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Properties and wettability of the superhydrophobic TiO_2 nanotube coating

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Abstract. By anodic oxidation and low-energy modification with lauric acid, superhydrophobic TiO_2 nanotube coating formed on the titanium dioxide. The two factors related to the superhydrophobility that roughness and surface energy were proved in the paper. The crystal structure, surface morphology, compositions and wettability were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), energy disperse spectroscopy (EDS) and contact angle measurements, respectively. Besides, the self-cleaning property and stability were studied. The result showed the coating exhibited superhydrophobicity with the contact angle (CA) 157±1° and the sliding angle (SA) 3.8±0.2°. The superhydrophobic TiO_2 nanotube coating showed excellent self-cleaning property to fly ashes and the moist soil. Besides, at room temperature and 180°, the stability of the coating was good.

1. Introduction

In the past few decades, titanium dioxide nanomaterials have attracted great attention as semiconductors. Because of their special physical and chemical properties, titanium dioxide nanomaterials have been studied in many applications, such as antibacterial material [1], solar cells [2], medical application [3] et al. Liao et al [4] have fabricated rutile TiO_2 nanorod arrays on FTO glass coated with TiO_2 seed layer by a hydrothermal method in order to improve the performance of dye sensitized solar cells. Wei et al [5] have constructed the nano brushite/TiO_2 nanotubes composited coating which shows excellent apatite-formation ability and cell biocompatibility. However, the titanium dioxide nanomaterials have high surface energy and the polarity of them is strong, especially for TiO_2 nanotubes which have a large specific surface area. The surface easily forms surface hydroxyl groups after adsorbing water molecules, which exhibits hydrophilicity and limits its application range.

Recently, superhydrophobic surface with a water contact angle bigger than 150° and a sliding angle lower than 10° has been a hot pot in surface modification research. The superhydrophobic surface has lots of applications, such as anti-fogging [6], self-cleaning [6, 7], corrosion resistance [8], oil/water separation [9]. Therefore, fabricating a superhydrophobic coating on nano-TiO_2 surface to decline the surface energy and expand the applications is necessary.

In this paper, superhydrophobic TiO_2 nanotube coating was fabricated on the titanium substrate by anodic oxidation and low-energy modification. The two keys that proper roughness and low surface energy to form superhydrophobic TiO_2 nanotube coating were discussed. Besides, the superhydrophobic TiO_2 nanotube coating exhibited good self-cleaning property and stability.

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2. Experimental

2.1 Material

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)(≥40wt.%), lauric acid ($C_{12}H_{24}O_2$), nitric acid (HNO_3), were obtained from Sinopharm Chemical Reagent Co.

2.2 Coating fabrication

In order to fabricate the superhydrophobic TiO_2 nanotube coating, three steps were as follows.

Pretreatment: to remove the grease and oxide layer on the surface of the substrate，Ti plate was firstly polished with sandpapers. Then, the Ti plate was ultrasonically rinsed with acetone, ethanol, and deionized water and dried at room temperature. At last, the cleaned Ti plate was activated by immersing in an acid solution.

Anodic oxidation: the pretreated Ti specimen was positive pole, and graphite plate was negative pole. The 1.5 mL/L HF aqueous was electrolyte for anodic oxidation. The anodization voltage was 20 V. After 2 h, it was taken out from the electrolyte immediately and deionized water was used to wash until the surface was neutral. Finally, the specimen was dried at ambient temperature.

Modification: the Ti plate coated with TiO_2 nanotube coating was immersed in an ethanol solution of lauric acid for 24 h in darks and subsequently dried at 60 ℃ for 20 min.

2.3 Characterization and measurements

The morphologies of the specimen surface were observed using field emission scanning electron microscope (FESEM, NovaNano SEM 450, FEI). 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 energy disperse spectroscopy (EDS, Oxford X-Max^N, FEI). The wettability of the surface was valued by the CA and SA, which were measured by a contact angle meter (SL200B, USA, KINO). For a specimen, the contact angle values took the average of five measurements with 3 μL water droplets and the measurement error of the contact angle was ± 1°.

