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Fabrication and characterization of superhydrophobic TiO_2 nanotube coating by a facile anodic oxidation approach

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ABSTRACT

Superhydrophobic TiO_2 nanotube coating was fabricated by anodic oxidation and lauric acid modification. Scanning electron microscope (SEM), X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FTIR) and energy disperse spectroscopy (EDS), and contact angle meter were employed to characterize the surface morphologies, surface crystal structures, chemical compositions, and contact angle of the superhydrophobic TiO_2 nanotube coating, respectively. The various properties of the superhydrophobic TiO_2 nanotube coating were assessed. Results showed that for the superhydrophobic TiO_2 nanotube coating the contact angle and sliding angle of is up to 157° and 3.8°. The superhydrophobic TiO_2 nanotube coating has good anti-icing, low adhesion, self-cleaning and anti-corrosion properties. Besides, for acid droplets, the contact angle is still > 150°.

1. Introduction

Inspired by superhydrophobic organisms in nature, such as lotus leaf [1,2], rose [2], butterfly wings [2,3], etc., bionic superhydrophobic surfaces have attracted much attention. The superhydrophobic surface with a contact angle of > 150° and a sliding angle of < 10° has a wide range of applications in many fields such as self-cleaning [4], oil-water separation [5], ice-resistance [6], and corrosion resistance [7], etc. Domestic and foreign researches indicate that the two necessary conditions for the construction of a superhydrophobic surface are proper rough structure and a low surface energy [8]. Generally, the most common steps are to fabricate micro and nano structures first and then modify the surface with low-energy modifiers. There are a series of methods for constructing superhydrophobic surfaces, including: template method [8,9], hydrothermal method [10], etching method [8,11], vapor deposition method [8,12], etc. However, for most methods, expensive equipment, materials, and complex processes limit their application in industry.

Recently, nanostructured materials have been widely used in the preparation of superhydrophobic surfaces. Within these nanostructure materials, TiO_2-based nanomaterials have aroused great interest and research because of their merits of large specific surface area [13], photoelectrocatalytic [14], and biocompatible abilities [15]. Currently, typical TiO_2 porous-nanostructure such as nanorods, nanoparticles and nanotubes, has been used to prepare superhydrophobic surfaces [16]. Xu et al. [17] have prepared TiO_2 nanorod arrays through hydrothermal method on fluorine-doped tin oxide coated glass substrates with a contact angle of 161.2 ± 1.3° and a small sliding angle of 7°. Li et al. [18] have fabricated superhydrophobic TiO_2 nanoparticles coating consisted of modified TiO_2 nanoparticles and polysiloxane resin, which exhibits good thermal stability, abrasion resistance and corrosion resistance. Huang et al. [19] have achieved nanoscale TiO_2 coating via reaction of octadecyl isocyanate (ODI) with TiO_2 particles, which can combine with various substrates by versatile film deposition methods and shows robust photocatalytic, self-cleaning and self-healing properties. Compared with the above nanostructures, TiO_2 nanotubes have an enlarged surface area so that the superhydrophobic layers can be easily created [20]. Furthermore, in combination with the biocompatibility and special electrical properties it can be established a wide area of application for TiO_2 nanotubes [21]. Yang et al. [22] have fabricated superhydrophobic TiO_2 nanotube array coating on titanium substrate using electrochemical anodic oxidation method, which exhibits excellent blood compatibility and remarkble performance in preventing platelets from adhering to the implant surface. However, for superhydrophobic TiO_2 nanotube coating, few studies have focused on the anti-icing, self-cleaning and anti-corrosion properties, etc.

In this work, we propose a facile method to prepare superhydrophobic surfaces on Ti substrates by anodic oxidation and modification in lauric acid. The anodic oxidation was utilized to form rough topography and then lauric acid modification was employed to make

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surfaces superhydrophobic. The various properties of the superhydrophobic TiO_2 nanotube coating were emphatically studied. Based on the characterization, the superhydrophobic TiO_2 nanotube coating in this work was found to have good anti-icing, low adhesion, self-cleaning and anti-corrosion properties. Besides, for acid droplets, the contact angle was still > 150°.

2. Experimental

2.1. Materials

TA2 titanium plates (40 mm × 20 mm × 1 mm) were purchased from Shenzhen Ode Fu Materials Co. Ltd, Guangzhou, China. Graphite plates (40 mm × 20 mm × 10 mm) were purchased from Beijing Jinglong Graphite Factory. Ethanol, acetone, hydrofluoric acid (HF) (≥ 40 wt%), lauric acid ($C_{12}H_{24}O_2$), nitric acid (HNO_3), sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Sulfuric acid (H_2SO_4) was obtained from West Long Chemical Co., Ltd in China.

2.2. Preparation of superhydrophobic TiO_2 nanotube coating

The fabrication process of superhydrophobic TiO_2 nanotube coating included anodic oxidation and modification, and the detailed procedures were as follows.

Before the anodic oxidation, Ti specimen was firstly polished with sandpapers of 600#, 1000#, 1500# along the horizontal direction and the vertical direction alternately, followed by ultrasonic cleaning in acetone, ethanol and deionized water for 20 min, respectively. Then the cleaned Ti specimen was activated by immersing in an aqueous solution that contained 30 mL deionized water, 24 mL HNO_3 and 6 mL HF for 30 s at room temperature. The purpose of the above steps was to remove the original oxide layer and impurities on the surface of the Ti substrate.

