Synthesis and photocatalytic properties of ultra-smooth TiO_2 thin films with superhydrophilicity

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Abstract

Functional TiO_2 films were fabricated on glass substrates by using modified dip coating method. The properties of the films including crystal structures, thickness, surface morphology and optical properties were studied. The film coated once possessed an ultra-smooth surface with a root mean square (RMS) roughness of 2.6 ± 0.7 nm, which was attributed to the effect of N_2 flow during the formation of film. The TiO_2 films exhibited superhydrophilicity without UV illumination and the superhydrophilic performance was enhanced with the increase of film thickness. Tests on degradation of dyes under UV illumination indicated that the annealing temperature and thickness of the TiO_2 films accounted for their photocatalytic performance. An increase of annealing temperature led to a decrease of the amount of defects and the recombination rate of electron-hole pairs. Because of change of film thickness, light absorption and amount of defects of the TiO_2 films influenced photocatalytic performance simultaneously.

Keywords: TiO_2 films; modified dip coating; superhydrophilicity; ultra-smooth;

1. Introduction

Semiconductor photocatalysts have boosted intriguing scientific research areas for the last decades that follows the extensively increasing demands in detoxification of organic pollutants and solar-energy conversion[1,2]. Since the water splitting phenomenon on TiO_2 electrode was first discovered by Fujishima in 1972[3], TiO_2 has attracted intensive interests for its potential applications in photocatalysis[4,5], environmental protection[6], sensors[7] and solar cells[8,9] owing to the advantages on photocatalytic performance, chemical stability and production cost. A variety of techniques have been used to prepare TiO_2 thin films including chemical vapor deposition (CVD)[10], sol-gel approaches[11-12], gold-assisted electrochemical etching[13], pulse laser deposition[14], sputtering[15,16], electrochemical anodization[17]. These procedures usually need rigid environments, complicated processes or expensive vessels.

In this research, a widely applicable and straightforward alternate method without formation of sols or gels has been developed to fabricate ultra-smooth titanium dioxide thin films, which exhibit efficient photocatalytic properties under UV illumination and superhydrophilicity without UV irradiation. The thin films are prepared by dipping glass substrates into a solution containing titanium precursor, followed by purging and drying with nitrogen flow and annealing in air.

2. Experimental:

2.1 Preparation of TiO_2 thin films

Ordinary microscope glass slides were used as substrates for TiO_2 film coating. Functional TiO_2films were prepared by using an improved dip coating method. A precursor solution was prepared by mixing tetrabutyl titanate ($Ti(OC_4H_9)_4$, TTBO) and isopropyl alcohol (IPA). The cleaned glass slide was then immersed into the precursor solution for 1 min and taken out quickly. After that, the slide was transferred to nitrogen flow with a rate of 500 sccm, in order to purge the remaining liquid on the glass surface. Such a procedure was repeated for several times. The samples were marked as TiO_2-x, in which x is the total coating times through the procedure above. Finally, the resultant samples were annealed at 200 – 500 °C in air for 5 h. In order to investigate the effect of N_2 flow in the preparation process, a sample marked as n-TiO_2 was fabricated by the same procedure excluding N_2 purging.

2.2 Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using an X-ray diffractometer XRD-6100x (Shimadzu, Japan) with Cu $K_{\alpha1}$ radiation (λ =0.154056 nm) and a Ni filter in a continuous scanning mode. The surface morphology of the specimens was obtained by an atomic force microscope (AFM) Nano Wizard II (JPK, Germany). The RMS roughness of the films was based on statistical results of the height distributions for the corresponding AFM images. The surface morphological features of the films were also observed using a field-emission scanning electron microscope (FE-SEM) SU1510 (Hitachi, Japan) operating at 15 kV. The thickness of TiO_2 thin film was determined by scanning an ellipsometer Alpha-SE (J.A. Woollam, USA). The water contact angles (WCAs) of TiO_2 thin films were measured by

