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A novel fabrication of a superhydrophobic surface with highly similar hierarchical structure of the lotus leaf on a copper sheet

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ABSTRACT

A novel and facile avenue was developed to successfully fabricate a regular hierarchical surface structure on a copper sheet via the combination of polydimethylsiloxane (PDMS) template and chemical etching method in this paper. The as-prepared hierarchical surface structure was comprised of uniform-sized microprotrusions and nanostructures which was similar to the natural lotus leaf. After modified by stearic acid, the surface was covered with a layer of hydrophobic chemical groups and became superhydrophobic. The values of its water contact angle and sliding angle were about 153° and 7°, respectively. Its wettability kept rather stable when it was exposed to humid conditions for 3 months. This study provides a new way to fabricate uniform surface microstructures that are highly similar to natural biological surfaces on metal materials.

1. Introduction

Superhydrophobicity with water contact angle higher than 150° and sliding angle less than 10° was discovered on the surface of lotus leaf in nature initially; then many scientists made great efforts to do a lot of investigations and found that superhydrophobicity was governed by two key factors namely low surface energy and rough surface topography [1–3]. In past years, superhydrophobicity has attracted increasing attention due to its importance in fundamental research and many potential application fields such as self-cleaning, anti-corrosion, and anti-frosting [4–8]. A variety of methods have been developed to mimic the lotus leaf surface for the fabrication of many artificial superhydrophobic surfaces [9–13]. However, most of them only mimicked the superhydrophobic property of lotus leaf, and few precisely mimicked its beautiful hierarchical surface structure. Despite the fact that some previous papers reported the artificial dual-scale superhydrophobic surface structures which were highly similar to the lotus leaf via template method or soft lithography technique, they were all based on resins or soft materials [14–19]. For example, in our previous work, we fabricated a highly similar surface microstructure with lotus leaf on a poly(vinyl chloride) film by nanocasting method using natural lotus leaf as template [20]. However, to the best of our knowledge, there is still no report about the fabrication of such highly similar lotus-leaf-like surface structure on metal materials such as copper sheet.

Copper is an important metal material used in many industrial fields and our daily lives [21,22]. Superhydrophobicity can endow the copper with special properties such as anti-frosting, anti-corrosion, and minimizing the resistance to flow in microfluidic devices. Thus, superhydrophobic coppers have greater potential applications even under bad conditions [5,22–24]. Although many techniques, such as solution immersion [25,26], electrochemical deposition [27,28], graft polymerization [29] and sol–gel method and [30–33], have been proposed to generate superhydrophobic surfaces on copper in the recent years, they cannot precisely prepare a surface microstructure which is very similar to the natural lotus leaf on a copper sheet.

In this work, for the first time, we present a novel method to fabricate a superhydrophobic surface with highly similar micro- and nanostructures of lotus leaf on a copper sheet via combining polydimethylsiloxane (PDMS) template with chemical etching technology. The fabrication process is very simple, efficient, inexpensive and environmentally friendly. Moreover, this method can

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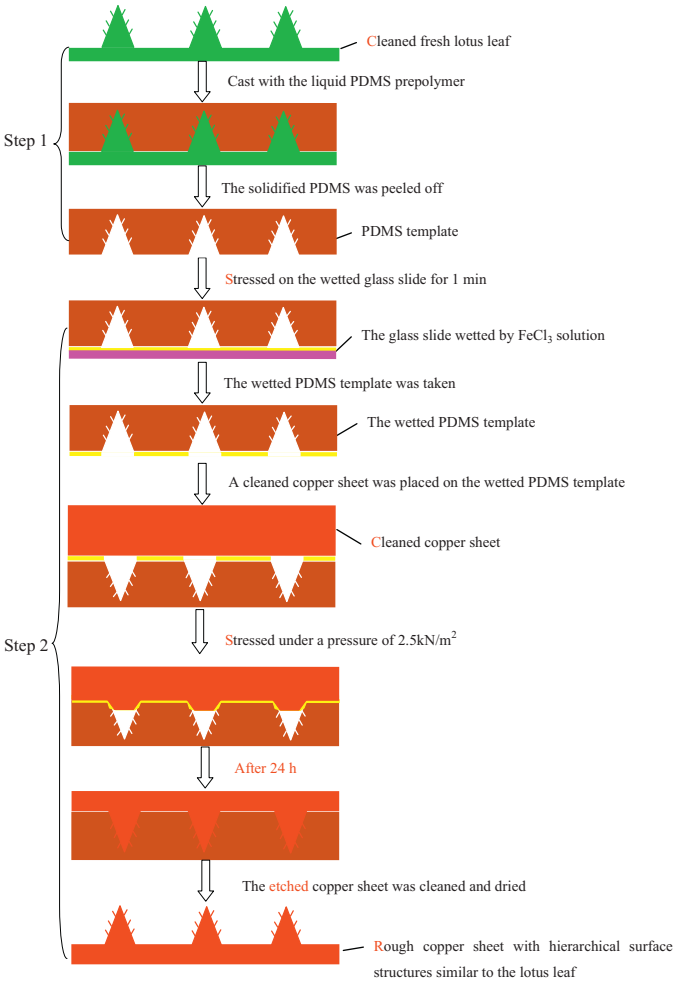

Fig. 1. Procedure scheme for fabricating the lotus-leaf-like surface structures.

also be utilized to fabricate many kinds of microstructures which are highly similar to other natural superhydrophobic surfaces such as wings of cicada on metal materials.

