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A facile electrochemical process to fabricate corrosion-resistant super-hydrophobic surface on copper substrate

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Abstract

A super-hydrophobic nickel film with hierarchical micro/nano scaled structure was deposited on copper substrate by one-step electrochemical process. The as-prepared surface shows excellent super-hydrophobicity with a high water contact angle of 160.3 ± 1.5° and a small sliding angle of 3.0 ± 0.5°. The surface morphology was characterized by scanning electron microscopy (SEM), and the surface exhibits accumulated hierarchical micro/nano structure. The energy-dispersive spectroscopy (EDS) and Fourier transform infrared spectra (FT-IR) were utilized to examine the surface chemical composition, and the results demonstrate that the nickel complex with organic acid was covered on copper. Furthermore, the potentiodynamic polarization tests indicate that the fabricated super-hydrophobic surface possesses better corrosion resistance in 3.5 wt.% NaCl solution, which can effectively protect the bare copper substrate. The existence of the super-hydrophobic film can be regarded as a barrier and thus provide a perfect air-liquid interface that inhibits penetration of the corrosive solution. This method of electrodeposition process is very simple, low-cost and effective, which offers a promising approach for mass production of super-hydrophobic surface on various metallic materials.

Keywords super-hydrophobic; electrochemical process; copper; nickel; corrosion-resistant

1. Introduction

Super-hydrophobic surface has attracted great attention due to their functions of self-cleaning, anti-icing and corrosion resistance [1]. Various approaches have been reported to fabricate super-hydrophobic surface, such as lithography [2], laser irradiation [3], chemical vapor deposition [4], and so on. It is known that surface roughness and surface chemical modification are two key factors to achieve super-hydrophobic properties [5]. But the traditional methods are still hampered by certain limitations including complicated process, sophisticated equipment and long process time [6]. What's more, strong toxic fluorocarbons is always used to lower surface energy, resulting in potential threat to human health and environment [7]. Thus, it is urgent to explore facile and economical method that can be scaled up in industrial level.

In this paper, one-step electrodeposition process was employed to fabricate super-hydrophobic nickel coating on copper substrate. The as-prepared surface exhibited excellent corrosion resistant property. Surface morphology and chemical composition were investigated to explain wettability change and corrosion resistant behaviour. This study is expected to find ways to produce super-hydrophobic surfaces for mass production on various metallic materials.

2. Experimental

2.1. Materials and reagents

The base material was copper with the dimensions of 30 mm x 10 mm x 1 mm. Ethanol, nickel chloride ($NiCl_2 \cdot 6H_2O$) and myristic acid of analytical grade were used as received.

2.2. Sample preparation

The detailed process is shown as follows. First, two cleaned copper substrates were polished with silicon carbide papers (up to 2000 grades), ultrasonically washed in acetone, ethanol, deionized water for 5 min in sequence, and subsequently dried in air. Second, 0.08 M nickel chloride and 0.1 M myristic acid were immersed in ethanol under constant stirring until 150 ml uniform electrolyte solution was obtained. Third, the two copper substrate were taken as anode and cathode in an electrolyte cell, and a direct current (DC) voltage of 30 V was performed to the electrodes with a distance of 2 cm. After 10 min electrolysis time, the working cathodic surface was rinsed with deionized water and then dried in air. Subsequently, the super-hydrophobic surface was achieved.

2.3. Characterization

The surface morphology of the obtained surface was observed by SEM (FEI, Quanta 250). The chemical composition was examined by EDS and FT-IR (Thermo Scientific, Nicolet iS50). The water contact angle was measured by a contact angle meter (AST, VCA optima) at room temperature. The corrosion resistance was evaluated by potentiodynamic polarization curves obtained at a sweep rate of 10 mV/s in a standard three-electrode cell configuration. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary electrode and conference electrode, respectively. The bare copper and fabricated super-hydrophobic sample were used as the working electrode with a surface area of 1 cm^2 exposed to corrosion medium. The measurements were performed in 3.5 wt.% NaCl solution at room temperature by an electrochemical workstation (CHI660D, China).

