

Superhydrophobic Coatings on Curved Surfaces Featuring Remarkable Supporting Force

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We present a facile route to prepare bionic superhydrophobic coatings with striking supporting forces by fabricating hierarchical micro-/nanostructures on curved surfaces. The hierarchical structure was synthesized by decorating silver nanoparticles on a monolayer array of polystyrene (PS) microspheres. The monolayer array formed on a flat surface was transferred on a curved surface using silver acetate solution, which can then be converted into silver nanoparticles through thermal decomposition. The fabricated superhydrophobic coating on a convex tube exhibited a strong water-repellent property and supplied a high supporting force when it was floated on water surface.

Introduction

Biomimetic research has recently revealed many interesting phenomena of natural organisms, such as self-cleaning effect of a lotus leaf (so-called lotus effect)^{1–3} that removes contamination on its surface and striking adhesive force of a gecko's foot.^{4,5} Such unique functionalities are attributed to the combination of hierarchical micro- and nanostructures on the surface of the natural organism. In particular, the lotus effect is related to the superhydrophobicity with a water contact angle (CA) larger than 150° and a sliding angle (SA) less than 10°,¹ which is caused by the combined effect of both a hierarchical micro-/nanostructure on the surface and a low surface-energy material covering the surface. This superhydrophobic property can be widely used for preventing the adhesion of water or snow to windows, antioxidation coating, self-cleaning utensils, and microfluidic devices.² Inspired by the lotus effect, various techniques to synthesize bionic superhydrophobic surfaces have been recently developed.^{7–14} In addition, the interesting feature of a water strider that can float and move quickly on water surface also results from the superhydrophobicity of the water strider's legs.⁶ A water strider's leg has special hierarchical structure consisting of microsetae with nanogrooves, which leads to the superhydrophobicity. A leg of a water strider gives a supporting force corresponding to 15 times the water strider's weight against water surface. Although various techniques to synthesize superhydrophobic surfaces have been developed, most of these techniques are restricted on flat substrates. However, to allow the striking water-supporting force to an object with curved surface, all of the outer surface of the object should be enclosed with superhydrophobic materials. So far, only a few methods to fabricate superhydrophobic surfaces that can mimic the legs of water striders have been investigated.¹⁵ Here, we present a novel and straightforward route to prepare superhydrophobic coatings on the outer surfaces of objects, including both flat and curved substrates. The fabricated superhydrophobic coating on a convex tube exhibited a strong

water-repellent property and supplied a high supporting force when it was floated on water surface.

Experimental Section

Materials Preparation. Commercialized monodispersed polystyrene (PS) spheres of different particle sizes, 1.3 μm (Soken, Chemisnow SX-350H) and 5.0 μm (Soken, Chemisnow SX-130H) in diameter, were dispersed in deionized water to prepare a suspension with the concentration of 2.5 wt %. Monolayer PS colloidal crystals were fabricated on glass substrates by spin coating of the suspension. The glass substrates were ultrasonically cleaned in acetone and then in ethanol for 1 h. Silver acetate (AgAc) aqueous solution (0.5 M) was prepared from silver(I) acetate powders (Kojima Chemicals Co. Ltd). Several small droplets (less than 0.5 mL) of nitric acid were added into the solution to facilitate solubilization, and the pH value of the solution was kept to ca. 3. The monolayer PS colloidal crystals were fabricated on glass substrates by spin coating.

Synthesis of the Superhydrophobic Coating. The fabrication process of the superhydrophobic coating on a curved substrate is illustrated in Figure 1. In previous studies, we reported that polymer colloidal monolayer on a substrate could be transferred onto another substrate.^{16,17} We applied this technique for the fabrication of the superhydrophobic coating on a curved surface using a precursor solution of silver nanoparticles as a medium. At first, a monolayer PS colloidal crystal was prepared on a glass substrate by spin coating.¹⁸ Subsequently, the colloidal monolayer on the substrate was gradually dipped into an AgAc solution with an inclination angle of about 30°. As a result, the colloidal monolayer was peeled off from the glass substrate and floated on the AgAc solution surface while retaining its integrity. Next, the colloidal monolayer was slowly picked up with a glass tube and accordingly the colloidal monolayer containing aqueous AgAc covered the outer surface of the tube, followed by drying the sample at room temperature. Finally, the samples were heated at 200 °C for 3 h in a vacuum oven. Glass tubes with two different outer diameters of 1.4 and 4.87 mm were used in the experiments. Due to the heating process, AgAc was transformed

