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## PAPER

# Controlled growth of CuO-Cu<sub>3</sub>Pt/Cu micro-nano binary architectures on copper substrate and its superhydrophobic behavior

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A facile, simple, novel method for controllable fabrication of a superhydrophobic surface was developed by spontaneous deposition and followed anneal on copper substrate. The surface morphologies, chemical compositions and hydrophobicity of the as-prepared surfaces were investigated using field emission scanning electron microscope, X-ray diffractometer, X-ray photoelectron spectroscopy and contact angle meter. The superhydrophobic surface was composed of hierarchical structure of CuO-Cu<sub>3</sub>Pt/Cu. At the optimal condition, the surface showed a good superhydrophobicity with a water contact angle of about 170±2° and a sliding angle of approximately 0±2°. Additionally, the formation mechanism of the superhydrophobic surfaces was studied. The as-prepared superhydrophobic surface exhibited good nonsticking behavior, long-term stability, and large buoyancy force, which offers possibilities to potential applications.

## Introduction

Wettability is an important property for a solid surface.<sup>1,2</sup> Stemmed from the discovery of self-cleaning nature of lotus,<sup>3,4</sup> superhydrophobic surfaces with water contact angle (WCA) greater than 150° and sliding angle (SA) lower than 5° have attracted widely researchers' interest worldwide because of their various special applications in fundamental research and potential industrial use, such as self-cleanness, oil-repellent surfaces, friction reduction, and corrosion resistance.<sup>5-11</sup> So far, according to the investigation on the natural superhydrophobic species, researchers have revealed that the micron or nanometer roughness and the use of low-surface-energy materials are necessary to obtain the superhydrophobicity of solid surfaces.<sup>12-15</sup> In the past few decades, various techniques such as electrochemical deposition method,<sup>16-18</sup> sol-gel method,<sup>19-21</sup> plasma fluorination method,<sup>22-24</sup> electrospinning method,<sup>25,26</sup> template method,<sup>27-29</sup> layer-by-layer self-assembly,<sup>30</sup> and other methods<sup>31-34</sup> have been proposed to prepare superhydrophobic surfaces.

Copper as an important engineering material received much attention in industries due to its high diathermanous and electric performance in addition to its good thermal and mechanical stability.<sup>35-37</sup> So, it is significant to prepare a self-cleaning and anticorrosion superhydrophobic surface for wide application of copper. So far, many studies have been focused on the preparation of superhydrophobic surfaces on copper substrates by means of various methods. For instance, Pei et al.

fabricated a superhydrophobic CuO film with dandelion-like structures on copper plate via a low-pressure oxidation method.<sup>38</sup> Jiang et al. reported a simple method of fabricating a super-hydrophobic surface on the copper substrate with the n-tetradecanoic, but which took a long time to carry out (about 3-5 days).<sup>39</sup> Wang et al. prepared a superhydrophobic surface with hierarchical nanowire CuO structure on copper plate via oxygen adsorption.<sup>40</sup> However, most of preparation processes are requiring time-consuming, organic modifiers, or special equipment to carry out. Therefore, it could be desirable to design a novel method for fabricating superhydrophobic surfaces on copper substrates. Compared with the methods described above, spontaneous deposition is an environmentally friendly, efficient, and low-cost method for introducing micro-nano structures on metal substrates. Our group had used the electroless galvanic deposition to coat zinc substrates with a textured layer of copper and obtained a high WCA of 162±2° without low surface energy materials to modify.<sup>41</sup> Pan et al. had obtained a novel kind of superhydrophobic copper boat via electroless deposition and then treated with n-dodecanoic acid.<sup>42</sup> Therefore, we hope to deposit another metal on copper substrate without low surface energy materials to modify.

In this study, we constructed superhydrophobic surfaces by immersing the copper substrate into platinum tetrachloride water solution and followed annealing. The whole process was facile to carry out and did not require organic modification and complex equipment. The morphologies,

chemical compositions, formation mechanism, effect factors, durability, and potential application of the superhydrophobic surfaces were also investigated.

## Experimental

### Materials

Platinum tetrachloride powder ( $\text{PtCl}_4$ , 99.8%), nitric acid ( $\text{HNO}_3$ , 65%~68%) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.5%) were purchased from China Beijing Fine Chemical. Co. Ltd. Copper substrates (99.9%) were obtained from Beijing Nonferrous Metal Research Institute.

