

FABRICATION AND OPTIMUM CONDITIONS OF A SUPERHYDROPHOBIC SURFACE USING A FACILE REDOX REACTION AND A SOLUTION-IMMERSION METHOD ON ZINC SUBSTRATES

IZDELAVA IN OPTIMALNI POGOJI ZA SUPERHIDROFOBNO POVRŠINO Z UPORABO REDOKS REAKCIJE IN Z METODO POTOPITVE V RAZTOPINO CINKOVIH SUBSTRATOV

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A superhydrophobic surface on a zinc substrate was prepared with a simple and economic redox reaction and a solution-immersion method, and the fabrication procedures and conditions were optimized. The effects of the reactant concentrations, reaction time, modifier types, modifier concentrations and modification time on the fabrication of the superhydrophobic surface were systematically studied by analyzing the water contact angle (CA) and SEM results. The results show that an excellent superhydrophobic surface was prepared when zinc plates were immersed in a 0.01-M CuSO₄ solution for 1 h and then modified with 5 % of mass fraction of lauric acid for 1 h. The water CA of the prepared surface was as high as 155.7°. The surface structure and composition of the superhydrophobic surfaces were characterized with SEM and FT-IR. The results show that the surface structure consists of a small number of particles and petal-like structures, and the product exhibits a long alkyl chain with a low surface energy, which contributes to the formation of the surface superhydrophobicity.

Keywords: superhydrophobic surface, cupric sulfate, redox reaction, solution immersion, optimum condition

Superhidrofobna površina na substratu iz cinka je bila pripravljena z enostavno in ekonomično redoks reakcijo in z metodo potopitve v raztopino ter z optimiziranjem postopkov in pogojev izdelave. Učinki koncentracij reagenta, reakcijski čas, modifikator učinka, njegove koncentracije in čas modifikacije pri izdelavi hidrofobne površine, so bili sistematično preučevani z analizo stika kota z vodo (CA) in s SEM- rezultati. Rezultat je pokazal, da je bila superhidrofobna površina odlično pripravljena, ko so bile cinkove plasti potopljene v 0,01-M CuSO₄ raztopino za 1 h in nato 1 h modificirane s 5 % lavrinske kisline. Kontaktni vodni kot pripravljene površine je 155,7°. Struktura površine in sestava superhidrofobne površine sta bili preiskovani s SEM in FT-IR analizo. Rezultati so pokazali, da je struktura površine sestavljena iz majhnega števila delcev in ima listno strukturo. Produkt ima dolgo alkilno verigo z nizko energijo površine, ki pripomore k formaciji superhidrofobnosti površine.

Ključne besede: superhidrofobna površina, bakrov sulfat, redoks reakcija, potopitev v raztopino, optimalno stanje

1 INTRODUCTION

Surface wetting is an important property, which is characterized by how a liquid makes contact with a solid surface. It depends upon the combined effects of the surface chemistry and surface morphology.^{1–3} In nature, various biological surfaces, such as lotus leaves and rice leaves, exhibit surface-wetting properties, which are beneficial for their subsistence.^{4–9} Superhydrophobicity and self-cleaning of lotus leaves were found to be a result of a waxy hierarchical surface structure.¹⁰ Rice leaves exhibit anisotropic dewetting behavior due to anisotropic hierarchical structures with ordered arrangements.¹¹ Superhydrophobic surfaces, which exhibit self-cleaning and non-wetting properties with a water contact angle (CA) larger than 150°, have drawn much attention both in scientific research and applications

based on their unique properties,^{12,13} such as anti-fogging,¹⁴ anti-icing,^{15,16} and self-cleaning.^{17,18} These properties are desirable for many industrial and biological applications such as anti-biofouling paints for boats, anti-sticking of snow for antennas and windows, self-cleaning wind shields for automobiles, metal refining, stain-resistant textiles, and anti-soiling architectural coatings.¹⁷

