Fogging occurs when moisture condensation takes the form of accumulated droplets with diameters larger than 190 nm or half of the shortest wavelength (380 nm) of visible light. This problem may be effectively addressed by changing the affinity of a material’s surface for water, which can be accomplished via two approaches: i) the superhydrophilic approach, with a water contact angle (CA) less than 5°, and ii) the superhydrophobic approach, with a water CA greater than 150°, and extremely low CA hysteresis. To date, all techniques reported belong to the former category, as they are intended for applications in optical transparent coatings. A well-known example is the use of photocatalytic TiO$_2$ nanoparticle coatings that become superhydrophilic under UV irradiation. Very recently, a capillary effect was skillfully adopted to achieve superhydrophilic properties by constructing 3D nanoporous structures from layer-by-layer assembled nanoparticles. The key to these two “wet”-style antifogging strategies is for micrometer-sized fog drops to rapidly spread into a uniform thin film, which can prevent light scattering and reflection from nucleated droplets. Optical transparency is not an intrinsic property of antifogging coatings even though recently developed antifogging coatings are almost transparent, and the transparency could be achieved by further tuning the nanoparticle size and film thickness. To our knowledge, the antifogging coatings may also be applied to many fields that do not require optical transparency, including, for example, paints for inhibiting swelling and peeling issues and metal surfaces for preventing corrosion. These types of issues, which are caused by adsorption of moisture, are hard to solve by the superhydrophilic approach because of its inherently “dry” nature. Thus, a “dry”-style antifogging strategy, which consists of a novel superhydrophobic technique that can prevent moisture or microscale fog drops from nucleating on a surface, is desired.

Recent bionic researches have revealed that the self-cleaning ability of lotus leaves and the striking ability of a water-strider’s legs to walk on water can be attributed to the ideal superhydrophobicity of their surfaces, induced by special micro- and nanostructures. To date, the biomimetic fabrication of superhydrophobic micro- and/or nanostructures has attracted considerable interest and these types of materials can be used for such applications as self-cleaning coatings and stain-resistant textiles. Although a superhydrophobic technique inspired by lotus leaves is expected to be able to solve such fogging problems because the water droplets can not remain on the surface, there are no reports of such antifogging coatings. Very recently, researchers from General Motors have reported that the surfaces of lotus leaves become wet with moisture because the size of the fog drops are at the microscale—so small that they can be easily trapped in the interspaces among micropapillae. Thus, lotuslike surface microstructures are unsuitable for superhydrophobic antifogging coatings, and a new inspiration from nature is desired for solving this problem.

In this communication, we report a novel, biological, superhydrophobic antifogging strategy. It was found that the compound eyes of the mosquito *C. pipiens* possess ideal superhydrophobic properties that provide an effective protective mechanism for maintaining clear vision in a humid habitat. Our research indicates that this unique property is attributed to the smart design of elaborate micro- and nanostructures: hexagonally non-close-packed (hcp) nipples at the nanoscale prevent microscale fog drops from condensing on the ommatidia surface, and hexagonally close-packed (hcp) ommatidia at the microscale could efficiently prevent fog drops from being trapped in the voids between the ommatidia. We also fabricated artificial compound eyes by using soft lithography and investigated the effects of micro- and nanostructures on the surface hydrophobicity. These findings could be used to develop novel superhydrophobic antifogging coatings in the near future.

It is known that mosquitoes possess excellent vision, which they exploit to locate various resources such as mates, hosts, and resting sites in a watery and dim habitat. To better understand such remarkable abilities, we first investigated the interaction between moisture and the eye surface. An ultrasonic humidifier was used to regulate the relative humidity of the atmosphere and mimic a mist composed of numerous tiny water droplets with diameters less than 10 μm. As the fog was...
directed through a polytetrafluoroethylene (PTFE) tube and blown toward the mosquito eyes, by using a LYNX stereo microscope with a high contrast stereo imaging ability we clearly observed that the tiny fog drops would not stay on the surface of the compound eyes although they could easily nucleate on the surrounding hairs as long as they were in contact with each other (Supporting Information, Movie 1). Figure 1 shows a representative optical photograph of a mosquito’s eyes after they were exposed to moisture for a long time. The eyes maintained a dry, clear state while the surrounding hydrophobic hairs nucleated a large number of drops with time. Thus, the mosquito eyes exhibited striking superhydrophobic antifogging properties.

