

Wettability of stearic acid modified chrome oxide layer on copper substrate

Bo Zhang^{1,2,3}, Haitao Feng^{1,3}, Feng Lin^{1,2}, Yabin Wang^{1,3}, Liping Wang^{1,2}, Yaping Dong^{1,3}, Wu Li^{1,4} ✉

¹Qinghai Institute of Salt Lakes, Chinese Academy of Sciences Xining 810008, Qinghai, People's Republic of China

²University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

³Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resource, Chinese Academy of Science, Xining 810008, Qinghai, People's Republic of China

⁴Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province, Chinese Academy of Science, Xining 810008, People's Republic of China

✉ E-mail: liwu2016@126.com

Published in Micro & Nano Letters; Received on 3rd August 2016; Revised on 27th October 2016; Accepted on 14th November 2016

A micronano structure superhydrophobic film was fabricated on copper substrate by electrodeposition of chrome oxide layer and surface modification of stearic acid. The fabricated film shows high water contact angle (165.4°) and low sliding angle (1.8°), and also performs well at corrosion resistance (protection efficiency, 99.9989%). The surface was characterised by scanning microscope, X-ray photoelectron spectroscopy and atomic force microscope.

1. Introduction: Superhydrophobic surfaces without rose petal effect draw increasing attention today for its unique water repellency and self-cleaning property [1]. The wettability of superhydrophobic surfaces can be characterised with water contact angle (CA, larger than 150°) and sliding angle (SA, lower than 5°) [2]. The superhydrophobic techniques can be applied to treat the surfaces of solar cell panel, ship and airplane for self-cleaning, anti-corrosion or anti-icing [3–6], or treat the surfaces of metal meshes for oil separation [7].

Several methods have been reported about fabricating superhydrophobic surface on copper substrate, such as etching in HCl solution and then modified with octadecanethiol [8], coating with multi-walled carbon nanotubes and silicone rubber [9], etching with bamboo-leaf-like polydimethylsiloxane template wetted by FeCl₃ solution and then modifying with stearic acid [10], oxidising in K₂S₂O₈-KOH mixture aqueous solution and then modifying with 1H,1H,2H,2H-perfluorodecyltriethoxysilane [11], and electrodeposition in mixed cerium chloride and myristic acid ethanol solution [12]. However, the reported methods still have some limitations, such as damage to the copper substrate surface, expensive raw materials, and complex fabricating steps.

In this work, we present a method of fabricating superhydrophobic film on copper substrate by electrodeposition of a chrome oxide (Cr₂O₃) layer which was reported to be of excellent corrosion resistance [13], and subsequent modification of stearic acid. The electrodeposition process is simple and has low requirements to instruments, and all the raw materials used in this work are of low price.

2. Experiment: Copper pieces of 1.5 × 1.5 × 0.2 mm were polished, and then ultrasonically cleaned with acetone, absolute ethanol and deionised water orderly. The pretreated copper pieces were taken as the working electrodes. A 2 × 2 × 0.2 mm platinum plate was chosen as the counter electrode, and 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution was chosen as the electrolyte. After 1 h of electrodeposition at the bath voltage of 4.0 V, the treated copper pieces were cleaned and dried, and then immersed into 0.05 mol·l⁻¹ ethanolic stearic acid solution for 12 h. After drying at 100°C for 1 h, the superhydrophobic film on copper substrate was obtained.

The surface of the fabricated superhydrophobic film were characterised by a JSM-5610LV scanning electron microscope (SEM), a PHI-5702 X-ray photoelectron spectroscopy (XPS), and a Nanoscope IIIa atomic force microscope (AFM). The corrosion

resistances of the samples were measured with an Autolab PGSTAT128N electrochemical workstation in 3.5 wt% NaCl aqueous solution at 25°C. A platinum gauze of 2.25 cm² and an Ag/AgCl electrode were chosen, respectively, as the counter and the reference electrode. The measurement was taken after immersing the samples in the electrolyte for 1 h to reach a stable state.

