# A Water Strider-Like Model with Large and Stable Loading Capacity Fabricated from Superhydrophobic Copper Foils

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**ABSTRACT** The present study reported the floating behavior of a water strider-like model on water surface. The artificial "legs" of the model were fabricated from round-shaped superhydrophobic copper foils that were prepared by simple solution-immersion processes in dilute ammonia and subsequent *n*-dodecanoic acid solutions. It was observed that four "legs" of the model, which had diameter of 2.0 cm and thickness of 50 $\mu$m, could support at least 6.15 g of weight on a water surface for more than 30 days. Results revealed that the loading capacity of the model depended on the wettability of the "legs"; and the superhydrophobic "legs" were indispensable for the large and stable loading capacity. The finding of this study shows an alternative application of 2D superhydrophobic surfaces and might help to the design of miniaturized aquatic devices.

**KEYWORDS:** water strider-like model • artificial legs • superhydrophobic copper foils • solution-immersion • ammonia solution • loading capacity • contact angles

## 1. INTRODUCTION

Over the past decades, special wettability properties of lotus leaves had been attracted much interest among researchers (1−4). Superhydrophobic surfaces, with water contact angle larger than 150° and sliding angle less than 10°, have many important potential applications in self-cleaning (1, 5), drag reduction (6−8), antifouling (9), anti-icing (10−12), nanostructure patterning (13), biomedical (14, 15) and microfluidic devices (16), and so on. It was revealed that surface roughness with micro/nanoscale binary structure was an important factor responsible for the superhydrophobicity (17−20). Therefore, artificial superhydropbobic surfaces have been constructed on various substrates by controlling surface topographies (21).

In nature, water striders are insects capable of walking quickly on a water surface using their highly water repellant (or superhydrophobic) legs (22). The hierarchical structures of strider legs, i.e., large numbers of submicrometer-sized hair with fine nanogrooves, allow this kind insect to literally scoot across water surface at high speed (23). Up until to now, mimicking the microstructure of strider legs to fabricate bioinspired aquatic devices had attracted considerable attention. Although artificial "legs" made from superhydrophobic wires exhibited interesting floating behavior (24, 25), the supporting forces associated with these "legs" were too small for practical applications. Recently, we fabricated miniature boats with striking loading capacity from superhydrophobic copper meshes (26), which offers possibilities to construct novel aquatic devices that have many important potential applications. However, the loading capacities of these boats are strongly dependent on the pore size of meshes and the long-term stability of the capacities is problematic. Therefore, constructing miniature aquatic devices with large and stable loading capacity through an easy and low-cost process still remains a challenge.

It is well-known that solution-immersion process is one of the simplest approaches for the fabrication of functional surfaces (27). In this study, we constructed a water strider-like model with large and stable loading capacity by using round-shaped superhydrophobic copper foils as artificial legs. In addition, the role of superhydrophobic surfaces in the loading capacity of the model was studied in detail. Although superhydrophobic copper plates had been fabricated through solution-immersion in ammonia (28, 29), few studies used these plates in miniature aquatic devices that might have important potential applications.

## 2. MATERIALS AND METHODS

In a typical experiment, copper foils with thickness of 50 $\mu$m were washed with 1.0 M HCl solution and distilled water successively, then the foils were immersed into a 0.030 M $NH_3$ solution for different duration time (28, 30). The resultant foils were taken out from the solution and dried. At last, the foils were treated with a 5 mM ethanol solution of *n*-dodecanoic acid ($n\text{-}C_{11}H_{23}COOH$) for 5 min (31, 32). After blow drying, the obtained copper foils were subjected to further characterizations. The reactions involved in the above procedures can be described as follows (30, 31)

$$Cu + NH_3 + O_2 \rightarrow Cu[NH_3]_n^{2+}$$

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$$\mathrm{Cu[NH_3]_n^{2+} + OH^- \rightarrow Cu(OH)_2}$$

$$\mathrm{Cu(OH)_2 + C_{11}H_{23}COOH \rightarrow Cu(OOCC_{11}H_{23})_2}$$

A water strider-like model was constructed by four pieces of round-shaped ($\phi = 2.0$ cm) superhydrophobic copper foils as "legs" and a sheet of rectangle copper plate as "body", and each "leg" was jointed to the "body" with a copper wire of 0.5 mm in diameter and 5 cm in length (Scheme 1). The maximal loading capacity of the model was measured by carefully adding quartz sands until its "legs" penetrated the water surface and the model started to sink.

