# Production and Characterization of Stable Superhydrophobic Surfaces Based on Copper Hydroxide Nanoneedles Mimicking the Legs of Water Striders

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The present work reports a simple and economic route for production and characterization of stable superhydrophobic surfaces from thin copper layers coated on arbitrary solid substrates. The thin copper layer was anodized in a 2 M aqueous solution of potassium hydroxide to form a thin film of copper hydroxide nanoneedles; then the film was reacted with *n*-dodecanethiol to form a thermally stable  $Cu(SC_{12}H_{25})_2$  superhydrophobic coating. The contact angle of the modified nanoneedle surface was higher than 150°, and its tilt angle was smaller than 2°. Furthermore, the surface fabricated on copper foil kept its superhydrophobic property after heating at 160 °C in air for over 42 h. This technique has also been applied for fabrication of copper wire with superhydrophobic submicrofiber coating to mimic water strider legs. The maximal supporting force of the superhydrophobic copper column has also been investigated in comparison to real water striders.

## Introduction

Superhydrophobic surfaces with water contact angles (CA) larger than 150° and tilt angles (TA) less than 5° have attracted extensive attention for their potential application in self-cleaning surfaces, microfluidic devices, and many other industrial processes.<sup>1-3</sup> Various techniques for achieving superhydrophobic surfaces including roughening the surfaces of hydrophobic materials (e.g., roughening hydrophobic polymer surfaces by thermal or solvent treatment, template syntheses, electrospinning, plasma polymerization or etching,<sup>4–7</sup> and solidification of melted alkvlketene dimmer,8 etc.) and modifying rough surfaces with materials of low surface free energies (e.g., coating waterproofing breathable fabrics<sup>9</sup> or thiol layers on copper or gold fractal surfaces,<sup>10,11</sup> coating perfluorosilane<sup>12–16</sup> or poly(tetrafluoroethylene) (PTFE)<sup>17</sup> on various roughened solid substrates, etc.) also have been developed in recent years. However, most of these approaches involve expensive and complex time-consuming procedures or are only applicable to special substrates, which prevent practical application on a large scale. Furthermore, there are few publications concerning the thermal stability of superhydrophobic surfaces. Recently, we successfully fabricated superhydrophobic surfaces on copper foils under mild conditions.<sup>18</sup> However, in these cases, a thin gold layer has to be deposited on the substrate for assembling a hydrophobic monolayer of alkylthiol. On the other hand, it is well known that electrochemical procedures can be accurately controlled and easily magnified on the large scale in industry. Fabrication of superhydrophobic surfaces through electrochemical approaches has been reported also.<sup>19,20</sup> However, in these cases, the electrochemical techniques were limited by the properties of the substrates.

Biomimicry is also one of the most important research areas in modern science.<sup>21,22</sup> Studying the biological microstructures and mimicking the structures to make the materials useful for human beings have attracted extensive attention.<sup>15,21</sup> Recently, water striders were focused on for their special ability to walk quickly on the water surface.<sup>23–25</sup> It was reported that the legs of water striders were columns in shape and covered by large numbers of submicrometer-sized hairs with fine nanogrooves. The hierarchical structures of strider legs make them superhydrophobic and generate high surface tensions, which make the water striders move quickly on the water surface.<sup>25</sup> Superhydrophobic coatings composed of dendritic gold clusters have recently been fabricated on a gold column by a layer-by-layer deposition method.<sup>26</sup> However, to date, no method has been developed for fabricating superhydrophobic submicrofiber coatings on column substrates.

Recently, we developed a method for fabrication of copper hydroxide nanoneedles on copper foil.<sup>27</sup> Here, we desire to demonstrate a simple way to fabricate thermally stable, lowcost, and large area superhydrophobic surfaces based on the copper hydroxide nanoneedles for various substrates. In this process a thin layer of copper was electroplated on a given substrate, then the copper layer was transformed into a nanoneedle film of copper hydroxide by anodization in an aqueous solution of potassium hydroxide, and finally the nanoneedle film was reacted with *n*-dodecanethiol to form a superhydrophobic surface. Replacing the copper foil with copper wire fabricates a submicrofiber superhydrophobic structure similar to that of a water strider's leg.

