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Flower-like Rh/Cu superhydrophobic coating via electrodeposition and its self-cleaning property

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Abstract. Rh/Cu superhydrophobic coatings with textured flower-like dual micro-nano structures were fabricated on copper substrates via electrodeposition of Rh followed by annealing treatment. The scanning electron microscopy and X-ray diffraction pattern were conducted to analyse the morphology and chemical composition of the coating surfaces, respectively. The water drops exhibited a water contact angle of $168\pm1^\circ$ and a sliding angle of $0\pm1^\circ$ on the coating surfaces which were obtained by etching in concentrated hydrochloric acid and nitric acid, electrodeposited at -1.0 V for 30 min and annealing in an oven at 180°C for 60 min. The prepared superhydrophobic coatings showed excellent water repellence and self-cleaning property due to its extremely high water contact angle.

1. Introduction

A superhydrophobic surface with a water contact angle (CA) above 150° and a sliding angle below 10° has a low affinity to water, which lead to the limitation of various phenomena on such a surface, for example, icing, contamination or oxidation, and corrosion [1]. The most typical superhydrophobic surface is the lotus leaf surface in nature. Water droplets on a lotus leaf can roll freely, thus remove contaminants on the blade. This natural phenomenon has aroused tremendous interests in revealing the essence of the superhydrophobicity and exploring methods of preparing artificial superhydrophobic materials [2-3]. The fundamental reason for the superhydrophobicity is the micro-nano dual rough structure. This kind of rough structure can effectively adsorb a large amount of air on the coating surface to reduce the contact area between the solid and the water, resulting in the superhydrophobicity. At the same time, the low surface energy of material is one of the reasons that lead to the superhydrophobicity.

Inspired by the lotus leaf, an extensive research on designing functional artificial superhydrophobic coatings has been carried out on a vast range of materials through a combination of rough surface roughening and low surface energy materials [4]. In this way, many efforts including electrodeposition [5, 6], chemical vapour deposition [7], layer-by-layer self-assembly [8], chemical replacement [9], sol-gel methods [10] and others have been devoted to obtaining the various artificial devices or coatings with special wettability.

It is well known that electrodeposition is an effective, easily controlled and reproducible technology, which has been widely used for manufacturing uniform coatings. Copper is a common life and industrial material with high thermal and electrical conductivity, mechanical workability and malleability. In this paper, we exploited a facile electrodeposition method to manufacture superhydrophobic coatings on copper substrates, which were fabricated by etching in $6\text{ mol}\cdot\text{L}^{-1}$



hydrochloric acid and 8 wt. % nitric acid for 8 min, electrodeposition of Rh at -1.0 V for 30 min and annealing in an oven at 180°C for 60 min without any modification of low surface energy substance. The wettability, surface morphology, chemical composition of the superhydrophobic coatings were investigated in detail. The prepared superhydrophobic coatings showed excellent water repellency and self-cleaning property.

2. Experimental

2.1. Reagents and Materials

Rhodium (III) chloride hydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Rh 38.8-39.2%), nitric acid (HNO_3 , 65%), hydrochloric acid (HCl, 36%-38%), acetone (CH_3COCH_3 , 99.5%) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.7%) were of analytical grade and used without further purification and were purchased from Sinopharm Chemical Reagent Co. Ltd. Copper sheets (2.0cm×1.0cm×0.1cm) were obtained from Beijing Cuibolin Nonferrous Metal Research Institute.

2.2. Pretreatment of the copper substrates and electrochemical preparation of superhydrophobic coatings

The copper substrates were cleaned under sonication in ethanol, acetone and distilled water respectively for 10 min to remove grease on the surfaces. Then the substrates were etched vertically in a mixture of 6 mol·L⁻¹ HCl and 8 wt. % HNO_3 solution for 8 min to remove oxide layer and roughen the surfaces, followed by rinsing with distilled water and drying in air.

The electrodeposition was conducted in a typical three electrodes cell with a copper substrate as working electrode, a saturated calomel electrode (SCE) as reference electrode, and platinum foil as counter electrode. The electrolyte is a mixture of 0.005 mol·L⁻¹ RhCl_3 and 0.1 mol·L⁻¹ KCl solution. Rh films were electrodeposited on copper substrate at a constant voltage of -1.0 V for 1800 s. After that, the surface was taken out from solution, rinsed slightly with distilled water and dried in air. Then the sample was placed in a petri dish covered with filter papers on both sides and annealed at 180°C for 1 h.