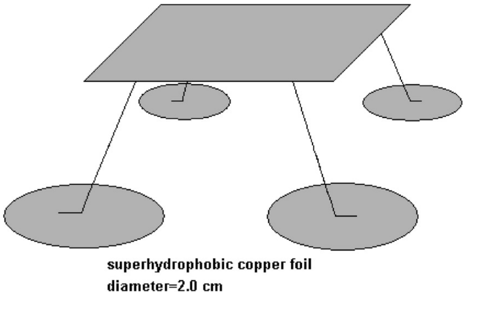
Water contact angle (CA) measurements were conducted by commercial instruments (OCA 20, DataPhysics Instruments GmbH, Filderstadt). A distilled water droplet of 4 $\mu$L was used as the indicator. Scanning electron microscopy (SEM) images were obtained with an H-7650. X-ray diffraction (XRD) analysis was carried out using a Shimadzu XRD-6000.

## 3. RESULTS AND DISCUSSION

First, the floating behavior of the water strider-like model on a water surface was investigated by carefully adding loads, for example, plastic claps. It is interesting to observe that the model can not only float freely on the water surface, but also exhibit a striking loading capacity. The model still stands on the water surface even it carries a 5.0 g of plastic clap (Figure 1a,b). Taking into account the net weight of the model, i.e., 1.1 g, the "legs" of the model can maximally support 6.15 g of weight on the water surface, which dramatically exceeds the maximum buoyancy forces produced by the "legs" themselves (i.e., 0.063 g). This result indicates that the superhydrophobic surfaces of the "legs" display striking water-repellent ability.

More interestingly, the model remains floating even if its "legs" are somewhat below the surface of the water, indicating that the superhydrophobic surfaces can prevent the "legs" from being wetted by water to some extent. Indeed, the photo taken from the side shows that each "leg" of the model makes a round-shaped water dimple (or meniscus), as shown in Figure 1c. The diameter of these dimples is about 28 mm and the vertical depth of the dimples reaches 3.8 mm (Scheme 2). The water dimple (or meniscus) greatly increases the water displacement volume of a single "leg" from 0.0157 cm$^3$ to at least 1.2 cm$^3$, which accounts for the large loading capacity of the model. The above results imply that the superhydrophobicity of the "legs" greatly contributes to the striking loading capacity of the model.

**Scheme 1. Illustration for a Water Strider-Like Model Fabricated from Superhydrophobic Copper Foils**



It is well-known that there two forces support the weight of the model. One is the buoyancy force ($F_b$), deduced by integrating the hydrostatic pressure over the "legs" area in contact with water (36). As shown in Scheme 2, $F_b$ of a single "leg" is equal to the water displacement of the rectangle region formed by dash line, i.e., $F_b = \rho\pi r^2(D + d)g$. Here, $\rho$, $D$, $d$, and $g$ are the density of water, thickness of copper foils, vertical depth of dimples, and gravity constant, respectively. The other is the curvature force, $F_c$, deduced by integrating the curvature pressure over this area or equivalently the vertical component of the surface tension, $\sigma\cos\theta$, along the contact perimeter (22, 33−35). For the "legs" in this study, curvature force can be described as $F_c = 2\pi r\sigma\cos\theta$. Here, $\sigma$ and $\theta$ are the water surface tension and contact angle, respectively. Therefore, the supporting force ($F_s$) for the strider-like model should be expressed by eq 1

$$F_s = 2\pi r\sigma\cos\theta + \rho\pi r^2(D + d)g \qquad (1)$$

It should be noted that the vertical depth of dimples ($d$) is dependent on the water contact angle of the "legs", as established by Jiang and Zheng co-workers (37)

$$\theta = \pi/2 + \arctan\sigma d + \arcsin(2\theta d/D) \qquad (2)$$

Equation 1 also indicates that the thickness ($D$) of copper foils might play a role in the vertical depth ($d$) of dimples and thereafter the supporting force of the "legs", which deserves further investigation. We can suppose that if the copper foil is extremely sharp on the edge, the supporting force might go up, as the meniscus would have to deform even more to wrap around the edge and wet the "legs".