3. Results and discussion

3.1. Surface morphology

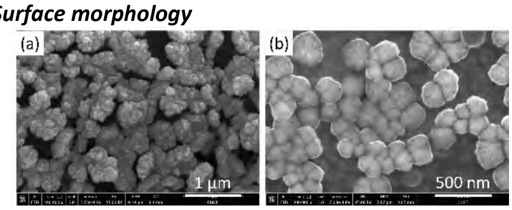

Figure 1. (a) SEM image of the as-prepared cathodic copper surface, (b) the corresponding high magnification.

Surface morphology of the obtained cathodic copper surface was characterized by means of SEM images. It can be seen from Fig. 1a that the bare copper surface was covered by the coating of the accumulated micro-scaled particles. High magnification image shows the rough surface with the nano-scaled cauliflower-like cluster. After the electrodeposition process in an electrolyte solution with applied DC voltage, the hierarchical micro/nano structure was formed on the cathodic copper surface. This unique surface structure can generate large amount of space in which air can be trapped, resulting in the suspension of water droplet on the fabricated copper surface. Thus, it implies that the surface morphology of copper was modified under electrochemical process, which made the surface be much rougher.

3.2. Chemical composition

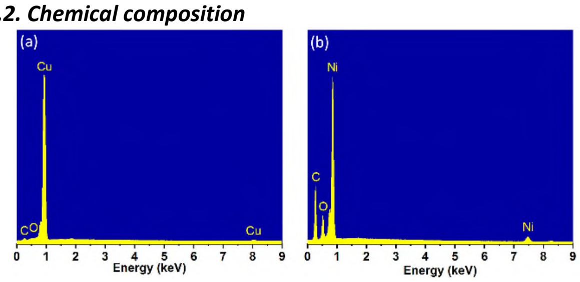

Figure 2. The EDS spectra of (a) the bare copper surface and (b) the as-prepared cathodic copper surface with nickel coating.

The EDS method was employed in order to analyse the surface chemical composition of the samples. Fig. 2 shows the EDS spectra of the bare copper and the as-prepared cathodic surfaces. It can be observed that after electrodeposition process, nickel film was generated on bare copper surface. At the same time, the relative contents of carbon and oxygen significantly increased.

Further investigation of surface chemical composition was conducted utilizing FT-IR. Fig. 3 plots the FT-IR spectrum of the cathodic copper surface. In high-frequency region, adsorption peaks at around 2920 and 2850 cm^{-1} are attributed to C-H asymmetric and symmetric stretching vibrations, respectively. In low-frequency region, the peaks at 1409 and 1545 cm^{-1} may stem from symmetric and asymmetric stretches of coordinated COO moieties [8]. Thus, it can be deduced that the obtained coating should be nickel complex with organic acid. The reaction process can be formulated as follows:

Cathode: $Ni^{2+} + 2e^- \longrightarrow Ni$; $2H^+ + 2e^- \longrightarrow H_2$;

$Ni^{2+} + 2CH_3(CH_2)_{12}COOH \longrightarrow Ni[CH_3(CH_2)_{12}COO]_2 + 2H^+$

Anode: $4OH^- - 4e^- \longrightarrow O_2 + H_2O$

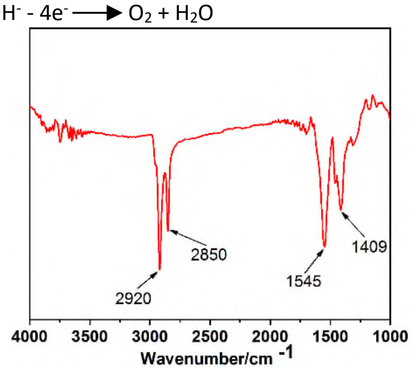

Figure 3. FT-IR spectrum of the as-prepared cathodic copper surface.

