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Fabrication of superhydrophobic and oleophobic surface on zinc substrate by a simple method

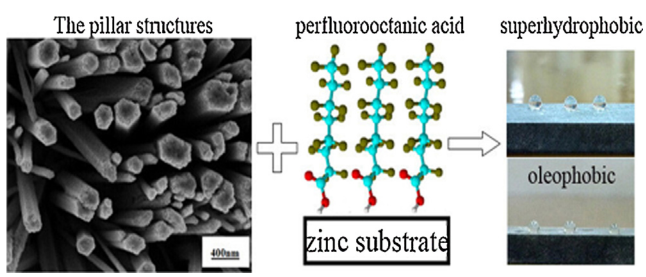
Li Hao, Yu Sirong*, Han Xiangxiang, Liu Enyang, Zhao Yan

College of Mechanical and Electronic Engineering, China University of Petroleum, Qingdao 266580, China

HIGHLIGHTS

- The superhydrophobic and oleophobic surface with hexagonal prisms was obtained.
- The contact angle of surface was correlated with the surface morphology.
- The surface morphology was related to the etching time and hydrothermal temperature.
- The improved wetting model was used to explain the experimental results.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports a simple approach for the preparation of superhydrophobic and oleophobic surface on zinc substrate. The surface was created by chemical etching and hydrothermal reaction, consisting of micro hexagonal prisms with about 4 μm in length, 0–1 μm in gap and 0.1–0.4 μm in diameter. The surface then became superhydrophobic and oleophobic with a fluoride coating, fabricated by chemically modified with perfluorooctanoic acid anhydrous ethanol solution. The effects of different process parameters, including chemical etching time and the hydrothermal temperature, on the surface morphology and wettability were examined using a scanning electron microscope (SEM) and a contact angle tester. The optimization of process parameters were obtained, namely, the chemical etching time was 90 s and the hydrothermal temperature was 95 °C. After zinc surface was treated using the optimum parameters, the results showed that the surface exhibited repellency toward distilled water and edible peanut oil with contact angles at 151.85° and 145.62°, respectively, and the sliding angle for distilled water was less than 10°.

1. Introduction

The nature provides inspiration and creation for many inventions about wettability, for example, the lotus leaves [1], the legs of water striders [2], the spider silk [3], the nepenthes pitcher plants [4], the peanut leaves [5], and wettability has been becoming more and more interesting in numerous scientific and technological fields. Superhydrophobic and oleophobic surface has broad prospect of application in engineering and daily life, such as improving the anti-corrosion [6], the drag reduction [7], the anti-frosting performance [8], and raising the hydrophobicity of textiles [9], etc. Therefore, finding the methods to create superhydrophobic and oleophobic surface is necessary.

Extensive literatures revealed that chemical composition and surface morphology both play important roles in the superlyophobicity/lyophobicity of general engineering materials [10]. However, even though a smooth solid surface was covered by a material (—CF_3 closely and orderly arranged) with a low surface free energy 6.7 mJ/m^2, the contact angle of water on it was only around 120° [11]. Therefore, it is very crucial to prepare

* Corresponding author. Tel.: +86 532 86983500x8708; fax: +86 532 86983300.
E-mail address: yusrchina@163.com (S. Yu).

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appropriate surface morphology on a solid surface in order to obtain a super-lyophobicity surface. Generally, the preparation of super-lyophobicity has two methods: one is to create a rough structure on a lyophobicity surface, and the other is to carry out surface modification on a rough surface using low surface free energy. A large number of approaches have been used to fabricate super-lyophobicity/lyophobicity surfaces, which involve the anodization and laser technology [12], the electrodeposition method [13], the electrospun method [14], the chemical etching method [15], hydrothermal reaction method [16], sputtering method [17]. Among these, chemical etching and hydrothermal reaction provide the advantages of great simplicity, low cost, and being suitable for almost any specimen type. Therefore, further development of above two methods to fabricate superhydrophobic and oleophobic surface is needed in experiments. Zinc is often applied as the coating metal of engineering material and widely used in many fields, therefore, achieving superhydrophobic and oleophobic properties on zinc surface has good application prospect and practical value. It is desirable to find a method which is less demanding conditions, simple operation, low cost and suitable for large-scale preparation for preparing superhydrophobic and oleophobic surface.

This work was inspired by the natural lyophobic biological materials and fabricated the rough surface with low free energy on the zinc substrate. Firstly, the sample surface was chemically etched by hydrochloric acid aqueous solution to create a rough surface with submicron structure. Then, obtain the rough surface with uniformly distributed hexagonal prism structures that were close to nanoscale after hydrothermal reaction. The zinc surface with hexagonal prism structures exhibited superhydrophobic and oleophobic properties after modified by low surface energy material.