#### **Experimental Section**

Synthesis of Cu(OH)<sub>2</sub> Nanoneedle Film. The fabrication procedure for Cu(OH)<sub>2</sub> nanoneedle film was reported previously.<sup>27</sup> Typically, growth of this film was carried out at room temperature in a one-compartment cell by use of a model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. A copper foil (99.9%) (washed successively with a 2.0 mol L<sup>-1</sup> HCl aqueous solution, acetone, and ethanol for ~5 min each under ultrasonication; finally, it was dried with a dry N<sub>2</sub> stream before experiment) or a substrate coated with a thin copper film was used as the working electrode (surface area = 3 cm<sup>2</sup>). The counter electrode was a stainless

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 TABLE 1: Composition of the Electrolyte Used for

 Electroplating Copper Film on Various Substrates

components	amount
copper pyrophosphate hydrate ( $Cu_2P_2O_7$ )	6 g
triammonium citrate ( $(NH_4)_3C_6H_5O_7$ )	32 g 2.5 g
H <sub>2</sub> O	100 mL
pH	8.5

steel sheet (AISI 304, surface area =  $3.2 \text{ cm}^2$ ). The electrolyte was a 2.0 mol L<sup>-1</sup> aqueous solution of KOH. The solutions were deaerated by dry nitrogen bubbling and maintained at a light overpressure during the experiments. Cu(OH)<sub>2</sub> nanoneedle film was electrochemically grown at a constant current density of 1.5 mA cm<sup>-2</sup> for 3 C cm<sup>-2</sup> at room temperature.

Synthesis of a Cu(OH)<sub>2</sub> Submicrofiber Column. Growth of submicrofibers on copper wires was carried out by anodization of a copper wire at 20 °C in a one-compartment cell by use of a model 273 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The copper wire was 140  $\mu$ m in diameter, which is almost the same size as that of a mature water strider's leg. Copper wire was used as the working electrode (surface area = 0.066 cm<sup>2</sup>). The counter electrode was a stainless steel sheet (AISI 304, surface area = 3.2 cm<sup>2</sup>). The electrolyte was a 2.0 mol L<sup>-1</sup> aqueous solution of KOH.

Growth of Copper Films on Different Solid Substrates. Clean stainless steel and (AISI 304) silicon wafer ( $10^{-3} \Omega$  cm) were used without any previous treatment; the glass and PTFE electrode was covered with a thin film of silver by silver mirror reaction. Copper film was electrochemically deposited at a constant current density of 10 mA cm<sup>-2</sup> for 20 C cm<sup>-2</sup> at 50 °C using copper foil as the counter electrode. The composition of the electrolytes is listed in Table 1. The as-prepared copper film electrode was washed with deionized water and dried with N<sub>2</sub> stream.

**Surface Treatment.** The as-prepared Cu(OH)<sub>2</sub> film was immersed in an ethanol solution of *n*-dodecanethiol (10 mmol  $L^{-1}$ ) for 1.5 h and then washed with ethanol and dried with N<sub>2</sub> stream before characterization. The as-prepared Cu(OH)<sub>2</sub> submicrofiber column was immersed in an ethanol solution of *n*-dodecanethiol (1 mmol  $L^{-1}$ ) for 3.5 h and then washed with ethanol and dried with N<sub>2</sub> stream before characterization. Pristine Cu(SC<sub>12</sub>H<sub>25</sub>)<sub>2</sub> was prepared by direct reaction of CuCl<sub>2</sub> aqueous solution with *n*-dodecanethiol at a molar ratio of 1:2. Pristine Cu(OH)<sub>2</sub> was prepared by direct reaction of CuCl<sub>2</sub> aqueous solution with *KOH* at a molar ratio of 1:2. Flat Cu(OH)<sub>2</sub> film was fabricated by planish Cu(OH)<sub>2</sub> particles under 5 MPa pressure using a GX Fourier transform infrared (FT-IR) spectrometer.