3. Experimental results

3.1 Micrograph and compositions

The surface appearance and SEM images of the superhydrophobic specimen were shown in figure 1. After anodic oxidation and modification, neat TiO_2 nanotube structure appeared on the surface of titanium substrate. Besides, the contact angle on this coating was up to 157±1°. It was because that the TiO_2 nanotube structure was easy for water droplet to be spheroidal after modification with lauric acid.

Because that TiO_2 is an amorphous phase at room temperature, the specimen was annealed at 400℃ for 2 h in vacuum environment. It could be seen from the figure 2 that two diffraction peaks appeared at 2θ =25.25°, 48.05° respectively assigned to the TiO_2 (101), TiO_2 (200), which was consistent with the standard powder diffraction peaks of TiO_2 anatase phase. The other peaks at 2θ = 35.08°, 38.38°, 40.13°, 52.97°, 62.92°, 70.60°, 76.15° were all assigned to the Ti. Compare with the pretreated specimen (figure 3(b)), O element was in certain content on the surface as shown in figure 3(a), indicating that the porous structure of surface was titanium dioxide formed after anodic oxidation. Besides, F appeared in the figure 3(b) was caused during the anodizing process that the generated titanium dioxide reacted with the HF electrolyte to facilitate the formation of the nanotube structure.

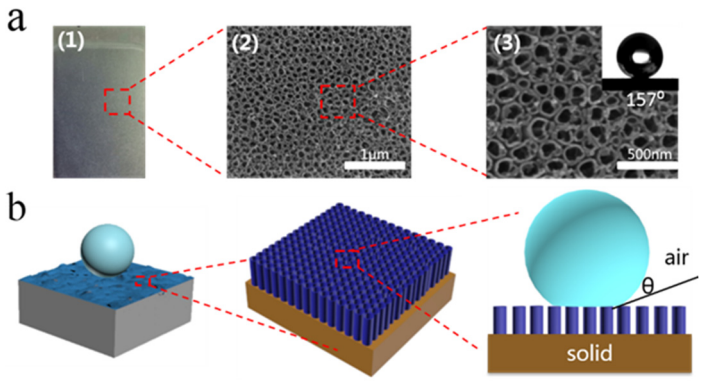


Figure 1. (a) Macro image 1) and micro image 2) and 3). (b) Schematic diagram of the state of water droplets on the microstructure.

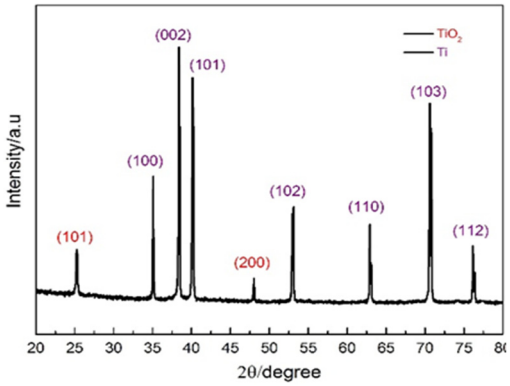


Figure 2. XRD pattern of the superhydrophobic TiO_2 nanotube coating treated at 400 ℃ for 2 h.

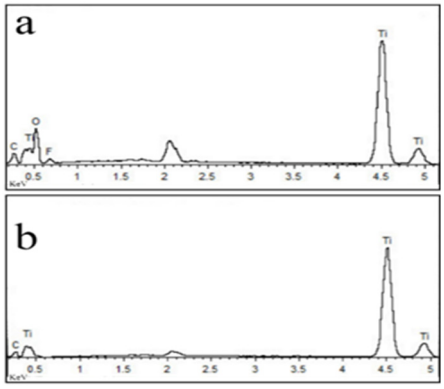


Figure 3. EDS spectra of TiO_2 nanotube coating a) and pretreated specimen b).