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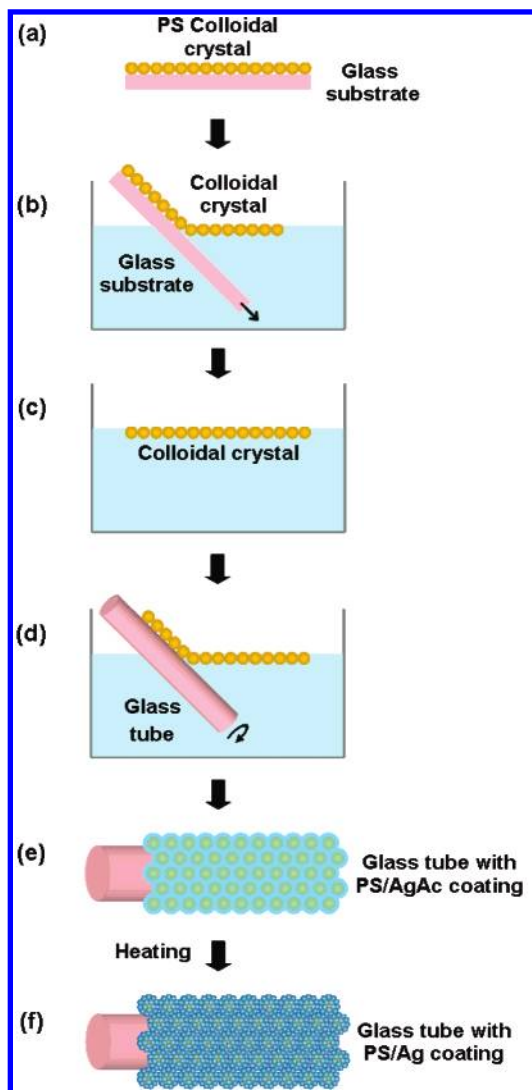


Figure 1. Schematic illustration of the fabrication process of a superhydrophobic coating on a curved surface. (a) A PS colloidal monolayer is fabricated on a flat substrate by self-assembly. (b) The colloidal monolayer on the substrate is gradually dipped into the AgAc solution, and then the monolayer is peeled off from the substrate. (c) The colloid monolayer floats on the solution surface. (d) The monolayer is picked by a glass tube with curved surface. (e) The PS colloidal monolayer with AgAc coating is formed on the curved surface. (f) After heating, the hierarchical structure consisting of micrometer-sized PS spheres and silver nanoparticles is prepared on the curved surface.

into silver nanoparticles,¹⁹ and consequently hierarchical structures that consist of PS microsphere arrays coated with silver nanoparticles were created. The photographs showing each process described above are displayed in Figure S1 in the Supporting Information.

Chemical Modification. The surfaces of the as-prepared samples were chemically modified with 1-dodecanethiol (Acros Organics Scientific Co.) to reduce the surface energy. Before the chemical modification, the samples were ultrasonically cleaned in both acetone and ethanol for 30 min, respectively.

Characterization. The morphologies of samples were characterized with a field emission scanning electron microscope (FESEM, FEI XL30 FEG). X-ray diffraction (XRD) measurement was performed to identify the crystal structure of as-prepared samples on a Rigaku D/MAX-RC XRD machine using Cu K α radiation. Static water CAs were measured with a G10 (KRÜSS GmbH) contact angle meter at room temperature. The weight of a water droplet used for the static CA measurements

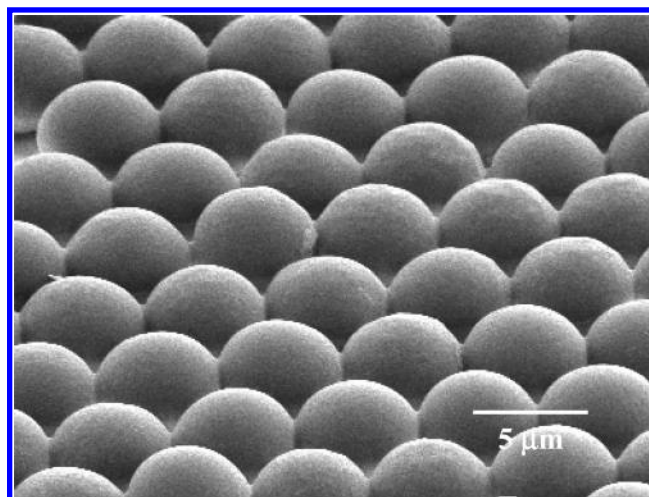


Figure 2. FESEM image of PS colloidal monolayer on glass substrate. PS sphere size: 5 μm .