Inspired by nature, a large variety of methods have been developed to synthesize a superhydrophobic surface by constructing rough micro-nanostructures and modifying the surface with chemical materials with a low surface free energy, such as the sol-gel method,¹⁹ electrohydrodynamics method,²⁰ plasma fluorination method,²¹ laser etching,²² chemical vapor deposition²³ and so on. Most of the methods need sophisticated and expensive equipment, so it is necessary to use a simple

method to fabricate a superhydrophobic surface. It is well known that solution immersion is a simple method to prepare a superhydrophobic surface. D. K. Sarkar and N. Saleema²⁴ prepared a leaf-like Ag micro-nanostructure on copper substrates by means of adjusting the concentration of the aqueous silver-nitrate solution and the reaction time. The water contact angle (CA) they got was about 162°. T. Ning, W. Xu and S. Lu²⁵ prepared a Pt micro-nanostructure on zinc substrates using solution immersion. They simply prepared a superhydrophobic surface using the replacement-deposition process. X. Hou, F. Zhou, B. Yu, W. Liu²⁶ prepared a superhydrophobic surface with hierarchical nanorods on zinc substrates by means of differential etching and hydrophobic modification. S. Wang, L. Feng, L. Jiang²⁷ fabricated a novel superhydrophobic surface merely by immersing a copper sheet into a solution of fatty acid at ambient temperature.

As a popular engineering material, zinc is widely used in industrial fields. Many ways have been used to fabricate a superhydrophobic surface on zinc substrates. H. Liu, S. Szunerits, W. Xu, R. Boukherroub²⁸ prepared a superhydrophobic surface on zinc substrates with a contact angle of 151° using a simple immersion technique. T. Ning, W. Xu, S. Lu²⁵ also introduced a simple way for constructing superhydrophobic surfaces with hierarchical flower-like micro-nanostructures using the deposition process.²⁵ The maximum CA value they got was about 171°. They also tested the stability of the prepared surface and proved that a pure platinum surface on a zinc substrate is stable. Nevertheless, the materials they used are not economic. It is necessary to find an economic material to fabricate a micro-nanostructure on a zinc substrate. In addition, economic surface modifiers with a lower surface energy can be used to promote the superhydrophobicity, such as lauric acid, myristic acid, palmitic acid and octadecanoic acid.

In this work, we tried to fabricate a superhydrophobic surface on a zinc substrate using a simple redox reaction and surface modification. The micro-nanostructure on the zinc substrates was created by immersing zinc plates in aqueous solutions of copper sulfate with different concentrations and for different times. The superhydrophobic surface was prepared by modifying the surface with different concentrations of the modifier and for different times. The conditions for preparing superhydrophobic surfaces were further optimized. The procedure is environmentally friendly, economic and easy to control.

2 EXPERIMENTAL PART

2.1 Materials

All the reagents used were of the analytical-reagent (AR) grade and used as received without further purification. A zinc substrate (10 × 10 × 0.2) mm with a purity of 99.9 % was obtained from Tianjin Damao Chemical Reagent Co. Ltd., China. Copper sulfate was purchased

from Tianjin Kaitong Chemical Reagent Co. Ltd., China. Lauric acid was purchased from Tianjin Tailande Chemical Reagent Co. Ltd., China. The other experimental chemicals of the analytical-reagent grade were purchased from Shanghai Chemical Reagent Co. Ltd., China.

2.2 Preparation of a micro-nanostructure on zinc substrates

Before the experiment, the surface of zinc was polished with abrasive papers to remove the oxides and then cleaned ultrasonically in sequence with alcohol and deionized water, each time for 10 min to remove the impurities of the zinc surface. After being dried at ambient temperature, dried zinc specimens were immersed in a CuSO₄ solution (a series of CuSO₄ solutions with the Cu²⁺ concentration ranging from 0.002 to 0.05 mol/L) for a few minutes at room temperature. Then the immersed specimens were rinsed with distilled water and finally dried at 120 °C in air for 20 min. The plate with the highest CA was considered for the optimized reaction time and reactant concentration.

2.3 Modification

The plates were etched using the optimized reaction time and solution concentration and then they were modified with different modifiers for 1h, such as lauric acid, myristic acid, palmitic acid and octadecanoic acid with a concentration of 5 % mass fraction in ethanol. The plate with the highest CA was considered for the optimized modifier. Then the plates were modified with the optimized modifier at different concentrations of (1, 2, 5, 10, 15, 20, 30 and 40) % mass fractions, and then the optimized concentration could be found.

2.4 Characterizations

Both CA values were measured with a contact-angle goniometer (FTA 1000, First Ten Ångströms Inc., USA) following the standard procedures. Water droplets were placed at four positions on one sample, and the averaged value was adopted as the contact angle. The volume of an individual water droplet used for the static CA measurements was about 5 µL. All Fourier transform infrared (FT-IR) spectra were obtained with a FT-IR spectrometer (Bruker Tensor 27, Germany). The micro-nanostructure of the superhydrophobic surfaces was observed with a scanning electron microscope (SEM, HITACHI, S-3400, Japan).