3.2 wettability

The wettability of the specimens treated under different conditions was shown in figure 4. Figure 4(a) indicated the wettability of the pretreated specimen with a CA about 87°, which meant that the pretreated specimen showed hydrophilic. Meanwhile, the unmodified TiO_2 nanotube coating exhibited stronger hydrophilicity with a CA about 34° (figure 4(c)). After modification by the lauric acid, the CA of the pretreated specimen and the TiO_2 nanotube coating attained to 105° and 158° respectively as shown in figure 4(b) and figure 4(d). And the modified pretreated specimen and modified TiO_2 nanotube coating exhibited hydrophobicity and superhydrophobicity.

Figure 5 showed the profile roughness and 3D topography of the specimens. The roughness of the TiO_2 nanotube coating was 2.07 μm which was bigger than that of the pretreated specimen whose roughness was 1.04 μm. Wenzel's equation (equation. (1)) was in the flowing [10]:

$$\cos\theta = \gamma \cos\theta_0 \quad (1)$$

where γ is a roughness parameter and the θ is contact angle affected by surface roughness. On the basis of the Wenzel's equation, if the surface showed hydrophilicity which meant the contact angle is smaller than 90°, then with the roughness increased, the contact angle became smaller and the hydrophilicity increased. On the contrary, if the contact angle of the surface was bigger than 90°, then with the roughness increased, the contact angle became bigger and the hydrophobicity increased even reached to superhydrophobicity. Figure 4 and figure 5 confirmed this view. After anodic oxidation, the roughness increased and the pretreated specimen was hydrophilic so that the CA of the unmodified TiO_2 nanotube coating was smaller (figure 4(a) and figure 4(c)). After modification, the pretreated specimen showed hydrophobicity, so the contact angle of the modified TiO_2 nanotube coating increased from 105

^{o} to 157^{o} (figure 4(b) and figure 4(d)). Besides, by comparing the figure 4(c) and figure 4(d), it could be found that the lower surface energy also was the key to fabricate superhydrophobic surface.

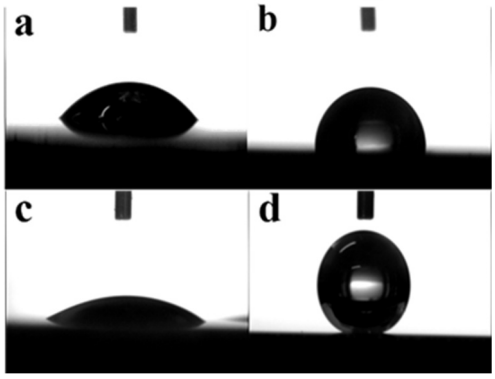


Figure 4. Wettability. a) Pretreated specimen. b) Pretreated specimen after modification. c) Unmodified TiO_2 nanotube coating. d) Modified TiO_2 nanotube coating.

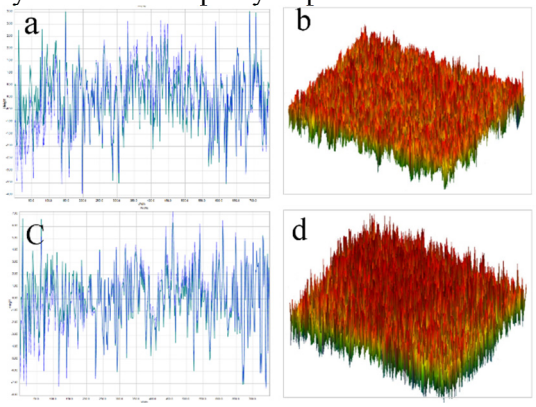


Figure 5. a) and c) The profile roughness of the pretreated specimen and the TiO_2 nanotube coating respectively. b) and d) 3D topography corresponding to a) and c).