### Preparation of samples

Copper plates sized  $1.0\text{cm} \times 1.0\text{cm} \times 0.1\text{cm}$  were cleaned ultrasonically with ethanol and distilled water for 5 min to remove the greasy and the oxide layer, respectively. Subsequently, they were etched with 22 wt%  $\text{HNO}_3$  for 6 min and followed by rinsed with distilled water. Then, the specimens were set perpendicularly in unplasticized poly vinyl chloride (UPVC) tube without bottom shown as our previous report,<sup>43</sup> and then were immersed in 0.002 mol/L  $\text{PtCl}_4$  aqueous solution for 60 min at room temperature and dried in air. Immediately afterward, the samples were placed in a Petri dish covered with filter papers and annealed at  $180^\circ\text{C}$  for 20 min in the oven. In the whole process, as shown in Fig. 1, the color of the surface of sample gradually changed from gold to gray when immersed in the  $\text{PtCl}_4$  solution, and then became blue when annealed.

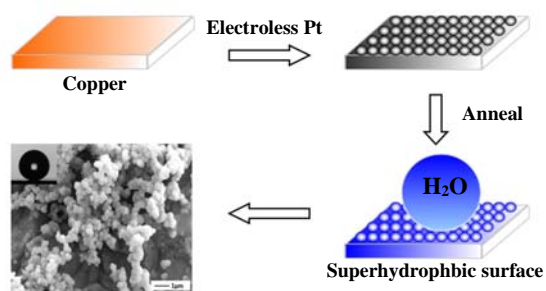


Fig. 1 Schematic illustration of fabricating a superhydrophobic surface

### Samples characterization

The surface morphologies of the obtained samples were analyzed using scanning electron microscopy (SEM, S-4800, Hitachi, Japan); The chemical compositional analysis of the surface of the sample was analyzed by X-ray photoelectron spectrometer (XPS, Model PHI 5300, Physical Electronics, USA), using 250 W Mg  $K\alpha$  ( $\lambda = 0.9891\text{ nm}$ ) X-ray as the excitation source; The microstructure was determined by an X-ray diffractometer (XRD, D8 ADVANCE, Bruker, Germany) operating with Cu  $K\alpha$  radiation at a continuous scanning mode (40 kV, 40 mA, and  $\lambda = 0.15418\text{ nm}$ ) and scanning rate of  $4^\circ/\text{min}$ ; Contact angles were measured with a contact anglemeter (FTÅ 200, Data physics Inc, USA) at ambient temperature. Water droplet (about  $8\text{ }\mu\text{L}$ ) was dropped carefully onto the surface. The average WCA value was determined by measuring five times at different positions of the same sample. All values of each sample were in a range of  $\pm 2^\circ$ . WCA images were captured by the video and measured

using a tangent algorithm due to the gravity of the droplet, which has been analyzed in detail in our previous paper.<sup>44</sup>

## Results and discussion

We are interested in fabricating superhydrophobic surfaces via rapid and convenient process without organic modification. The superhydrophobic surfaces were obtained via spontaneous deposition on copper substrates in  $\text{PtCl}_4$  aqueous solution at room temperature, and followed anneal.

### Contact angle measurement

The WCAs of the samples were measured by contact anglemeter, as shown in Fig. 2. The WCA of the untreated surface of sample is approximately  $66^\circ$ , indicating hydrophilicity (Fig. 2a). After treated with the  $\text{PtCl}_4$  solution, the WCA increases to  $130^\circ$ , indicating hydrophobicity (Fig. 2b). However, after anneal treatment, the surface of sample successfully becomes superhydrophobic with a WCA of  $170^\circ$  as shown in Fig. 2c. The results clearly indicate that replacement deposition and anneal processes are both important in the fabrication of superhydrophobic surfaces.

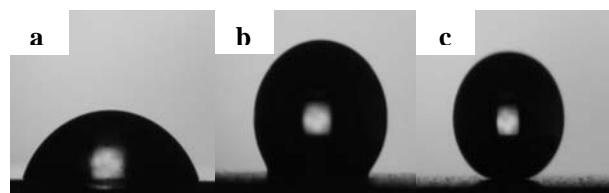


Fig. 2 Images of the WCAs on the Cu surfaces: (a) untreated copper, (b) reacted in 0.002 mol/L  $\text{PtCl}_4$  aqueous solution for 60 min and (c) after annealed at  $180^\circ\text{C}$  for 20 min.