The wettability measurements were took on a XG-CAMB CA analyser with 4.5 µl water droplet, and the water CA and SA data were obtained by averaging five measurements. The analyser can determine CA results with two decimal precision, and the listed results are all within the first decimal.

3. Result and discussion: In Fig. 1a, it could be seen that the surfaces of the bare copper is smooth, and its water CA is 82.2°. After modification in 0.05 mol·l⁻¹ ethanolic stearic acid solution for 12 h, the copper sample surface is still smooth, and the water CA increases to 116.4° (Fig. 1b). It infers that the stearic acid modification helps to increase the hydrophobicity of the copper surface. The water CA of the copper sample after electrodeposition in 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution for 1 h is only 10.2° (Fig. 1c), and it should be attributed to the extremely increased surface area [14].

The copper after electrodeposition in 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution for 1 h and a subsequent modification in 0.05 mol·l⁻¹ ethanolic stearic acid solution for 12 h, shows excellent superhydrophobicity. The high water CA (165.4°) and low SA (1.8°) of the sample indicates that the fabricated surface is of both excellent water repellency and low hysteresis.

Figs. 1d and f show that the fabricated superhydrophobic surface inherits the micronano morphology of the copper sample after electrodeposition. Stearic acid modification reduces the surface energy of the Cr₂O₃ layer and makes it hydrophobic. According to Wenzel model, if the surface is hydrophobic, the larger the true surface area is, the higher the water CA is, and it should be the cause of the high water CA of the fabricated superhydrophobic surface [14].

The excellent superhydrophobicity of the stearic acid modified Cr₂O₃ surface can also be attributed to the phenomena of 'Capillarity' and 'Cushion effect' [15]. The surface topography of the fabricated superhydrophobic film is shown in Fig. 1h. The superhydrophobic film surface consists of several micron-sized hills and valleys, and multiple nano-sized embossments exist on the surface of the hills and valleys. Thus, the fabricated surface has a micronano structure which was reported to be important for

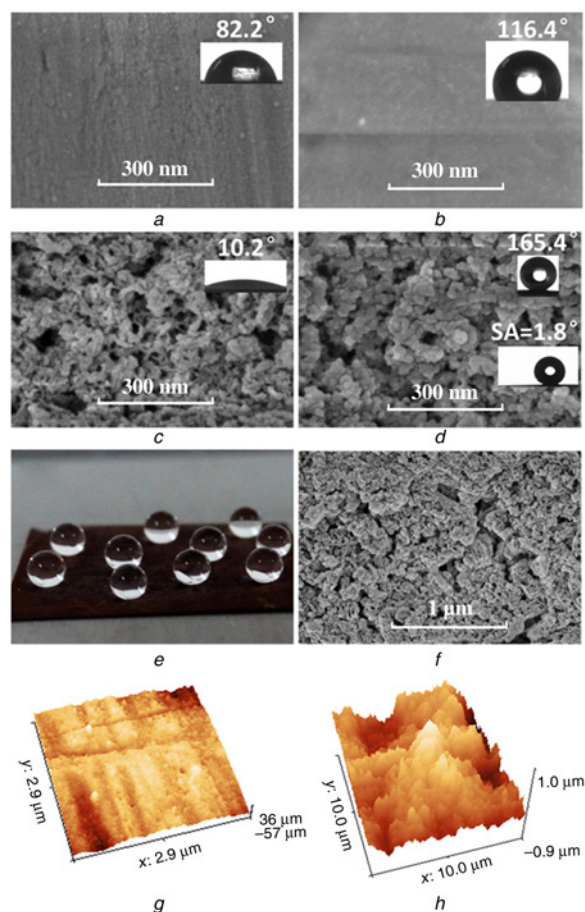


Fig. 1 SEM images and water CA results of
a Bare copper
b Copper after modification
c Copper after electrodeposition
d and *f* Copper after electrodeposition and modification
e Photograph of water droplets on the superhydrophobic film. AFM topographies of
g Bare copper
h Copper after electrodeposition and modification