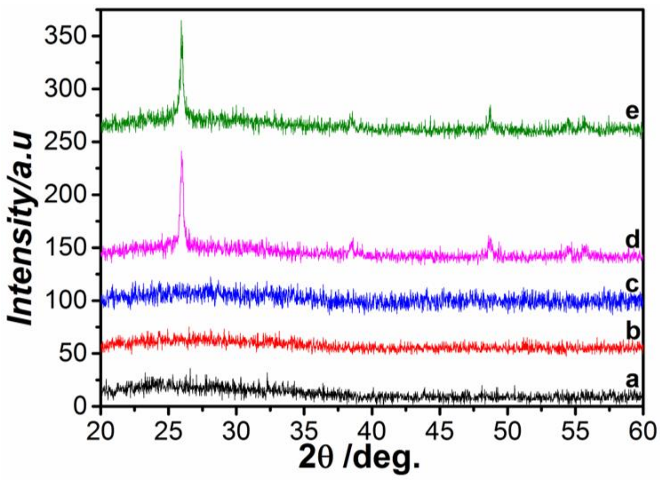

Figure 1. XRD patterns of the as-prepared TiO_2 (a) and TiO_2-1 thin films annealed at 200°C (b), 300 °C (c) ,400 °C (d) and 500 °C (e).

using CAM 200 (KSV instrument, Finland) without UV irradiation at ambient temperature. Water droplets were automatically generated with a volume of 5 μL. Samples were stored in a dark box for 48 h before measurements. Photocatalytic activities of samples were evaluated by degradation of methylene blue under light irradiation of a 500 W high-pressure mercury lamp. In each experiment, TiO_2 film on glass substrate as a photocatalyst was placed into 3.5 ml methylene blue solution (1×10^{-5} M) in a quartz vessel and the solution was stirred for 1 h in dark to reach absorption equilibrium between the catalyst and the solution. The solution was then exposed to light irradiation. After irradiation for a given time, the film was removed out of the solution, and the concentration of the solution was determined using UV–Vis spectra (Shimadzu UV-3600).

3. Results and discussion:

3.1 Structures and morphology

Figure 1 shows the X-ray diffraction patterns of the TiO_2-1 thin films prepared on glass slides, which were annealed in air for 5h at 200 °C, 300 °C, 400 °C and 500 °C, respectively. The diffraction peaks indicated that annealing over 400 °C has greatly improved the crystallinity of the samples. The peaks shows the films are in accordance with anatase TiO_2 structures.

Figure 2 (a) and (c) shows FE-SEM images of the TiO_2-1 thin film annealed at 400°C in air for 5h and