Next, in order to obtain the TiO_2 nanotube coating, the pretreated Ti specimen and graphite plate were used as anode and cathode, respectively. At 20 V DC voltages, the two electrodes, whose gap distance was 40 mm, were placed in HF aqueous electrolyte for 2 h (Fig. 1). In this work, in order to investigate the effect of HF content on the superhydrophobicity of the coating, the additive amount of HF for 150 mL HF aqueous solution was 0, 0.5, 1.5, 2.5 and 3.5 mL. After the anodic oxidation, the specimen was cleaned by deionized water and dried at ambient temperature.

Finally, the Ti surface coated with TiO_2 nanotube coating was immersed in a 0.02 mol/L ethanol solution of lauric acid for 24 h in darks and subsequently dried at 60 °C for 20 min.

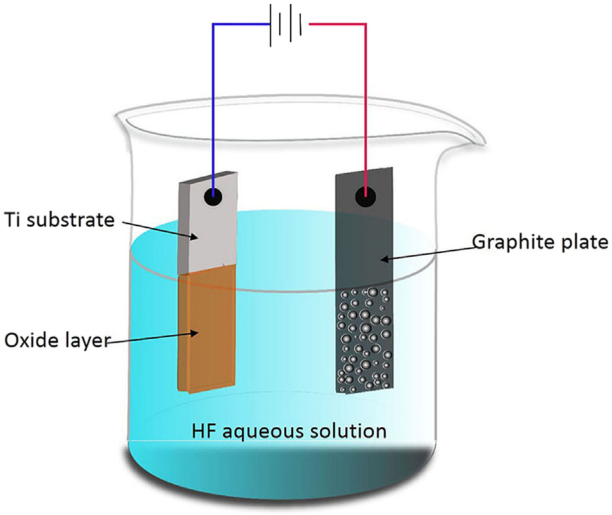

Fig. 1. Schematic illustration for anodic oxidation.

2.3. Characterization and tests

The morphologies of the specimen surface were observed using field emission scanning electron microscope (FESEM, NovaNano SEM 450, FEI). The crystal structures of the specimens were measured with X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical B.V.). The X-ray source was a Cu target, which was operated at 40 kV and 40 mA within the 20–80° range. The chemical compositions of specimen surface were analyzed by Fourier transform infrared spectrometer (FTIR (Nexus, Thermo Nicolet)) and energy disperse spectroscopy (EDS, Oxford X-Max^N, FEI).

The contact angle (CA) of specimen surface was measured by a contact angle meter (SL200B, USA, KINO) with digital image analysis software. CA values were the averages of at least five measurements performed at different positions with 3 μL water droplets. In the SA measurements, one side of the specimen was placed on the glass slide. The sliding angle of water droplet (8 μL) on the specimens could be determined by increasing the number of slides till the water droplet starts to slide.

In order to prove the low adhesion of the superhydrophobic surface, the 3 μL water droplet was contacted and separated with the superhydrophobic surface through the movement of the needle, and the process was recorded by the photos. Besides, the self-cleaning was also tested. The specimen consisting of substrate and superhydrophobic coating was inclined about 3.8°. Tens of microns of fly ash were uniformly sprinkled on the surface of the specimen. Water droplet with a size of 8 μL was dropped on the surface of the substrate and superhydrophobic coating, respectively.

The anti-icing property of the superhydrophobic coating was tested at −20 °C in cryogenic box (DW-45W28, China, Jiesheng). 3 μL of droplets were dropped onto three specimens as shown in Fig. 12-(1), and icing-delay time was recorded. Besides, in this work, the wettability of the superhydrophobic coating over a wide range of pH was observed through measuring CA of the specimens. Acidic and alkaline solutions of different pH values were prepared with concentrated sulfuric acid and sodium hydroxide, respectively, and the CA were tested with 3 μL droplet.

The anti-corrosion property of the superhydrophobic coating was evaluated by polarization curve in 3.5 wt% NaCl solution using electrochemical workstation (CS310, China) at room temperature. A standard three-electrode system was used in the electrochemical tests, with saturated calomel electrode (SCE) as the reference electrode, graphite plate as the counter electrode, and the specimens with an exposed area of 1 cm^2 as the working electrode. Before the tests, the specimens were immersed in the 3.5 wt% NaCl solution for 90 min to stabilize. The potentiodynamic polarization curves were obtained at a scan rate of 0.333 mV/s and measured three times under the same conditions for reproducibility.

3. Results and discussion

3.1. Microstructure and formation mechanism of superhydrophobic TiO_2 nanotube coating

SEM images of Ti specimen surface under different processing conditions were shown in Fig. 2. Fig. 2(a) indicated that there is no special structure on the pretreated specimen, only the uneven structure appeared by the etching of the aqueous solution (30 mL deionized water, 24 mL HNO_3 and 6 mL HF). After the anodic oxidation and modification, TiO_2 nanotubes were formed on the Ti substrate with average 90 nm inner diameter and 18 nm wall thickness. Meanwhile, cavities existed between the neat nanotubes as shown in Fig. 2(b, c).

Combining microscopic morphology and chemical reactions that