3 RESULTS AND DISCUSSION

3.1 Influence of the reactant concentration and time

The effects of the CuSO₄ concentration and reaction time on the surface wettability of the obtained surfaces were meticulously studied using CA measurements (**Figure 1**). The zinc plates were immersed in the solu-

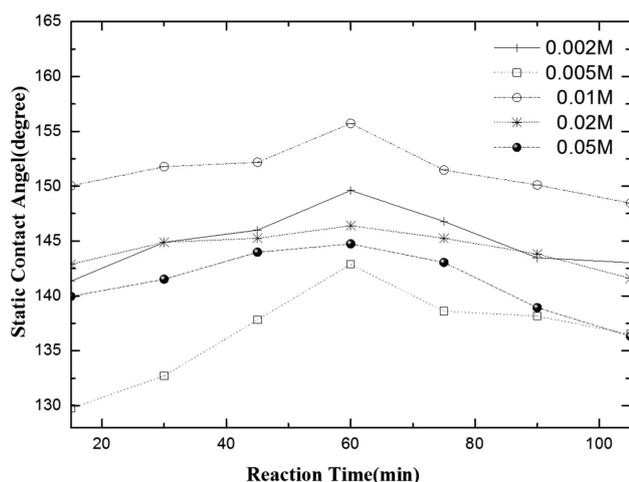


Figure 1: Curves of the water contact angle of the prepared samples as a function of the concentration of the CuSO_4 solution and reaction time

tions with different CuSO_4 concentrations ranging from 0.002 to 0.05 M for different times. Then the reaction products were modified with 5 % mass fraction of lauric acid-ethanol solution for 1 h. As shown in **Figure 1**, the water CAs of the surfaces varied significantly depending upon the concentration of the CuSO_4 solution under the condition of a constant reaction time and the reaction time under the condition of a constant CuSO_4 concentration.

With an increase in the CuSO_4 concentration, the values of the CA increase at first. When the CuSO_4 concentration is 0.01 M, the CAs obtain their maximum values. As the CuSO_4 concentration continues to grow, the CAs decrease. In addition, the CAs reach their maximum values when the reaction time is 1 h for different concentration curves. It therefore indicates that 0.01 M is the optimum concentration and 1 h is the optimum reaction time. The change trend of the CAs may be a result of an increase of the amount of the deposition product formed on the surface and the resulting changes in the surface roughness. With an increase in the CuSO_4 concentration, the quantity of deposition increases under the constant reaction time. As the reaction time increases, the quantity of the product also increases under the constant CuSO_4 concentration. In fact, M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe²⁹ found that surfaces with a water contact angle of 150° could be developed by introducing a proper roughness to the materials with low surface energies. Thus, when the product quantity reaches a certain value, the value of the surface roughness is proper, resulting in the maximum CA.

3.2 Influence of the kind of modifier

Figure 2 shows the water CA for the zinc surfaces, reacted for 1 h and modified with different modifiers (lauric acid, myristic acid, palmitic acid and octadecanoic acid) for 1 h. The CA is 155.7° , 149.3° , 148.6° , and

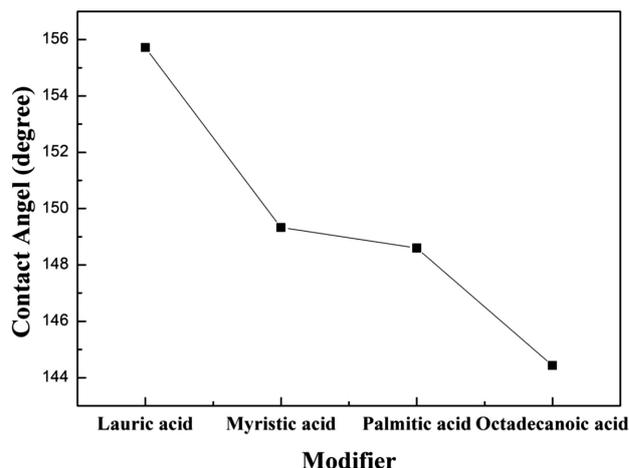


Figure 2: Curves of the contact angle versus the modifier types. The modifiers are lauric acid, myristic acid, palmitic acid and octadecanoic acid

144.4° when the surface is modified with lauric acid, myristic acid, palmitic acid and octadecanoic acid, respectively. The cause of this phenomenon is the same mass fraction because lauric acid's molecular weight is minimum, and the numbers of myristic acid's or palmitic acid's molecules in the unit volume are lower than the number of molecules of lauric acid. It can be concluded that among these modifiers, lauric acid is the most powerful for achieving the best superhydrophobicity.