2.3. Sample characterization

All characterizations were conducted under an ambient atmosphere at room temperature. The water contact angle (CA) was measured with a water drop volume of 8 μL using a contact-angle meter (FAT200, Dataphysics Inc. USA) at five different locations on the surface, and averaged to the value, and the error was in the range of ±1°. The chemical composition information of the surface was acquired by X-ray powder diffractometer (XRD, D8 ADVANCE, Bruker, Germany) at a continuous scanning mode between a 2Theta range of 35 to 100 and a scanning rate of 5°/min. The surface morphology of each sample was characterized by scanning electron microscope (FEI SEM Nova NanoSEM430).

2.4. Self-cleaning property test

Cover the chalk powder with a thickness of 1 mm on the copper substrate, the coating after electrodeposition without annealing and the coating after annealing, and observe whether the water drop can take away the chalk from these surfaces with a slight lean.

3. Results and discussion

3.1. Wettability and morphology of each sample.

Figure 1 shows the water CAs of surfaces obtained under different treatment conditions, reflecting the obvious change of wettability with different treatments. As seen in figure 1a, the water CA of bare Cu substrate is 63±1°. After etching, the CA reaches 106±1° as seen in figure 1b, which decreases to 76±1° after electrodeposition as shown in figure 1c. While the water CA increases to 168±1° exhibiting

superhydrophobicity after annealing at 180°C for 1 h as shown in figure 1d. All of these phenomena suggest that the diverse treatments especially annealing on surface wettability are important. The sample after annealing exhibits complete water repellence which is in line with the Cassie–Baxter model [11]. The Cassie–Baxter model states:

$$\cos\theta' = f_1\cos\theta - f_2 \quad (1)$$

where f_1 and f_2 represent the area fractions of the solid-liquid interface and air-liquid interface, respectively; θ' and θ are apparent water CA on rough composite surface and intrinsic water CA on smooth surface, respectively. Here, f_1 is 0.015 and f_2 is 0.985 considering that $\theta = 63\pm1^\circ$, $\theta' = 168\pm1^\circ$ and $f_1 + f_2 = 1$, which means that the contact area of the solid and water droplet occupies about 1.5% of the total composite area. Thereby the coating exhibits water repellence.

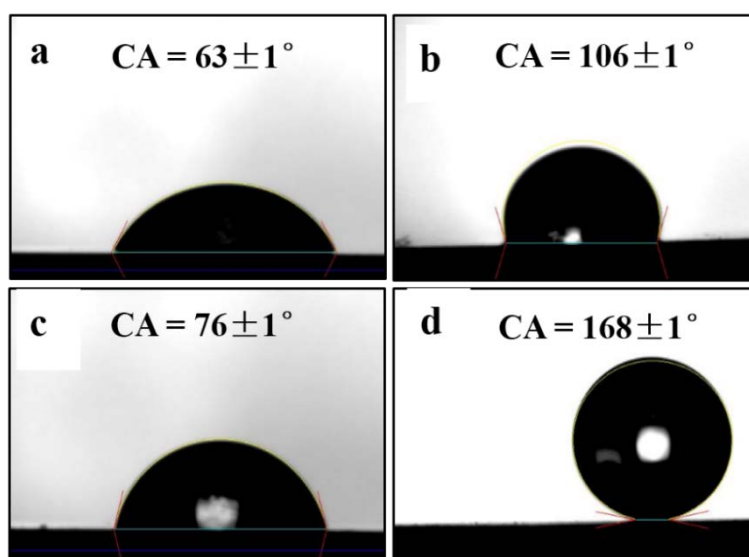


Figure 1. Images of the water CAs on the surfaces: (a) bare copper substrate; (b) after etching with a mixture of 6 mol·L⁻¹ HCl and 8 wt. % HNO₃ solution for 8 min; (c) electrodeposited at -1.0 V for 1800 s; (d) after annealing at 180°C for 1 h

Figure 2 shows the SEM images of samples treated with different conditions at different magnifications. From the SEM image of figure 2a, the bare copper substrate is relatively smooth. While etching in a mixture of 6 mol·L⁻¹ HCl and 8 wt. % HNO₃ solution, as shown in figure 2b, the surface becomes rough. After electrodeposition, it can be seen in figure 2c₁ that the surface develops into many ravines and densely packed spherical particles which grows upward and have an average diameter of 300 nm in figure 2c₂. After annealing treatment at 180 °C for 1h, it can be clearly seen in figure 2d₁ that every original sphere turns into smaller flower-like nanospheres, which have diameters ranging from 40 to 100 nm as shown in figure 2d₂. This change of morphology before and after annealing makes the surface form more grooves, which can adsorb more air, thereby reducing the contact area between the droplet and the solid surface and exhibiting excellent superhydrophobicity.

