



Fabrication of Superhydrophobic Surfaces of TiO₂ Coatings Modified with 1-Octadecanethiol†

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Nanoscaled rough surface modified by low-surface-energy materials has been widely used for preparation of superhydrophobic materials. In the present work, a superhydrophobic TiO₂ micro/nanostructured coating modified with 1-octadecanethiol was fabricated by a facile dip-coating process. As hydrophobization treatment by 1-octadecanethiol, the TiO₂ surface changed from hydrophilic (36°) to superhydrophobic (151°), which could be attributed to the synergistic effect of the improved roughness of TiO₂ and the formation of self-assembled monolayer with low surface energy.

Key Words: TiO₂, Superhydrophobic, 1-Octadecanethiol, Dip-coating process.

INTRODUCTION

Superhydrophobic surfaces, with a water contact angle more than 150°, have attracted great interest for both fundamental research and practical applications¹. Conventionally, superhydrophobic surfaces have been produced mainly in two ways². One is to create appropriate rough structure on hydrophobic substrates, in which research methods used mainly include chemical vapor deposition, template synthesis, laser etching, self-assembly, sol-gel method and other methods. The other is to modify a rough surface by low-surface-energy materials. The low-surface-energy materials commonly used are fluoride alkyl silane, fluorine polymer and wax. As an important inorganic functional material, titanium dioxide (TiO₂) possesses various kinds of applications in the fields of sensors, electronic components, solar battery and self-cleaning materials due to its low cost and unique properties³. Herein, the TiO₂ micro/nanostructured aggregate was successfully obtained by hydrothermal reaction and then the 1-octadecanethiol (ODT) with low surface energy was used for hydrophobization treatment. The surface showed good superhydrophobic property and stability.

EXPERIMENTAL

The micro/nanostructured TiO₂ were synthesized by the method of Li *et al.*⁴. The synthesis process is as follows: potassium titanium oxalate (2 mol) was dissolved in 20 mL of

distilled water, followed by the addition of 30 % H₂O₂ (15 mL) and 37 % HCl (1 mL) under stirring. The mixed solution was transferred to a sealed 50 mL Teflon-lined autoclave, heated at 150 °C for 8 h and then cooled to room temperature naturally. The white precipitate was collected, washed with distilled water and absolute alcohol several times and then dried in a vacuum at 80 °C for 12 h. The obtained TiO₂ samples were dispersed in an ethanol solution of 1-octadecanethiol with constant stirring for 2 h at 75 °C to complete a self-assembly process. The suspension was then used to fabricate coatings by dip-coating onto glass slides eroded by acids and dried in an oven at 80 °C until the ethanol evaporated completely.

The X-ray diffraction were recorded with Philips X'Pert Pro Super diffract meter with CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$). The field emission scanning electron microscopy (FESEM) was performed on JEOL JSM-6700F. The contact angles of the coating were measured with a contact angle meter C20 (Kono, America).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the as-obtained TiO₂ sample. All the observed peaks of the pattern can be indexed to a pure tetragonal rutile phase (JCPDS card, 21-1276) with lattice constants = 4.593 Å and c=2.958 Å. No peak for other types was observed, showing the high purity and well crystallinity of the samples.

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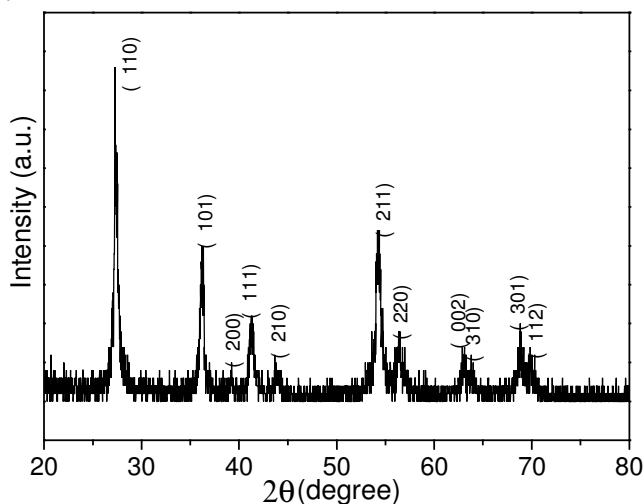


Fig. 1. XRD pattern of the as-obtained TiO₂ sample

Fig. 2 shows SEM images of the TiO₂ sample at different magnifications. From Fig. 2a, it is observed that the products exhibit rough structure aggregated by a large number of nanoparticles. A magnified SEM image showing the close observation of the aggregate is presented in Fig. 2b. It reveals that these aggregate are constructed from many short TiO₂ nanorods and irregular TiO₂ nanoparticles with size in the range of 100–200 nm and they aggregate with each other to form the microscale hierarchical structure.

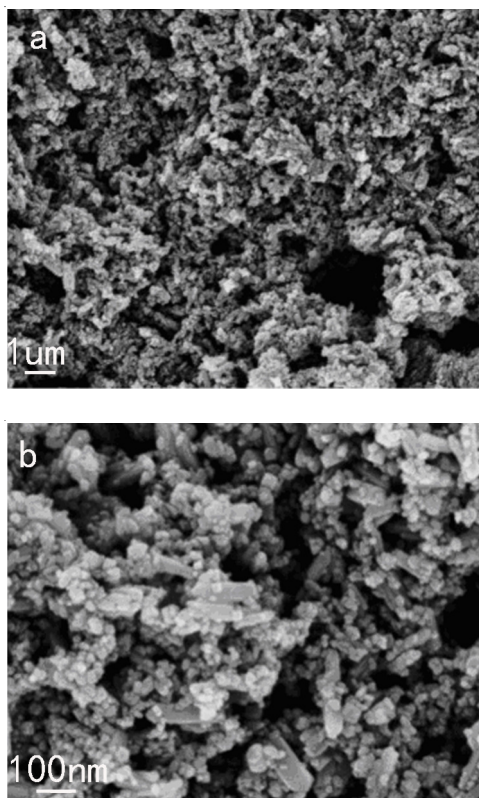


Fig. 2. SEM images of the untreated TiO₂ coating at different magnifications

Fig. 3 shows SEM images of hydrophobization-treated TiO₂ coating with 1-octadecanethiol. From the images, we can see that the surface morphology of the samples has been changed after the modification with 1-octadecanethiol, indicating that

