Miniature Boats with Striking Loading Capacity Fabricated from Superhydrophobic Copper Meshes

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ABSTRACT A novel kind of miniature boat that might have many potential applications was fabricated from superhydrophobic copper meshes for the first time. These boats not only floated freely on a water surface but also exhibited striking loading capacities. By selection of the pore size of copper meshes, a loading capacity greater than 11.0 g could be readily achieved for a boat of 8.0 cm^3 in volume. The large loading capacity is believed to arise from the air film surrounding the superhydrophobic surfaces of boats. The results of this study present new applications of artificial superhydrophobic surfaces in areas of miniature aquatic devices.

KEYWORDS: miniature boats • copper meshes • superhydrophobicity • pore size • loading capacity

INTRODUCTION

Superhydrophobic properties of solid surfaces have attracted intensive interest during the past decade because they play an important role in biological processes and have many potential applications (1, 2). Much effort has been devoted to the design and fabrication of superhydrophobic surfaces by mimicking the surfaces of lotus leaf, rice leaf, and so on (3−5).

In nature, water striders are kinds of insects that can stand and walk freely on a water surface using their water-resistant legs (6−11). Recently, Jiang et al. revealed that the striking water repellence and fast-propulsion abilities of water striders arise from their superhydrophobic legs. They attributed the superhydrophobicity of the legs to the cooperative effect of hierarchical micro/nanostructures and a low-surface-energy wax coating (12, 13). This finding may help us to design and fabricate novel drag-reducing and fast-propulsion aquatic or air devices (14, 15). Up to now, some reserachers had tried to fabricate aquatic devices by mimicking the legs of water striders. However, the application of this sort of technology to full-sized boats and ships is exceedingly problematic because water repellence produced by these artificial legs is of little practical usage (16, 17).

Here, we report a novel kind of miniature wire boat fabricated from superhydrophobic copper meshes for the first time. The entire procedure is carried out using readily available materials and laboratory equipment under ambient conditions. The boats can not only float freely on a water surface but also exhibit a large loading capacity. Moreover, the boats are able to recover their superhydrophicity in the case of physical damage. Despite the fact that superhydrophobic meshes had been used in oil−water separation (18−22), no study on aquatic devices was reported.

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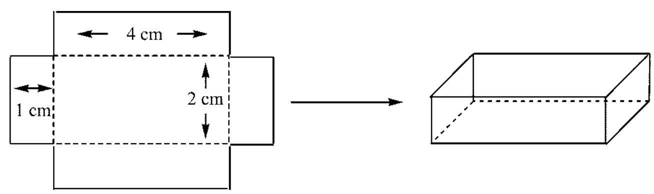
Scheme 1. Illustration for the Fabrication of a Miniature Boat



EXPERIMENTAL SECTION

Copper meshes used in this study were purchased from Hebei Anping Mesh Co. Ltd., Hebei, China, and were knitted by copper wires about 200 μm in diameter. The pore sizes of these meshes are in the range of 50−1000 μm. The weights of copper meshes are in the range of 17.5−22.4 mg cm^{-2}. The fabrication of a miniature boat was conducted as follows. A sheet of copper mesh (4 cm × 6 cm) was enfolded into a boat of 4 cm × 2 cm × 1 cm in size according to the diagram illustrated in Scheme 1. Then the boat was successively washed with a 1.0 M HCl solution and acetone for 2 min to remove surface impurities. The dried boat was immersed in an aqueous solution of $AgNO_3$ (20 mM) for 20 s (23). After being washed with water and blown by dry air, the boat was immersed in an ethanol solution of *n*-dodecanoic acid (5 mM) for another 5 min to tune the surface free energy (24). Finally, the boat was washed with acetone and dried in air. Water contact angles of boat surfaces are about 157° (see the Supporting Information).