Recent bionic research has indicated that the supernatural macroscopic functions of certain biosurfaces are derived from special microscopic structures and morphologies.[8–11,20,21] To explore the origin of such marvelous superhydrophobic antifogging properties, we first investigated the microscopic structure and morphology of mosquito eyes in detail. Figure 2a shows a scanning electronic microscopy (SEM) image of a single mosquito eye. The mosquito eye is a compound structure composed of hundreds of microscale hemispheres, which act as individual sensory units called ommatidia. These ommatidia are uniform with a diameter of ca. 26 μm and organize in an hcp arrangement (Fig. 2b). By using high-resolution field-emission SEM, we observed that the surface of each micro-hemisphere was covered with numerous, fine, nanoscale nipples (Fig. 2c). Increased magnification revealed that these nipples are very uniform, with average diameters of (101.1 ± 7.6) nm and interparticle spacings of (47.6 ± 8.5) nm; they organize in an approximately hexagonal ncp array (Fig. 2d).

According to Cassie’s principle for surface wettability,[22] such hierarchical micro- and nanostructures may be considered as heterogeneous curved surfaces composed of air and solids. Similar to the surfaces of lotus leaves[8,9] and water strider’s legs,[11] air may become trapped in the spaces between the nanonipples and micro-hemispheres to form a stable air cushion that acts as an effective water barrier, greatly reducing the contact of tiny fog drops with the eye surface. Chandler and co-workers have reported that it is theoretically difficult for a hydrogen-bonded network of water molecules to invade the voids in nanomaterials such as parallel hydrophobic plates with a critical separation of ca. 100 nm at room temperature and atmospheric pressure.[23] As a result, air is firmly trapped in the small voids between these neighboring nanonipples, which possess an average interparticle spacing of 47.6 nm. In this case, water surface tension is strong enough to cause the micrometer-sized fog drops to contract, assuming a perfect spherical shape because of negligible weight. Moreover, the loose arrangement of nanonipples on hcp micro-hemispheres makes an extremely discrete and nonplanar triple-phase (liquid-air-solid) contact line, which is energetically favorable for driving the spherical fog drops effortlessly from the surface.[24] Thus, the combination of hexagonally ncp nanonipples at the nanoscale and hcp ommatidia at the microscale on the surface of mosquito eyes may induce ideal antifogging properties via a superhydrophobic approach.

Although mosquito eyes and lotus leaves are both superhydrophobic, the difference in their surface microstructures gives rise to different biological behavior: the former is antifogging for microscale fog drops while the latter is self-cleaning for millimeter-scale raindrops. It has been reported that the arrangement of lotus papillae at the microscale is random and diffuse with a spacing larger than fog drop diameters.[8] Accordingly, the tiny fog drops are easily trapped in the spaces between the papillae so that the lotus leaf surface may become wet during a long exposure to moisture.[18] In comparison, the mosquito ommatidia at the microscale assume a compact hcp arrangement with triangular voids less than 3 μm, which effectively prevent the plunge of fog drops, while the hexagonally ncp nanonipples trap a stable air cushion, thus preventing microscale fog drops from condensing on the corneal surface.

Because of the microscale size and the spherical design of mosquito eyes, it is difficult to quantitatively characterize their CA value by using the conventional sessile drop method.

**Figure 1.** A photograph of antifogging mosquito eyes. Even though they are exposed to moisture, the surface of the eyes remains dry and clear while the surrounding hairs nucleate many drops.

**Figure 2.** a) An SEM image of a single mosquito eye. b) An hcp micro-hemisphere (ommatidia). c) Two neighboring ommatidia. d) Hexagonally ncp nanonipples covering an ommatidial surface.
To better understand the contribution of the nanonipple and the micro-hemisphere structure to the water-resistance of the surface, we must fabricate artificial compound eyes. Recently, research groups engaging in biomimetic design and optical device research have fabricated 2D microlenses (micro-hemisphere arrays) that mimic the hcp ommatidia by various methods including the melting of a patterned photoresist,[25] soft lithography,[26] three-beam interference lithography,[27] and self-assembly of monodisperse polymer beads.[28,29] Very recently, Lee et al. have proposed a novel, biologically inspired, 3D optical synthesis to prepare artificial compound eyes consisting of microscale ommatidia on a hemispherical polymer dome that is 2.5 mm in diameter.[30] However, further patterning of the nanonipple structure on the surface of arrayed micro-hemispheres has remained a technological challenge until now.

