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Fabrication of flower-like copper film with reversible superhydrophobicity–superhydrophilicity and anticorrosion properties

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ABSTRACT

Reversible surface wetting behaviors between superhydrophobicity and superhydrophilicity is a hot topic research due to its potential applications in engineering. In the present work, a superhydrophilic copper film with flower-like structures was fabricated on zinc plate by a facile method of electroless deposition, and water contact angle on the copper film is 0°. After being modified by dodecanethiol (DDT), the superhydrophilic film was converted to be superhydrophobic with a water contact angle larger than 152° and a gliding angle lower than 5°. Interestingly, the superhydrophobic copper film was switched back to superhydrophilic after being annealed at 300 °C for 30 min and restored to superhydrophobic again after remodification with DDT, and the reversible switch between superhydrophobicity and superhydrophilicity could be repeated several times. Compared with the bare zinc plate and unmodified copper film, the superhydrophobic copper film modified by DDT possesses good anticorrosion properties due to the trapped air in the hierarchical structure of the "flower pits".

1. Introduction

In nature, lotus leaves and the legs of a water strider possess unusual superhydrophobicity [1–3]. Superhydrophobic surfaces with a water contact angle (WCA) greater than 150° and a glide angle (GA) lower than 5° have attracted extensive attention due to their considerable potential values in fundamental research and industrial applications, including impermeable textiles [4], anti-corrosion [5], self-cleaning coatings [6], oil-water separation [7,8], microfluidic devices [9] and biotechnology [10]. It is well documented that superhydrophobicity is determined by a combination of dual-scale structures and low surface free energy material. Inspired by the superhydrophobicity in nature, considerable efforts have been devoted to constructing superhydrophobic surfaces, including wet chemical oxidation [11], electro deposition [12], dip coating [13], hydrothermal [14], spray deposition [15], chemical vapor deposition [16] and sol–gel [17]. To date, smart surfaces with switchable wettability between superhydrophobicity and superhydrophilicity are of greater importance because of their numerous industrial applications. Versatile external stimuli were employed to switch surface wetting behavior, such as light illumination [18,19], temperature [20], solvents [21], electrical potential [22] and pH [23].

Generally, water contact angles on metal surfaces are low because of its high surface energy and flat surfaces, therefore, it is necessary to obtain superhydrophobicity to roughen metal surface and modify the rough surface with low surface free energy material. In the literature [24–26], reversible transition of superhydrophobicity-to-superhydrophilicity on brass was achieved by alternating current etching, chemical etching and electrodeposition. The wetting cycle between superhydrophobicity and superhydrophilicity can be controlled by annealing, plasma treatment and remodification with low surface energy material [24–26]. The technique adopted above often needs special equipment for etching or plasma treatment. In this paper, we adopt a simpler and more versatile strategy for constructing switchable copper film with chrysanthemum-like structures on zinc substrate, and the wettability cycles between superhydrophobicity and superhydrophilicity were achieved through adsorbing/desorbing the low surface free energy of dodecanethiol (DDT). Compared with bare zinc plate and unmodified copper film, superhydrophobic copper film exhibits good anticorrosion properties.

2. Experimental

2.1. Materials

Zinc plates with a purity of 99.9% were obtained from Shanghai Chemical Reagent Company of Chinese Medical Group; $CuSO_4 \cdot 5H_2O$ were purchased from Tianjin Baishi Chemical Co., Ltd. China.

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2.2. Pretreatment of zinc plates

The plates with 1.5 cm × 1.5 cm were ultrasonically degreased in acetone, absolute ethanol and distilled water for 10 min, respectively. After degreasing, the plates were put in an oven at 75 °C for 10 min.

2.2.1. Electroless deposition

Zinc plates were vertically dipped in 0.0625 M $CuSO_4$ for different times, after which they were taken out and dried in air at room temperature for 10 min, and then, they were dried in an oven at 75 °C for 20 min.

2.3. Surface modification

Electroless deposited zinc substrate was immersed in an absolute ethanol solution of DDT (5 wt.%) at room temperature for 24 h, then the samples were taken out, rinsed with absolute ethanol and dried in an oven at 75 °C for 15 min. Finally, the samples were kept in a desiccator for the following characterizations.

2.4. Characterizations

The surface chemical states of the copper films were analyzed on a PHI-5702 X-ray photoelectron spectroscope (XPS) using Al Ka radiation. The crystal structures were characterized using a D/MAX-2400 (RIGAKU, Japan) X-ray diffract meter with Cu Ka radiation. The surface morphologies were observed by FE-SEM (JSM 6701F). Surface roughness was determined by surface roughness tester 2206 (Harbin Measuring & Cutting Tool Group Co., Ltd., China). Contact angles were measured by using DSA100 contact angle meter (Krüss, Germany) at room temperature; droplets of 8 μL were placed at five different positions for one sample.