**Characterizations.** Water contact angles were measured by a contact angle system, OCA 20, made by Dataphysics Instruments GmbH (Germany). The size of the water droplet was 5  $\mu$ L. The static contact angle measurement was carried out after the droplet deposited on the surface for 20 s. The contact angle value was obtained by measuring five different positions of the same sample. The tilt angles were measured five times for each sample by tilting the sample with a 5  $\mu$ L drop on it until the drop began to slide. Scanning electron micrographs (SEM) were taken out by use of a FEI Sirion 200 scanning electron microscope. Ion concentrations were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES), model Vista-MP (VARiAN Co.). X-ray diffraction (XRD) was carried out using a D8 Advance (Bruker) X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Thermogravimetric analysis was carried out using a TGA 2050 system (TA Co.). X-ray photoelectron spectra (XPS) were taken on a PHI Quantera SXM (PE Co.) X-ray photoelectron spectrometer.

#### **Results and Discussion**

The synthesis and characterization of Cu(OH)<sub>2</sub> nanoneedles fabricated on copper foil have already been described previously.<sup>27</sup> The as-prepared Cu(OH)<sub>2</sub> nanoneedle film has a highenergy surface with a contact angle close to 0°. To fabricate a superhydrophobic surface we treated the film with a 10 mmol  $L^{-1}$  ethanol solution of *n*-dodecanethiol for 1.5 h in order to lower its surface energy. Figure 1 illustrates the SEM images of the nanoneedle film before (A) and after (B) treatment with *n*-dodecanethiol. It is clear from this figure that the morphology of the thiol-modified nanoneedle surface (thiol-MNS) is different from that of pristine Cu(OH)2 nanoneedle film. The appearance of the nanoneedle surfaces was changed, and the nanoneedles themselves adhered together into bundles to form a highly rough surface, indicating reaction of n-dodecanethiol and Cu(OH)<sub>2</sub> nanoneedles. Chemical reaction caused the destruction of the Cu(OH)<sub>2</sub> nanocrystal and the morphology to change. The copper concentration of 25 mL of thiol solution after treating a 3 cm<sup>2</sup> copper foil with Cu(OH)<sub>2</sub> nanoneedles was measured to be only 0.25 mg  $L^{-1}$  by an inductively coupled plasma-atomic emission spectrometer, indicating that the as-prepared thiol-MNS is insoluble in the solvent. After thiol modification the water contact angle of the nanoneedle surface was measured to be as high as 155°, and its tilt angle was tested to be smaller than 2° (see insert of Figure 1B). The contact angle of the droplet changed from 155° to 160° after exposure to an ambient environment for 30 min, which indicates the surface is stable with time. In comparison, a flat copper foil was also treated with n-dodecanethiol through the same chemical procedures. The contact angle of the modified flat copper surface was measured to be only 110°. This result indicated that the nanostructures of the n-dodecanethiol-modified Cu(OH)2 nanoneedle surface (thiol-MNS) strongly enhanced its hydrophobicity.

