Effects of oxidation processes and microstructures on the hydrophilicity of copper surface

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ABSTRACT

A rapid, economical method to achieve superhydrophilic copper surfaces is proposed in the present study. Different microstructures could be obtained by different oxidation processes, namely, hydrogen peroxide (H_2O_2) oxidation, thermal oxidation, and their combination, and the effects of the various processes and microstructures on the hydrophilicity were investigated. The results revealed that an optimal oxidation time and solution concentration enable copper surfaces have superhydrophilicity. The superhydrophilicity, with contact angle close to 0°, was attained on a copper plate surface first by thermal oxidation and then by H_2O_2 oxidation. However, for a porous wick surface, only H_2O_2 oxidation is required to achieve excellent superhydrophilicity.

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1. Introduction

Recently, the wettability of material surfaces has attracted considerable attention due to its importance in both basic research and practical applications. Superhydrophilicity is an extreme wetting property wherein a water droplet can completely spread over the surfaces with a contact angle (CA) equal or close to 0° [1]. Some scholars considered surfaces superhydrophilic when they have a CA < 10° [2]. Due to their unique wetting characteristics, superhydrophilic surfaces have potential in the fields of anti-fogging coatings [3], oil-water separation [4], heat transfer [5], and other applications.

Surface chemical composition and roughness are the two main factors affecting surface wettability. Some authors suggested that superhydrophilicity is mainly caused by surface hydroxyl, carboxyl, and other polar groups gathering on the surface [6]. Others suggested that the surface microstructure is an important factor in determining superhydrophilicity [7]. Various microstructures on solid surfaces, such as nanowires [8], nanorods [9], and nanofilms [10], can be obtained using different methods. There are currently many methods for preparing superhydrophilic surfaces, such as electrochemical methods [11], sol-gel methods [12], replica molding [13], and layer-by-layer assembly [14].

Copper is an important industrial material. Although many methods can be utilized to prepare superhydrophilic copper surfaces, they often involve expensive equipments or complex processes, and producing large-area superhydrophilic surfaces is difficult. Herein, a rapid, economical method that achieves superhydrophilicity on copper surfaces is presented. The effects of various microstructures on the hydrophilicity were studied using H_2O_2 oxidation, thermal oxidation, or their combination.

2. Experimental procedures and methods

Two types of copper materials were used. One was a smooth copper plate polished with 2000 mesh sandpaper, and the other consisted in sintered porous wicks using copper powder with a particle diameter of 88 μm. The porous wicks were sintered in a furnace at a temperature of 850 °C for 3 h. Before the experiments, the copper plate and porous wick were first rinsed with deionized water and then dried in an oven at 60 °C for about 10 min for subsequent use.

2.1. H_2O_2 oxidation

First, the polished copper plates were immersed in a HNO_3 solution at a concentration of 15% by weight (i.e., 15 wt%) for 15 min to remove the oxide film from the surface and then rinsed with deionized water and dried in the oven for 10 min at 60 °C. Then, the samples were divided into two groups. One group was immersed in various H_2O_2 solutions for 8 h at concentrations of 3, 6, 9, 15, and 30 wt%. Another group was immersed in a 30 wt% H_2O_2 solution

for 2, 4, 8, 16, and 24 h to study the effects of immersion time (t). After the copper plates were removed, the samples were prepared using a series of processes, such as rinsing and drying.

The results of the above study indicated that 30 wt% and t = 8 h are the optimal H_2O_2 solution concentration and immersion time, respectively. Thus, the sintered porous wicks were directly immersed in a H_2O_2 solution of 30 wt% concentration for 8 h to modify the surfaces.

If these prepared superhydrophilic surfaces were kept in pure water or a vacuum, the superhydrophilicity could last for several months. If they were in clean air, the superhydrophilicity could last for 2–3 days. However, if the air was not clean, the superhydrophilicity quickly disappeared within 3 h.

2.2. Thermal oxidation

The copper plates were heated in the sintering furnace under air. The temperature in the furnace was ramped up over a period of 50 min and maintained at 300 °C for 1.5 h. Then, the heating elements were turned off, and the furnace was cooled under the natural convection conditions. The samples were not taken out until their temperatures were close to room temperature in the furnace, which took about 4 h.