superhydrophobicity [16]. Multiple nano-sized depressions exist in this micronano structure surface, and these depressions allow air to be trapped within the surface. When the surface was immersed into water, water forms convex shapes between the air/liquid interfaces because of the extremely high hydrophobicity of the trapped air, and thus is blocked from permeating into the fabricated superhydrophobic film [17, 18].

Fig. 1*e* is the photograph of the fabricated superhydrophobic film on copper substrate. The surface shows a homogeneous deep black-brown colour, and the water droplets on the surface are all of sphere shapes. The phenomenon confirms that the fabrication of a superhydrophobic film on copper substrate was successful.

The composition of the deep black-brown layer obtained after electrodeposition in 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution for 1 h was analysed by XPS, and the results are shown in Figs. 2*a* and *b*. The binding energy positions of Cr2p_{1/2} and Cr2p_{3/2} peaks in Fig. 2*b* (respectively, at 576.6 and 586.3 eV) and the obtained atomic ratio of Cr and O (1:1.57) confirm that the main substance of the deep black-brown layer is Cr₂O₃ [19, 20], and the result is supported by the reported literatures [21, 22]. The XPS spectra in Fig. 2*a* shows that the carbon peak of the copper sample after both electrodeposition and stearic acid modification is much higher than that of the bare copper, and it indicates that the absorption of stearic acid to Cr₂O₃ layer surface is strong.

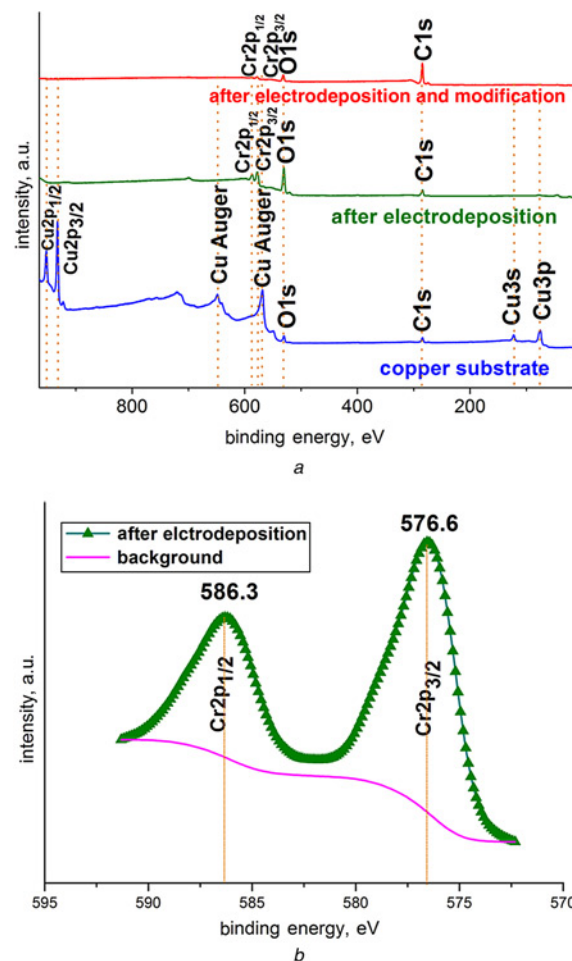


Fig. 2 Composition of the deep black-brown layer obtained after electrodeposition in 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution for 1 h was analysed by XPS

a XPS spectra of the copper substrate, copper substrate after electrodeposition, copper substrate after electrodeposition and without modification, and copper substrate after both electrodeposition and stearic acid modification

b Peaks of Cr2p_{1/2} and Cr2p_{3/2} in the XPS spectra of the copper substrate after electrodeposition

We choose stearic acid for surface modification on the Cr₂O₃ layer for both its low cost and none toxicity. Moreover, stearic acid molecule consists of a carboxyl head group and a long hydrophobic alkyl chain, and the carboxyl group can react with metal oxides and forms a chelate bond with the metal atom [23, 24]. Just as shown in the XPS spectra, the absorption of stearic acid to Cr₂O₃ layer surface is strong.

