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A novel combination approach for the preparation of superhydrophobic surface on copper and the consequent corrosion resistance

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ABSTRACT

In this paper, superhydrophobic surfaces on copper substrates are prepared by combining the etching and calcination treatment processes. The surface morphologies, wettability, chemical composition and corrosion resistance are characterized by means of scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), water contact angle, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The achieved superhydrophobic surface has a contact angle as high as 157.6° and a persistent corrosion resistance in a 3.5 wt.% NaCl aqueous solution. This method could provide an effective route to fabricate superhydrophobic surface with inhibitive and self-cleaning properties for various applications.

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1. Introduction

Copper (Cu), due to its good electrical and thermal conductivities, and high mechanical properties [1,2], has been widely used in industrial, military, life and other areas, such as condenser and heat exchanger on the ship, various instruments of the elastic element, tubing, pump, medical equipment, optical instruments, decorative materials, metal artwork and a variety of household appliances [3–5]. However, hydroxides and fluorides could be easily formed on copper in air, some non-oxidizing acid (hydrochloric acid, sulfuric acid, etc.), salt solutions and various organic acids [6]. Thus, the corrosion problems of copper have attracted great attention [7–9]. Superhydrophobic film is very effective to improve the corrosion resistance of copper [10]. The film could increase the copper surface contact angle with water, and prevent the corrosive medium from contacting with the copper surface.

In nature, there are many different types of organisms with the special surface wettability [11–13]. For example, lotus leaves exhibit high superhydrophobic and self-cleaning function, which is known as the "lotus effect". The Micro-nano papillae structure on the surface is responsible for the superhydrophobic properties of lotus leaves [14]. It is expected that special hierarchical micro/nano structures are required to fabricate superhydrophobic surfaces [15,16]. To further improve the quality of superhydrophobic surfaces, low surface energy material modifications to the rough surface may be essential [17]. For the past decade, a lot of methods including template [18], chemical etching [19], oxidation [20], electrodeposition [21,22], and sol-gel methods [23,24], have been used to produce special hierarchical micro/nano structures on metal substrates. For example, Yuan et al. [18] fabricated a regular multi-scale hierarchical structure on a copper foil by combing the template and etching approaching using the back surface of fresh bamboo leaf as the original template. The further treatment by stearic acid resulted in the superhydrophobic property with the water contact angle of 160.0°. The corrosion resistance of this sample, however, has not been tested.

In this work, a facile and low-cost method is developed to fabricate superhydrophobic surfaces on the copper substrate. It involves chemical etching in an ammonia solution and consequent calcination in air at 340 °C. The surface is then further modified in an ethanol solution containing stearic acid [25]. This superhydrophobic surface shows high corrosion resistance in a 3.5 wt.% NaCl solution.

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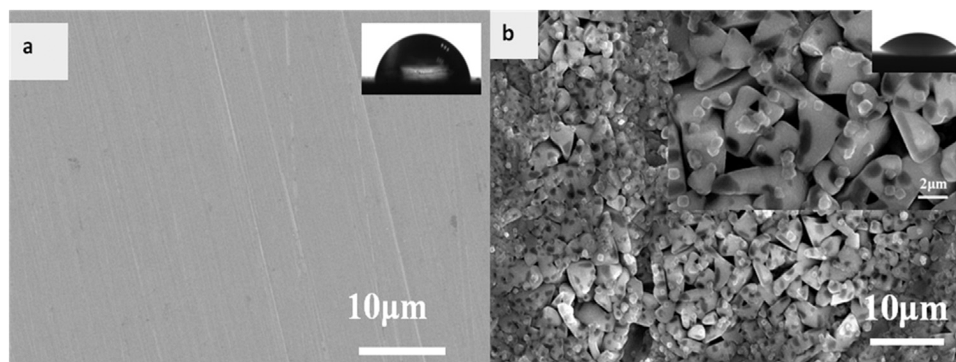


Fig. 1. SEM images of bare copper (a) and etched copper with 10 wt.% ammonia solution (b).

Table 1
Polarization parameters of bare copper, etched copper with 10 wt.% ammonia solution for 20 h, calcined treatment copper at 340 °C for 10 min in air and superhydrophobic copper modified with an ethanol solution of stearic acid for 3 h in 3.5 wt.% NaCl solution.

