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A Simple Method for Fabrication of Bionic Superhydrophobic Zinc Coating with Crater-like Structures on Steel Substrate

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Abstract

Surface modification with superhydrophobicity is a popular and challenging research field on metals. In this work, a simple method was used to fabricate a bionic superhydrophobic zinc coating with crater-like structures on pipeline steel surface. This method involved electrodeposition of zinc coating and chemical reaction in perfluorooctanoic acid ethanol solution. The perfluorooctanoic acid with low surface free energy was not only used for chemical etching but also used for fluorinated modification. The contact angle of water on such superhydrophobic zinc coating was up to 154.21˚, and the sliding angle was less than 5˚ due to the micro crater-like structures and the low surface free energy. Moreover, the prepared superhydrophobic zinc coating demonstrated excellent self-cleaning property and great stability at room temperature, and the contact angle of water on this coating remained stable after storage in air for more than 80 days. This superhydrophobic zinc coating will open much wider applications of electrodeposition metal coating, including self-cleaning property, and can be easily extended to other metals.

Keywords: bionic surface, superhydrophobic coating, electrodeposition, crater-like structure, self-cleaning

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1 Introduction

Superhydrophobic surface has attracted tremendous attention owing to its potential applications in the fields of self-cleaning[1], anti-corrosion[2], anti-icing[3], fluid drag reduction[4], oil/water separation[5], *etc*. During the past two decades, superhydrophobic surfaces inspired by the lotus-leaf effect have been extensively studied for these purposes[6]. In order to prepare a superhydrophobic surface on solid substrates, it is necessary to fabricate microstructures and decrease the surface free energy.

Many methods have been developed to fabricate superhydrophobic surfaces, such as chemical etching[7], anodic oxidation[8], solution-immersion[9], electrodeposition[10], electrostatic spinning[11], template[12], and shot blasting[13], due to their wide range of applications in industrial production. Among these methods, the electrodeposition method is low-cost, simple, and does not require severe condition[14,15], for example, expensive material or complex procedure. Moreover, surface morphology plays a key role in fabricating superhydrophobic surface because the micro/nano structure can trap air to prevent the spreading of water droplet when it is deposited on the solid surface[16]. So far, various surface morphologies have been prepared for achieving superhydrophobicity, for instance, square pillar structure[17], convex structure[18], pyramid structure[19], inverted trapezoid structure[20], re-entrant structure[21], and over-hanging structure[22]. Furthermore, long chain fatty acid and silane are often used as the modified materials due to the low surface energy, and they can be absorbed onto the substrate surface[23].

In industrial production, pipeline steel as an important metal has extensive applications, especially for transportation. The adhesion of water mixture on steel surface directly affects the production and transportation. Therefore, it is necessary to fabricate a superhydrophobic surface with self-cleaning property on pipeline steel. Furthermore, as a traditional technology, electrodeposition of zinc coating is usually used for protecting the metals from corrosion[24]. Meng *et al.* prepared superhydrophobic surfaces on many common metals, including zinc, by an electrochemical reaction in per-

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fluorocarboxylic acid solution[25]. Hence, preparing a superhydrophobic electrodeposition zinc coating on pipeline steel surface is viable.

In this paper, we reported a method for fabrication of a superhydrophobic zinc coating with crater-like structures on pipeline steel surface. This simple and inexpensive method consisted of electrodeposition of zinc coating and electrochemical reaction in perfluorooctanoic acid ethanol solution. In addition, the influences of experimental conditions on the surface morphology and wettability were discussed. The self-cleaning property and the durability of the superhydrophobic zinc coating were also investigated.

2 Materials and experiment

2.1 Materials

X90 pipeline steel was obtained from TGRC of China and cut into the size of 20 mm × 50 mm × 3 mm. Zinc plate (99.9 wt.%) was obtained from the common market in China and cut into the size of 20 mm × 50 mm× 5 mm. Zinc sulfate heptahydrate ($ZnSO_4·7H_2O$, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd in China. Sulfuric acid (H_2SO_4), anhydrous ethanol and acetone were all of analytical grade and purchased from West Long Chemical Co., Ltd in China. Perfluorooctanoic acid (PFOA, 90%) was purchased from aladdin in China.

2.2 Fabrication of superhydrophobic zinc coating

The steel and zinc samples were polished with sandpaper of 2000#, and then ultrasonically cleaned in anhydrous ethanol and in distilled water for 5 min, respectively, for degreasing. After being cleaned, the steel samples were processed with pretreatment using alkali and acid solution, which was detailed in Ref. [26].

Next, the electrodeposition of zinc coating on steel surface was implemented by immersing the steel (cathode) and the zinc (anode) samples in the aqueous solution including 240 $g·L^{-1}$ of $ZnSO_4·7H_2O$ (pH adjusted by H_2SO_4 to about 4), and the distance between the anode and the cathode was fixed at 2 cm. A direct current (4 $A·dm^{-2}$) was conducted to electrodes for 15 min to 40 min, followed by another current density (9 $A·dm^{-2}$) quickly for 1 min to 6 min. The temperature of the electrodeposition solution was 25 ˚C, and the effective area of the steel sample was fixed to 20 mm × 35 mm with the rest place covered by electrical tape.

Finally, the steel sample was processed with chemical etching and fluorinated modification using perfluorooctanoic acid (PFOA) ethanol solution[27]. To be more specific, the steel sample with zinc coating was immersed in a beaker with 100 mL of 0.01 $mol·L^{-1}$ PFOA ethanol solution for 11 days at room temperature. Then, the sample was left in a petri dish at room temperature to dry.

2.3 Characteristics

A field emission Scanning Electron Microscope (SEM, Nova NanoSEM 450, FEI) was used for investigating the surface morphology of the prepared samples, and the sample for SEM test was coated with platinum (Cressington, 108Auto) to increase the surface conductivity. An X-ray Diffraction (XRD, X'Pert PRO MPD, PANalytical B.V.) was used for examining the crystal structure of the sample surface. An Energy Disperse Spectroscopy (EDS, Oxford X-MaxN, FEI) and a Fourier Transform Infrared (FTIR, NICOLET 8700, Thermo) were used to record the chemical compositions of the sample surface.

The wettability of the coating surface was tested by contact angle meter (SL200B, USA, KINO) using about 5 μL of water droplet at the ambient temperature. At least five different positions for each sample surface were measured for the calculation of the average Contact Angle (CA). Sliding Angle (SA) was the inclining angle of the tested surface when a water droplet about 8 μL starts rolling. The self-cleaning property of the superhydrophobic coating was tested by deposition of fly ash on the surface, and then the surface was cleaned by the directed rolling water droplet of about 8 μL. The digital pictures were obtained at different moments in time.

3 Results and discussion

3.1 Surface morphology and wettability of the steel under different conditions

To investigate the impact of different experimental conditions on the surface morphology of the steel sample, the SEM images of the steel surface are given in Fig. 1. After the first step electrodeposition (4 $A·dm^{-2}$, 20 min), it can be seen from Fig. 1a that the hexagon structures with textures were nearly parallel to the substrate surface, and this was because the faster non-epitaxial growth of the nuclei reduced the free energy of the system[28]. Furthermore, as shown in Fig. 1b,