To further understand the role of superhydrophobic surfaces in the supporting forces of the "legs", we fabricated a series of artificial "legs" by using round-shaped copper foils with contact angles ranging from 95° to 160°, and each "leg" had a diameter of 2.0 cm and a weight of 0.10 g. The fabrication of these copper foils was achieved by controlling the concentrations of ammonia solutions and immersion time (see Figures S1 and S2 in the Supporting Information). For the purpose of comparison, a blank copper foil with contact angle of 97.1° was also investigated as an artificial "leg" in study. The supporting forces of the "legs" before and after superhydrophobization treatments were measured carefully by adding quartz sands. It was observed that the wettability of the copper foils strongly affected the maximal depth of dimples and the loading capacity of the "legs" (Figure 2). Within experiment error, the maximal dimple depth and loading capacity of these "legs" increase as the contact angle is increased from 95 to 160°. A blank copper "leg" can only form a dimple with a maximal depth of 2.6 ± 0.19 mm and the maximum loading capacity is less than 1.10 g. This result suggests that even if the surface of a copper foil is normal hydrophobic (e.g., CA = 101.6°), the "leg" can offer sufficient upward force to support it standing

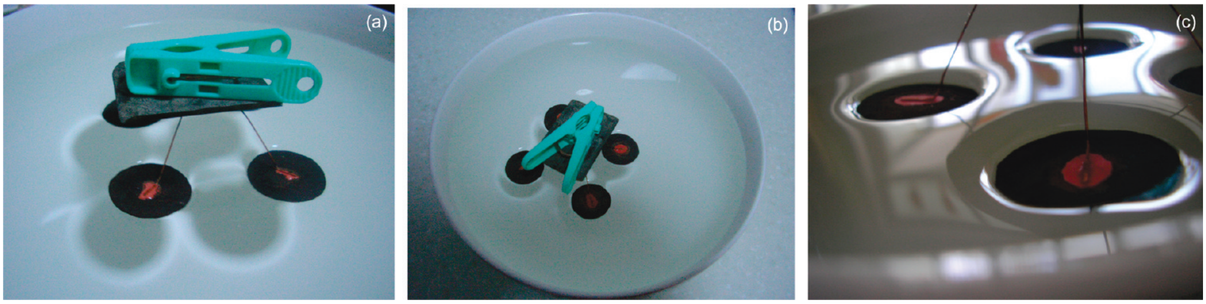


**FIGURE 1.** Water strider-like model carrying a 5.0 g plastic clap floating on the water surface: (a) side view of the model, (b) top view of the model, (c) dimples around the "legs" of the model. The net weight of the model is 1.1 g, and each "leg" has a diameter of 2.0 cm. The copper foils used in the model had a contact angle of 155.4°.