The as-prepared superhydrophobic surface also exhibits nonsticking behavior. As it can be seen from Fig. 3, when a  $8\text{ }\mu\text{L}$  droplet detached from the syringe, the droplet is hardly able to stick to the surface put flat on the test table without any tilting and instantaneously rolls off without any adhesion, indicating a SA of around  $0 \pm 2^\circ$  on the surface.<sup>45</sup>

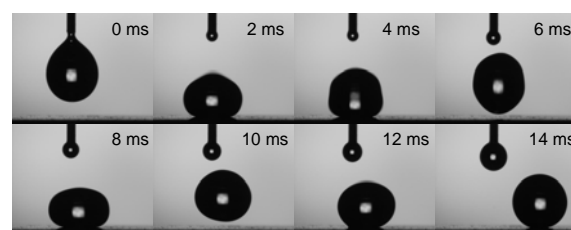
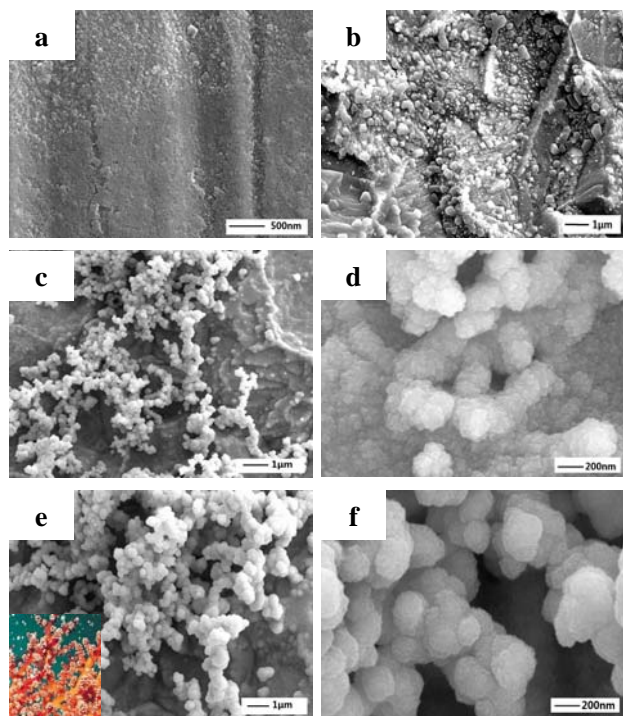


Fig. 3 Successive snapshots obtained from the full rebound of a  $8.0\text{ }\mu\text{L}$  droplet on the superhydrophobic surface.

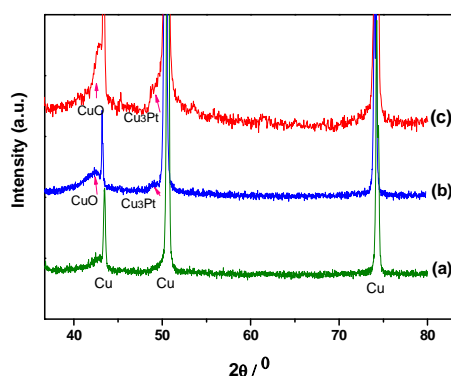
### Morphology and microstructure

To obtain a better understanding of the change of WCA, SEM images are used to research the morphologies of the surfaces of samples (Fig. 4). Fig. 4a and 4b are the SEM images of the surfaces of the samples before and after treatment with  $\text{HNO}_3$ , respectively, showing different roughness on the copper surfaces. When the copper substrate was reacted in 0.002 mol/L  $\text{PtCl}_4$  solution for 60 min, the resulting surface is densely covered by many nanospheres, which forms coralline-like structures as shown in Fig. 4c. Moreover, the nano-sized

