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Effect of surface morphology on wettability conversion

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Effect of surface morphology on wettability conversion

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Abstract: A hierarchical structural surface of TiO\textsubscript{2} film with reversibly light-switchable wettability between superhydrophobicity and superhydrophilicity on metal substrate was fabricated through simply dip-coating method from TiO\textsubscript{2} precursor solution containing TiO\textsubscript{2} nanoparticles with the average diameter 25 nm (P25), followed by heat-treatment and modification with fluoroalkylsilane (FAS) molecules. The morphology, phase and crystallographic structure, and chemical composite of the as-prepared TiO\textsubscript{2} film were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The wettability of TiO\textsubscript{2} film was characterized by a drop shape analyzer. The water contact angle of superhydrophobic TiO\textsubscript{2} film was up to 165.6°. Under UV irradiation, the water contact angle decreased and the superhydrophobic TiO\textsubscript{2} film became superhydrophilic because of hydroxyl groups absorption on the TiO\textsubscript{2} surface. Meanwhile, the surface morphology of TiO\textsubscript{2} film, which resulted from the TiO\textsubscript{2} nanoparticles added in TiO\textsubscript{2} precursor solution, had a significant effect on the wettability conversion of TiO\textsubscript{2} film and enhanced the switch from hydrophobicity to hydrophilicity. The wettability could be reversibly switched between superhydrophobicity and superhydrophilicity via alternation of UV exposure and dark storage.

Keywords: TiO\textsubscript{2}; morphology; wettability; reverse conversion

1 Introduction

Solid surface wettability is one of the most important properties of materials, which strongly depends on both surface chemical composition and geometrical microstructure \cite{1}. One extreme case of wettability properties, namely superhydrophobic surface with a water contact angle greater than 150°, has aroused considerable interest in recent years because of their potential applications in self-cleaning surfaces, microfluidic devices, textile industries, and possibly anti-icing applications \cite{2–4}. It is demonstrated that superhydrophobic surface can be prepared through either fabricating micro-nanostructured surface on low surface free energy materials or chemically modifying the micro-nanostructured surface with low surface free energy materials, or both \cite{5}. Up to now, a large number of superhydrophobic surfaces have been generated through various techniques, and the micro-nanostructured superhydrophobic films reported have covered various materials, such as polymers, carbon nanotubes, oxides, metals, and so on \cite{6–11}. The oxides, especially the oxide semiconductors, have attracted more attention in recent years.
Oxide semiconductors play an outstanding role in many aspects of science and engineering owing to their unique optical, semiconducting, catalytic, magnetic, and piezoelectric properties [12–15]. Therefore, they have practical applications as a key component for the fabrication of piezoelectric transducers, transparent conductive oxides, sensors, light-emitting diodes, and optoelectronic devices. In recent years, there has been increasing interest in the wettability of oxide semiconductors as smart materials [16–22]. Among the large family of oxide semiconductors, TiO₂, with the direct band gap energy of 3.55–3.75 eV, has been widely used in photocatalysts, hydrogen generation, gas sensing, solar cells, and so on [23–25]. However, the wettability of TiO₂ has not been fully studied, especially its wettability conversion [17]. Few of publications on wettability conversion of TiO₂ films have been reported, in contrast to the huge number of literatures on TiO₂ films [26,27]. Herein, we report a method for preparation of a superhydrophobic TiO₂ film, which consists of fabricating a micro-nanostructured TiO₂ film from TiO₂ precursor solution containing TiO₂ nanoparticles and modifying the resultant film with fluoroalkylsilane molecules. The effect of surface morphology of TiO₂ film on the wettability conversion is investigated.

2  Experimental details

2.1  Preparation of TiO₂ film

In our experiment, all reagents are analytical grade and used without further purification. Specific process of preparation is as follows.