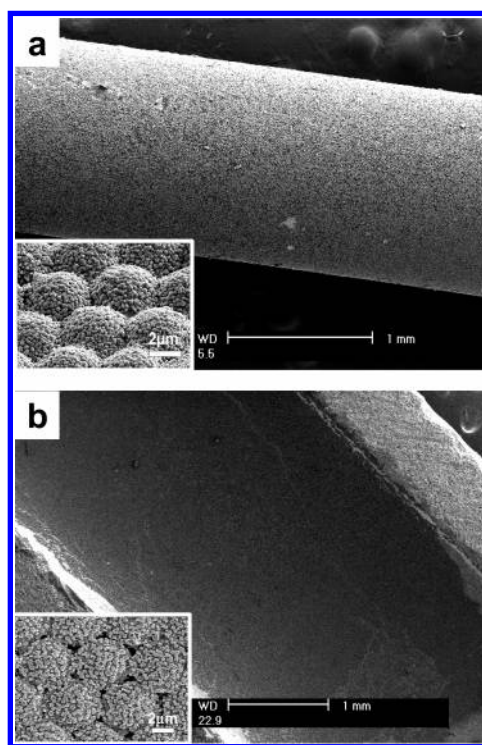


Figure 3. FESEM images of the hierarchical structure on (a) an outer surface of a glass tube (outer diameter: 1.4 mm) and (b) inner surface of a glass tube (inner diameter: 3.0 mm). The insets are magnified images of the PS spheres of 5 μm in diameter.

was 3 mg. CA values were obtained by averaging five measurement results on different areas of the sample surface.

Results and Discussion

Figure 2 displays the PS colloidal monolayer with sphere size of 5 μm on the glass substrate, which takes on the hexagonal close-packed alignment. Figure 3a shows a typical FESEM image of the fabricated hierarchical micro-/nanostructure on a convex glass substrate. Close-packed arrays of monolayer PS spheres with 5 μm in diameter completely covered the glass substrates, and nanoparticles with an average size of 180 nm were uniformly decorated on the PS spheres. Using the same strategy, such a hierarchical micro-/nanostructure was also fabricated on a concave surface of the inner wall of a glass tube (Figure 3b). X-ray diffraction spectra revealed that the

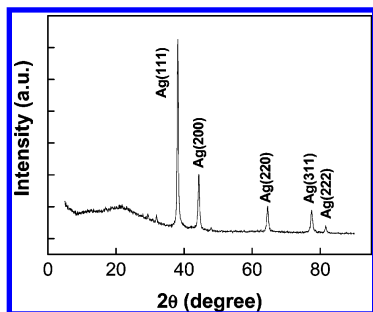


Figure 4. XRD spectrum of the nanoparticles synthesized on the PS monolayer.

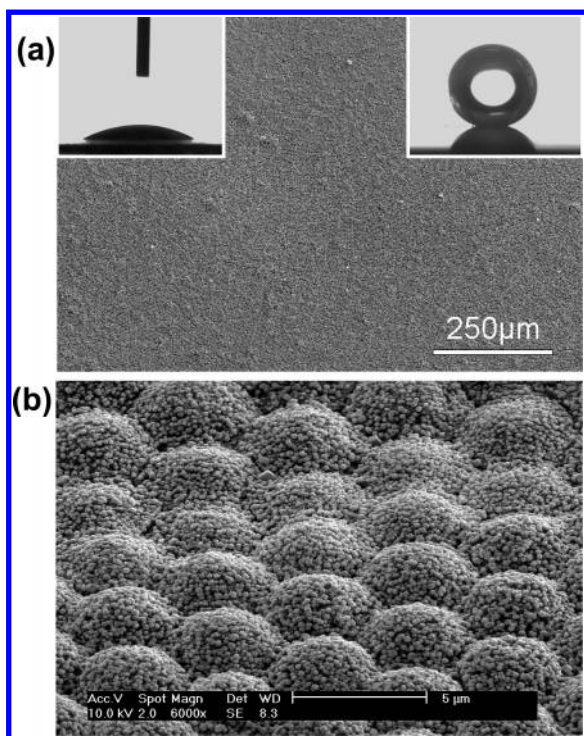


Figure 5. (a) FESEM images of the superhydrophobic coating fabricated on a flat glass substrate and water droplet shapes on its surface. The insets on left and right top are water droplet shapes before and after the surface modification, respectively. The water CAs were 29° (left) and 168° (right), respectively. (b) Magnified FESEM image of the coating surface.