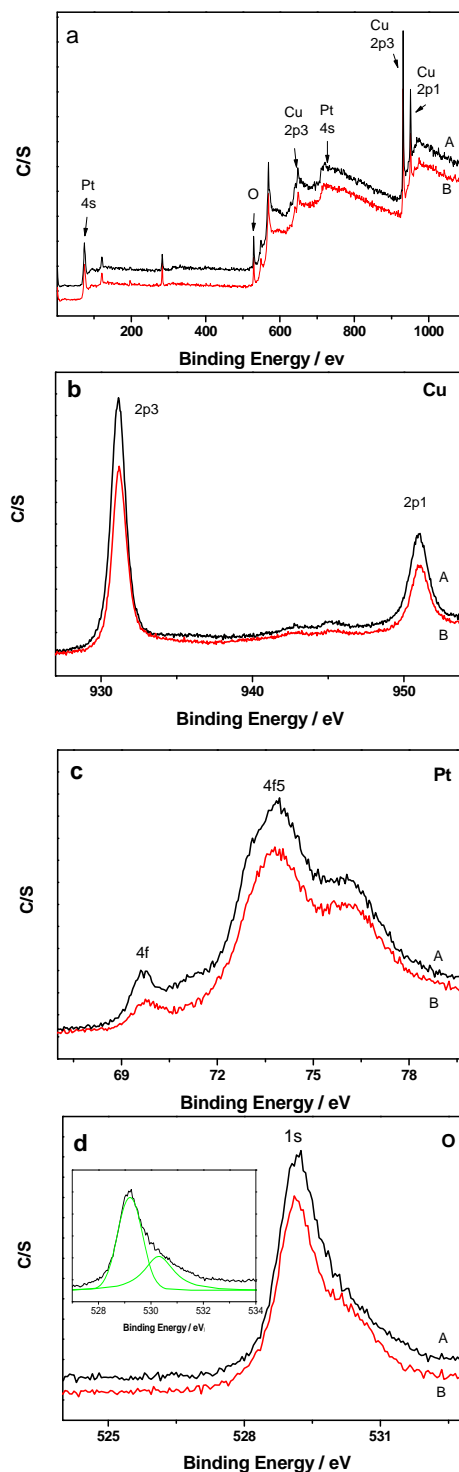
particles grow along the protuberant parts of the copper surfaces. The average diameter of particles in the structures is about 120 nm (Fig. 4d). Amazingly, the surface treated with anneal is composed of the dense and uniform particles on the copper substrate, exhibiting a coralline-like nanostructure, might be sufficient to take effect in increasing the porosity and surface roughness (Fig. 4e). After annealing, the particles become inerratic nanospheres with an average diameter of about 200 nm (Fig. 4f). That is, a certain degree of hierarchical structures is formed on the rough copper substrate. Due to the surface of air cushion, which can keep the water droplet away from the surface, the water droplet can easily bounce on this surface and finally roll off.



**Fig. 4** SEM of the surfaces of samples: (a) untreated copper, (b) copper after treatment with  $\text{HNO}_3$  aqueous solution, (c) and (d) reacted in the  $\text{PtCl}_4$  solution, (e) and (f) after anneal. The inset of (e) is the morphology of coralline.



**Fig. 5** XRD spectra of the samples: (a) the untreated copper, (b) treatment with  $\text{PtCl}_4$  solution, and (c) after anneal



**Fig. 6** XPS spectra of the samples: (A) before anneal; (B) after anneal. The inset of (d) is the fitted curve of B.

The superhydrophobic property of the sample results from both the surface morphological structures and chemical compositions. Fig. 5 shows XRD pattern of the samples. As a comparison, the XRD pattern of the bare copper substrate is also recorded and shown in Fig. 5a. Sharp peaks are attributed to the copper substrate (JCPDS Card No. 04-0836). After deposition of Pt for 60 min, two new peaks appear in the region



35–80° (Fig. 5b). The new two broad peaks at  $2\theta = 42.2^\circ$  and  $49.2^\circ$  are assigned to the diffraction peak of CuO (200) and diffraction peak of Cu<sub>3</sub>Pt (200) with the cubic phase (JCPDS No. 35-1358, No. 35-1091), respectively. However, after anneal, the peak at around  $42.2^\circ$  and  $49.2^\circ$  become more distinctly, indicating that the size of CuO-Cu<sub>3</sub>Pt gradually increase (Fig. 5c). These broad peaks also confirm the existence of nano-sized grains in the major overlay. This agrees well with the results of SEM observations.