To study the influence of immersion time to the wettability of the fabricated surface, we immerse the copper samples after electrodeposition in 2 mol·l⁻¹ chromic acid and 0.05 g·l⁻¹ sodium nitrate aqueous solution for 1 h into 0.05 mol·l⁻¹ ethanolic stearic acid solution for different times, and the results are shown in Fig. 3. The water CA increases with the immersion time, and reaches the highest value of 165.4° at 12 h. After 12 h, the CA decreases slowly with the immersion time, and there should be two reasons. First, the excessively absorbed stearic acid fills the multiple depressions on the Cr₂O₃ layer and makes the surface become smooth and gradually lose its ability of trapping air which can block water from penetrating the sample surface, and the surface area decrease along with the surface smoothing should also cause the water CA decrease [14]. Second, stearic acid corrodes and changes the micronano structure morphology of the Cr₂O₃ layer after long time of immersion, and finally leads to the weakening of superhydrophobicity.

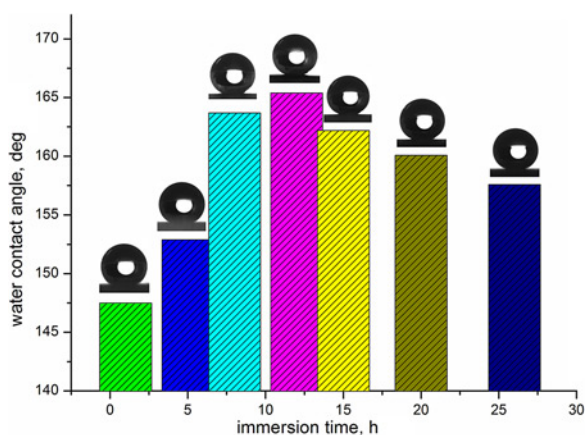


Fig. 3 Water CA results of the electrodeposited copper samples immersed in $0.05 \text{ mol}\cdot\text{L}^{-1}$ ethanolic stearic acid for different time

The corrosion resistance of the fabricated superhydrophobic surface was measured in contrast to those of the bare copper, the copper after electrodeposition in $2 \text{ mol}\cdot\text{L}^{-1}$ chromic acid and $0.05 \text{ g}\cdot\text{L}^{-1}$ sodium nitrate aqueous solution for 1 h, and the copper after modification in $0.05 \text{ mol}\cdot\text{L}^{-1}$ ethanolic stearic acid solution for 12 h. The results are listed in Fig. 4, and the corrosion currents of the samples were calculated according to the tangent intersection point of the anodic and cathodic Tafel lines [25].

The corrosion current of the fabricated superhydrophobic surface is 2.2135 nA , which is much lower than those of the other three samples. The protection efficiency of the superhydrophobic surface is as high as 99.9989%, which is calculated with the following equation

$$\eta = \frac{(i_{\text{corr}} - i'_{\text{corr}})}{i_{\text{corr}}} \times 100\% \quad (1)$$

where i_{corr} and i'_{corr} , respectively, represent the corrosion current of the bare copper, and the fabricated superhydrophobic surface [26].