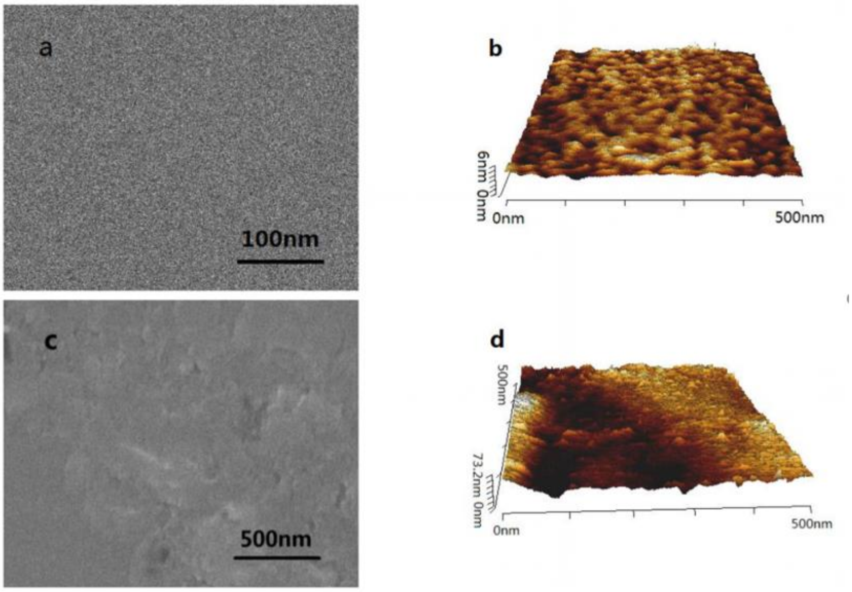

Figure 2. FE-SEM and AFM images of the TiO_2 thin film annealed at 400 °C in air for 5 h (a, b) and the n-TiO_2 sample prepared by the same procedure excluding N_2 purging (c, d).

the n-TiO_2 thin film prepared by the same procedure excluding N_2 blowing. Figure 2 (b) and (d) exhibits the AFM image of the corresponding samples. It is obvious that the annealed TiO_2-1 film possessed an ultra-smooth surface. The calculated RMS roughness of the annealed films is 2.6 ± 0.7 nm, which is consistent with the result of SEM image. The SEM image of the n-TiO_2 sample prepared shows a rough surface and the analysis of AFM image yield an RMS roughness of 9.1 ± 6.5 nm, which is significantly larger than that of annealed TiO_2-1 film.

The formation of ultra-smooth surface of the annealed TiO_2-1 films may be attributed to the effect of N_2 blowing, which is demonstrated in Figure 3. Without N_2 flow, a much thicker layer of solution remained

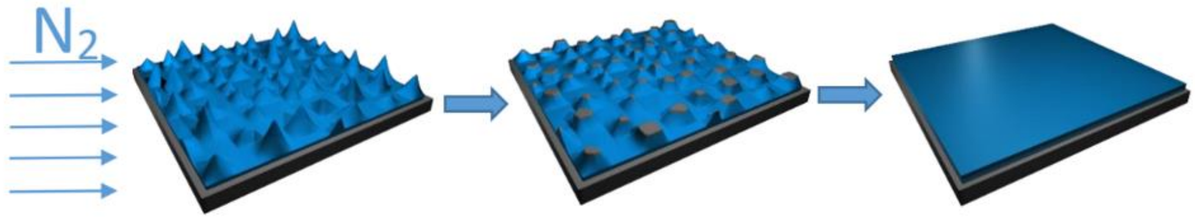

Figure 3. Schematic of formation of TiO_2 thin filmfacilitated by N_2 flow.

on the substrate and liquid droplets were generated before the evaporation of solvent since the glass surface was not superhydrophilic, which resulted in a rougher surface.

Ellipsometric analysis of TiO_2 films were performed at an incidence angle of 70° with optical range of 350–900 nm. The thicknesses of TiO_2 films after annealing at 400 °C obtained by spectroscopic ellipsometry were shown versus the corresponding coating times in Figure 4. The thicknesses of TiO_2-1, TiO_2-2, TiO_2-3 and TiO_2-5 films were measured to be 76 nm, 236 nm, 389 nm and 705 nm, respectively. The linear correlation between the thickness and coating times showed that the fabrication method can offer