2.3. Compound oxidation

To study the effects of compound oxidation on the hydrophilicity of the copper surface, thermal oxidation and H_2O_2 oxidation were combined to modify the copper surface. First, according to the method in Section 2.1, the copper plate was oxidized in a 30 wt% H_2O_2 solution for 8 h, then thermal oxidation was carried out following the steps in Section 2.2, which was called H_2O_2 + - thermal oxidation. Conversely, these two oxidation processes were reversed for some samples, keeping the wt% and t unchanged, which was called thermal + H_2O_2 oxidation.

Water droplets (5 μl) were dripped onto samples oxidized under different conditions to measure their CAs. The microstructural morphology of the copper surfaces was characterized by scanning electron microscopy (SEM) and atomic force microscope (AFM).

3. Results and discussion

Fig. 1(a) shows the effects of the H_2O_2 solution concentrations on the contact angles (t = 8 h). In the figure, the CAs decrease with the increase in the H_2O_2 concentrations. At low H_2O_2 concentrations, the decreases in CAs are more drastic with increasing concentrations. At high H_2O_2 concentrations ($\geq$9 wt%), the CAs tend to increase more gently. Fig. 1(b–d) shows SEM images of copper plate surfaces oxidized by H_2O_2 at different concentrations. As shown in Fig. 1(b), when the concentration is low, 5 wt%, the surface microstructures exhibit clusters, and the corresponding CA is 32.6°. The clustered structures gradually change into nanosheets with increasing H_2O_2 concentrations (see Fig. 1(c), CA = 11.8°). In particular, the nanosheets become thinner and more densely packed with further increase in concentration (Fig. 1(d)), in which each sheet has a thickness of ~10 nm. Thus, this copper plate exhibited higher surface roughness, and its hydrophilicity was improved. At 30 wt% H_2O_2 and t = 8 h, the CA was about 5.7°.

Fig. 2 shows the effects of the immersion time in 30 wt% H_2O_2 solution on the contact angles and microstructures. As shown in Fig. 2(a), the CAs rapidly decrease with the increases in t for t < 4 h and then gradually decrease for 4 h < t < 8 h. For t > 8 h, the immersion time has little effect. Fig. 2(b) shows many clusters on the copper plate surface for t = 2 h. Each cluster includes many small oxides nanosheets. With the increase in t, the clusters converted into sheets, and gradually became smaller (Fig. 2(c)). At
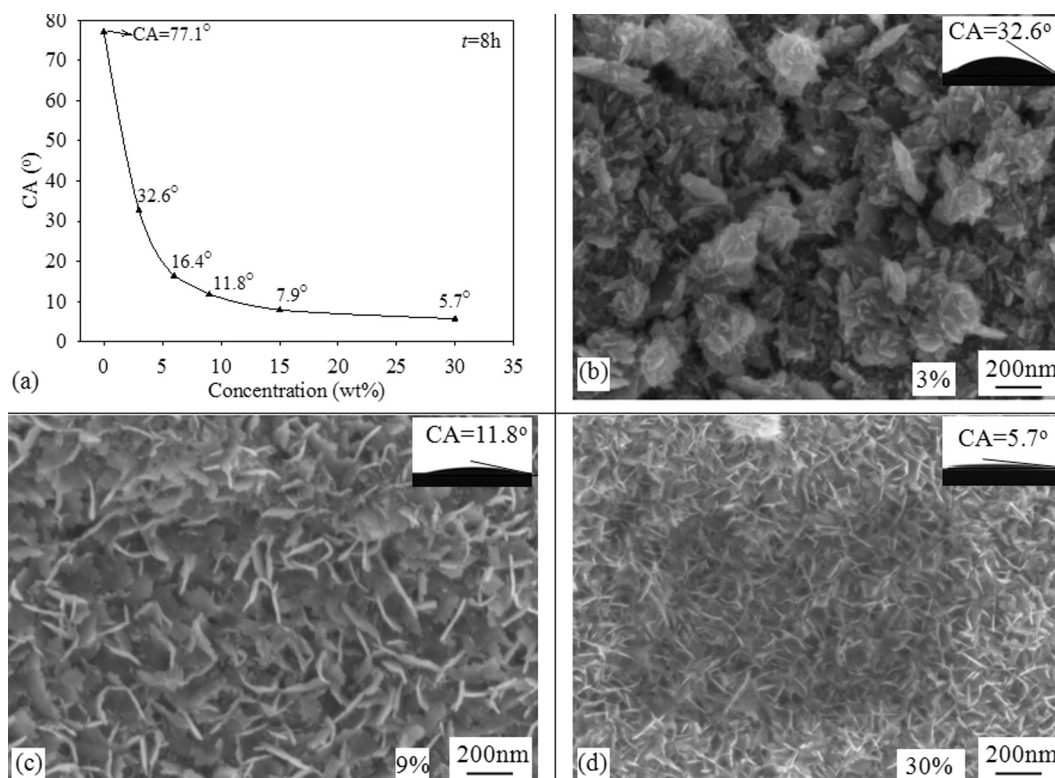