2. Experimental

2.1. Materials

In these experiments, 36% hydrochloric acid and 95% ethanol were obtained from Changsha Huihong Chemical Reagent Plant of China. Iron trichloride ($FeCl_3$) and stearic acid were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. The copper sheets (purity > 99.5%), prepolymer of PDMS and its catalyzers were provided by Shanghai Jing Xi Chemical Technology Co., Ltd.

2.2. Preparation of PDMS template

The PDMS template was prepared as sketched in step 1 of Fig. 1. Firstly, a fresh lotus leaf was cleaned by water for 5 min to remove the contaminant deposited on its surface. Secondly, the prepolymer of PDMS and its catalyzers were mixed and stirred for 10 min. Then, the liquid mixture was cast on the cleaned surface of lotus leaf. After curing at room temperature for 24 h, the solidified PDMS was peeled off the lotus leaf surface, and a porous PDMS template with a complementary topographic surface structure of the lotus leaf was obtained.

2.3. Fabrication of superhydrophobic copper

Firstly, 10 g $FeCl_3$ was dissolved in 50 ml ethanol to form uniform solution. Subsequently, a copper sheet and a glass slide were all ultrasonically cleaned by hydrochloric acid solution for 10 min and ethanol for 15 min. Then, the glass slide was vertically immersed in the $FeCl_3$ solution for 20 min. After vertically drawn out from the solution, the glass slide was horizontally placed on a desk, and then the porous PDMS template was wetted with a thin layer of $FeCl_3$ solution by gently pressing it on the wetted glass slide for 1 min. Next, the cleaned copper sheet was covered on the wetted PDMS template and a moderate pressure of about 2.5 kN/m^2 was exerted on them for 24 h. As a result, a rough hierarchical surface structure, which was highly similar to that of the lotus leaf surface, was obtained on the copper sheet. The schematic diagram of the fabrication process for the lotus-leaf-like hierarchical surface structure is shown in step 2 of Fig. 1. Finally, the rough copper sheet with the lotus-leaf-like hierarchical surface structure was vertically immersed in a stearic acid–ethanol solution (0.004 M) for 45 min at room temperature, and then the rough copper sheet was vertically drawn out. After drying for 1 h at room temperature, a superhydrophobic copper sheet with highly similar hierarchical surface structure of lotus leaf was obtained.

2.4. Characterization

The surface morphologies of the samples were observed by scanning electron microscopy (SEM) of HITACHI S-3000N and FEI Quanta 200. The chemical compositions were determined by X-ray diffractometry (XRD, D8 Advanced) and Fourier Transform Infrared spectroscopy (FTIR, Nicolet 380). The contact angles were measured by sessile drop method with a Dataphysics OCA20 instrument equipped with a CCD camera at ambient temperature. The sliding angle was measured by tilting the sample stage and recorded when the water droplet began to move in the downhill direction.

3. Results and discussion

In order to fabricate a beautiful highly similar surface microstructure of the lotus leaf on a copper sheet, we designed a novel method which included two steps: preparation of PDMS template with a negative structure of lotus leaf surface and fabrication of lotus-leaf-like surface structure on a copper sheet as shown in Fig. 1. From Fig. 1, we know that the first step is to fabricate PDMS template using natural lotus leaf as original template (shown in step 1 of Fig. 1), which is similar to our previous work [20]. It was reported that PDMS was one of the most optimized materials to prepare complementary topographic surface structure of the lotus leaf because the prepolymer of PDMS flowed easily and could permeate into the micro- and nanostructures of lotus leaf due to its low viscosity and surface tension, and the solidified PDMS was a flexible material and could be easily peeled off the lotus leaf [34]. Therefore, PDMS was chosen as the material to precisely prepare the complementary topographic surface structure of the lotus leaf in this experiment. In step 2 (shown in Fig. 1), the top surface of PDMS template was wetted with a thin layer $FeCl_3$ solution by pressing it on a wetted glass slide. Considering that the PDMS template was hydrophobic, the ethanol was selected as the solvent of $FeCl_3$ to increase the wettability of $FeCl_3$ solution on PDMS template.

Fig. 2a shows the SEM image of the lotus leaf surface, and Fig. 2b is the higher magnification SEM image of a protrusion on the surface of lotus leaf. From Fig. 2a and b, we can see that the surface structure of the lotus leaf is comprised of many microprotrusions with the diameter ranging from 5 to 10 μm, and the interval distances among the adjacent microprotrusions are between 10 and 40 μm

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