The maximal loading capacity of a miniature boat was measured by carefully adding silica sands until its upper edges were flooded by water and the boat started to sink. Then the silica sands were collected, dried, and weighed. Scanning electron microscopy (SEM) images were recorded on a JEOL 6500 FEGSEM operating at 2.5 kV.

RESULTS AND DISCUSSION

At first, a miniature boat was put on a water surface and its floating behavior was investigated by carefully adding loads, as displayed in Figure 1. It is found that the boat can

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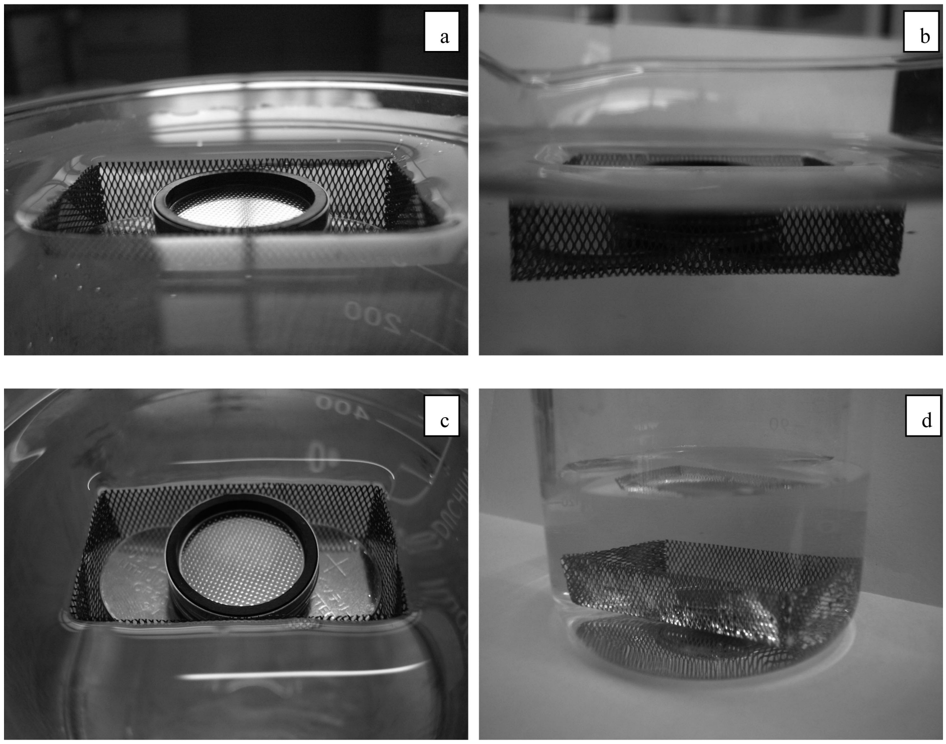

FIGURE 1. Optical images of a miniature boat floating on water surface, (a and b) side view, (c) top view; (d) the boat sunk down in ethanol solution. Pore size of copper mesh used is about 930 μ.

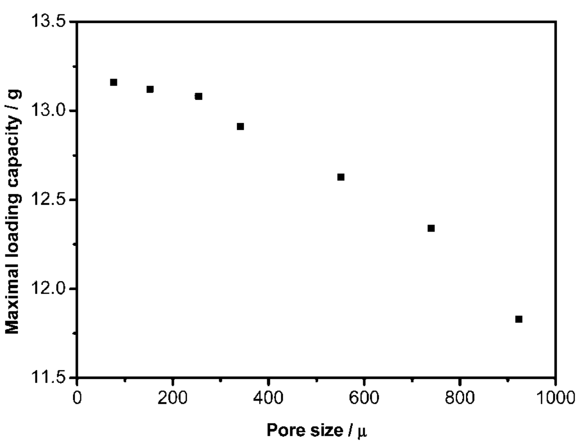

FIGURE 2. Dependence of the maximal loading capacities of boats on the pore sizes of copper meshes. Boat size: 4 cm × 2 cm × 1 cm. The weights of boats are not included.