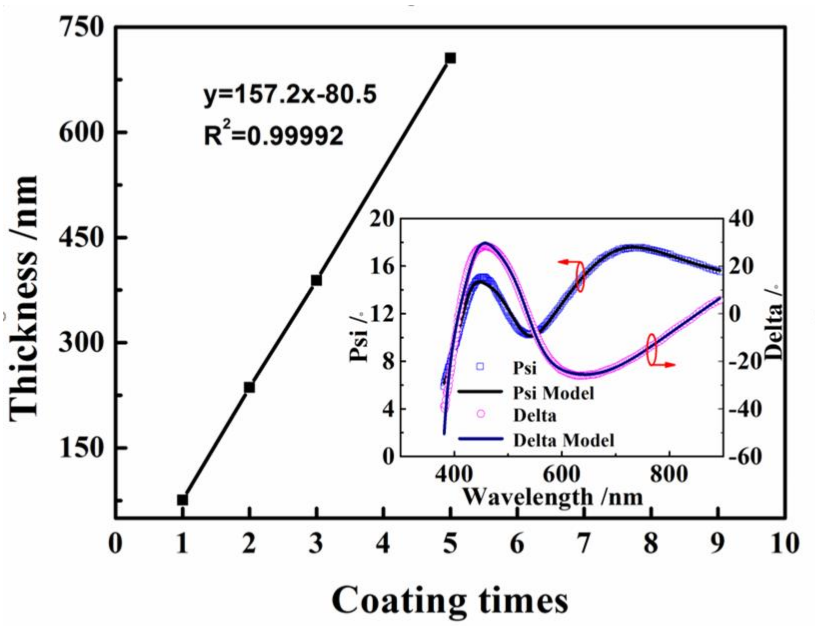

Figure 4. Relationship between the film thickness and coating times. A linear fit to the data is displayed. Inset is the measured ellipsometric parameters and fittings of the data to the EMT model for the TiO_2-1film on glass substrate annealed at 400 °C in air.

control of the thickness of the TiO_2 films. The measured data of Δ (delta) and ψ (psi) were fitted using the Bruggeman effective-medium theory (EMT)[18], as shown in the inset of Figure 4. The effective dielectric function was calculated by considering the sample type of a TiO_2 layer on a glass substrate. The EMT model extracts the refractive index of the TiO_2 layer as a function of wavelength, which yields an value of 1.92 ± 0.03 in the visible wavelength range, lower than that (~2.5) of bulk TiO_2[18].

3.2 Superhydrophilicity

By measurement of WCAs, the surface wettability of TiO_2 films was investigated. Figure 5 shows water spreading behaviors of the TiO_2 films coated with different times. The equilibrium WCAs were eventually close to zero, which showed the superhydrophilicity of all films. With the increase of film thickness, the time for the droplets to expand fully on contact surface decreased. The performance follows the Tanner's power-law behavior[20] described as $\theta \propto (t + t_0)^{-n}$, where θ is the contact angle, t is time from droplet deposition, t_0 is a constant, n is a power parameter and its value increases with the thickness of the superhydrophilic film[21]. In our results, the time t and the power parameter n are negatively correlated, which is in good agreement with the correlation of Tanner's power law.