nanoparticles decorating the PS spheres were silver crystals (Figure 4), which resulted from thermal decomposition of AgAc. The curved glass substrates made it difficult to investigate the water-repellent property of the hierarchical structures on the substrates by measuring the water contact angle (CA) of the surfaces, because a water droplet easily rolled down due to the superhydrophobic property of the surface. Therefore, we prepared the hierarchical structure on a flat glass substrate and measured water CAs (Figure 5a). The morphology of the hierarchical structure on the flat glass substrate (Figure 5b) was very similar to those on the curved glass substrates (insets of Figure 3). The water CA of the as-prepared hierarchical structure was measured to be 29° , showing hydrophilicity (the inset at left top in Figure 5a). However, the wettability of the structure was changed from hydrophilicity into superhydrophobicity after the chemical modification of the surface with 1-dodecanethiol, which is a kind of low surface-free energy material: the water CA was dramatically increased to 168° (the inset at right top in Figure 5a). In addition, the modified surface exhibited a small SA of about 2° . In the process of CA measurement, we found it difficult to add a water droplet on the fabricated superhydro-

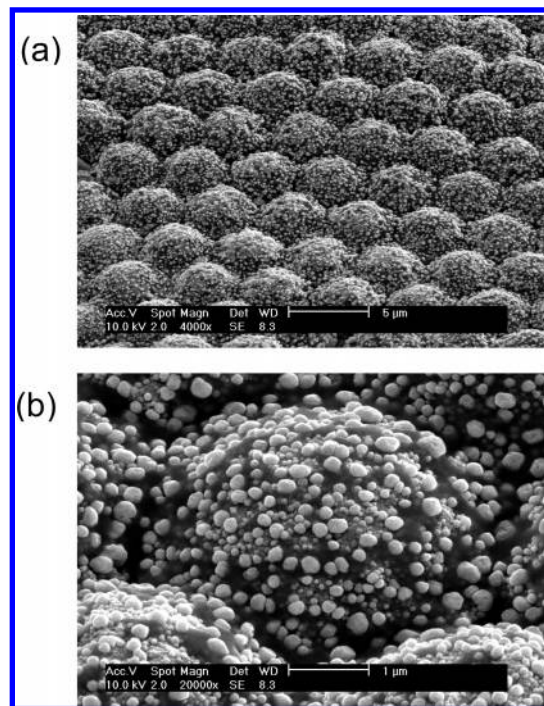


Figure 6. (a) FESEM image of the hierarchical structure fabricated with a reduced AgAc solution of 0.3 M and at a heating temperature of 200°C for 3 h. (b) A magnified image of a part in (a).

phobic coating on the flat substrate (Figure S2), demonstrating that the surface has a very low adhesive force and very small CA hysteresis.²⁰ The fact of superhydrophobicity with a very low SA and the difficulty in dropping water on the surface provide strong evidence for the lotus effect of the synthesized surface with the hierarchical micro-/nanostructure.

In the presented method, the distribution of silver nanoparticles on microspheres can be controlled by changing the concentration of AgAc precursor. The number of nanoparticles coated on the microspheres decreased with decreasing precursor concentration. This is because lower precursor concentration induced thinner AgAc coating on the PS spheres. If the precursor concentration was relatively low (to say 0.3 M), silver nanoparticles were not completely coated on the PS spheres (Figure 6a) because of the incomplete coating of AgAc on the PS spheres (Figure 6b). These resulted in smaller surface roughness and corresponding lower water CAs as compared to the optimized precursor concentration of 0.45–0.65 M. Moreover, a well-controlled heating temperature was also crucial for the successful synthesis of the superhydrophobic coating. Heating temperature below 180°C was insufficient to convert AgAc precursor to silver nanocrystals on the PS spheres. At a heating temperature above 220°C , PS spheres were gradually decomposed and the hierarchical structures collapsed (glass transition temperature T_g of PS is nearly 100°C),¹⁹ leading to the decrease in the CA. The experimental results showed that the temperature in the range of $195\text{--}215^\circ\text{C}$ was the optimum value for the formation of the superhydrophobic coatings. Heating treatment has two important roles: first, decomposition of AgAc coating into silver nanoparticles and, second, enhancing the mechanical stability of the synthesized superhydrophobic coating. A bare monolayer colloidal crystal can be easily peeled off from the substrate. However, the PS spheres can be slightly melted during the heating process. Because the heating temperature was higher than T_g of PS, the PS spheres adhered tightly to the substrate, and furthermore the silver nanoparticles produced in the heating process were embedded into PS spheres (Figure 6b). Conse-