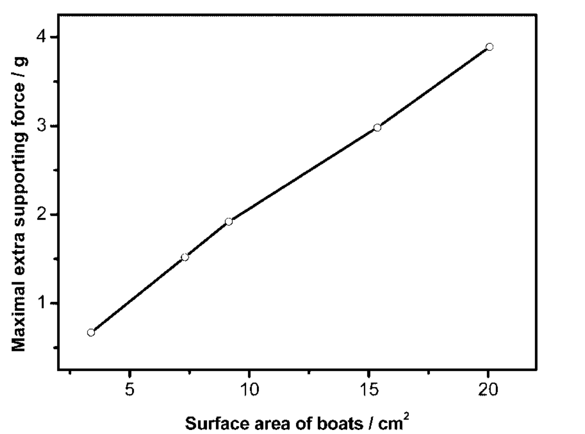

FIGURE 3. Dependence of the maximal extra supporting forces on the outer surface areas of the boats. The pore size of the copper mesh used is about 930 μm.

not only float freely over a water surface but also exhibit striking loading capacity. Water does not penetrate into the boat during the process of loading weight. Interestingly, the boat is able to keep floating even if its upper edges are below the water surface, as shown in Figure 1b,c. A loading capacity larger than 11.0 g is readily reached in this case, which exceeds the maximum buoyancy force calculated for the boat (i.e., 8.0 g). In contrast, the boat cannot float over (but rather sink quickly) the surfaces of organic solvents including ethanol, acetone, and petroleum ether (Figure 1d). For the purpose of comparison, we had constructed a bare boat using a sheet of pristine copper mesh. Under the same conditions, water will penetrate into the bare boat when 3.3 g of load is added. By comparison, we demonstrate that the superhydrophobicity is responsible for the interesting floating behavior of the boat.

Then a series of boats were fabricated by superhydrophobic copper meshes with different pore sizes, and the maximal loading capacities of the boats as a function of the pore sizes are plotted in Figure 2. Within experimental error, the maximal loading of these boats decreases as the pore size is increased from 50 to 1000 μm, indicating that the loading capacities are strongly dependent on the pore sizes of the copper meshes. As seen in Figure 2, the optimal pore size for a boat with the largest loading capacity is about 50−250 μm. It should be noted that the weights of the miniature boats are not considered in this study because the ratio of the boat weights to the maximal loading capacities is only about 3.2−3.4%. In addition, we believe that the shape of the mesh wires may affect the loading capacities