**Scheme 2. Schematic Illustration for the Dimples around the "Legs" of the Water Strider-Like Model**

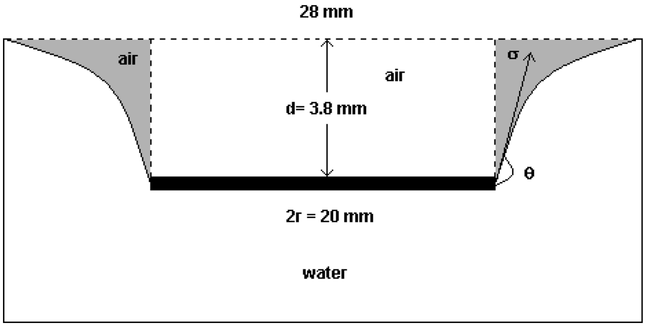


**Table 1. Curvature Force ($F_c$) and Buoyancy Force ($F_b$) Calculated for the "Legs" with Different Contact Angles**

| contact angle (deg) | curvature force ($F_c/g$) | buoyancy force ($F_b/g$) |
|---|---|---|
| 97.1 | 0.263 ± 0.030 | 0.817 ± 0.060 |
| 101.6 | 0.280 ± 0.034 | 0.820 ± 0.066 |
| 120 | 0.394 ± 0.020 | 0.946 ± 0.059 |
| 130.1 | 0.383 ± 0.013 | 1.077 ± 0.056 |
| 141.8 | 0.385 ± 0.013 | 1.125 ± 0.056 |
| 148.8 | 0.401 ± 0.006 | 1.159 ± 0.053 |
| 155.4 | 0.380 ± 0.007 | 1.200 ± 0.050 |

on water surface. In contrast, a single superhydrophobic "leg" with contact angle of 155.4° can repel the water surface to form a dimple with a maximal vertical depth of 3.8 ± 0.2 mm, where the maximal loading capacity is approximately 1.57 g. Therefore, coating a "leg" with superhydrophobic film increases its maximal supporting force about 40%. The results demonstrate that the superhydrophobic property of the "legs" plays a crucial role in the large supporting force. It is believed that the superhydrophobic surfaces prevent the "legs" from being wetted by water and thus resulting in large $F_s$, which guarantees the model floating on the water surface when it carries a weight of 6.15 g. Table 1 summarizes the contribution of $F_c$ and $F_b$ to the supporting forces of the "legs" with different wettability. It is revealed that the curvature force and buoyancy force account for about 25 and 75% of the total supporting forces, respectively.

Another characteristic associated with the loading capacity of the model is its long-term stability. Figure 3 shows the effect of floating time on the maximum loading capacity of the model. After standing on the water surface for 30 days, the model remains a loading capacity around 6.15 g, suggesting the long-term stability of the supporting forces of the "legs". This result forms contrast with that of the miniature boat fabricated from copper meshes. In that case, the mesh boats would sink after floating on water surface for a long time (26). We also compared the present result with the model strider using 1D superhydrophobic wires as artificial "legs" (24, 25, 36, 37). By comparison, the "legs" constructed from the superhydrophobic copper foils possess much larger and more stable loading capacity, which is an important feature for the practical application of superhy-