The anticorrosion effect was evaluated by means of potentiodynamic polarization using a classic three electrode cell of CHI660B electrochemical workstation (Shanghai CH Instrument Ltd). A platinum wire, a saturated calomel electrode (SCE) and a superhydrophobic copper film were employed as counter electrode, reference and working electrode, respectively. The voltage scan rate is 10 mV s^{-1} at room temperature. Three electrodes were immersed in 3.5 wt.% NaCl aqueous solution for 10 min allowing the system to be stabilized.

3. Results and discussion

To obtain rough copper clusters on zinc substrate, we immersed zinc substrates in 0.0625 M $CuSO_4$ aqueous solution for different times, and then copper clusters were deposited on zinc plate due to the following chemical reaction:

$$Zn + Cu^{2+} = Cu + Zn^{2+}.$$

Fig. 1 presents the morphologies of the copper film constructed by different deposition duration. With the deposition time of 15 s, copper nanopores with a diameter of approximately 100 nm and microrods with 600 nm length grow on zinc substrate which was covered by copper spots and took on different shapes (as shown in the inset of Fig. 1(a), white bar corresponds to 100 nm). As deposition time increased to 30 s, copper nano flowers with chrysanthemum-like shape with a diameter range of 0.5 μm–1 μm began to grow out, as shown in

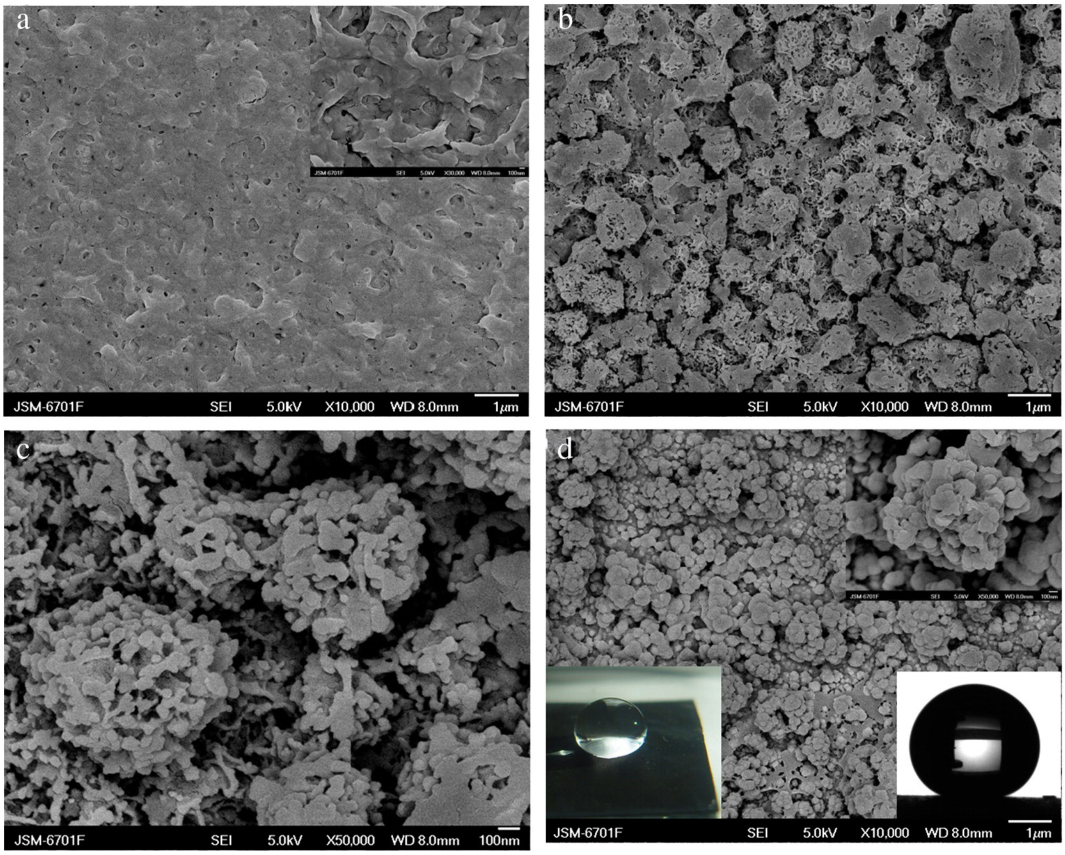

Fig. 1. FESEM images of copper crystals deposited on zinc plate with different times, (a) 15 s, (b)–(c) 30 s and (d) 90 s. Insets of (a) and (d) are the magnified images, white bars correspond to 100 nm. The insets at lower left and lower right in (d) are the digital camera image and optical micrograph of water droplet.

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