Fig. 6 shows the XPS spectra of the samples. The curves labeled with (A) and (B) in the graphs are the samples coated platinum before anneal and after anneal, respectively. Fig. 6a shows the total XPS for the sample, which reveals that Cu and Pt exist on the surfaces whether the sample was annealed or not. What is more, during anneal, no new substance is found. Fig. 6b shows the XPS of the copper element. It can be easily seen that the peaks at 934.4 and 954.4 eV are attributed to Cu 2p<sup>3/2</sup> and Cu 2p<sup>1/2</sup> of copper(II), respectively, demonstrating CuO composition. The clear Pt peaks, appearing at 69.9 and 74.1 eV, confirm that the copper substrate is covered by platinum (Fig. 6c). The peak positions for Cu-Pt alloy are consistent with the previous literatures.<sup>46,47</sup> Fig. 6d shows the XPS spectra of the oxygen element. There is no change about the peaks locate at 529.3 eV in the curve A and B, but a new peak is found at 530.3 eV in the curve B as shown in the inset of Fig. 6d. It indicates Cu is oxidized to CuO on the surface. This result is in conformity with the XRD result.

### Influence factors of wetting behaviors

In order to prepare the superhydrophobic surfaces preferably, a series of influencing factors should be considered, such as concentration of aqueous solution, reaction time, anneal time, and anneal temperature. Fig. 7 shows the effect of different concentration of PtCl<sub>4</sub> solution on the wetting behaviors. It firstly increases from 93° to 132° with the increase of concentration of PtCl<sub>4</sub> and reaches the maximum value of 170° at 0.002 mol/L, and finally decreases to 140°. The result reveals the concentration of PtCl<sub>4</sub> aqueous solution has a great effect on wettability of the samples.

Fig. 8 shows the surface morphologies of CuO-Cu<sub>3</sub>Pt/Cu surfaces prepared at different concentration of PtCl<sub>4</sub> solution. It can be easily found that all the surfaces are composed of coralline-like CuO-Cu<sub>3</sub>Pt/Cu binary architectures and the sizes of CuO-Cu<sub>3</sub>Pt gradually increase with the increase of solution concentration. When the concentration of PtCl<sub>4</sub>

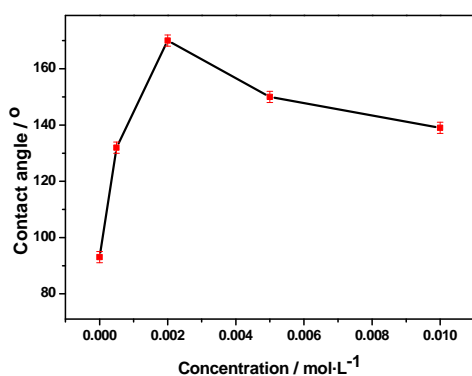


Fig. 7 WCAs of the as-prepared surfaces at different concentration of PtCl<sub>4</sub> aqueous solution.

solution was 0.0005 mol/L, the copper substrate is barely covered by a few thin particles with an average diameter of about 50 nm (Fig. 8a). Moreover, particles mainly extend along the protuberant parts of copper surface. When the concentration of PtCl<sub>4</sub> solution was 0.002 mol/L, countless particles form an interconnected granular structure on a large area of the copper substrate as shown in Fig. 8b. It looks like coralline structures and numerous grooves in which can trap a lot of the air. Compared with Fig. 8b and c, the shape of the hierarchical structures stays almost unchanged. However, the size of nanoparticle grows bigger and the copper substrate is covered more densely. When the concentration of PtCl<sub>4</sub> solution increased above a certain threshold of 0.010 mol/L, the average diameter of particles is found to be approximately 200 nm, and the roughness of the copper substrate is clearly shown to be changed (Fig. 8d).