Fig. 1. Effects of the H_2O_2 concentration on the contact angles and microstructures.
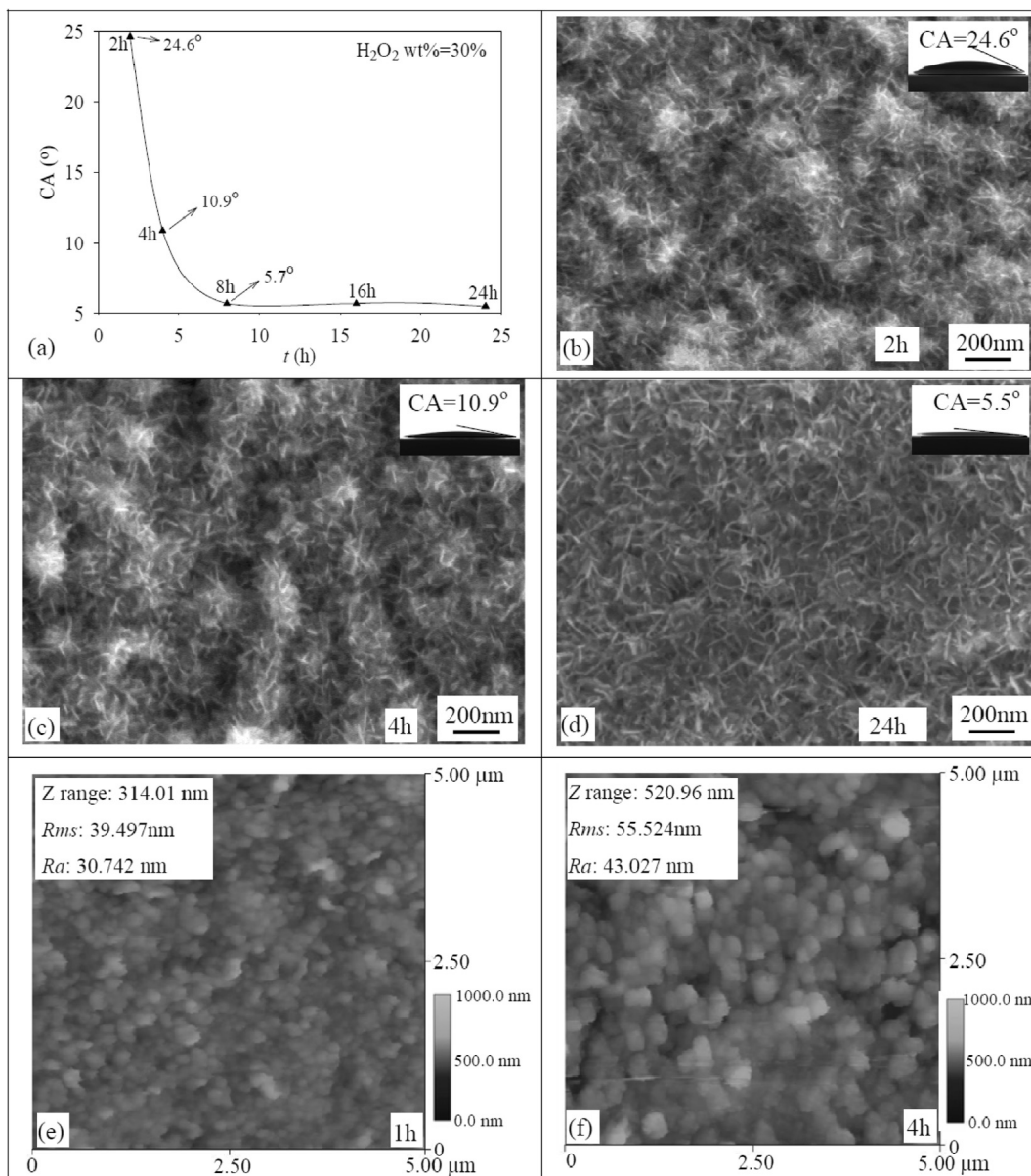
Fig. 2. Effects of the immersion time on the contact angles and microstructures.