3.2. Chemical compositions of the superhydrophobic coating

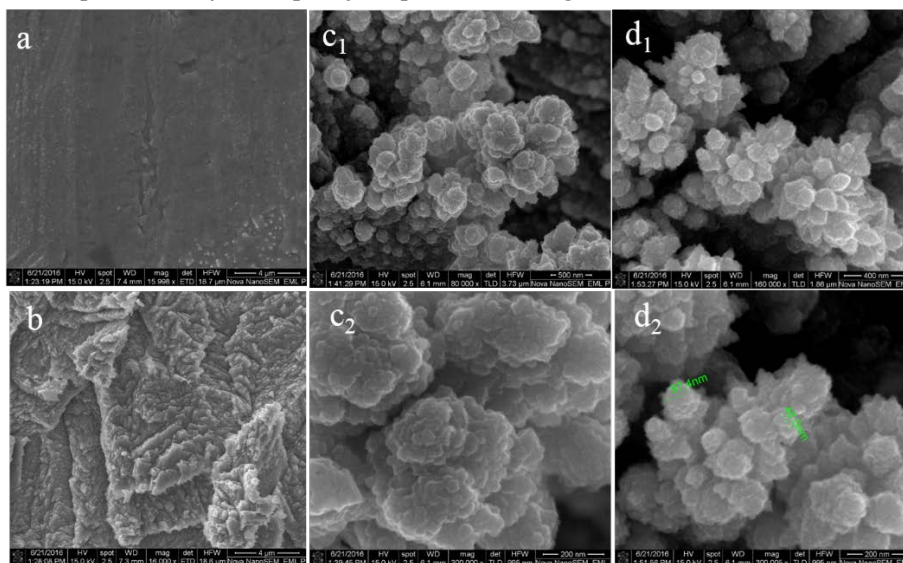


Figure 2. SEM images of each surface: (a) bare copper substrate; (b) after etching with a mixture of $6 \text{ mol} \cdot \text{L}^{-1}$ HCl and 8 wt. % HNO_3 for 8 min; (c_1 and c_2) electrodeposited at -1.0 V for 1800 s; (d_1 and d_2) after annealing at 180°C for 1 h.

3.2.1 XRD analysis. X-ray powder diffractometer (XRD) was applied to ascertain the elemental composition of the surfaces which could affect the surface wettability. The XRD patterns of bare copper substrate, electrodeposited coating before and after annealing treatment were analysed as shown in figure 3. The symbols of $\diamond$ and $*$ present the peaks of Cu and Rh, respectively. The sharp diffraction peaks in figure 3a belong to pure metal copper substrate (JCPDS Card No. 04-0836), namely Cu (111), Cu (200), Cu (220) and Cu (311). Compared with the XRD patterns of the bare copper substrate, new diffraction peaks appear for the surface after electrodeposition at about 41.0° , 69.8° , 84.3° as shown in figure 3b, which are indexed to (111), (220), and (311) planes of cubic Rh (JCPDS Card No. 05-0685), suggesting that Rh was deposited onto the Cu surface during the electrochemical process. From figure 3c, there are no new peaks illustrating no new substance is formed after annealing treatment.

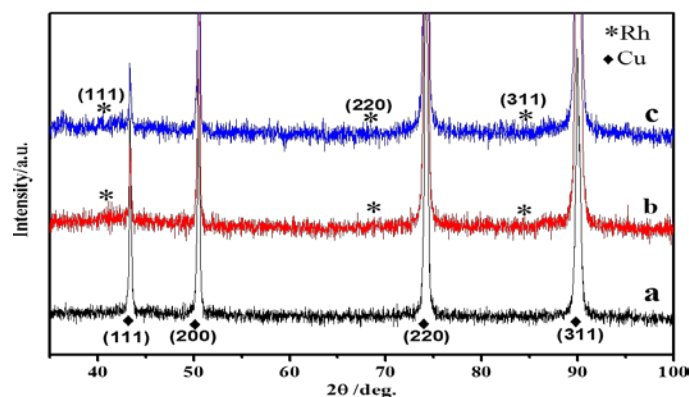


Figure 3. XRD patterns of the samples: (a) bare copper substrate; (b) electrodeposited at -1.0 V for 1800 s; (c) after annealing at 180°C for 1 h.