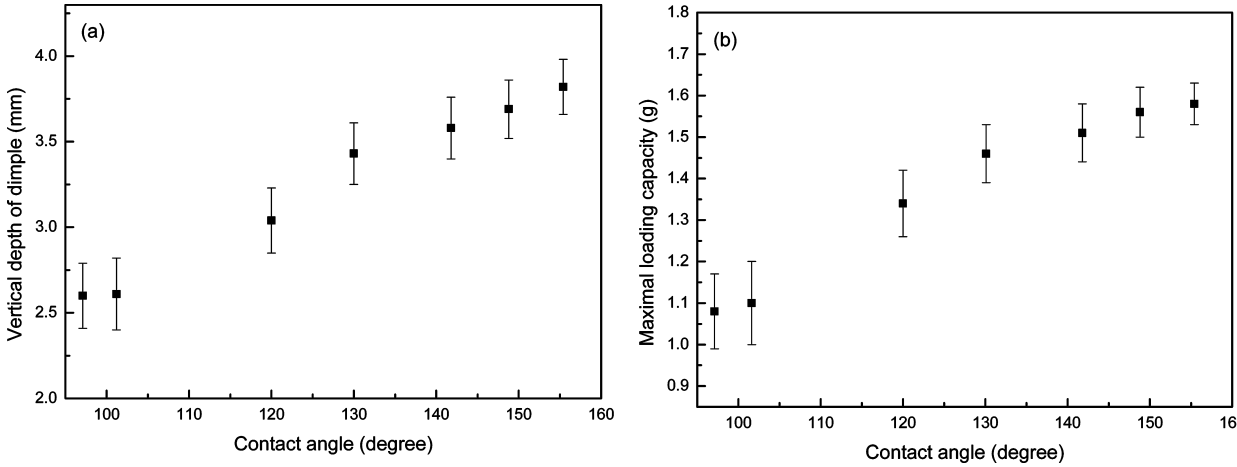


**FIGURE 2.** Effect of water contact angle on (a) the vertical depth of dimples and (b) the maximal loading capacity of the "legs".

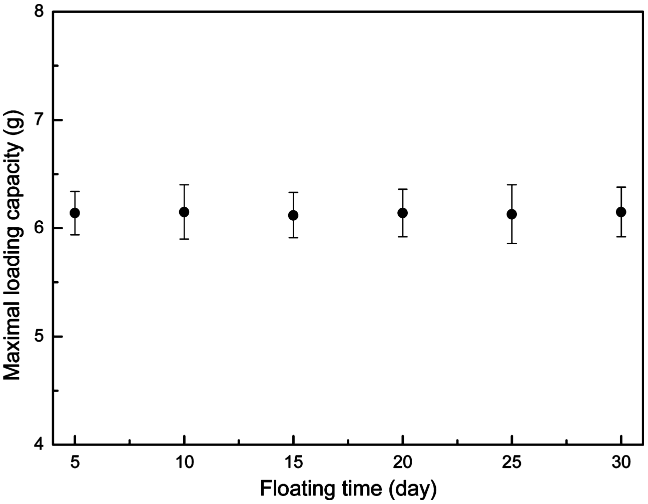


**FIGURE 3. Relationship between floating time and the maximal loading capacity of the model. The copper foils used in the model had a contact angle of 155.4°.**

drophobic surfaces in miniature aquatic devices. In addition, the superhydrophobic "legs" can emerge out through the water surface when they sink and then refloat again, indicating the superhydrophobic surfaces of the "legs" provide additional buoyancy force under water. This characteristic is important for an aquatic device if it is dragged into the water by some external forces.

The superhydrophobic property of the copper foils is believed to arise from the micro/nanometer hierarchical structures of flowerlike clusters formed on their surfaces. Figure 4 shows the surface morphologies of the copper foils after immersion in 0.03 M $NH_3$ for different duration time. These surfaces are covered with flower-like clusters with a size of a few micrometers. All these flowerlike clusters are built from nanosheets of a few tens of nanometers in width and a few hundred of nanometers in thickness, indicating the presence of binary structure at both micrometer and nanometer scales. The composition of flowerlike clusters is $Cu(OH)_2$, as demonstrated by XRD measurement (see Figure S1a in the Supporting Information). It is considered that air can be effectively trapped in the space between individual nanosheets of the flowerlike clusters (4), which form a cushion at the foil—water interface that prevents the foil from being wetted. Therefore, a water droplet trends to "float" on the trapped air rather than directly contact with the clusters, leading to the superhydrophobic property. We also reveal that the wettability of the copper foils depends on not only the immersion time in ammonia solution but also the concentration of ammonia (see Figures S1b and S2 in the Supporting Information). A concentration around 0.03 M and an immersion time of 48 h are ideal for high water repellence. It is noticed that the copper foils can withstand