3.3 Photocatalytic property

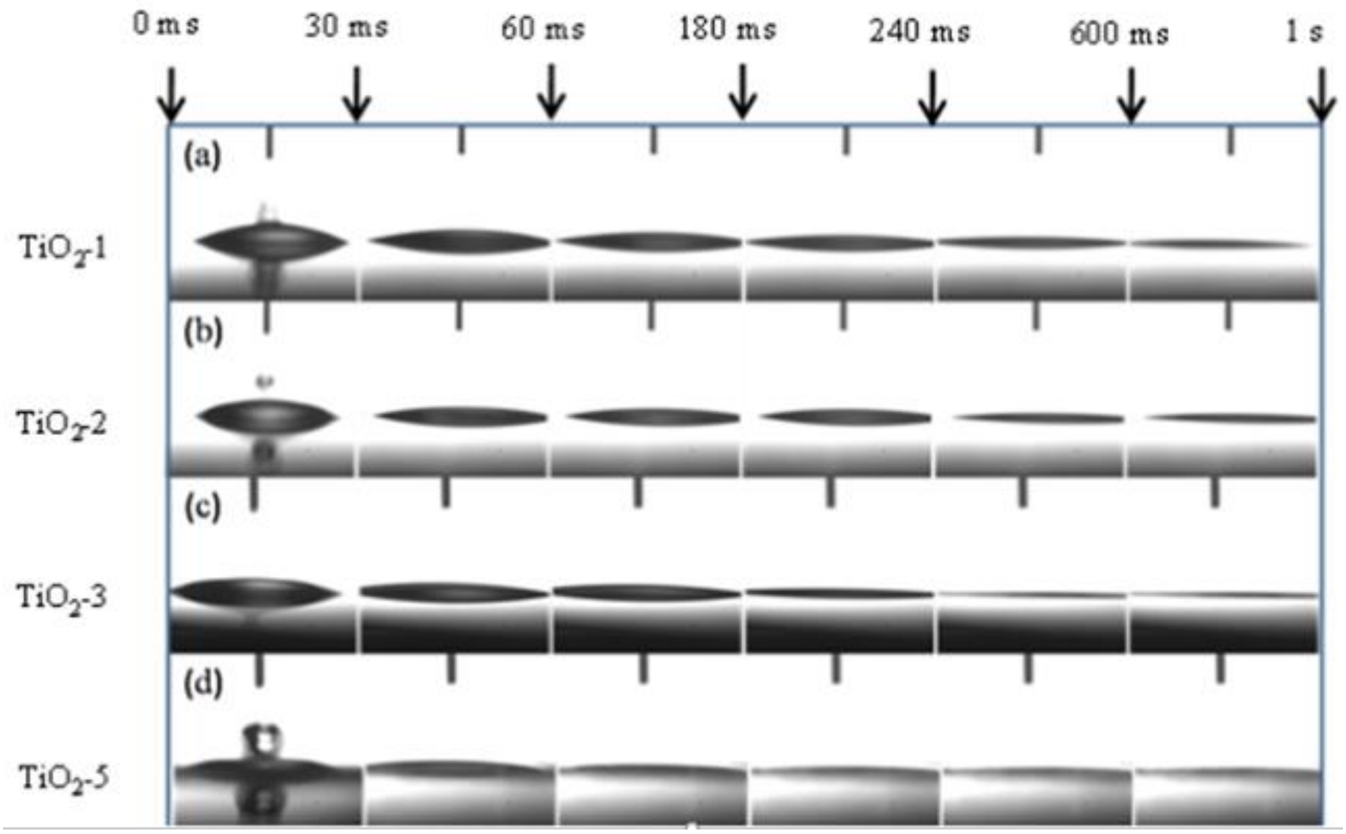

Figure 5. Optical images of water spreading behaviors on TiO_2-1(a), TiO_2-2(b), TiO_2-3(c), TiO_2-5(d) thin films annealed at 400 °C.

By investigating the photocatalytic degradation of methylene blue on TiO_2 thin films, the effects of the thickness and annealing temperature of the films on photocatalytic properties were taken into account, which is shown in Figure 6. Figure 6 (a) shows the degradation rate on TiO_2-1, TiO_2-2, TiO_2-3 and TiO_2-5 films annealed at 400 ˚C. With the film coating times $x \leq 3$, the degradation efficiency of dyes increased with x. However, the efficiency dropped apparently for the films with $x>3$. Neglecting difference of reflection effect on the surface, the number of photons absorbed by the films has a positive correlation with the film thickness in a moderate range. However, if the thickness of the film exceeds a critical value, photons will not be able to travel through the films and an increase of thickness will not enhance light absorption. In addition, charge carriers generated by lights may diffuse towards the substrate because of the concentration gradient, which impedes their contact with dye molecules.[19] Figure 6 (b) shows the degradation rate on TiO_2-1 annealed at 200˚C, 300 ˚C, 400˚C and 500˚C. The degradation efficiency increased with the annealing temperatures, which is consistent with the fact that the increase of annealing temperature led to the improvement of crystallinity and less defects, i.e., lower recombination rate of electron-hole pairs.