4. Conclusions: In summary, the fabrication of a micronano structure superhydrophobic film on copper substrate by electrodeposition of Cr_2O_3 and modification of stearic acid was proposed. The obtained superhydrophobic surface is compact and homogenous, and shows excellent superhydrophobicity (CA 165.4° , SA 1.8°). The fabrication process is simple and of low

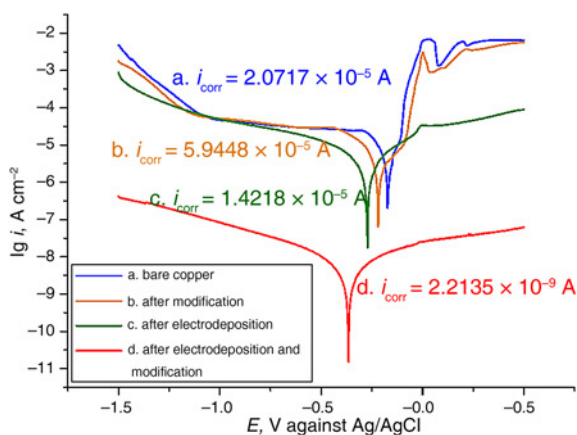


Fig. 4 Polarisation plots of copper substrate, copper after modification, copper after electrodeposition, and copper after both electrodeposition and modification

cost, and has potential application in the fields such as anti-corrosion (protection efficiency, 99.9989%).

5. Acknowledgments: This research was supported by Youth Guidance Fund of Qinghai Institute of Salt Lakes, Chinese Academy of Sciences (grant nos. Y460111036 and Y460101035) and Applied Basic Research Fund of Qinghai Science and Technology Department, Qinghai Province of China (2014-ZJ-707).

6 References

- [1] Wong T.S., Kang S.H., Tang S.K.Y., *ET AL.*: 'Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity', *Nature*, 2011, **477**, (7365), pp. 443–447
- [2] Zhang P., Lv F.Y.: 'A review of the recent advances in superhydrophobic surfaces and the emerging energy-related applications', *Energy*, 2015, **82**, pp. 1068–1087
- [3] Jelle B.P.: 'The challenge of removing snow downfall on photovoltaic solar cell roofs in order to maximize solar energy efficiency-research opportunities for the future', *Energy Build.*, 2013, **67**, pp. 334–351
- [4] Gang W., Zhixiang Z., He W., *ET AL.*: 'Low drag porous ship with superhydrophobic and superoleophilic surface for oil spills cleanup', *ACS Appl. Mater. Interfaces*, 2015, **7**, (47), pp. 26184–26194
- [5] Ball P.: 'Engineering shark skin and other solutions', *Nature*, 1999, **400**, pp. 507–509
- [6] Mohamed A.M.A., Abdullah A.M., Younan N.A.: 'Corrosion behavior of superhydrophobic surfaces: A review', *Arab. J. Chem.*, 2015, **8**, (6), pp. 749–765
- [7] Yanlong S., Wu Y., Xiaojuan F., *ET AL.*: 'Fabrication of superhydrophobic-superoleophilic copper mesh via thermal oxidation and its application in oil–water separation', *Appl. Surf. Sci.*, 2016, **367**, pp. 493–499
- [8] Guo J., Yang F., Guo Z.: 'Fabrication of stable and durable superhydrophobic surface on copper substrates for oil–water separation and ice-over delay', *J. Colloid Interface Sci.*, 2016, **466**, pp. 36–43
- [9] Mokarian Z., Rasuli R., Abedini Y.: 'Facile synthesis of stable superhydrophobic nanocomposite based on multi-walled carbon nanotubes', *Appl. Surf. Sci.*, 2016, **369**, pp. 567–575
- [10] Zang D., Wu C., Zhu R., *ET AL.*: 'Porous copper surfaces with improved superhydrophobicity under oil and their application in oil separation and capture from water', *Chem. Commun.*, 2013, **49**, (75), pp. 8410–8412
- [11] Yuan Z., Bin J., Wang X., *ET AL.*: 'Fabrication of superhydrophobic surface with hierarchical multi-scale structure on copper foil', *Surface Coat. Technol.*, 2014, **254**, pp. 151–156
- [12] Liu Y., Li S., Zhang J., *ET AL.*: 'Corrosion inhibition of biomimetic super-hydrophobic electrodeposition coatings on copper substrate', *Corros. Sci.*, 2015, **94**, pp. 190–196
- [13] Chen D., Huang A., Gu H., *ET AL.*: 'Corrosion of Al_2O_3 – Cr_2O_3 refractory lining for high-temperature solid waste incinerator', *Ceram. Int.*, 2015, **41**, (10, Part B), pp. 14748–14753
- [14] Yamaguchi M., Suzuki S., Sasaki S., *ET AL.*: 'Fabrication of nano-periodic structures and modification of the Wenzel model to estimate contact angle', *Sensors Actuators A Phys.*, 2014, **212**, pp. 87–92
- [15] Cho Y.J., Jang H., Lee K.-S., *ET AL.*: 'Direct growth of cerium oxide nanorods on diverse substrates for superhydrophobicity and corrosion resistance', *Appl. Surf. Sci.*, 2015, **340**, pp. 96–101
- [16] Chu F., Wu X.: 'Fabrication and condensation characteristics of metallic superhydrophobic surface with hierarchical micro-nano structures', *Appl. Surf. Sci.*, 2016, **371**, pp. 322–328
- [17] Liu K., Cao M., Fujishima A., *ET AL.*: 'Bio-inspired titanium dioxide materials with special wettability and their applications', *Chem. Rev.*, 2014, **114**, (19), pp. 10044–10094
- [18] Wang P., Zhang D., Qiu R., *ET AL.*: 'Super-hydrophobic film prepared on zinc as corrosion barrier', *Corros. Sci.*, 2011, **53**, pp. 2080–2086
- [19] Desimoni E., Malitesta C., Zamboni P.G., *ET AL.*: 'An X-ray photoelectron spectroscopic study of some chromium oxygen systems', *Surf. Interface Anal.*, 1988, **13**, (2–3), pp. 173–179
- [20] Allen G.C., Harris S.J., Jutson J.A., *ET AL.*: 'A study of a number of mixed transition metal oxide spinels using X-ray photoelectron spectroscopy', *J. Appl. Electrochem.*, 2000, **30**, pp. 1069–1079