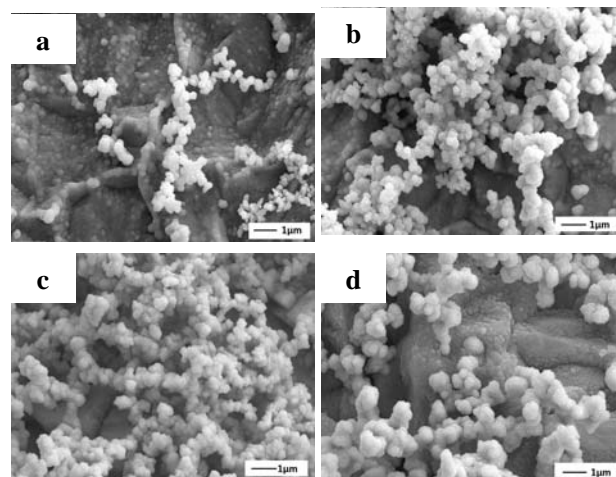


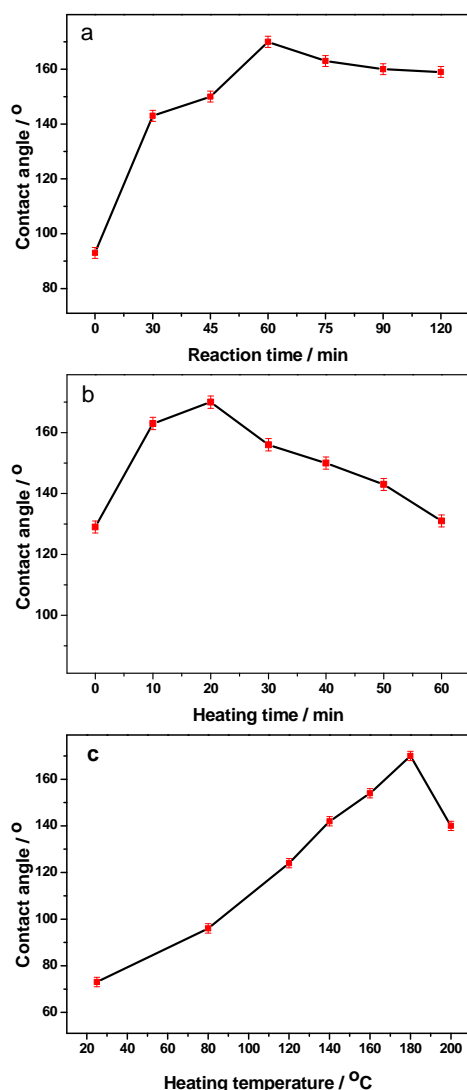
Fig. 8 SEM images of the prepared samples obtained at various concentration of PtCl<sub>4</sub> solution: (a) 0.0005 mol/L, (b) 0.002 mol/L, (c) 0.005 mol/L, and (d) 0.01 mol/L, while other conditions kept constant.

In addition to the effect of concentration discussed, superhydrophobic characteristics of the samples also depend on the reaction time, anneal time and anneal temperature. Fig. 9a shows the WCAs of the samples immersed in 0.002 mol/L PtCl<sub>4</sub> solution for different time. When the reaction time increased from 0 min to 120 min, the average WCA increases from 93° to 170°, and then decreases to 150°. The optimal reaction time is 60 min. Fig. 9b shows the relationship between WCAs and anneal time. As clearly seen in Fig. 9b, when the anneal time is lower than 20 min, the advancing contact angles gradually increase with an increase in the anneal time. However, when the anneal time is larger than 20 min, the WCAs sharp decrease. Fig. 9c shows changes in the WCAs of the sample surfaces after anneal at various anneal temperature values for 20 min. The result indicates that the anneal temperature has a great effect on the wettability of the sample and the optimal condition is 180°C.

The above results indicate that the optimal superhydrophobic surface with a WCA as high as of 170° and a SA as low as about 0±2° will be obtained by immersing the copper sheet in 0.002 mol/L Pt aqueous solution for 60 min and annealing at 180°C for 20 min.

### Theoretical explanation for superhydrophobicity

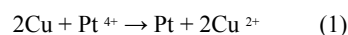
According to the characteristics of surface morphologies and compositions above, the possible growth mechanism for



**Fig. 9** WCAs of the as-prepared surfaces at different reaction time (a), different anneal time (b) and different anneal temperature (c).

coralline-like CuO-Cu<sub>3</sub>Pt/Cu micro-nano binary architectures is considered as consisting of the following steps: Firstly, tetravalent platinum in the aqueous solution is deoxidize to Pt atom by Cu atom on the copper substrate. Obviously, the longer the growth time and the higher the concentration of Pt are, the larger the size of Pt particles is, resulting in the larger surface roughness. Secondly, Pt atoms will come into the crystal lattices of copper or interstices among them and then form Cu<sub>3</sub>Pt alloy, causing crystal copper defects. As shown in the SEM images of Fig. 8, when the concentration of PtCl<sub>4</sub> aqueous solution is low, nano-spheres of Cu<sub>3</sub>Pt is gradually formed on the surfaces. However, when the concentration of PtCl<sub>4</sub> aqueous solution is increased, the effective micro-nano binary architectures disappear on the prepared surfaces, owing to kinetics of chemical reaction balances. Thirdly, when the sample is annealed, the Cu atom at active lattices defects on the surface is oxidized by O<sub>2</sub> in air to CuO. When anneal temperature is lower than 180°C, it is too low to form crystalline grain CuO quickly to change the surface

morphologies. Once the anneal temperature is higher than 200°C, the morphologies of CuO-Cu<sub>3</sub>Pt would be destroyed and superhydrophobic surface disappear. The main reactions in the system are shown in the following equations: (scheme 1)



