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Design of submicron structures with superhydrophobic and oleophobic properties on zinc substrate

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ABSTRACT

A superhydrophobic and oleophobic surface was demonstrated on Zn substrate via a composite method using chemical etching, hydrothermal reaction, and fluorinated modification. The surface morphology with aligned ZnO rods that grew almost perpendicularly on Zn substrate and had flat hexagonal crystallographic planes played a key role in the achievement of the superhydrophobicity and oleophobicity. The Zn surface with aligned ZnO rods was then made superhydrophobic and oleophobic with maximum distilled water and peanut oil contact angles (CAs) of 152° and 146°, respectively, by further fluorinated modification, and the sliding angle (SA) for distilled water was less than 10°. Moreover, on the basis of the classical models (Wenzel's and Cassie's model), an improved model was established to analyze the influence of the surface morphology on the wettability. The effect of the experimental parameters including the hydrothermal temperature and the concentration of the chemical etching agent on the surface morphology and the wettability were examined, and then the optimum parameters were obtained. This method is simple and inexpensive, and has potential application in depositing Zn coating that can provide both corrosion resistance and oleophobicity to the substrate metals.

1. Introduction

Many breakthroughs in the wettability have been achieved via investigating of the superhydrophobicity phenomenon displayed by nature, including the lotus leaves [1], the nepenthes pitcher plants [2], the geckos' foot [3], and the spider silk [4], which provides inspiration and creation for numerous research groups in the field of science and technology. The understanding of the functions provided by objects and processes found in nature has guided us to imitate and fabricate hydrophobic or oleophobic films because the superhydrophobic or oleophobic surfaces could provide many practical applications, such as corrosion resistance [5], self-cleaning property [6], drag reduction [7], and oil–water separation [8].

To date, researchers have developed a large number of efficient methods to fabricate superhydrophobic or oleophobic surfaces [9–12]. It has been revealed that the combination of the surface morphology and the low-surface-energy material can achieve superhydrophobicity or oleophobicity [13]. So far, in order to obtain artificial superhydrophobic or oleophobic surfaces, a great many of different surface morphologies have been fabricated successfully, for example, the pillar morphology [14–16], the overhanging morphology [17], the convex and concave morphologies [18], the trapezoid morphology [19], the sinusoid and paraboloidal morphologies [20], etc.

Recently, ZnO microstructure that can increase surface roughness, resulting in the superhydrophobicity of the substrate surface with a fluorosilane coating, has become the subject of the extensive investigations. Moreover, the hydrothermal method reported for the fabrication of the superhydrophobic surface is less time-consuming and without any post-treatment procedure [21–23]. Hence, the development of this simple and effective method to fabricate superhydrophobic surface is necessary. However, in aforementioned articles, the source of zinc ions was provided by hydrothermal solution. Fang et al. [24] prepared the radial growth (perpendicular to the surface) of ZnO nanofibers on Zn substrate by hydrothermal reaction, and Zn was used as not only the substrate but also the source of zinc ions. On the other hand, to the best of our knowledge, this morphology combined with surface modification can achieve superhydrophobicity [25]. However, it would increase the adhesion of the surface when the surface structure was single-scale or small enough at nanometer scale [26], we shall optimize the preparation technology to fabricate the superhydrophobic and oleophobic surface with submicron structure on Zn substrate to decrease the adhesion.

In this article, after Zn substrate was etched, the aligned ZnO rods that were almost perpendicular to the surface in-situ grew on the Zn substrate via simple hydrothermal method, and the superhydrophobic and oleophobic surface was obtained after fluorinated modification. Moreover, the effect of the experimental parameters including the hydrothermal temperature and the concentration of the chemical etching agent on the morphology and the wettability of the Zn substrate surface were studied by an improved model.

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2. Experiment

2.1. Chemicals and materials

Pure Zn plate was used as the substrate material and its chemical compositions were listed in Table 1. All the materials and reagents were used as received. The hydrochloric acid (HCl, 36–38%) was used as the chemical etching agent. The ammonia/ethanol aqueous solution was used as the hydrothermal solution. The perfluorooctanoic acid (PFOA, a low surface energy material, purity 90%) was used for the fluorinated modification.

2.2. Fabrication of ZnO submicron structures

The Zn substrates ($10 \times 30 \times 2$ mm^3) were successively polished with sandpapers to 2000#, subjected to ultrasonic treatment in anhydrous ethanol and acetone for 5 min, respectively, to remove the oil and contamination, and dried with a hair dryer. Then, the prepared specimens were immersed in HCl aqueous solution (0.5, 0.8, 1.0, and 1.2 mol/L, respectively) with the volume of 50 mL for chemical etching. After being etched for 90 s at room temperature (about 20 °C), the specimens were ultrasonically cleaned in distilled water and anhydrous ethanol for 5 min, respectively. Finally, the cleaned and etched Zn specimens were immersed in an ammonia/ethanol aqueous solution (100 mL) containing ammonia water (5 mL), anhydrous ethanol (50 mL), and distilled water (45 mL) in a teflon-lined stainless steel reaction autoclave followed by heating at a desired temperature (85, 95, 105, 115, and 125 °C, respectively) for 24 h. After the hydrothermal treatment, the Zn samples were ultrasonically cleaned in distilled water and anhydrous ethanol for 5 min, respectively, followed by being dried again with a hair dryer.