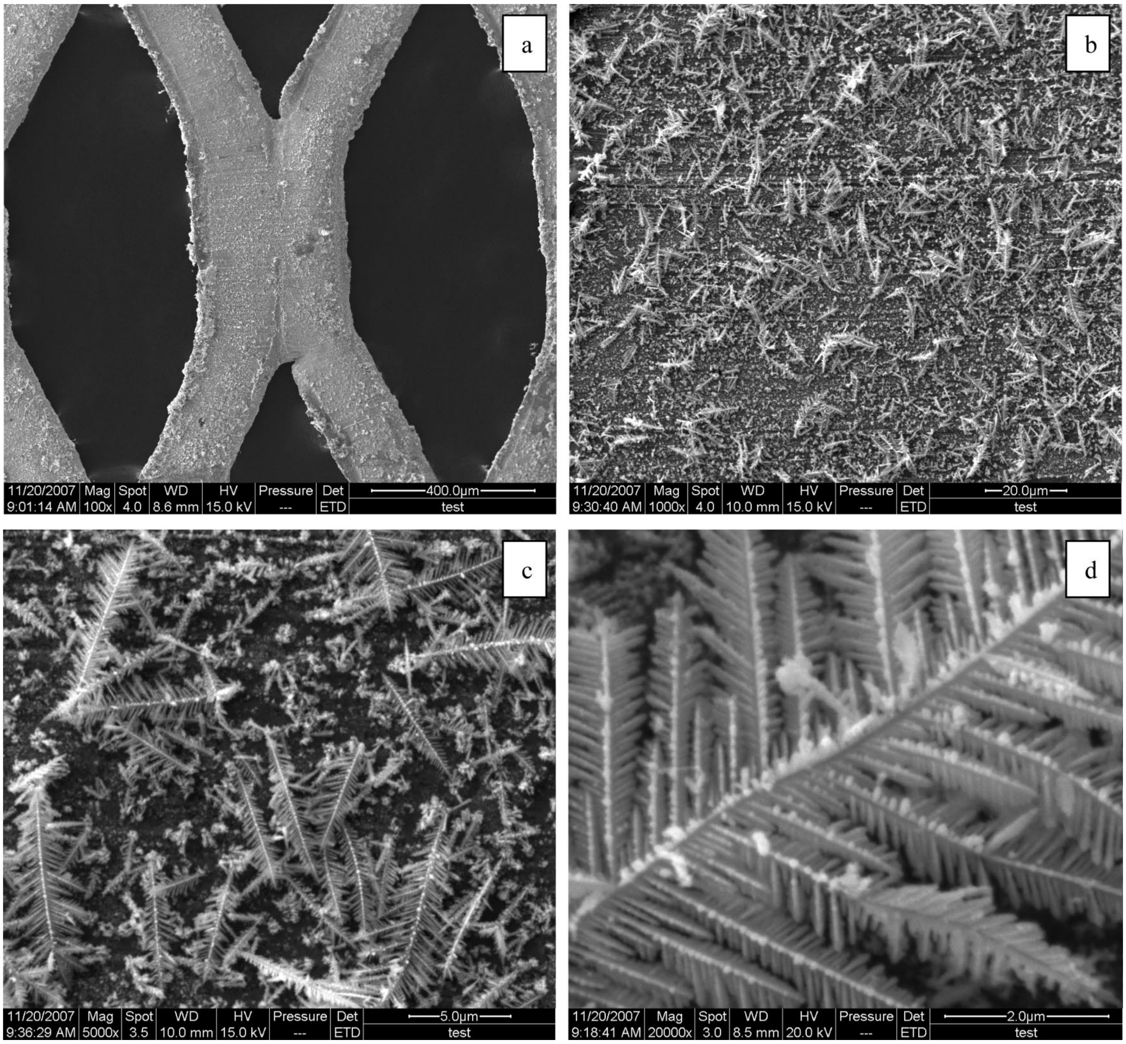

FIGURE 4. SEM images of silver deposits on copper meshes; (a) ×100, (b) ×1000, (c) ×5000, and (d) ×20 000.

of the boats. For the purpose of comparison, we have fabricated a similar boat using a sheet of copper foil. Under the same conditions, the loading capacity of this boat is about 13.8 g (or 14.4 g when the boat weight is considered), which is only 1.05 times greater than the maximum loading capacity of wire boats.

As demonstrated above, the large loading capacity (F) of these boats arises from their superhydrophobic surfaces. Owing to the plastron effect (25), a film of air will surround the superhydrophobic surfaces, thus preventing boats from being wetted and/or penetrated by water. Therefore, the first contribution to the loading capacity is the buoyancy force (F_b) associated with boat volumes. Second, because the outer surfaces of the boats are surrounded by an air film, we speculate that a thickness (d) of a few millimeters will produce sufficient additional buoyancy force. For example, an air film of 1.5 mm will provide about 3.0 g of extra buoyancy force for a boat of 20 cm^2 in surface area, implying that we cannot ignore the loading capacity produced by the air film (F_f). Third, it is observed that these boats remain floating even if their upper edges are lower than the water surface, indicating that the superhydrophobic upper perimeters prevent the boats from being submerged. As a result, another contribution to the loading capacity is the surface tension force (F_s) related to the upper perimeter, which is equivalent to $l\mathbf{Y}\cos\theta$ ($\mathbf{Y}$ is the water surface tension, θ the contact angle, and l the contact perimeter) (26−30).