3.2.2 EDS analysis. Energy-dispersive spectroscopy (EDS) was applied to further confirm the chemical composition. The EDS spectra of bare copper substrate and superhydrophobic coating after annealing are shown in figure 4a and figure 4b respectively. For bare copper substrate, there is only Cu element as shown in figure 4a. As seen in figure 4b, the Rh element appear after electrodeposition and annealing treatment, further indicating that Rh was deposited onto the Cu surface successfully.

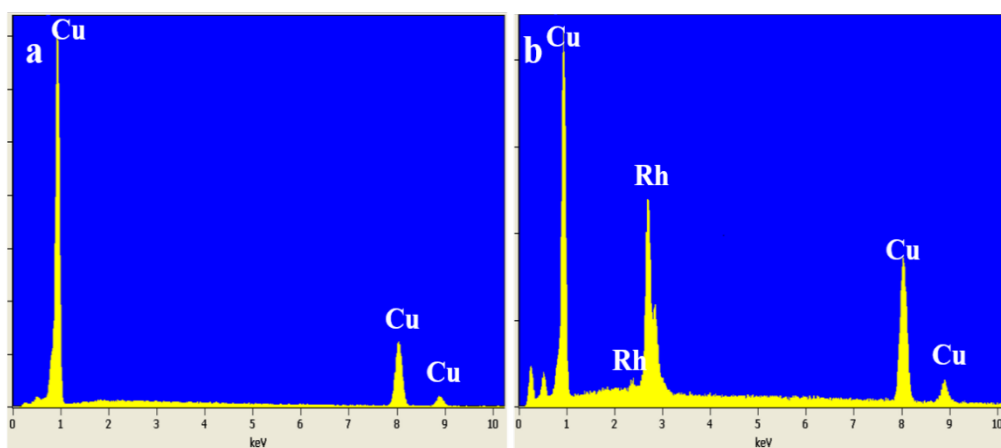


Figure 4. EDS spectra of the samples: (a) bare copper substrate; (b) superhydrophobic coating after annealing at 180°C for 1 h

3.3. Self-cleaning property of the superhydrophobic coating

Self-cleaning property of superhydrophobic coating has been a hot spot in the field of surface technology. The behaviours of water droplets on the bare copper substrate, the coating before and after annealing all covered with chalk powder are shown in figure 5. It can be seen in figure 5a that the water droplets detached from the syringe and chalk powder remained and adhered to the copper surface. From figure 5b, the water droplets on the coating before annealing cannot take away chalk powder, which was same as the situation of figure 5a. As the water droplets detached from the syringe rolled down on the superhydrophobic coating after annealing, chalk powder were removed adequately and the surface remained dry as shown in figure 5c illustrating the prepared superhydrophobic coating has self-cleaning ability. The self-cleaning ability of superhydrophobic coating might have important potential and practical applications in industrial field.

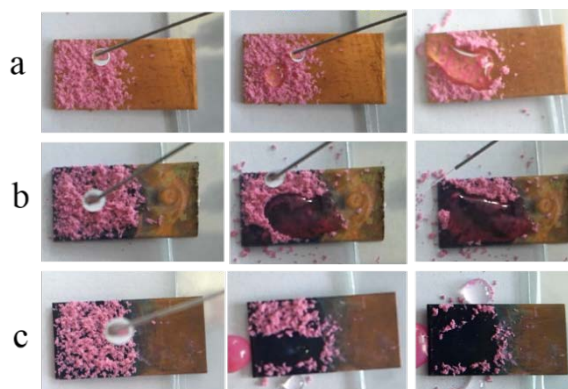


Figure 5. Self-cleaning property test: (a) bare copper substrate; (b) surface before annealing; (c) superhydrophobic coating after annealing.

4. Conclusion

In summary, Rh/Cu superhydrophobic coatings with flower-like structures were manufactured by electrodeposition method without modification of organic low surface energy materials. The micro-nano structures play important roles on the superhydrophobicity. The wettability, surface morphology, and chemical composition of the prepared superhydrophobic coatings were evaluated in detail. The fabricated superhydrophobic coatings showed self-cleaning property, which have potential industrial applications.

Acknowledgements

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