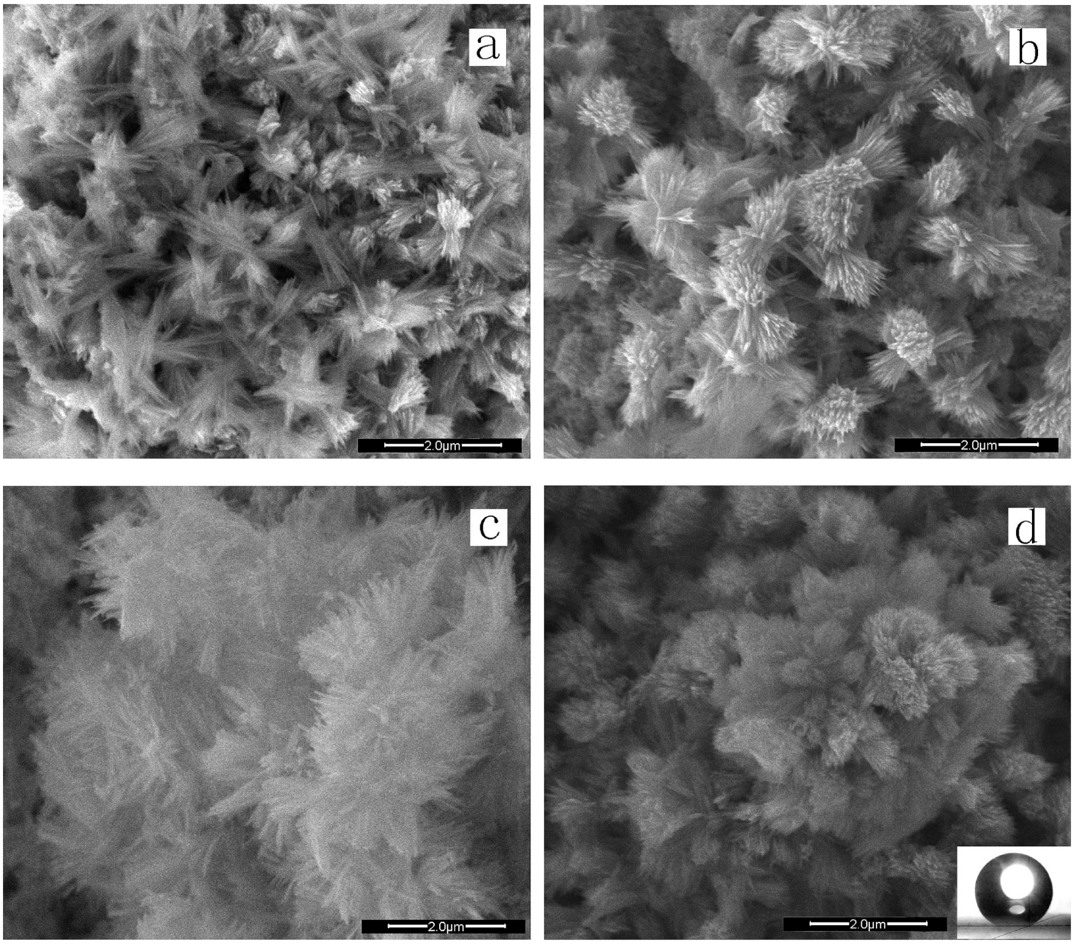


**FIGURE 4. SEM images of copper foils immersed in 0.03 M $NH_3$ for (a) 24, (b) 48, (c) 72, and (d) 96 h; inset is the optical image of a water droplet on the resulting copper foils after *n*-dodecanoic acid modification.**

slight mechanical damage such as scratching by sharp objects and still keep high contact angles, indicating good mechanical stability of the superhydrophobic surfaces.

## 4. CONCLUSIONS

In summary, a water strider-like model with large and stable loading capacity was constructed by using round-shaped superhydrophobic copper foils as artificial "legs". The flowerlike $Cu(OH)_2$ clusters formed on the "legs", which were governed by not only immersion time but also the concentration of ammonia, mainly accounted for the large loading capacity of the model. We have also studied the effect of hydrophobic property on the supporting forces of the "legs" on the water surface. Although normal hydrophobicity was sufficient to support an artificial "leg" when it only floated on the water surface, our study implied that superhydrophobic surface was still indispensable for a leg having large and stable loading capacity. It is anticipated that these bioinspired miniature models can be used in aquatic robot, water pollution monitor, and marine surveillance, etc.

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**Supporting Information Available:** Effects of immersion time in ammonia solutions and the concentrations of ammonia solutions on the surface morphologies and wettability of copper foils (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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