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Fabrication of non-flaking, superhydrophobic surfaces using a one-step solution-immersion process on copper foams

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ABSTRACT

Non-flaking superhydrophobic surfaces were prepared using a simple one-step solution-immersion process on commercially obtained copper foam substrates. Copper foams were immersed in a 0.05 M ethanolic stearic acid solution at room temperature for several days. This formed coverage of copper stearate with micro- and nano-scale hierarchical surface morphology. The surface of the copper foam after 4 days of immersion demonstrates superhydrophobicity with a water contact angle of 156°. A sliding angel of 4° for a 5 μL droplet indicates excellent non-sticking behavior. Compared with a flat copper plate, the superhydrophobic surfaces based on copper foams are much more robust and mechanically stable. This work provides a promising strategy for scalable fabrication of superhydrophobic surfaces on 3D porous structures.

1. Introduction

Some biological materials have special wettability. Artificial lotus-leaf-like superhydrophobic surfaces have a water contact angle (CA) greater than 150° and a sliding angle (SA) of less than 10°. Interdisciplinary fields including biology, physics, chemistry, materials science and engineering thermal physics have investigated such materials [1–4]. Ongoing efforts have been devoted to exploring the fabrication of superhydrophobic surfaces for practical applications such as oil-water separation [5], friction reduction [6], corrosion prevention [7], highly functional microfluidic devices [8–10], and drop-wise condensation [11]. As a widely used industrial material, copper is attractive for its high electrical and thermal conductivity, mechanical workability, and malleability; however, it is susceptible to corrosion. It has recently been reported that forming superhydrophobic films on copper surfaces can effectively improve their corrosion resistance [12–14]. So far, copper with superhydrophobic surfaces has been fabricated using various strategies. These techniques include electroless galvanic deposition [15], sol–gel processing [16], surface oxidation [17], electro-deposition [18], electro-plating [19], and etching [20]. Both micro- and nano-scale hierarchical structures and low-surface-energy materials are vital to the superhydrophobicity of a surface. As such, most fabrication procedures are divided as two steps where the hierarchical roughness is created first and subsequent modifications include low-surface-energy coatings.

The one-step solution-immersion method is one of the simplest approaches to fabricate superhydrophobic surfaces on various substrates, including zinc, silicon and steel [21]. The first report of a one-step solution-immersion process to create superhydrophobic films on copper substrates was by Jiang and co-workers [22]. In their work, hierarchical roughness and low-surface-energy were obtained simultaneously by immersing a copper plate into a fatty acid solution. Direct-current electro-deposition on copper substrates using ethanol solutions of *n*-tetradecanoic acid [23] or stearic acid [24] as electrolytes and spray-coating methods using copper stearate [25] can shorten the preparation time needed for the one-step processes. However, these approaches require additional processing steps and control of other key parameters, making them more complicated than the simple solution-immersion method. Because of its relatively few experimental parameters and long preparation time, the one-step solution-immersion method is particularly appropriate for exploring how the surface morphology evolves with preparation time, and allows us to capture details that might perhaps not be observed if we used faster approaches.

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The as-prepared superhydrophobic films are composed of copper fatty acid carboxylates. As there is a phase interface between the substrate and the superhydrophobic film, heat or external mechanical forces may affect the robustness of the films. However, stability is a key factor in developing the practical use of superhydrophobic films. Further investigation into increasing film stability should be carried out. Discontinuous surfaces can allow stress to be released at the edges and prevent heterogeneous layers from detaching [26]. Using copper with a discontinuous surface (rather than a flat one) as the substrate in the one-step solution-immersion approach may allow formation of a superhydrophobic surface with more robust adhesion to the substrate. 3D porous copper films have a discontinuous copper surface and have been prepared using a hydrogen bubble dynamic template. Superhydrophobicity after treatment with *n*-hendecane thiol has been demonstrated [27]. Open cell copper metal foams are a commercial obtained 3D porous material widely utilized in flat heat pipes and thermal spreaders because of its high surface area and capillary pumping capacity [28]. And their wetting properties, such as wettability transition, have been studied intensively [29]. If they can be applied to the fabrication of superhydrophobic surfaces, the preparation of 3D porous films can be simplified.

In this study, we selected copper metal foam as the substrate for fabricating a superhydrophobic surface. The superhydrophobic surface is prepared by immersing copper foam into a ethanol solution of stearate acid, with chemical reactions occurring between the copper and stearate acid. In contrast to the superhydrophobic surfaces more commonly formed on flat copper plates, the superhydrophobic surfaces prepared on the copper foam show a large surface area and non-flaking copper stearate coverage of the micro- and nano-scale hierarchical morphology. An abrasion test shows that the superhydrophobicity of the copper foam surface is more stable than that of the flat copper plate.

