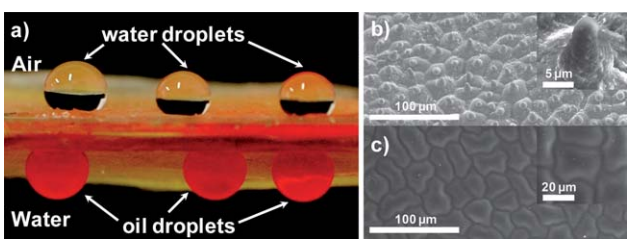


Fig. 3 a) The Janus interface material is floating on the water surface, and the water droplets can stay on its upper side in the shape of spheres in air and the oil (n-hexane dyed red) droplets are on its lower side in the shape of spheres in water. b) SEM images show the micro-/nanoscale hierarchical structure on the upper side of the lotus leaf is replicated by PDMS. c) The tabular and slightly convex papillae on the lower side of the lotus leaf are also replicated by epoxy resin.

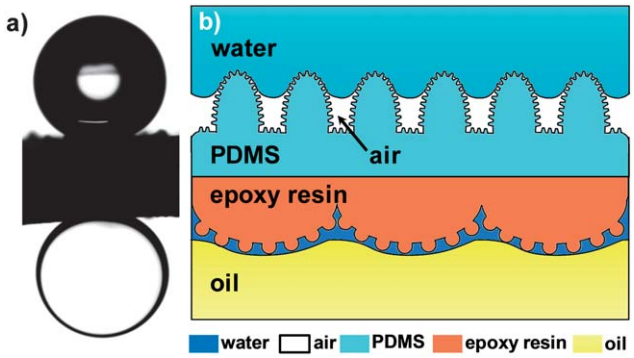


Fig. 4 Schematic illustrations of liquid droplets in contact with Janus interface material. (a) The Janus interface materials are floating on the water surface. A water spherical droplet is on its upper side in air and an oil (n-hexane) droplet is on its lower side in water. (b) The top surface of micro-sized papillae (cyan) on the artificial upper side of the lotus leaf is only partly wetted with water (blue), and the trapped air results in superhydrophobicity in air. The artificial lower side (orange) is completely wetted with water (blue). The nanogrooves on the lower side reduce the contact area between oil (yellow) and the lower side, which achieves underwater superoleophobicity.

between the oil and the surface has been proved to be the main reason for achieving superoleophobicity. The papillae on the lower side of the lotus leaf also result in underwater superoleophobicity. The nanogroove structures on the papillae further reduce the contact area between oil and the lower side (Fig. 4). Eqn (1) was obtained by combining three Young's equations under different conditions, which can be used to calculate the contact angle in a solid/water/oil three-phase system.[23] For a rough surface composed of solid and water, the Cassie model is expressed as eqn (2).

$$\cos\theta = \frac{\gamma_{o\text{-}g}\cos\theta_o - \gamma_{w\text{-}g}\cos\theta_w}{\gamma_{o\text{-}w}} \quad (1)$$

$$\cos\theta' = f\cos\theta + f - 1 \quad (2)$$

where $\gamma_{o\text{-}g}$ is the oil/gas interface tension, θ_o is the OCA in air, $\gamma_{w\text{-}g}$ is the water/gas interface tension, θ_w is the contact angle of water in air, $\gamma_{o\text{-}w}$ is the water/oil interface tension, θ is the contact angle of an oil droplet on a smooth surface in water, f is the area fraction of solid, and θ' is the contact angle of an oil droplet on a rough surface in water. Here, the oil used is 1,2-dichloroethane and its interfacial tension $\gamma_{o\text{-}g}$ in air is 24.15 mN m^{-1}.[37] The water surface tension $\gamma_{w\text{-}g}$ in air is 73 mN m^{-1} and the 1,2-dichloroethane/water interfacial tension $\gamma_{o\text{-}w}$ is 28.1 mN m^{-1}.[38] In air, the 1,2-dichloroethane contact angle measured on a smooth epoxy resin surface θ_o is nearly 10° (Fig. S4a†), and the water contact angle θ_w is about 66.0° (Fig. S4b†). As a result in eqn (1), $\cos\theta = -0.210$, thus $\theta = 102.2°$, indicating the flat epoxy resin behaved as an underwater oleophobic surface. The OCA in water on flat epoxy resin is about 110.0° (Fig. S4c†). Eqn (2) can be utilized to calculate the area fraction of f. Substituting θ and θ' into eqn (2), $f = 0.13$ can be obtained, indicating the lower side of the Janus interface material is relatively smooth, which is consistent with the experiments (Fig. 2c) and further verify our proposed mechanism[23] in a previous report.

In conclusion, we fabricated Janus interface materials with in-air superhydrophobicity on one side and underwater superoleophobicity

on the other side inspired by the Janus feature of lotus leaves. Underwater superoleophobicity on the lower side of a lotus leaf offers a new insight into revealing its special surface wettability and helps us thoroughly understand integrated multi-functional characteristics in biological systems. In addition to bringing an alternative branch of Janus materials, this study will also initiate new progress in the field of lotus-related bionics and accelerate the developing of bio-inspired multi-functional interface materials. Looking to the future, emerging efforts will focus on developing bio-inspired multi-functional material systems.

Acknowledgements

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