2.1.1  Preparation of TiO₂ precursor

TiO₂ precursor was prepared through sol–gel method [28]. First, 8.2 mL tetra-n-butyl titanate was dissolved in 5.8 mL ethanol. The other 5.8 mL ethanol was mixed with 0.4 mL water and 0.25 mL 68% aqueous solution of nitric acid, and 0.6 g TiO₂ nanoparticles with the average diameter 25 nm (P25, containing 80% anatase and 20% rutile) were added and ultrasonically dispersed. Then the mixture was added dropwise to the former solution under ice-cooled condition with vigorous stirring. 0.5 g poly(ethylene glycol) (PEG, M ≈ 2000) was added to the solution as soon as the 0 ℃ mixing was finished. The container was sealed with stirring to dissolve PEG completely under atmosphere, and then the TiO₂ precursor solution was stirred for another 24 h.

2.1.2  Process of TiO₂ film

The glass substrate pre-cleaned was immersed in TiO₂ precursor solution for 5 min, and withdrawn with the rate of 3 mm·s⁻¹. After drying naturally in the ambience, such an operation was repeated two times. Then the specimen was sintered at 450 ℃ for 60 min with a heating rate 5 ℃·min⁻¹.

2.1.3  Surface modification

The prepared specimen was placed into a 1.0 wt% ethanol solution of CF₃(CF₂)₇CH₂CH₂Si(OCH₃)₃ (FAS), which had been hydrolyzed by the addition of a threefold molar excess of water. The specimen was left in this solution for 1 h, washed with ethanol, and placed in an oven at 140 ℃ for 1 h.

2.2  Measurement and characterization

TiO₂ gel was obtained from the TiO₂ precursor heated at 80 ℃ for 20 h. The thermal property of the TiO₂ gel was characterized by thermogravimetric analysis (TG, STA 409 PC luxx, Netzsch, Germany) operating in atmosphere at a heating rate of 10 ℃·min⁻¹ from room temperature to 700 ℃. The phase and the crystallographic structure of the TiO₂ film were characterized by an X-ray diffractometer (XRD, D/max-2550, Rigaku Co., Tokyo, Japan) with Cu Kα radiation (λ = 0.154 nm) at a scan rate of 8 (°)·min⁻¹ ranging from 20° to 80°. The surface topography and structure of the TiO₂ film were characterized by a field-emission scanning electron microscope (FE-SEM, LEO-1530, Carl Zeiss Co., Oberkochen, Germany) operating at 15 kV. Dynamic light scattering (DLS) size distribution of TiO₂ aggregated particles in the TiO₂ precursor solution containing P25 particles was measured by laser diffraction particle size analyzer (Zetasizer ZS, Malvern Instruments Ltd., Malvern, UK). The chemical composition of the TiO₂ film modified with FAS was analyzed on an X-ray photoelectron spectroscopy (XPS) equipped with a standard monochromatic Al Kα source (hv = 1486.6 eV). Water contact angles were measured with a drop shape analyzer (DSA100, Kruss, Germany) at ambient temperature. Water droplets were dropped carefully onto the surface and the average value of five measurements at different positions of the sample was adopted as the contact angle. The wettability conversion tests of TiO₂ film were carried out under UV irradiation from a low pressure Hg tube (Philips TUV 8 W, the strongest emission at 254 nm).
3 Results and discussion

Figure 1 shows the TG pattern of the TiO\textsubscript{2} gel obtained from the TiO\textsubscript{2} precursor without TiO\textsubscript{2} P25 nanoparticles heated at 80 °C for 20 h. The result shows that the organic matter in TiO\textsubscript{2} gel is decomposed before 450 °C completely, which indicates that an annealing treatment at a temperature equal to or greater than 450 °C may be required to eliminate the organism residing in the TiO\textsubscript{2} gel.