On the basis of the above analysis, the supporting force (F) for the boat having a size of $a \times b \times c$ (a = length, b = width, and c = height) should be given by

$$F = F_b + F_f + F_s = abcg + [ab + 2(a + b)c]dg + 2(a + b)\gamma\cos\theta \quad (1)$$

Here, g is the gravitational constant. For a miniature boat perimeter $2(a + b) \ll 1$ m, F_s calculated by $2(a + b)\mathbf{Y}\cos\boldsymbol{\theta}$ ($\mathbf{Y}$ is 72.8 mJ m^{-2} for water at room temperature) is negligible compared to its maximal loading capacity. Then the supporting force F can be described as

$$F = F_b + F_f = abcg + [ab + 2(a + b)c]dg \quad (2)$$

It is reasonable that the extra supporting force (F_e) for a boat mainly arises from the air film surrounding its surface, which can be illustrated as

$$F_e = F_f = [ab + 2(a + b)c]dg \quad (3)$$

Equation 3 suggests that F_e is strongly dependent on the outer surface area of the boat. This conclusion is supported by the experiments conducted on boats with various sizes. Figure 3 plots F_e vs the outer surface area of these boats. It is interesting to find that the maximal F_e is linear with the outer surface area of the boat.

Using eq 2, one is able to understand the loading capacities of miniature boats. If an intact air film surrounds the outer surface of a boat, the loading capacity is equivalent to the buoyancy force associated with the volume of both the boat and the air film. In the case that the air film is penetrated by water, a dramatic decrease in the displaced volume and the interface area of boat—air will take place, leading to a significant reduction in F_b and F_f. Consequently, the loading capacities of miniature boats mainly originate from the air film surrounding their outer surfaces, but it still depends on the displaced volume of water and does not violate Archimede's principle.

Another interesting characteristic associated with miniature boats is the reparability of their superhydrophobic surfaces. For example, immersing a damaged boat (e.g., scraped by a sharp object) into the above $AgNO_3$ and *n*-dodecanoic acid solutions successively will lead to the regeneration of superhydrophobic coatings. This feature is very important for the practical application of an aquatic device if accidental physical damage is unavoidable.

The superhydrophobicity of boat surfaces is considered to originate from the binary roughness of silver deposited on copper meshes, as shown in Figure 4. The silver deposits are leaflike dendrites with a length of 7 μm and a width of 2.0 μm, and each dendrite is composed of smaller dendrites consisting of nanoscale crystals, indicating the presence of hierarchical structures on both micro- and nanometer scales. The binary structures together with low-surface-energy alkyl groups lead to the superhydrophobicity and striking loading capacity of the boats (3, 4). After storage for 1 month, boat surfaces still keep a contact angle of 156°, suggesting long-term stability of the superhydrophobic coatings (see the Supporting Information).

CONCLUSION

In summary, novel miniature boats with remarkable loading capacities are constructed by superhydrophobic copper meshes for the first time. The pore sizes of copper meshes and outer surface areas of the boats exert a significant impact on the loading capacity. It is believed that the large loading capacity of miniature boats is mainly ascribed to the air film surrounding the superhydrophobic meshes. Though application of this technology to full-sized boats and ships is difficult, these novel boats will find their small-scale applications in fields such as aquatic robots, environmental surveillance, and microfluidity. The air film on superhydrophobic surfaces may dramatically reduce the flow resistance and fluidic drag; we expect that the present finding may be extended to the design of novel superfloating and drag-reducing aquatic devices.

Supporting Information Available: Optical image of a water droplet on boat surfaces, immersion time in *n*-dodecanoic acid vs contact angle, XPS spectra of boat surfaces, and storage time vs contact angle. This material is available free of charge via the Internet at http://pubs.acs.org.

ARTICLE

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