2. Experiment

2.1. Materials and reagents

Zinc substrates were provided by Shanghai Ailiai Metallic material Co., Ltd. Anhydrous ethanol, acetone, ammonia hydroxide (NH_4OH, 25–28%), hydrochloric acid (HCl, 37%) were obtained from West Long Chemical Co., Ltd. and perfluorooctanoic acid (PFOA, 90%) was purchased from Aladdin.

2.2. Preparation of the rough surface

This technique is simple and economical. Firstly, zinc substrates (10 mm × 30 mm × 2 mm, 99.9%) were polished with sandpaper to 2000 # and cleaned. Then, the prepared zinc substrates were carried out using 1.0 mol/L hydrochloric acid (HCl) aqueous solution for different time (30, 60, 90, 120 and 150 s, respectively) at room temperature (about 20 °C) and cleaned in successive cleaning of anhydrous ethanol and distilled water in an ultrasonic cleaning instrument. Finally, the samples were immersed in a mixed solution containing ammonia hydroxide (5 mL), anhydrous ethanol (50 mL), and distilled water (45 mL) in a Teflon-lined stainless steel reaction still which was heated and kept at a constant temperature (85, 95, 105, 115 and 125 °C, respectively) for 24 h. After the hydrothermal treatment, the zinc substrates were taken out, cleaned, and dried with a hair dryer.

2.3. Surface modification

After the rough surface was fabricated, the zinc substrates were chemically modified by 0.01 mol/L perfluorooctanoic acid anhydrous ethanol solution (PAAES) for 11 days. The substrates were then taken out and dried at room temperature for 24 h.

2.4. Contact angle measurements

Contact angles were measured at a contact angle tester (SL200B, USA, KINO) which consists of a manual liquid deposition system and a computer-based image processing system. Distilled water and edible peanut oil were used as the test liquids, and about 2.5 μL of the liquid droplet was deposited on the specimen surface. Every testing result was an average of more than three different areas of the substrate. The measurement error of the contact angle is ±1°.

2.5. Surface characterization

The surface morphologies of the samples were investigated by a field-emission scanning electron microscope (FESEM, Zeiss Ultra55, Ti Photonics and S4800, Hitachi Limited) equipped with EDS system for elemental analysis. The X-ray powder diffraction data were examined using a X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical B.V.) equipped with a Cu Kα radiation source. Fourier transform infrared spectrum (FTIR) data were collected on a Fourier transform infrared spectrometer (FI-IR, NICOLET 8700, Thermo).

2.6. Theoretical background

Theoretical basis about a droplet on a rough surface can be attributed to Wenzel [18] and Cassie [19] models. The Wenzel and Cassie equations presented two possible equilibrium states for a droplet on the rough surface. When a droplet contacts a rough surface without air pockets, the static contact angle is given by Wenzel equation [18]. While if it is composite contact and the fractional area with air pockets, the static contact angle is given by Cassie equation [19]. On the basis of these two models, the researchers have been made some theoretical models, for instance, the square pillars model [20], the mushroom-type model [21], the pit model [22], the trapezoid pillar model [23].

In this paper, we depicted a model roughness structure made of hexagonal prisms arranged in a regular array and considered the geometry of flat-top in Fig. 1a. Let the length of the hexagon side be a, height be H and the gap of the nearest parallel edges of two hexagons be b, then the length of the square side is $\sqrt{3}a + b$ (Fig. 1b). For the general case, where the diameter of droplet size is much larger than $\sqrt{3}a + b$, a droplet only contacts the flat-top of the pillars in the composite interface, and the cavities are filled with air. For this case, we defined two surface characteristic values: $\alpha = H/a$, $\beta = b/a$, then Wenzel equation and Cassie equation were evolved into:

$$\begin{aligned}\cos\theta_w &= \left(1+\frac{6aH}{(\sqrt{3}a+b)^2}\right)\cos\theta_y \\ &= \left(1+\frac{6(H/a)}{(\sqrt{3}+(b/a))^2}\right)\cos\theta_y \\ &= \left(1+\frac{6\alpha}{(\sqrt{3}+\beta)^2}\right)\cos\theta_y\end{aligned} \tag{1}$$

and:

$$\begin{aligned}\cos\theta_c &= \frac{3\sqrt{3}a^2/2}{(\sqrt{3}a+b)^2}(\cos\theta_y+1)-1 \\ &= \frac{3\sqrt{3}/2}{(\sqrt{3}+(b/a))^2}(\cos\theta_y+1)-1 \\ &= \frac{3\sqrt{3}/2}{(\sqrt{3}+\beta)^2}(\cos\theta_y+1)-1,\end{aligned} \tag{2}$$