Figure 2 displays the XRD patterns of TiO\textsubscript{2} films. All the diffraction peaks in the pattern of TiO\textsubscript{2} film fabricated from the TiO\textsubscript{2} precursor solution without P25 nanoparticles can be well indexed as a pure anatase of TiO\textsubscript{2}, which is in good agreement with the standard data file (JCPDS Card No. 21-1272). The strong and sharp diffraction peaks reveal that the TiO\textsubscript{2} is well crystallized. However, the XRD pattern of TiO\textsubscript{2} film containing TiO\textsubscript{2} nanoparticles displays that the film is mainly composed of anatase phase, and comprises little amount of rutile phase which comes from TiO\textsubscript{2} P25 nanoparticles added into TiO\textsubscript{2} precursor solution.

The SEM images of the TiO\textsubscript{2} films taken with different magnifications are shown in Fig. 3. Figure 3(a) presents a typical SEM image of TiO\textsubscript{2} film prepared from the TiO\textsubscript{2} precursor solution without TiO\textsubscript{2} P25 nanoparticles, which shows that the film is flat. Its high magnification SEM image (Fig. 3(b)) exhibits that the film is composed of the grains of about 50 nm. However, the surface morphology of TiO\textsubscript{2} film fabricated from the TiO\textsubscript{2} precursor solution with TiO\textsubscript{2} P25 nanoparticles (Figs. 3(c) and 3(d)), which exhibits that the morphology of the TiO\textsubscript{2} film is composed of nanoparticles with size about 50–100 nm and the relatively small nanoparticles are aggregated to form clusters with size about 500 nm, is very different from the one fabricated from the TiO\textsubscript{2} precursor without P25 nanoparticles. As a result, the TiO\textsubscript{2} film containing TiO\textsubscript{2} P25 nanoparticles shows hierarchical structure.

The TiO\textsubscript{2} films are modified with low surface free energy material FAS, and the wettability is investigated. Before modified with the low surface free energy material FAS, the water droplets could easily spread out on the original TiO\textsubscript{2} films without and with TiO\textsubscript{2} P25 nanoparticles, which means that the as-prepared original TiO\textsubscript{2} films are hydrophilicity. After modified with FAS, the water contact angle of the TiO\textsubscript{2} film without TiO\textsubscript{2} P25 nanoparticles is 118.4° which is inserted in Fig. 3(a). The FAS is one of the widely used self-assembled monolayer molecules to form organic thin film on various oxide substrates to lower the surface free energy. The hydrophobicity of TiO\textsubscript{2} film without TiO\textsubscript{2} P25 nanoparticles may be mainly owing to the low surface free energy of FAS. While, the TiO\textsubscript{2} film with TiO\textsubscript{2} P25 nanoparticles displays excellent superhydrophobic property with the water contact angle of 165.6° after modified with the low surface free energy material FAS (Fig. 3(c)), which could be owing to the complex surface structure containing hierarchical features and the low surface free energy. Higher surface roughness and lower surface free energy play important roles in the superhydrophobicity of the TiO\textsubscript{2} film with TiO\textsubscript{2} P25 nanoparticles. The more excellent hydrophobicity of TiO\textsubscript{2} film with P25 nanoparticles than that without P25 nanoparticles after modified with the low surface free energy material.
FAS indicates that the TiO$_2$ P25 nanoparticles added into the TiO$_2$ precursor solution have an important influence on formation of superhydrophobicity.

The typical XPS survey spectra of TiO$_2$ films with TiO$_2$ P25 nanoparticles before and after being modified with FAS are shown in Fig. 4. A strong fluorine peak locates at 687 eV and also the peaks of C, O, and Ti are observed in this case. This demonstrates that the TiO$_2$ surface is covered by the FAS film which greatly reduces the free energy of the surface.

The particle size of the TiO$_2$ precursor solution containing TiO$_2$ P25 nanoparticles was measured by the laser diffraction particle size analyzer. The result suggests that the TiO$_2$ P25 nanoparticles in the TiO$_2$ precursor solution obviously generate aggregation with a size range of 150–1200 nm (most frequent size 1000 nm) (Fig. 5), which plays an important role in forming hierarchical structure of TiO$_2$ surface. The hierarchical structure of surface likely leads to the efficient trapping of numerous air pockets in the TiO$_2$ film surface which makes the TiO$_2$ surface minimal contact with the water and contributes greatly to the superhydrophobicity as often discussed in literature [29].