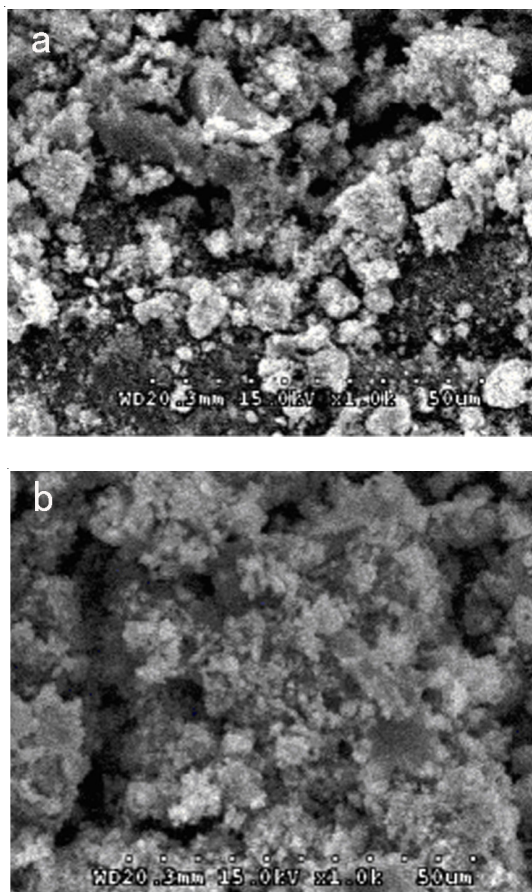
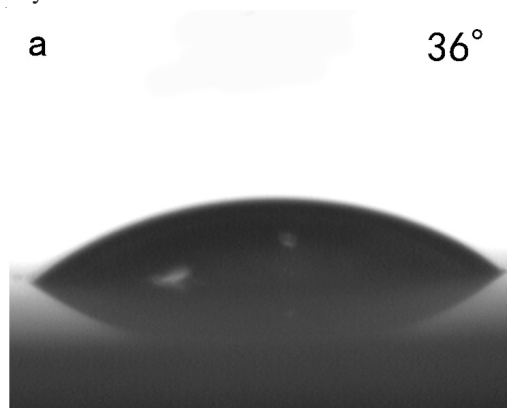


Fig. 3. SEM images of the hydrophobization-treated TiO₂ coating

a self-assembled monolayer was formed on the TiO₂ surface. More pores are engendered in the flocculence-like microstructures, which may improve the surface roughness or trap more air.

The surface wettability of the as-prepared coatings has been evaluated by the water contact angle measurement. As shown in Fig. 4, the contact angle of untreated TiO₂ coating was measured to be 36°, showing its hydrophilic nature. However, after the hydrophobization treatment with low-surface-energy 1-octadecanethiol, the contact angle of the coating was measured to be 151°, exhibiting the good superhydrophobicity. Moreover, it is worthwhile to note that the water droplets are extremely unstable on the surface of the superhydrophobic TiO₂ coating. Even the surface remains horizontal, the water droplets also roll down easily, resulting in the contact angle hard to measure. It indicates the surface possess a very small contact hysteresis.



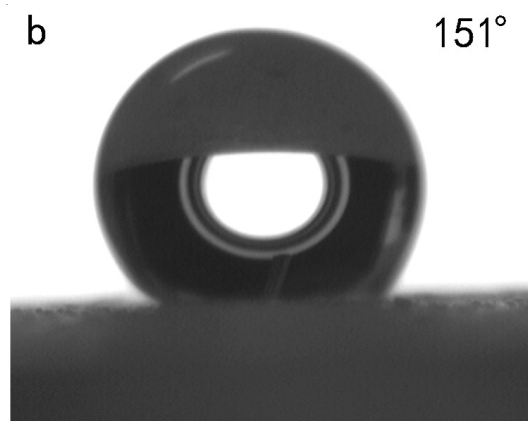


Fig. 4. A water droplet on (a) pure TiO₂ coating (b) modified TiO₂ coating

As we know, surface roughness and chemical composition are determinant factors of the surface wetting property. In our reactive system, the micro/nanostructured TiO₂ were obtained and subsequently modified with 1-octadecanethiol. On one hand, the micro/nano hierarchical structure of TiO₂ could provide the structural groundwork for the superhydrophobicity. On the other hand, the surface of TiO₂ nanoparticles were covered with a self-assembled 1-octadecanethiol monolayer, which can effectively decrease the surface free energy and increase the

hydrophobicity. Therefore, both the structure effect of the TiO₂ and the formation with self-assembled monolayer with low surface energy make the coating superhydrophobicity.

Conclusion

A simple method of fabricating super hydrophobic surface of 1-octadecanethiol modified TiO₂ micro/nanostructure is presented. Combining the surface topography provided by the TiO₂ micro/nanostructure and the low-surface-energy layer formed by 1-octadecanethiol adsorption render the coating superhydrophobicity. The superhydrophobic coating may be applicable for multiple fields such as optoelectronic industries and biochemistry field.

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