Figure 3 outlines a procedure for fabricating artificial mosquito compound eyes that involves three main steps. First, we used photolithography to fabricate hexagonally np circular photoresist posts on a glass slide (Fig. 3a). Based on the parameters of mosquito ommatidia, the diameter and the height of the posts were set to ca. 20\(\mu\)m with a ca. 5\(\mu\)m spacing between two neighboring posts. When the sample was heated at 160 °C for 5–15 min, the circular photoresist posts on the slide melted into a hemisphere shape (Fig. 3b) because the interfacial energy was minimized.[25] Next, the micropattern of the photoresist hemisphere array was replicated on a polydimethylsiloxane (PDMS) stamp (Fig. 3c) by a two-step soft-lithography process.[31] As shown in Figure S1 of the Supporting Information, the liquid PDMS prepolymer was cast on the photoresist hemisphere array and then cured at 60 °C in an oven for 3 h. After it was cooled to room temperature, the solidified PDMS film comprising a negative micropattern was removed. According to the vapor-phase assembly method,[32] such a concave hemisphere micropattern was further modified with monolayers of self-assembled fluoroalkylsilane (FAS) molecules and used as the master for making PDMS stamps with a convex hemisphere micropattern through soft lithography. We then patterned a monolayer of colloidal crystals on the surface of PDMS hemispheres to mimic the nanonipples on the mosquito ommatidia by using a typical lift-up soft-lithography technique.[33] As shown in Figure 3d, the PDMS stamp patterned with micro-hemisphere arrays was brought into conformal contact with a monolayer of silica nanospheres on a silicon substrate and subsequently hot-pressed at 100 °C, 0.2 \(\times\) 10\(^5\) Pa for 3 h. After the cooled PDMS stamp was carefully peeled from the substrate, we obtained compound-eye micro- and nanostructures (Fig. 3e).

Figure 4a shows a typical optical photograph of an artificial compound eye, which was composed of a large number of uniform PDMS hemispheres. We clearly observe that these PDMS hemispheres have uniform diameters of ca. 22 \(\mu\)m and assume an hcp arrangement (Fig. 4b). Further magnification revealed that the surface of each PDMS micro-hemisphere has approximately \(1.85 \times 10^9\) spheres mm\(^{-2}\) (Fig. 4c). These nipplelike silica spheres have a uniform diameter of 100 nm and also arrange in an hcp structure. Subsequently, the as-prepared, artificial, compound-eye counterparts were chemically modified with a self-assembled monolayer FAS molecules with a water CA of 109° on a flat surface.[32] Figure 4d shows a photograph of a spherical water droplet on the artificial compound-eye surface.
sphere structures could greatly enhance the water-resistant property of the surface. However, it is noted that the surface of the artificial counterpart is far less hydrophobic than the mosquito eyes because the nanostructure (Fig. 4c) that assembled on the surface of the PDMS micro-hemispheres was not as perfectly organized as the mosquito nanonipple structures shown in Figure 2c and d because of limitations in the fabrication method. These nipplelike nanospheres exhibited some local defects, which could reduce the fraction of air trapped in the voids between the nanospheres, thus decreasing the water CA and surface hydrophobicity.\(^{[22]}\) As a result, the surface quality of the artificial analogue was insufficient for preventing microscale fog drops from condensing on the surface. In addition, the transparent PDMS micro-hemisphere films became hazy after the uniform nanospheres were assembled onto the surface of the micro-hemispheres, which could result from the enhanced scattering and reflectivity effects of visible light on the defect points of the nanoparticle monolayer. Thus, the construction of perfect hexagonally ncp nanonipple structures on the surface of arrayed micro-hemispheres remains a technological challenge for future work.