3.3 Influence of modifier concentrations

Figure 3 shows the water CA for the zinc surfaces reacted for 1 h and modified with a lauric acid-ethanol solution with concentrations of (1, 2, 4, 5, 10, 15, 20 and 25) % for 1 h. The CA is 144.5° , 146.4° , 150.6° , 155.7° , 145.9° , 144.0° , 142.8° and 141.0° . The CAs of the surfaces vary significantly depending upon the concentration of the lauric acid solution under the conditions of constant reactant concentrations and reaction time

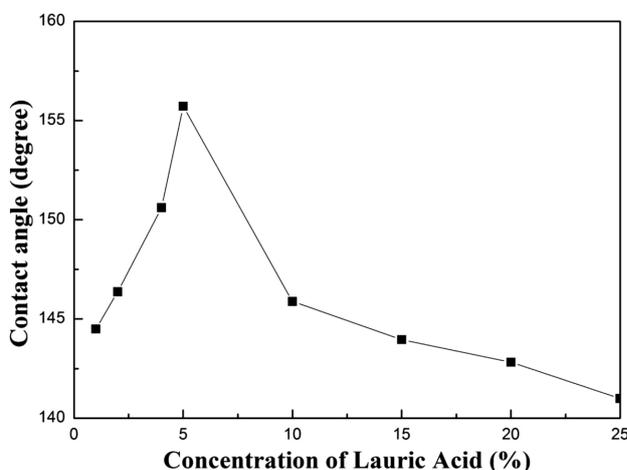


Figure 3: Curves of the contact angle versus the lauric-acid concentration

(0.01M CuSO_4 concentration and 1 h reaction time). When the concentration of lauric acid is 5 % mass fraction, the water CA reaches the maximum value of about 155.7° . This indicates that for the lauric-acid modifier, 5 % of mass fraction is the optimum concentration. When the concentration of lauric acid is less than 5 % of mass fraction, the CAs of the surfaces increase with the concentration of lauric acid. When the lauric-acid concentration is increased, there are more deposit products on the surface structure, which may damage the prepared micro-nanostructure on the zinc plate so that the deep-seated rough structure obtained with a redox reaction cannot play an effective role in the preparation of the final surfaces, which results in a decrease in the water CA.

3.4 Influence of the modification time

Figure 4 shows the water CAs for the zinc surfaces reacted for 1 h and modified with 5 % mass fraction of lauric acid for different modification times of (0.5, 1, 1.5, 2, 3, 4) h and 5 h. The CA is 147.3° , 155.7° , 147.7° , 145.3° , 145.2° , 145.2° and 144.6° , respectively. It is clear that 1 h is a suitable modification time. The reason for this is the fact that a chemical reaction taking 0.5 h is not completed and the surface modification is not completed either. On the other hand, if the chemical-reaction time is greater than 1 h, a layer of lauric-acid self-assembled molecular film forms on the micro-nanostructure surface, covering the original micro-nanostructure.

3.5 Surface micro-nanostructure and composition of superhydrophobic surfaces

Figure 5 shows digital images and the wetting property of water droplets on the untreated surface and the prepared superhydrophobic surface using water-contact-

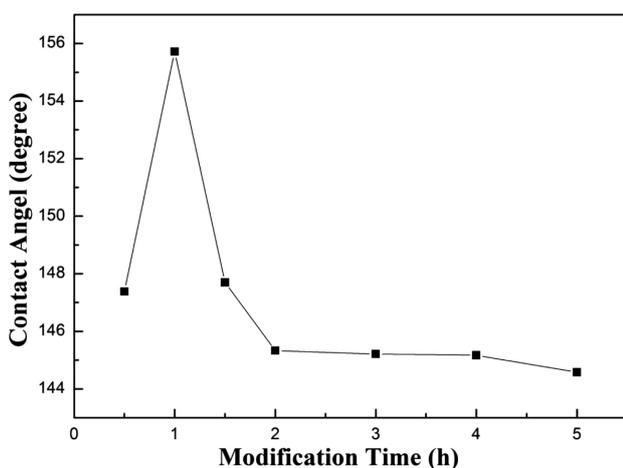


Figure 4: Water contact angles of the prepared samples for different modification times ranging from 0.5 h to 5.0 h