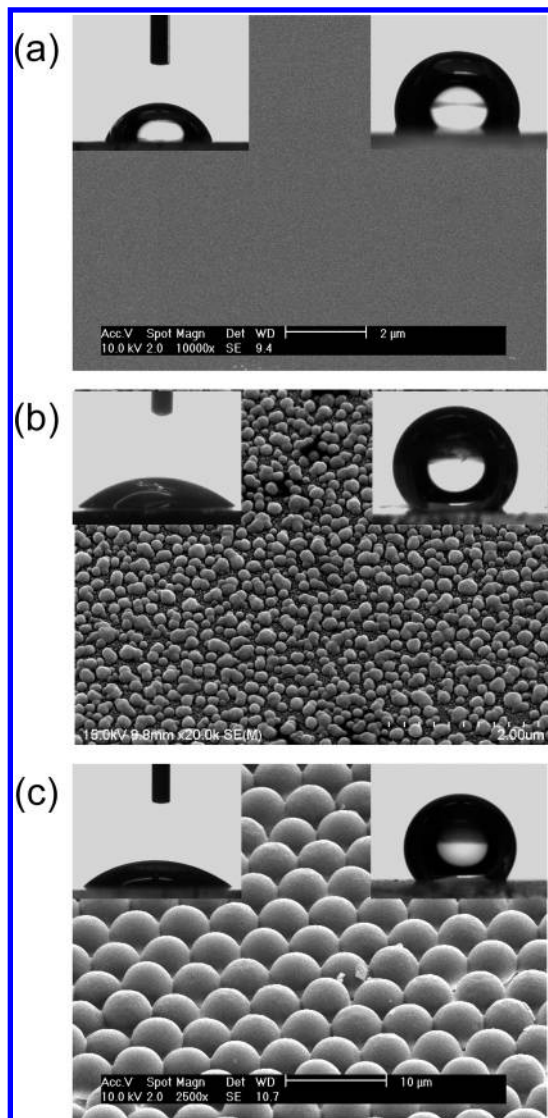


Figure 7. FESEM images and measurement results of water contact angles for (a) a flat silver film surface, (b) a silver nanoparticle film, and (c) a colloid monolayer with a thin silver coating. Insets at left (right) top of the figures are the droplets before (after) the chemical modification. The water CAs before and after the modification were (a) 68° and 110°, (b) 41° and 135°, and (c) 43° and 129°, respectively.

quently, the heating process leads to the formation of highly durable superhydrophobic coatings: the coatings were not detached from a substrate even when the substrate was ultrasonically washed in water for 1 h. The superhydrophobic coatings can also be produced with PS spheres of different sizes. For example, when such a hierarchical structure was synthesized from PS colloidal monolayer of 1.3 μm sphere size on a glass substrate, the surface also took on superhydrophobicity with a water CA of 163° and a SA of about 6° after the modification with thiol.

The superhydrophobicity of the hierarchical structures can be explained by the equation presented by Cassie and Baxter:²¹

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (1)$$

where θ_r and θ are the CAs of a rough surface and a native flat surface, and f_1 and f_2 ($=1 - f_1$) are the area fractions of a water droplet in contact with the surface and with air on the surface, respectively. To measure θ , a flat and uniform silver film with the thickness of 30 nm was prepared by plasma sputtering of Ag on a glass substrate. The water CA of the flat silver film