Furthermore, the superhydrophobic property of thiol-MNS was tested to be thermally stable. The water contact angle of thiol-MNS described above did not show any change even when the surface had been kept in air at 200 °C for 2 h (Supporting Information, Figure S1). When the modified nanoneedle surface was heated at 160 °C in air for a very long time (42 h), the surface still exhibited the superhydrophobic property with a water contact angle as high as 154° and tilt angle smaller than 2°. The surface will not decrease even when bending the copper substrate to over 120°. After heat treatment at 160 °C the surface retains its superhydrophobic property even when the surface was rubbed by a piece of paper. Cu(OH)<sub>2</sub> is thermally unstable and can be easily decomposed into CuO at temperatures higher than 150 °C as demonstrated by the TGA curve shown in Figure 2 (solid line).<sup>28</sup> Therefore, the thermal stability of modified film implies that n-dodecanethiol was not simply adsorbed on the Cu(OH)2 surface. In fact, Cu(OH)2 can react with *n*-dodecanethiol following the equation  $Cu(OH)_2$  +  $2C_{12}H_{25}$ -SH  $\rightarrow$  Cu(SC<sub>12</sub>H<sub>25</sub>)<sub>2</sub> + 2H<sub>2</sub>O. Thus, the nanoneedles were covered with hydrophobic alkyl chains after chemical treatment. Cu(SC<sub>12</sub>H<sub>25</sub>)<sub>2</sub> exhibits a decomposition temperature of approximately 250 °C (Figure 2, dashed line); the Cu(SC12H25)2 coating enhanced the thermal stability of thiol-MNS. As shown in Figure 2, dotted line, the thiol-modified nanoneedles decompose in two steps. The first step in the temperature range of 170-200 °C is attributed to dehydration of Cu(OH)<sub>2</sub> of the nanoneedle host, and the second step in the temperature



**Figure 1.** SEM images of the film before (A) and after (B) treatment with an ethanol solution of *n*-dodecanethiol (10 mmol  $L^{-1}$ ) for 1.5 h (the nanoneedles were deposited at a constant current density of 1.5 mA cm<sup>-2</sup> in 2.0 mol  $L^{-1}$  KOH solution for 3C cm<sup>-2</sup>). Insert of B: digital camera image of a water droplet on the film after treatment at room temperature (drop weight = 20 mg).



**Figure 2.** TGA traces for as-prepared  $Cu(OH)_2$  nanoneedles (solid line), the thiol-modified nanoneedles (dotted line), and pristine  $Cu(SC_{12}H_{25})_2$  (dashed line) prepared by direct reaction of  $CuCl_2$  and  $C_{12}H_{25}SH$  at a molar ratio of 1:2 (the samples were heated in air at a rate of 20 °C min<sup>-1</sup>).

scale of 220–250 °C is attributed to decomposition of the  $Cu(SC_{12}H_{25})_2$  skins of the thiol-modified nanoneedles. According to the TGA data we can calculate that the film was composed of 76%  $Cu(OH)_2$  and 24%  $Cu(SC_{12}H_{25})_2$  (by weight). It was found that the dehydration reaction changed the nanoneedle morphology little and the  $Cu(SC_{12}H_{25})_2$  coating made the superhydrophobic surface stable at temperatures as high as 200 °C.

High-resolution X-ray photoelectron spectral results also confirmed that the surfaces of Cu(OH)2 nanoneedles were converted to  $Cu(SC_{12}H_{25})_2$  after reaction with *n*-dodecanethiol. The XPS spectra of the surfaces of as-prepared Cu(OH)<sub>2</sub> nanoneedle film (a), thiol-modified nanoneedle film (b, thiol-MNS), and a pure copper foil after thiol treatment (c) are shown in Figure 3. As can be seen from this figure, no obvious S  $2p_{3/2}$ peak was found in the spectrum of as-prepared Cu(OH)2 nanoneedle film. However, the spectrum of thiol-MNS showed two S  $2p_{3/2}$  peaks. The peak at 162 eV is related to the sulfur of Cu(SC12H25)2, and that at 163.5 eV is associated with the sulfur of free *n*-dodecanethiol.<sup>29,30</sup> Accordingly, on thiol-MNS, most of the n-dodecanethiol molecules changed into the corresponding copper salt, while on the copper foil surface, most of the thiol molecules are in the free state. Thus, it is reasonable to conclude that n-dodecanethiol reacts with Cu(OH)<sub>2</sub> much easier than with metallic copper. Furthermore, there is a strong O 1s peak at 531.2 eV in the spectrum of as-prepared Cu(OH)<sub>2</sub>

film.<sup>31</sup> However, after treating with *n*-dodecanethiol, this O 1s peak is greatly weakened while a strong C 1s peak of alkane at 284.8 eV appears. These results provided additional evidence for reaction of Cu(OH)<sub>2</sub> and *n*-dodecanethiol. There is a weak carbon peak in the C 1s spectrum of as-prepared Cu(OH)<sub>2</sub> film, which is attributed to a trace amount of impurity.