3.3 Self-cleaning property

Like lotus leaves, superhydrophobic surfaces tend to have self-cleaning effects. The test about the self-cleaning property of the superhydrophobic TiO_2 nanotube coating was shown in figure 6. Fly ash and moist soil were sprinkled evenly on the surface of the inclined specimen. About 10 μL water droplet was dropped from a height of 2 cm. As shown in figure 6(b), the water droplets carried away the fly ash, and the original coating surface was exposed again. Moreover, for the moist soil which was stickier and had smaller size than fly ashes, the superhydrophobic TiO_2 nanotube coating still has self-cleaning properties (figure 6(a)). The reason was that when the impact pressure of the droplet is high enough, the air pockets will be repelled as a result of droplet invade the pillars to catch the dirt particles.

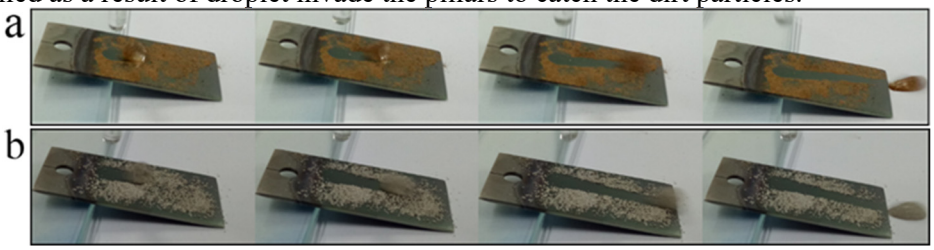


Figure 6. Dirt (a) moist soil, b) fly ashes) removal test at the superhydrophobic TiO_2 nanotube coating.

3.4 Stability

In order to study the stability of the superhydrophobic TiO2 nanotube coating, the CA and SA were measured after staying at room temperature for a long time and treated at 180° for different time. In Qingdao, China, from April to November 2018, the CA and SA were measured once a month. It could be found from the figure 7(a) that the CA and SA remained about the same. Besides, the coating was placed in a 180° incubator, and the CA and SA were recorded every 2 hours. Figure 7(b) showed that the CA and SA were still stable after 12 h. From the above results, the superhydrophobic TiO2 nanotube coating has good stability.

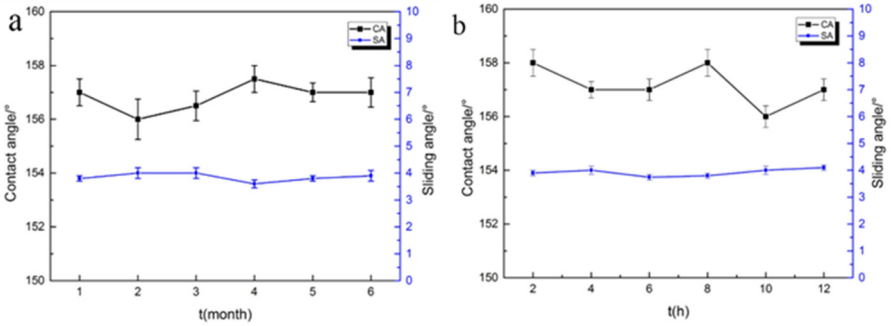


Figure 7. CA and SA of superhydrophobic TiO_2 nanotube coating stayed at a) room temperature and b) the incubator of 180°.

4. Conclusion

The superhydrophobic TiO_2 nanotube coating was constructed with the CA of 157±1° and SA of 3.8±0.2°. After the anodic oxidation and low-energy modification with lauric acid, the wettability changed from hydrophilicity to superhydrophobicity, which indicated the roughness and surface energy were the key factors to the wettability. The superhydrophobic TiO_2 nanotube coating showed good self-cleaning property especially for the moist soil which was stickier. Besides, after staying at room temperature for 6 months and treated at 180° for 12 h, the CA and SA remained about the same, which confirmed the excellent stability of the coating.

Acknowledgments

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