When the TiO$_2$ films are irradiated with UV light for 2 h, they show hydrophilicity (Fig. 6). Changes in water contact angle, as a function of irradiation time, show that the TiO$_2$ film with TiO$_2$ P25 nanoparticles turns from superhydrophobicity with water contact angle of 165.6° to hydrophilicity with water contact angle of 30.2° after 2 h irradiation, whereas the water contact angle of the TiO$_2$ film without TiO$_2$ P25 nanoparticles changes from 118.4° to 52.6° after 2 h irradiation. While TiO$_2$ films are irradiated with UV light, photoexcited electrons and positive holes are produced, and certain redox reactions induced by the photoexcited
electrons and holes may produce extra hydroxyl groups and oxygen vacancies on the surface which could result in the hydrophilicity of TiO$_2$ film [9,26]. It is obvious that the hydrophobicity–hydrophilicity conversion rate of TiO$_2$ film with TiO$_2$ P25 nanoparticles is faster than that of TiO$_2$ film without TiO$_2$ P25 nanoparticles, and that is mainly governed by the surface morphology of TiO$_2$ film. It is confirmed that rough structure of the surface has a profound influence on wettability.

As described by Wenzel’s equation:
\[
\cos \theta' = r \cos \theta
\]

where $\theta'$ is the apparent water contact angle on a rough surface, $\theta$ is the intrinsic water contact angle on a flat surface, and the surface roughness $r$ can enhance both the hydrophilicity and the hydrophobicity of the surface [3]. For the surface mainly composed of FAS $(\theta > 90^\circ$ for a smooth FAS surface), since $r > 1$ for a rough surface in comparison with a smooth area, the water contact angle $\theta'$ of rough surface will increase with the surface roughness $r$, which means that rough surface can enhance the hydrophobicity of surface, and the larger roughness, the more hydrophobicity. Similarly, for the TiO$_2$ film irradiated with UV light, its surface is covered with numerous hydroxyl groups and shows hydrophilicity, and therefore $\theta$ is less than $90^\circ$. The water contact angle $\theta'$ of rough surface will increase with the surface roughness $r (r > 1)$, that is to say the rough surface can enhance the hydrophilicity, and the larger roughness, the more hydrophilicity. Therefore, for a stimuli-responsive surface, the responsive wettability may be amplified by introducing surface roughness.

When the hydrophilic TiO$_2$ film from UV-irradiated hydrophobic TiO$_2$ film is placed in dark for 10 days, the hydrophilic TiO$_2$ film with TiO$_2$ P25 recovers to hydrophobicity with water contact angle $156.7^\circ$. However, the hydrophilic TiO$_2$ film without TiO$_2$ P25 recovers its water contact angle just to $86.9^\circ$. The conversion has been repeated more than 5 times (Fig. 7). When the TiO$_2$ film is placed in dark, oxygen atoms could replace the oxygen vacancies gradually, and the wettability reconverts from hydrophilicity to hydrophobicity. The conversion rate from hydrophilicity to hydrophobicity of TiO$_2$ film with TiO$_2$ P25 nanoparticles is faster than that of TiO$_2$ film without TiO$_2$ P25 nanoparticles, which mainly attributes to the surface morphology of TiO$_2$ film.
4 Conclusions

In summary, we have fabricated hydrophobic TiO2 film from TiO2 precursor solution containing TiO2 nanoparticles. TiO2 nanoparticles added in TiO2 precursor solution make the TiO2 film show hierarchical structural rough surface. And the rough surface of TiO2 film can distinctly enhance the wettability conversion of TiO2 film between hydrophobicity and hydrophilicity. This research will provide a theoretical and experimental basis for light controlled switch and light controlled dynamic self-cleaning materials.

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