**Scheme 1.** The main reactions in the formation of superhydrophobic surface.

There are two models can account for theoretically wetting properties. One is the Wenzel model,<sup>48</sup> in which water drop will penetrate to the grooves of the rough surface. The other model is the Cassie-Baxter model,<sup>49</sup> where the superhydrophobic surface is regarded as a porous medium composed of air pockets. Generally, the nonsticking superhydrophobic surface, for the superhydrophobic sample with a high WCA of 170° and a low SA of 0±2°, can be explained by the Cassie-Baxter model. The apparent contact angle is formulated as:

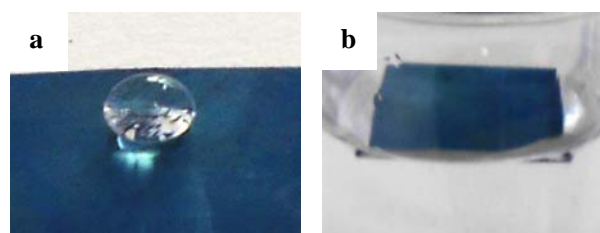
$$\cos\theta_A = f_1 \cos\theta - f_2 \quad (4)$$

In this equation,  $f_1$  and  $f_2$  are ratios of solid surface and air in contact with liquid, respectively, and  $f_1 + f_2 = 1$ . Where  $\theta_A$  (170°) is the WCA of the superhydrophobic surface of the sample,  $\theta$  (66°) is the WCA of the smooth copper surface. It is easy to deduce from this equation that by increasing the fraction of air ( $f_2$ ), the WCA of the rough surface ( $\theta_A$ ) will be increased. According to equation 4, the value of  $f_2$  of the superhydrophobic Cu surface is estimated to be 0.969, which means that the air occupies about 96.9% of the contact area between the water droplet and the composite surface. Thus, the high values of  $f_2$  suggest that the micro-nano binary structures on the surfaces are responsible for the better superhydrophobicity.

### Stability and application evaluation

The environmental stability and durability of the superhydrophobic samples have been investigated. After exposed the coralline-like superhydrophobic sample surface to air for 12 months, the value of the WCA did unchanged still, indicating that the superhydrophobic surface has long-term stability and durability.

It is well-known that the super buoyancy force is a highly important parameter for the practical application of materials on water. In this study, the floating ability of the superhydrophobic surface was evaluated by a simply approaches. Copper plate sized 2.0 cm×2.0 cm×0.01cm was treated the same as the above method. The water droplet on the blue superhydrophobic surface is shown in Fig. 10a. As we all know, the untreated copper sheet will sink in water, however, when the superhydrophobic sample was laid down on to the water, it floats on the surface of the water. The result clearly indicated that the film has a good flotative property as shown in Fig. 10b. It is believed that the superhydrophobic surfaces prevent the sample from being wetted by water and thus results in large buoyancy force, which offers possibilities to construct novel aquatic devices, might have important potential applications.



**Fig. 10** The optical images of the superhydrophobic sample: (a) the water droplet on the superhydrophobic surface and (b) floating on the surface of the water.

## Conclusions

In summary, a superhydrophobic surface was successfully fabricated on copper substrates via a facile, simple, time-saving process in this study. The fabrication process was easily controllable by varying the reaction conditions. What is more, generated CuO-Cu<sub>3</sub>Pt/Cu micro-nano binary architectures without further modification of additional low-surface-energy substance had long-term stability and durability. Furthermore, the growth mechanism of CuO-Cu<sub>3</sub>Pt/Cu architectures was proposed in detail. The superhydrophobic surface with large buoyancy force might have potential practical application. This facile and low-cost application method is not only favorable for the promising applications of copper material for various industrial items, but also offer an effective strategy to fabricate superhydrophobic surface on other metallic materials.

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## Notes and references

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