In summary, we have discovered a novel biological anti-fogging strategy by using a superhydrophobic approach. Research has indicated that the combination of hexagonally ncp nipples at the nanoscale and hcp ommatidia plays a crucial role in creating the ideal superhydrophobicity for preventing microscale fog drops (moisture) from condensing on the eye surface. Moreover, the development of configurable soft-lithography methods by using PDMS allows the bio-inspired creation of superhydrophobic compound-eye-like microstructures consisting of arrays of micro-hemispheres covered with nipplelike nanospheres. In addition, it was reported that the anti-reflective nanonipples on the insect’s ommatidia can cause the destructive interference of reflected light from the ommatidial surface to enhance the efficiency of photon capture\(^{[20,21]}\) which supplies mosquitoes with good vision in a dim habitat. Because the adhesive force of dust particles to rough micro- and nanostructures is far less than that of the particles with spherical beads,\(^{[8]}\) fog drops may take the particles away from the superhydrophobic eye surface, thereby achieving cleaning in a humid habitat even though the particles are pervasive in the air. Thus, we believe that these findings could provide an inspiration for designing novel superhydrophobic materials in the future, which may be developed into multifunctional coatings with antifogging, anticorrosive, easy-cleaning, and antireflective properties based on the requirements of different application.

**Experimental**

*Antifogging Characterization of Mosquito Eyes: A mosquito was placed on a sample holder under a LYNX optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera and connected to a desktop computer. A YC-D205 ultrasonic humidifier (Beijing YADU Science and Technology Co, P. R. China) was used to generate a fog composed of numerous microscale water beads, most of which had diameters in the range 5–10 μm. This fog was directed and blown toward the mosquito eyes through a PTFE tube with a 3 cm diameter.*

*Fabrication of Artificial Compound-Eye Structures: Ordered arrays of circular photoresist posts were fabricated by using photolithography. Glass substrates were cleaned by sonication in acetone and ethanol for 15 min each. Because the required photoresist layer must be very thick and the typical photoresist materials are not practical because of their lower viscosity, a high-viscosity positive photoresist (BP-215, Beijing Chemical Reagent Institute) was selected. A layer (ca. 10 μm) of positive photoresist was spin-coated onto the slides at 2000 rpm and placed in an oven at 88 °C for 18 min. The slides were then removed from the oven and allowed to cool to room temperature. Subsequently, a second layer (ca. 10 μm) of photoresist was spin-coated onto the solidified samples at 2000 rpm and baked in an oven at 90 °C for 30 min. This photoresist layer was exposed to a 1000 W UV light source through a transparent mask patterned with 20 μm circles spaced 5 μm apart. This approach was used to generate circular photoresist posts after developing (0.5 wt% NaOH solution), rinsing with deionized water, and flow drying under nitrogen. According to Whitesides and co-workers\(^{[25]}\), after the samples were heated at 160 °C for 5–15 min, the circular photoresist posts on the slides melted and formed hemispheres because of the minimization of interfacial energy. The resulting hemisphere arrays of photoresists were replicated on a PDMS stamp, which in turn was used as the master to replicate the PDMS stamp with features of hcp microscale hemisphere arrays (for more details, please see Supporting Information, Fig. S1). Monodisperse silica nanospheres with average diameters of 100 nm were prepared in ethanol according to the Stöber method\(^{[34]}\). The silica nanospheres were centrifuged in ethanol, and the precipitate was redispersed in water. A 10–20 μL drop of the colloidal suspension was applied to a slightly tilted silicon substrate. The evaporation of the suspension took place in a closed chamber with control over temperature and ambient humidity. Such colloidal nanospheres self-assembled to form crystalline solids\(^{[35]}\). In a typical lift-up process, a PDMS stamp with patterned features was brought into conformal contact with an obtained crystal film on a silicon substrate, and the sample was hot-pressed (100 °C, 0.2×10 MPa, 3 h). The PDMS stamp was carefully peeled away after the sample was cooled to room temperature. The obtained artificial compound-eye microstructures were modified by self-assembling a monolayer of low-surface-energy FAS with a water CA of 10° on a flat surface.

SEM images of micro-hemispheres of mosquito eyes were obtained on a HITACHI S-3000N scanning electron microscope in a low-vacuum mode. SEM images of arrayed nanonipples and artificial compound-eye structures were taken with a JEOL JSM-6700F field-emission scanning electron microscope at 3.0 kV. CAs were measured on a Dataphysics OCA20 CA system at ambient temperature. Water droplets (3.0 μL) were dropped carefully onto the surface of artificial compound-eye counterparts. The average CA value was obtained by measuring at five different positions.

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