As mentioned above, as-prepared Cu(OH)2 nanoneedles film shows a superhydrophilic property. We found that the flat surface of a pellet formed by pressing Cu(OH)<sub>2</sub> particles under 5 MPa pressure (see Experimental Section) has a water contact angle of 62°. A Wenzel equation is usually used to describe the contact angle on the rough surface in this situation,<sup>32</sup> cos  $\theta^* = r \cos \theta$  ( $\theta^* = \text{contact angle on the rough surface; } \theta =$ contact angle on the flat surface, r = ratio of the actual over the apparent surface area of the substrate). Thus, r for the superhydrophilic Cu(OH)<sub>2</sub> nanoneedle surface was calculated to be about 2.2. Modifying the film with *n*-dodecanethiol produces a hydrophobic surface, and surface roughness enhances its contact angle to over 150°. In this situation air trapped below the water droplet can significantly enhance the surface hydrophobicity and the contact angle is usually described by<sup>33,34</sup> cos  $\theta^* = -1 + \varphi_s(1 + \cos \theta)$  ( $\theta^* = \text{contact angle on the rough}$ surface,  $\theta = \text{contact}$  angle on the flat surface,  $\varphi_s = \text{fraction of}$ solid in contact with water). n-Dodecanethiol treated flat Cu(OH)<sub>2</sub> film mentioned above has a water contact angle of about 110°; the thiol-MNS has a water contact angle of 155°. Accordingly,  $\varphi_s$  of the thiol-MNS was calculated to be 14.2%, indicating that about 86% of the total surface area was trapped with air.

It is well known that electroplating of copper on various solid substrates such as a microprinting circuit or plastic can be easily realized. Thus, the electrochemical approach for fabrication of thermally stable superhydrophobic surfaces described above can be extended to other substrates. Here, we used two conductive (stainless steel sheet and silicon wafer) and two insulating (glass and polyethylene tetrafluoride, PTFE) substrates as examples. First, a thin layer of copper was electrochemically deposited on the surface of each substrate at 10 mA  $cm^{-2}$  for 20 C  $cm^{-2}$ . The insulating substrates were precoated with a thin layer of silver by use of the silver mirror reaction.<sup>35</sup> Then, a surface of Cu(OH)<sub>2</sub> nanoneedles was achieved on the substrate through the same electrochemical procedures described above. Figure 4A, B, C, and D shows typical SEM images of as-prepared copper hydroxide nanoneedle film on a stainless steel, silicon wafer ( $10^{-3} \Omega$  cm), glass, and PTFE sheet, respectively. As can be seen, the nanoneedles constructed a rough porous surface on each substrate. The inserts of Figure 4A and B are profile SEM images of the samples. They clearly demonstrate that the



**Figure 3.** High-resolution XPS spectra of as-prepared  $Cu(OH)_2$  nanoneedle film (a) and the same film (b) or a copper foil (c) after treatment with *n*-dodecanethiol.

film coated on stainless steel is compact, even when the surface is lacerated by a knife, while the quality of the film coated on silicon, glass, or PTFE was relatively worse. The thiol-MNS fabricated from these surfaces also exhibited superhydrophobicity with a contact angle larger than 151° and tilt angle less than 2° and also can resist a high temperature of 200 °C (Figure 4). After the hea treatment, the superhydrophobic layer still adhered firmly on SS substrate while delamination occurred at the interface of the superhydrophobic coating and silicon, glass, or TFEE substrate due to their different mechanical and thermal properties.