2. Experimental

Copper foams of 99.9% purity, 0.88 porosity, with 90 pores per inch (PPI) and a thickness of 2.5 mm were commercially obtained. Experimental results testing the copper plates (99.9% purity, 0.8 mm thickness) were compared with that of the copper foam samples. In this study, the copper foams and plates were cut into square pieces with side lengths of 2.0 cm. In the cleaning procedure, the copper foams and plates were sequentially washed with acetone, ethanol, 2 M HCl, and deionized (DI) water in an ultrasonic bath followed by drying with nitrogen gas. The cleaned substrates were then immersed in an ethanolic stearic acid solution (0.05 M) at room temperature. They were finally rinsed thoroughly with ethanol and DI water, and then dried in air.

Abrasion tests were carried out as described in Refs. [20,30,31]. A copper substrate with a superhydrophobic surface was subjected to a pressure of 5 kPa. As cotton fibers can be hooked by the copper foam, common A4 paper was used as a sliding base rather than the cotton fabric used in the reference.

Field-emission scanning electron microscope (FE-SEM) images were obtained at 10 kV using LEO 1530 FE-SEM. Fourier transform IR (FTIR) data were collected on a Varian 3100 instrument using the KBr method as the transmission mode. Some powder was scraped from the resultant surfaces, and mixed with KBr to make a palette. X-ray photoelectron spectroscopy (XPS) data were obtained on PHI-5300 ESCA with the C 1s reference at 284.8 eV. Water CAs and SAs were measured by a contact angle meter at room temperature (OCA15EC, DataPhysics Instruments GmbH, Germany). At least five different sections were tested for each sample. 5 μL was used for all individual water droplets.

3. Results and discussion

As shown in Fig. 1(a), the bare copper foam has a 3D porous frame with pore size of less than 400 μm. Its surface is relatively flat, without any deposits, as can be seen from the magnified FE-SEM image of the copper skeleton (inset in Fig. 1(a)). Fig. 1(b)–(g) respectively illustrate the surface morphologies of the copper foams prepared with immersion times of 4 h, 2 days, and 4 days. The panoramic surface morphology of a 4 h immersion time sample (Fig. 1(b)) is similar to that of the bare copper foam, in that the outline of the copper foam skeleton is still smooth. However, there is also indication of many self-assembled clusters of a copper compound. This compound was later confirmed to be copper stearate, and the coverage of the clusters on the substrate is not dense (Fig. 1(c)). The inset in Fig. 1(c) gives a high-magnification image of the self-assembled cluster, showing that the folded copper stearate nanosheets are entangled with each other. When the immersion time increased to 2 days, the outline of the skeleton became rougher, as shown in Fig. 1(d) and the pore size was reduced as the result of copper stearate cluster growth. The magnified FE-SEM images in Fig. 1(e) reveal that dense clusters are formed and completely cover the substrate. For immersion times of 4 days, the skeleton of the 3D porous structure became thicker and rougher, and the pore size decreased significantly to ∼100 μm (Fig. 1(f)). The surface is now heavily covered with the self-assembled clusters. Flowerlike self-assembled clusters are also observed to have formed on top of previously laid-down cluster layers, as shown in Fig. 1(g). These cluster-flowers with the scale of about 10–20 μm are composed of nanosheets, separated by a few microns (within one cluster-flower); adjacent cluster-flowers are also separated by several-micron gaps. This indicates that hierarchical micro-/nano-structures can be formed on the surface of the copper foams. Fig. 1(h) shows a photograph of the complete blue coating that forms on the copper foam after immersion for 4 days.

The one-step solution-immersion process was also carried out on flat copper plates. To make a straightforward comparison, the surface morphologies of copper plates, prepared using the same immersion times as those used to treat the copper foams shown in Fig. 1, were characterized by FE-SEM, and the images are presented in Fig. 2. Fig. 2(a) shows that after an immersion time of 4 h, the copper plate is sparsely covered by some deposits. These deposits are separated, flower-like clusters, about 15 μm across (Fig. 2(b)). When the immersion time increased to 2 days, more and more deposits were formed, but some of them flaked off, as shown in Fig. 2(c) and (d). Even when the immersion time was increased to 4 days, a continuous coating was not formed (Fig. 2(e) and (f)). This is also apparent from the photograph of the copper plate prepared using an immersion time of 4 days (Fig. 2(g)). In contrast to the complete blue coating on the copper foam shown in Fig. 1(h), the coverage of the copper plate substrate is incomplete, and white. The different colors of the coatings on the copper foam and copper plate can be attributed to their different thicknesses.

Copper carboxylate has been reported to be produced by utilizing the chemical reactions between copper and fatty acid in the ethanol solution [22,24]. Cu^{2+} ions are released from the substrates through the oxidation of copper and immediately react with stearic acid molecules to form copper stearate. The reaction can be expressed as follows:

$$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O \quad (1)$$

$$Cu^{2+} + 2CH_3(CH_2)_{16}COOH \rightarrow Cu[CH_3(CH_2)_{16}COO]_2 + 2H^+ \quad (2)$$

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