2.3. Fluorinated modification

After the ZnO submicron structure was fabricated on Zn substrate, it was chemically modified through being immersed in 0.01 mol/L PFOA anhydrous ethanol solution (PAAES) with the volume of 50 mL for 11 days at room temperature (about 20 °C). In order to prevent the volatilization of anhydrous ethanol, the beaker was sealed with plastic wrap. The fluorinated surface was then left in a petri dish at room temperature for 24 h prior to the contact angle measurement. The superhydrophobic and oleophobic Zn surface was finally obtained under optimized experimental parameters. A scheme of the fabrication process is shown in Fig. 1. Depending on the optimized concentration of HCl aqueous solution and hydrothermal temperature, this process resulted in the formation of oriented ZnO submicron structures surmounted with PFOA film after fluorinated modification.

2.4. Characterizations

The morphology of the surface was observed by a field-emission scanning electron microscopy (FESEM, Zeiss Ultra55, Ti Photonics) equipped with EDS system for elemental analysis. The surface chemical compositions were obtained using a fourier-transform infrared spectrophotometer (FTIR, NICOLET 8700, Thermo). The crystal structure of the specimen was analyzed using an X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical B.V.) equipped with a Cu Kα radiation within the range from 20° to 80°. The contact angle measurements were conducted on an optical goniometer (SL200B, USA, KINO) at ambient temperature. Distilled water and peanut oil droplets (about 2.5 μL) were gently deposited on the testing surface using a microsyringe, and the data was an average of over three independent measurements for each sample. The measurement error of the goniometer was ±1°.

Table 1
Chemical compositions of the Zn substrate (wt.%).

Zn	Cd	Cu	Fe	Pb	Sn
99.9977	0.0004	0.0001	0.0002	0.0014	0.0001

3. Results and discussion

3.1. Surface morphology

The surface morphology of the Zn substrates was controlled by adjusting the experimental parameters. Fig. 2 shows the surface morphology of the substrate variation with the hydrothermal temperature. Prepared Zn plates were immersed in a 1 mol/L HCl aqueous solution for 90 s and in an ammonia/ethanol aqueous solution at a constant temperature, ranging from 85 °C to 125 °C, for 24 h, respectively. When the hydrothermal temperature was 85 °C, the surface (Fig. 2(a)) was mainly covered by compact acicular structure, and the cauliflower-like structure was sparsely interspersed on the surface. Increasing the temperature to 95 °C, the surface mainly contained oriented submicron rod-like structures (Fig. 2(b)) and the top of the rod was flat hexagon. Once the temperature continued to increase (105 °C), the aggregates of the submicron structures exhibited sparsely on the surface while the size of the submicron structure almost unchanged (Fig. 2(c)). For further higher hydrothermal temperature (115 °C and 125 °C), the aggregates of oriented submicron structures were obvious and the diameter of the submicron structure became larger, resulting in the decrease of the spacing among the oriented submicron structures (Fig. 2(d)–(e)). From these FESEM images, one can observe that the diameter of the submicron structures increased with the increase of the hydrothermal temperature. On the other hand, the spacing among the oriented submicron structures decreased when the temperature increased. According to La Chatelier's principle, forming precipitations is exothermic, resulting in the increase of the heat content, then the equilibrium shifts to the reactants. This decreases the nucleation rate when the concentration of ionic is a constant value. Therefore, there will be less crystal nuclei at higher temperature, which explains the reason why the diameter of oriented submicron rod-like structure becomes larger with the increase of temperature. It revealed that the morphology of the as-prepared surface was strongly influenced by the hydrothermal temperature, and this was also mentioned in related literature [27]. Those results showed clearly that oriented submicron rod-like structures can be fabricated by using this straightforward process.

Zn as the reactive metal is easy to obtain crevices and gaps in the surface via chemical etching (Fig. 3) because the reaction rate between each crystal plane and HCl aqueous solution is different. Therefore, in order to investigate the influence of the concentrations of HCl aqueous solution on the surface morphology (Fig. 4), the Zn substrates were immersed in different concentrations of HCl aqueous solution, ranging from 0.5 mol/L to 1.2 mol/L, for 90 s and then in an ammonia/ethanol aqueous solution at 95 °C for 24 h. As shown in Fig. 4(a), when the concentration was 0.5 mol/L, the surface was composed of a large number of needle-like structures and most of them were uniform. In addition, few rod-like structures existed sporadically on the surface. Once the concentration increased to 0.8 mol/L, the surface morphology (Fig. 4(b)) was mainly composed of rod-like structures, but these structures were relatively sparse. Increasing the concentration to 1.0 mol/L, as illustrated in Fig. 4(c), the surface contained a great number of aligned ZnO rod-like structures that grew almost perpendicularly on the substrate and had flat hexagonal crystallographic planes. The diameter of the rod-like structure was about 0.5 μm and the spacing among the oriented submicron rod-like structures was from 0.2 to 2 μm. Moreover, a literature found that the surface with single submicron structures is the structural basis for the formation of Cassie's state when the droplets were static on the surface [28]. The diameter of the rod-like structure became small again (Fig. 4(d)) which was similar to Fig. 4(a), in other words, the oriented submicron rod-like structures were not obvious when the concentration further increased. This was