- [21] Saiddington J.C., Hoey G.R.: 'Microscopic study of the formation of cathodic films on iron during electrolysis of chromium plating solutions at various $\text{CrO}_3\text{:SO}_4$ Ratios', *J. Electrochem. Soc.*, 1970, **117**, (8), pp. 1011–1020
- [22] Soragni E., Fontanesi C., Barnani G., *ET AL.*: 'Dynamic aspects of the electroreduction of chromic acid solutions', *Appl. Surf. Sci.*, 1989, **37**, (1), pp. 111–134
- [23] Gurav A.B., Lathe S.S., Vhatkar R.S., *ET AL.*: 'Superhydrophobic surface decorated with vertical ZnO nanorods modified by stearic acid', *Ceram. Int.*, 2014, **40**, (5), pp. 7151–7160
- [24] Xu J., Xu J., Cao Y., *ET AL.*: 'Fabrication of non-flaking, superhydrophobic surfaces using a one-step solution-immersion process on copper foams', *Appl. Surf. Sci.*, 2013, **286**, pp. 220–227
- [25] Maho A., Denayer J., Delhalle J., *ET AL.*: 'Electro-assisted assembly of aliphatic thiol, dithiol and dithiocarboxylic acid monolayers on copper', *Electrochim. Acta*, 2011, **56**, (11), pp. 3954–3962
- [26] Appa Rao B.V., Iqbal M.Y., Sreedhar B.: 'Electrochemical and surface analytical studies of the self-assembled monolayer of 5-methoxy-2-(octadecylthio)benzimidazole in corrosion protection of copper', *Electrochim. Acta*, 2010, **55**, (3), pp. 620–631