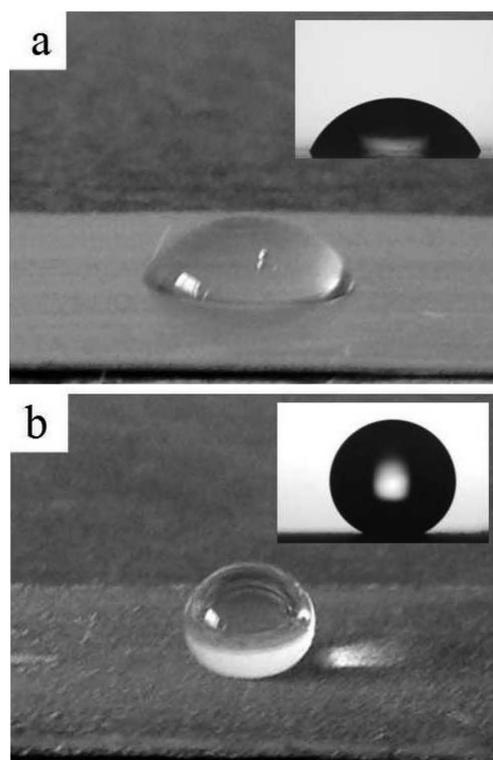


Figure 5: Photographs of a water droplet on the surfaces of: a) untreated zinc substrate and b) zinc substrate treated under the optimum condition. The insets correspond to the water contact angles

angle measurements, demonstrating the superhydrophobicity of the prepared surface. The water contact angle of the untreated zinc substrate is 64.1° (the inset in **Figure 5a**) while the treated zinc substrate surface exhibits a water-contact-angle value of 155.7° (the inset in **Figure 5b**). A smooth zinc surface is hydrophilic, but a rough modified zinc surface becomes superhydrophobic. It is well known that the roughness structure and the chemical composition of a surface result in the wettability of a solid surface. A successful fabrication of a superhydrophobic surface is believed to be a cooperative effect of a surface structure prepared with a redox reaction and a surface modification with low-surface-energy materials.

The surface micro-nanostructure was further studied with scanning electronic microscopy (SEM) as shown in **Figure 6**. There are obvious differences as the reaction time changes from 15 min to 105 min. **Figures 6a** and **6b** are SEM images of a 15-min reaction at $2000\times$ and $6000\times$ magnifications, respectively. The results show that a small amount of particles and petal-like structures formed on the zinc substrate. The average diameter of the particles is about 400 nm, as shown in **Figure 6b**; that is, a certain micro-nanostructure is formed, which makes the contact angle to be about 150° . **Figures 6c** and **6d** are SEM images of a 1-h reaction at $2000\times$ and $5000\times$ magnifications, respectively. Compared with