Anodization of a copper column was also successfully achieved. Figure 5 shows the typical scanning electron micro-



**Figure 4.** SEM images of as-prepared  $Cu(OH)_2$  nanoneedle films grown at a constant current density of 1.5 mA cm<sup>-2</sup> in 2.0 mol L<sup>-1</sup> KOH solution and coated on different substrates: (A) stainless steel, (B) silicon wafer, (C) glass, (D) PTFE. Insets of A: optical picture of a water droplet on the thiol–MNS on stainless steel (drop weight 5 mg) and a profile image of the film (the lower one). Inset of B: profile images of the film coated on a silicon wafer.



**Figure 5.** SEM and TEM images of as-prepared Cu(OH)<sub>2</sub> submicrofibers deposited at a constant current density of 2 mA cm<sup>-2</sup> in 2.0 mol L<sup>-1</sup> KOH solution for 1500 s. T = 20 °C. (A) overall image,; (B) magnified image, (C) TEM image. Inset: SAED pattern.

graphs (SEM) of a copper column after anodization in a 2.0 mol L<sup>-1</sup> aqueous solution of KOH at a constant current density of 2 mA cm<sup>-2</sup> for 3 C cm<sup>-2</sup>. As can be seen, the copper wire was coated compactly with submicrofibers. Figure 5B is a magnified view of the as-prepared submicrofibers, which demonstrated that they are  $\sim 5 \mu m$  in length and 150–300 nm in diameter. The morphology of the copper column surface is



**Figure 6.** SEM images of as-prepared copper hydroxide submicrofibers after treatment with an ethanol solution of *n*-dodecanethiol (1 mmol  $L^{-1}$ ) for 3.5 h (the fibers were deposited at a constant current density of 2 mA cm<sup>-2</sup> in 2.0 mol  $L^{-1}$  KOH solution for 3 C cm<sup>-2</sup>): (A) overall view and (B) magnified view.

similar to that of water striders' leg. Our energy-dispersive X-ray spectroscopy (EDX) measurement affirms a strict stoichiometric ratio of Cu:O = 1:2, which reveals that the as-prepared submicrofibers were composed of Cu(OH)<sub>2</sub>. XRD measurement of the as-prepared product on the copper foil (instead of copper wire) is in agreement with the orthorhombic phase Cu(OH)<sub>2</sub> (JCPDS 13-420). Figure 5C is a transmission electron micrograph (TEM) of an as-prepared Cu(OH)<sub>2</sub> submicrofiber. The selected area electron diffraction (SAED) pattern of a 300 nm wide fiber (inset, Figure 5C) indicates that the fiber is a single crystal. According to the features of the diffraction pattern, Cu(OH)<sub>2</sub> fibers are arranged parallel to their (010) planes and the preferential growth direction of the single-crystal fibers is their [100] direction.

It is known that water striders can move quickly on the water surface due to its superhydrophobic legs with submicrofibers. To fabricate a superhydrophobic surface, the copper column with Cu(OH)2 submicrofiber coating was immersed in an ethanol solution of *n*-dodecanethiol (1 mmol  $L^{-1}$ ) for 3.5 h, then washed with ethanol, and dried with N2 stream. Figure 6 illustrates the SEM images of the submicrofibers fabricated on the copper column after thiol treatment. The overall view of the thiolmodified surface (Figure 6A) is similar to that of the column surface with submicrofibers (Figure 5A). Figure 6B is a magnified view of the column surface shown in Figure 6A. It is clear from this image that the surface morphology of the thiolmodified submicrofiber surfaces is obviously different from that of pristine Cu(OH)<sub>2</sub> fibers. The original smooth surfaces of  $Cu(OH)_2$  fibers were roughened by the reaction with *n*-dodecanethiol. When a water droplet was dropped onto the copper wire surface it rolled off quickly. As it is hard to measure the static contact angle of the wire surface, instead of the copper column, we used a flat copper foil with  $1.5 \times 1 \text{ cm}^2$  for measuring the water contact angle (after anodization and thiol treatment, the surface morphology of the copper foil is similar to that of the copper column described above). The contact angle of the thiol-treated copper foil with submicrofibers was measured to be 155°, and its tilt angle was tested to be smaller than 2°, which revealed that the surface was superhydrophobic.