Samples	E_{corr} (mV *vs.* SCE)	β_a (mV dec^{-1})	i_{corr} (A cm^{-2})	η_p (%)
Bare	−352	104.28	4.318×10^{-6}	\
Etched	−287	58.2	6.981×10^{-7}	83.83
Calcined	−277	93.3	1.047×10^{-7}	97.57
Superhydrophobic	−238	52.73	2.354×10^{-8}	99.45

2. Experiment

2.1. Materials

Cu (≥99.5 wt.%) foils were purchased from Xiangwei Machinery Co., LTD., YangZhou, China. All chemical reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received.

2.2. Specimen preparation

Copper samples (50 mm × 10 mm × 3 mm) and electrodes (10 mm × 10 mm) were abraded with different grades of emery paper (1#, 3#, 6#), cleaned ultrasonically with alcohol and deionized water respectively, and dried via Blast Oven. The dried copper and copper electrode were etched with a 50 mL ammonia solution (10 wt.%) at room temperature for 20 h, and then the samples and electrodes were washed with alcohol and deionized water, and dried again. After that, these samples and electrodes were calcined in air at 340 °C for 10 min.

2.3. Superhydrophobic surface preparation

The copper surfaces which had been etched and calcined were modified in a 0.1 mol/L ethanol solution of stearic acid at room temperature for 3 h. The obtained superhydrophobic copper samples were washed with alcohol and deionized water, and then dried for further characterization.

2.4. Characterization

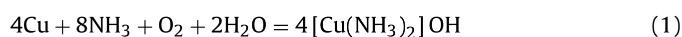
The surface morphologies and chemical compositions of the samples were investigated with a scanning electron microscopy (SEM, SU-1500, Hitachi, Japan), and an X-ray diffraction (XRD, Cu Kα radiation, Bruker, D8 Advance, Germany). The contact angle (CA) was measured by K100-MK2 Almighty Tension Meter (KRUSS Germany), and the shape of water drops dripping on sample surface was tested with a JC 2000C1 CA system at ambient temperature.

The electrochemical corrosion behavior was conducted in a 3.5 wt.% NaCl aqueous solution at room temperature via an electrochemical workstation (CHI 660E, CH Instruments Inc.). The workstation was equipped with a standard three-electrode system: the Pt electrode was used as the counter electrode, and the calomel electrode (SCE) and the copper sample were used as the reference electrode and working electrode, respectively. Before electrochemical experiments, these copper samples with an area of 1 cm^2 were immersed in the NaCl solution for 1000 s to achieve a stable open circuit potential (OCP vs. Ag/AgCl). The potentiodynamic polarization curves were measured between −0.15 V and 0.15 V (vs. OCP) with the scanning rate of 1 mV/s. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of 100 kHz–0.05 Hz at the OCP with the amplitude of voltage of 5 mV.

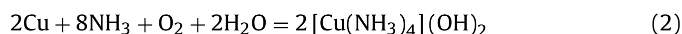
3. Results and discussion

3.1. Surface morphology

The geometrical characteristics of the surfaces before and after etching, calcining and modification were investigated by SEM images. Fig. 1a shows the morphology of Cu surface without any treatment. It is very smooth with the CA of 76.5°. After the etching treatment (20 h in 10 wt.% ammonia solution), there are irregular shaped cell-like projections with the depth of several micrometers in the surface. This surface shows a very small CA of 21° (Fig. 1b). The Cu atoms on the surface may be dissolved in the ammonia solution via reactions (1) and (2):



$$4Cu + 8NH_3 + O_2 + 2H_2O = 4\,[Cu(NH_3)_2]\,OH \qquad (1)$$



$$2Cu + 8NH_3 + O_2 + 2H_2O = 2\,[Cu(NH_3)_4]\,(OH)_2 \qquad (2)$$

After the calcining treatment, a more rough structure can be formed on the substrate. Vertically oriented peak-like projections appears to be the results of the etching process (Fig. 2a). These peak-like projections show nearly uniform size with approximate 600 nanometers in thickness and two micrometers in width (Fig. 2b). The Cu ion diffusion through the grain boundaries results in more irregular hump of Cu layers in the role of high-temperature calcination stress in the copper film, which could also support the compressive stress relaxation mechanism.

Once the surfaces were modified in an ethanol solution of stearic acid for 3 h, catkin-like structure with a size of several micrometers in the surface can be observed on the copper surface (Fig. 3a). In a magnified image (Fig. 3b), catkin-like structure with about 100 nanometers in thickness and 30 micrometers in width can be cleared observed. This unique surface showed a CA of 157.6°. It is the kind of copper carboxylate [23,24], which copper oxides on the etched surface could rapidly be reacted with stearic acid. Since the modified reaction belongs to the Metathesis reaction [25], the mod-

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