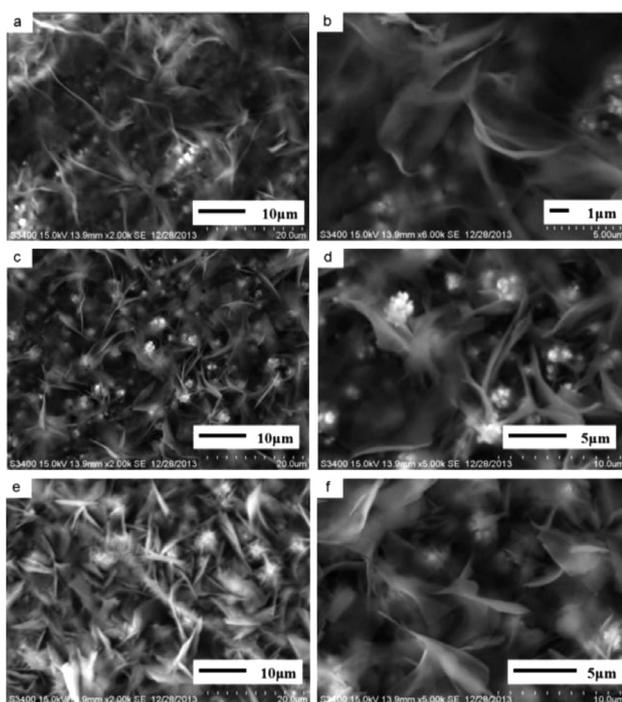


Figure 6: SEM images of the superhydrophobic surfaces on zinc substrates reacted in a 0.01 M CuSO_4 solution for different times and modified with 5 % of lauric acid-ethanol solution for 1 h: a) 15 min reaction, 2000 \times ; b) magnified part of a), 6000 \times ; c) 1 h reaction, 2000 \times ; d) magnified part of c), 5000 \times ; e) 105 min reaction, 2000 \times ; f) magnified part of e), 5000 \times

Figures 6a and **6b**, the petal-like structures become dense and the average diameter of the particles increases to about 1 μm . A certain degree of hierarchical structure is formed when the reaction time rises to 1 h. This kind of hierarchical structure will keep the air in the interspaces when a droplet drops on the surface structure. Combined with the surface modification with a layer of low-surface-energy materials, the contact angle reaches

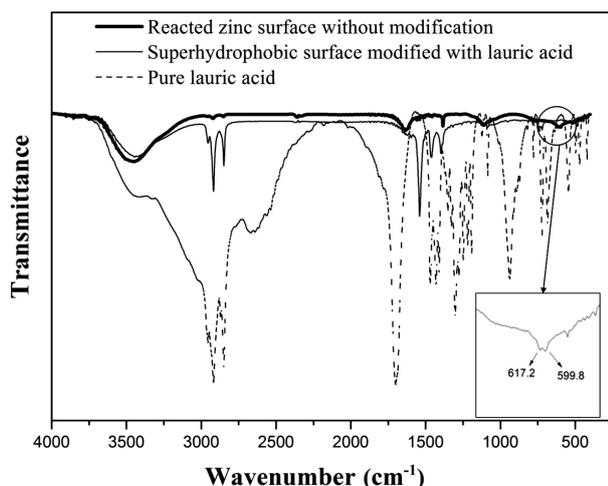


Figure 7: FT-IR spectra of lauric acid (dotted line), the zinc surface reacted for 105 min without a modification (solid line), and the superhydrophobic surface reacted for 105 min and modified with 5 % mass fraction of lauric acid-ethanol solution for 1 h (thick line)

about 155.7°. However, when extending the reaction time to 105 min, the petal-like micro-nanostructure becomes bigger as shown in **Figures 6e** and **6f**. The contact angle decreases to 148.5°.

Figure 7 shows the change in the surface composition of the prepared superhydrophobic surfaces on the zinc substrates. The two peaks at 599.8 cm^{-1} and 617.2 cm^{-1} that appeared in the FT-IR spectra of the reacted zinc surface without a modification are the Cu-O stretching.^{30,31} Compared with the reacted zinc surface without a modification, there are two new peaks at 2849 cm^{-1} and 2918 cm^{-1} in the FT-IR spectra of the superhydrophobic surface, which were identified as the symmetric and asymmetric vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups of lauric acid, respectively. What is more, the stretching vibration of the free C=O band from lauric acid at 1701 cm^{-1} disappeared and a new band appeared at 1539 cm^{-1} . This goes to prove the C=O stretching vibration of coordinated COO^- moieties to Cu^{2+} ions. Thus, the results demonstrate that $\text{CH}_3(\text{CH}_2)_{10}\text{COO}^-$ and Cu^{2+} formed a bond of $\text{Cu}(\text{CH}_3(\text{CH}_2)_{10}\text{COO})_2$ on the zinc surface. The combination of the product with a low surface energy and the micro-nanostructure allows the prepared surface to have superhydrophobic properties.

4 CONCLUSIONS

In summary, we have prepared superhydrophobic surfaces on zinc substrates using a simple redox reaction and the solution-immersion method. This fabrication strategy is based upon the replacement process and modification. In addition, we also investigated the optimum conditions. The results confirmed that the surface could be prepared by immersing zinc plates in a 0.01 M CuSO_4 solution for 1 h, using 5 % mass fraction of lauric acid-ethanol solutions to modify the surface for 1 h. The corresponding water CA of the surface was as high as 155.7°. The present work provides a simple and economic method for preparing commendable superhydrophobic zinc surfaces, which holds bright prospects in our daily life due to its simple and economic process.

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