t = 24 h, the clusters almost disappeared, and only nanosheets existed on the surface (Fig. 2(d)), which exhibited a CA of 5.5°. Fig. 2(e, f) present AFM images for t = 1 and 4 h, respectively, revealing the relationship between CAs and surface roughness. The roughness increases with increasing t, and the CA increases with increasing roughness. According to the Wenzel model [15], for a hydrophilic surface, the surface wettability can be enhanced by increasing the surface roughness.

Fig. 3 shows the microstructures of the copper plate surfaces after different oxidation treatments and their corresponding contact angles. As shown in Fig. 3(a), after thermal oxidation, the surface was covered with a layer of oxides. The oxides were crystalline with a size of ~100 nm and many gaps between them (CA = 37.1°). The micromorphology of the copper plate surface treated by H_2O_2 + thermal oxidation (Fig. 3(b)) is similar to that in Fig. 3(a), but with smaller, more densely packed features (~30 nm), and the corresponding CA was 11.3°. After H_2O_2 oxidation (see Fig. 3 (c)), the surface was covered with many oxides nanosheets, and the contact angle was 5.7°. After thermal + H_2O_2 oxidation, the surface was covered with a layer of flower-shaped oxides. Each flower

was made up of many nanosheets, and the corresponding CA was approaching 0°. Thus, the surface with flower-like structures exhibited the most improved superhydrophilicity of the three different surface structures, and the nanosheets structures are more effective than globular structures for wettability. To possess good superhydrophilicity, the surface structures should be smaller, thinner, more densely packed, and more compact to improve surface roughness. In addition, gaps are required to produce sufficient capillary suction to spread the liquid as quickly as possible.