Figure 7 (a), (b) and (c) shows the degradation rate of methylene blue on as-prepared TiO_2-1, TiO_2-2, TiO_2-3 and TiO_2-5 films and the films annealed at 200˚C or 300˚C. With increasing coating times, the degradation rate decreased. The XRD results have demonstrated the formation of these amorphous TiO_2 films with the annealing temperatures less than 400˚C. With comparison to crystalline TiO_2 films,

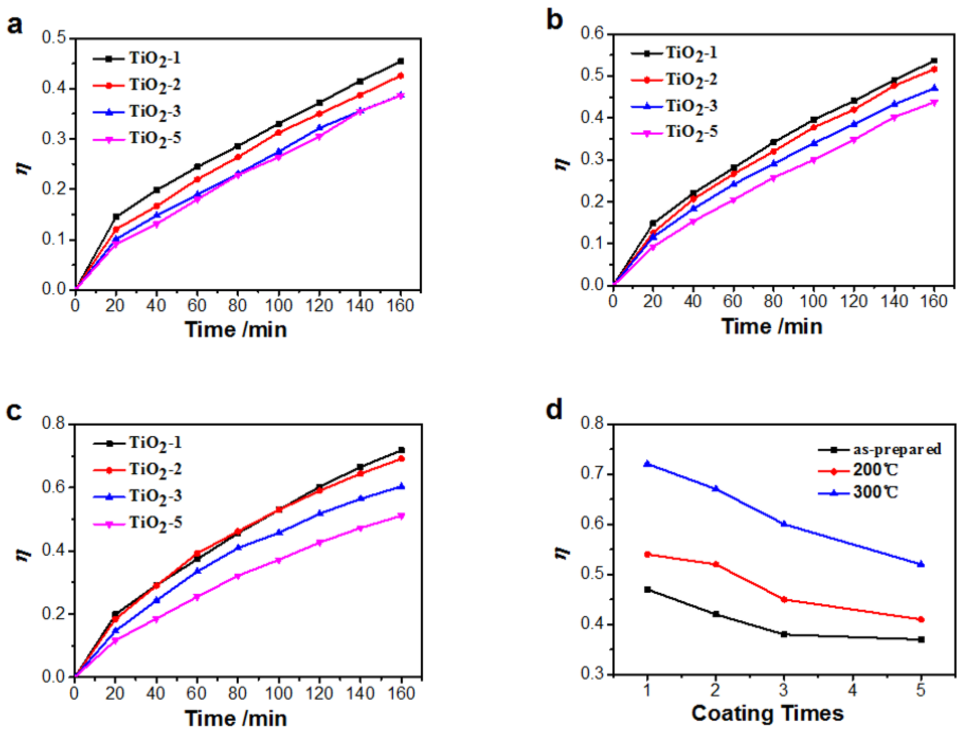

Figure 7. Degradation rate of methylene blue on the as-prepared TiO_2-x films(a) and the films annealed at 200°C (b) and 300°C (c), respectively; Degradation rate of methylene blue on theTiO_2-x films with UV illumination for 160 min (d).

amorphous TiO_2 films possessed a large amount of defects, which resulted in a high recombination rate of electron-hole pairs and dominated the photocatalytic activity. Figure 7 (d) shows the effect of annealing temperature on the degradation rate. With increasing annealing temperatures, all TiO_2-x films showed increasing degradation rates due to decreasing defects.

4. Conclusion

In summary, an easy modified dip coating method has been used to fabricate ultra-smooth TiO_2 layers on glass slides. After annealing at the 400˚C, the TiO_2 films exhibit an anatase structure and the RMS roughness of TiO_2-1 film measured by spectroscopic ellipsometry is 2.6 ± 0.7 nm. Tests on degradation of dyes under UV illumination indicated that the annealing temperature and thickness of the TiO_2 films account for their photocatalytic performance. A high annealing temperature resulted in a small of amount of defects and a low recombination rate of electron-hole pairs. Thickness of TiO_2 films may affect light absorption and amount of defects simultaneously. All the TiO_2films showed superhydrophilicity without UV illumination. The hydrophilicity of the films was enhanced with the increase of film thickness. All these properties showed promising applications in self-cleaning coating, anti-UV light and sterilization.

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