To deeply understand the behavior of water striders on the water surface, we investigated the maximal supporting force of



Figure 7. Model constructed for mimicking a water strider.

the superhydrophobic copper column (which is similar to the legs of water striders). To simplify the measurement, a model was constructed to mimic the water striders. As shown in Figure 7, the body of the spider model was made of an oval plane of polyethylene tetrafluoride (PTFE). Six superhydrophobic copper columns (blue parts, 1.5 cm each) were arranged symmetrically at the two sides of the plane. The unmodified copper wires (1 cm each, yellow parts) were fixed 120° to the plane. The angle between the superhydrophobic wire and the pristine copper wire was also about 120°. To prevent the water surface from being pierced by the sharp tip of the superhydrophobic copper wire, part of the wire end (about 3 mm) was bent vertical to the water surface. During the test process the model spider was put onto the water surface carefully and additional weight was loaded until its feet were completely immersed in the water. The maximal supporting force of each superhydrophobic foot of the spider model was measured to be about 83 dynes; this value is close to that of the real water striders.<sup>25</sup> We also used thioltreated smooth copper wires (CA =  $110^{\circ}$ ) as the feet of a spider model for comparison. The experimental results indicated that the maximal supporting force of each foot was measured to be only 29 dynes, which suggests that the superhydrophobic submicrofibers morphology is the principal factor for water repellency.

It is known that the weight of a static water strider model is supported mainly by two kinds of forces. One is the buoyancy force,  $F_{\rm b}$ , deduced by integrating the hydrostatic pressure over the body area in contact with the water; the other is the curvature force,  $F_{\rm c}$ , deduced by integrating the curvature pressure over this area or equivalently the vertical component of the surface tension,  $\sigma \sin \theta$ , along the contact perimeter.<sup>23,36</sup> Here,  $F_c$  is the more important factor. When  $Mg = F_b + F_c$ , the maximal supporting force was obtained (where M is the mass sum of the spider model and the additional load and g is the gravitation constant). The superhydrophobic submicrofibers coatings on the copper wire is effective for preserving air in the pores and forming a cushion at the wire-water interface that prevents the wire from being wetted and causes a large  $F_{\rm c}$ . In contrast to other superhydrophobic coatings, the submicrofiber coating has deep pores in high number density, which makes the surface of the wire-water interface hard to be wetted by water under static pressure. This may help us to understand why water striders choose the hierarchical structure of micrometer-sized tiny hairs with fine nanogrooves.

## Conclusion

We developed a simple way to fabricate a thermally stable superhydrophobic surface with high contact angles and a low tilt angle by combination of the electrochemical technique and surface reaction. The method described here can be easily extended to any other substrates, such as stainless steel, silicon wafer, glass, and PTFE, for fabricating thermally stable superhydrophobic coatings. Moreover, as electroplating of copper film is a low-cost and mature technology in industry, the method described here can be easily magnified to a large scale. Furthermore, we successfully applied the fabrication method of superhydrophobic copper wires with submicrofibers structures, which is similar to the leg of water striders. The superhydrophobic wire causes a much larger curvature force than that of a thiol-treated smooth copper wire. This work may help us to understand why water strider can move quickly on the water surface and why it chooses the hierarchical structure of micrometer-sized tiny hairs with fine nanogrooves.

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**Supporting Information Available:** Detailed information of the water contact angle at different treated temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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