Fig. 4 shows the microstructures on the surface of sintered porous wick. In Fig. 4(a), many copper particles have been sintered together. The surface of the sintered wick before oxidation is relatively smooth. However, after H_2O_2 oxidation, the surface is rough and covered with a layer of oxides (Fig. 4(b)). Fig. 4(c, d) shows higher magnification images of the surface in Fig. 4(b), wherein the structures of oxides are similar to those on the copper plate surface treated using the same oxidation conditions. Fig. 4(d) shows leaf-like structures with a size of ~100 nm and a thickness of ~5 nm. Thus, the interaction between the porosity and surface modification through H_2O_2 oxidation imparted
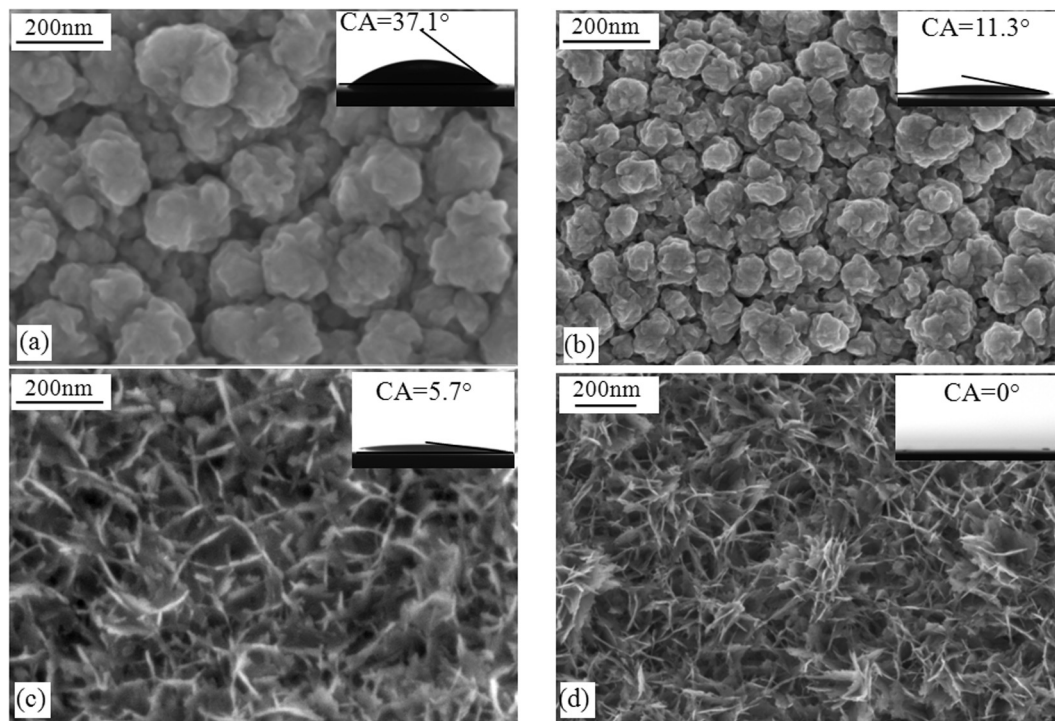
Fig. 3. SEM images and corresponding contact angles after (a) thermal oxidation, (b) H_2O_2 + thermal oxidation, (c) H_2O_2 oxidation, (d) thermal + H_2O_2 oxidation.
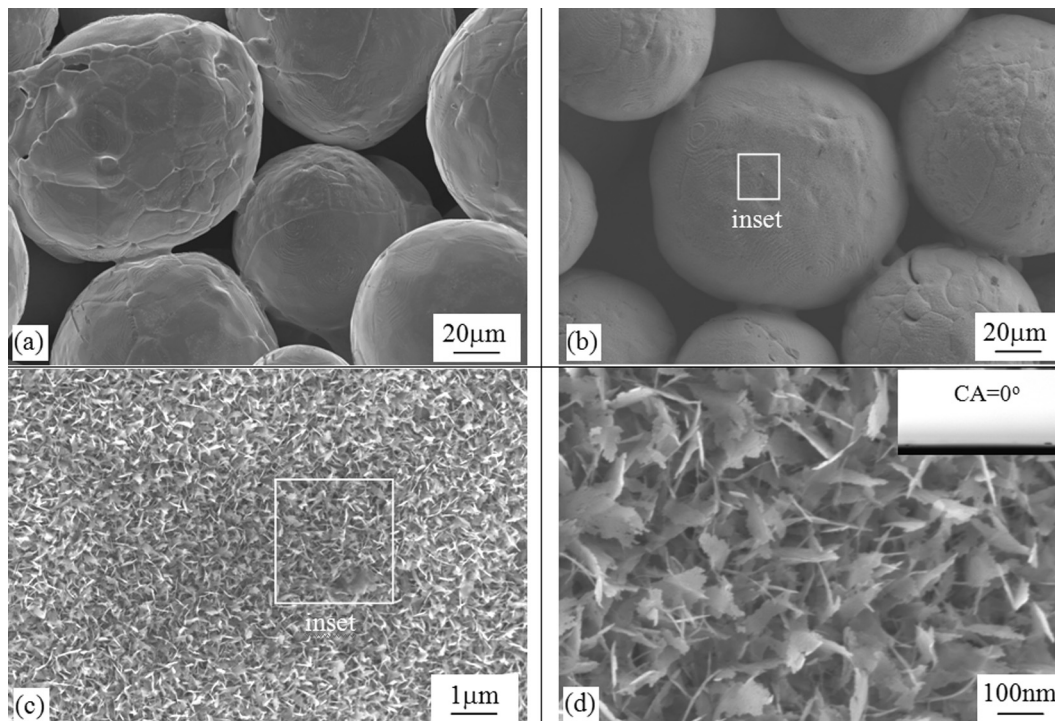

Fig. 4. SEM images of sintered porous wick (a) before and (b–d) after H_2O_2 oxidation.

sintered porous wick with superhydrophilicity. The corresponding CA approaches 0°.

4. Conclusions

Superhydrophilic surfaces can be produced on a copper plate surface by the combination of thermal and H_2O_2 oxidations. In con-

trast, for sintered porous wicks, only H_2O_2 oxidation is required to achieve excellent superhydrophilicity on the copper surfaces. For the H_2O_2 oxidation process, 30 wt% and $t = 8$ h are the optimized parameters for preparing superhydrophilic surfaces. Flower-like structures with many nanosheets are more effective at improving the hydrophilicity of surfaces than pure sheet and globular structures.

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