3.3. Surface wettability

To evaluate the surface wettability, water contact angles of bare copper substrate and the fabricated cathodic copper surface were measured at 3 different positions. The results demonstrate that the contact angle was only 83.0 ± 3.5° for bare copper surface, while the contact angle value of the obtained cathodic copper surface dramatically increased to 160.3 ± 1.5° with a small sliding angle of 3.0 ± 0.5°. Due to the change of surface morphology, the cathodic copper surface had more air in the hierarchical micro/nano structure. Meanwhile, nickel complex with organic acid could lower surface free energy and render the surface to exhibit super-hydrophobic property. It implies that both surface morphology and surface chemical composition have considerable influences on the surface wettability.

3.4. Corrosion resistance

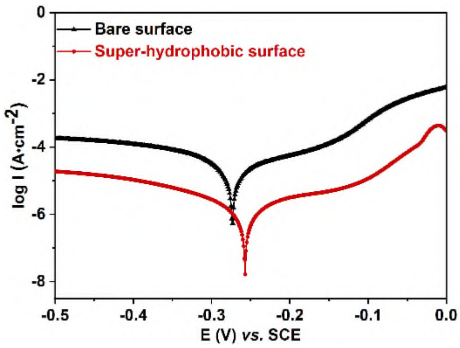

Figure 4. Potentiodynamic polarization curves of the bare and super-hydrophobic copper surface in 3.5 wt.% NaCl solution.

Corrosion resistance behaviour of the bare and super-hydrophobic copper surfaces were measured in 3.5 wt.% NaCl solution by potentiodynamic polarization method (shown in Fig. 4). By Tafel extrapolation method, corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (*CR*) can be calculated and then presented in Table 1. Generally, a surface with positive-going E_{corr} and combined low I_{corr} is regarded to possess excellent anti-corrosion property. Therefore, the results demonstrate that the super-hydrophobic copper surface exhibits better corrosion resistance than the bare copper substrate. In addition, the super-hydrophobic surface shows very low *CR*, 16-fold decline from the bare copper. It is concluded that the super-hydrophobic surface has a good anticorrosion protection for the bare copper substrate.

Table 1 E_{corr}, I_{corr} and *CR* of the bare and super-hydrophobic copper surfaces

Sample	E_{corr} (mV)	I_{corr} ($A\cdot cm^{-2}$)	*CR* ($mm\cdot a^{-1}$)
Bare	-0.27	4.8×10^{-5}	5.6×10^{-1}
Super-hydropobic	-0.25	3.0×10^{-6}	3.5×10^{-2}

4. Conclusions

In this work, the corrosion resistant and super-hydrophobic nickel coating was successfully achieved on bare copper substrate by a facile electrodeposition process. The as-prepared surface showed a contact angle of 160.3 ± 1.5° and a small sliding angle of 3.0 ± 0.5° after it was deposited at 30 V for 10 min. The wettability of the coating was attributed the hierarchical micro/nano cauliflower-like structure and nickel myristate with low surface energy. The fabricated nickel coating displayed excellent anticorrosive property than the bare copper substrate. This effective method can be used for mass production of surfaces with super-hydrophobicity on various metallic materials.

References

[1] Liu K, Tian Y and Jiang L 2013 *Prog. Mater. Sci.* **58** 503-64

[2] Ellinas K, Tserepi A and Gogolides E 2011 *Langmuir* **27** 3960-69

[3] Müller F, Kunz C and Gräf S 2016 *Materials* **9** 476

[4] Liu Y, Yu Z, Zhou S and Wu L 2006 *Appl. Surf. Sci.* **252** 3818-27

[5] Celia E, Darmanin T, Taffin E, Amigoni S and Guittard F 2013 *J. Colloid Interface Sci.* **402** 1-18

[6] Yang Z, Tian Y, Yang C, Wang F and Liu X 2017 *Appl. Surf. Sci.* **414** 313-24

[7] Si Y, Guo Z and Liu W 2016 *ACS Appl. Mater. Interface* **8** 16511-20

[8] Chen Z, Hao L and Chen C 2012 *Colloids Surf. A* **402** 1-7