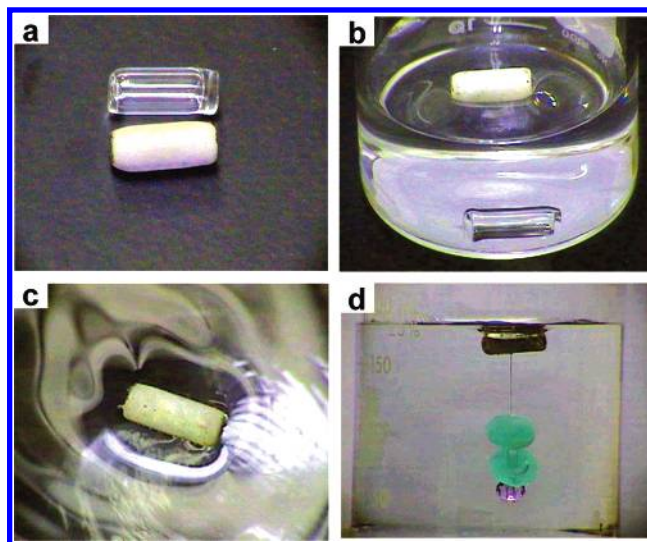


Figure 8. (a) Photographs of a bare glass tube (left) and a glass tube with the superhydrophobic coating (right), respectively. (b) The behavior of the two tubes when slowly dropped on water surface. (c) The glass tube with the superhydrophobic coating on water surface. Deformed meniscus is clearly seen on the water surface near the tube. (d) The glass tube with the superhydrophobic coating weighted with plastic beads.

was 68°, and the film was transformed into hydrophobicity with a water CA of 110° after the surface modification (Figure 7). From the measured values of θ_r (168°) and θ (110°), f_2 for the superhydrophobic coating in Figure 5 is calculated to be 96.7%. This reveals that the synthesized superhydrophobic coating produces a large amount of air traps between the microstructure of the PS colloidal crystal and the silver nanoparticles on the colloidal crystal, and that the air traps prevent the contact between water and the solid surface. This suggests that such a superhydrophobic coating is not easily wetted due to the large air fraction on the surface, although it is submerged in water.

To demonstrate the water-repellent property of the superhydrophobic coating, we prepared such a coating on a glass tube (Figure 8a) and measured the supporting force of the tube. Both ends of the tube were sealed to prevent water from permeating into the inside of the tube. The outer diameter, the inner diameter, and the length of the tube were 4.87, 3.05, and 13.15 mm, respectively. The weight of the tube was 332 dynes, which is about 300 times heavier than a water strider (an adult *Gerris remigis*).²²

Surprisingly, when a glass tube with the superhydrophobic coating was dipped into water and then taken out, no water droplet was found on the surface of the tube, exhibiting that the coating has an excellent water-repellent property. As displayed in Figure 8b, a bare glass tube sank to the water and finally dropped down to the bottom of vessel. However, the glass tube covered with the hierarchical structure can easily float on the water surface. Moreover, deformed meniscus is clearly seen on the water surface near the tube (Figure 8c), reflecting that strong supporting force was produced by the superhydrophobic coating on the tube. For measuring the maximum supporting force, the glass tube was weighted with plastic beads through a thin plastic wire that was fixed at the middle of the glass tube until the glass tube sank to the bottom of the vessel (Figure 8d).

The maximum supporting force is obtained when $mg = F_b + F_c$. Here, m is the total mass of the glass tube, the plastic beads, and the thin wire that make the weighted tube sink to the water bottom. g is the acceleration of gravity. The total

weight mg is supported by a combination of two forces, the buoyancy force (F_b) and the curvature force (F_c).^{15,22} F_b can be determined by integrating the hydrostatic pressure over body area in contact with water. F_c is associated with the surface tension, and thus this is the more important factor characterizing the non-wetting property of the superhydrophobic coating than F_b . The total weight mg was measured to be 1420 dynes, which is around 4.3 times the weight of the glass tube. In addition, the maximal curvature force was calculated to be 386 dynes (see the Supporting Information), which is 4.5 times larger than that of a leg of water strider (an adult *Gerris remigis*) reported by Lu and his co-workers.²² The results show that a very high supporting force was produced by the fabricated superhydrophobic coating, which can effectively capture the air in the interstices among the micro-/nanohierarchical structures.

Conclusion

In conclusion, we present a novel and facile route to prepare bionic superhydrophobic surfaces with a striking supporting force by synthesizing hierarchical microsphere/nanocrystal structures on curved surfaces. Because the superhydrophobic surface consists of regularly ordered structure, the whole surface has uniform superhydrophobicity. The route can be used for miniaturized aquatic devices operating on water or under water and lossless liquid transportation channels. In addition, the surface coated with the hierarchical structure may show superhydrophilicity if the structure is chemically treated with a high surface-energy material, as we reported previously.²³ Next, coating of such a hierarchical structure on an object can also be used for improving heat transfer between the object surface and water flowing outside the object.

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Supporting Information Available: Additional experimental images and calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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