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TiO_2 optical coating layers for self-cleaning applications

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Abstract

TiO_2 films deposited by various coating techniques were investigated for self-cleaning applications. The optical coating layers of TiO_2 films prepared from a sol–gel precursor were deposited on glass substrates using spin coating, dip coating and screen printing techniques. Effects of film deposition techniques on crystal structure, microstructure, thickness, photocatalytic activity, hydrophilicity and optical properties of the films were investigated using XRD, AFM, SEM, surface profilometer, UV–vis spectrophotometer and contact angle measurement. Dip coating the TiO_2 optical film two and three times resulted in superhydrophilic surfaces. Increasing number of dipping times was found to increase the photocatalytic activity.

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1. Introduction

Self-cleaning applications using semiconducting powders or thin films have become a subject of increasing interest especially in the last 10 years. The self-cleaning property has been known to be a mutual effect between photocatalysis and hydrophilicity. The photocatalysis property help decompose the organic substances that come into contact with the surface and thus prevent them from building up. The hydrophilicity makes the cleaning more effective as the water spread over the surface rather than remaining as droplets which help collect the dirt better, make the surface dry faster, and moreover, prevent the undesirable water streaking or spotting on the surface [1–3]. TiO_2 is one of the most widely used materials for self-cleaning application because its thermo stability and photocatalytic properties [4–9]. The ability to engineer the TiO_2 to have superhydrophilic property on surfaces is also an advantage [1–3].

In this study, TiO_2 films were prepared from titanium precursor solution by various techniques to compare differences in film morphologies, photocatalytic activities and hydrophilicity. The effects of deposition techniques on the hydrophilicity and photocatalytic activity of the TiO_2 films are evaluated by measuring the contact angle of water on the films and the photocatalytic decolorization of aqueous methylene blue, respectively.

2. Experimental procedure

2.1. Preparation of TiO_2 precursor solution

To obtain a stable TiO_2 sol, a precursor solution was prepared following Legrand-Buscema et al. [10]. First, 0.3 M titanium-isopropoxide (TTIP, Fluka) was dissolved in isopropanol (IPA, Fluka) and stirred at room temperature for 30 min. Then, acetylacetone (Acac, Merck) was added to make 10:3 molar ratio of titanium isopropoxide to acetylacetone. The mixture was used as chelating agent to stabilize the solution. The mixture was then stirred for 30 min more. Acetic acid (Lab-scan) was added afterward to help initialize hydrolysis by creating esterification reaction with isopropanol. Transparent yellow solution was obtained.

2.2. Preparation of P25 Degussa TiO_2 solution for coating

A mixture of P25 Degussa TiO_2/Terpineol anhydrous (Fluka)/Ethyl cellulose (Fluka) having weight ratio of 1:7:1 was prepared. The mixture was stirred vigorously and continuously until homogeneous white solution was obtained.

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The TiO_2 precursor and P25 Degussa TiO_2 mixture were used for film fabrication by dip coating, spin coating and screen printing. Soda lime glass slides (30 mm × 20 mm × 1.5 mm) were used as substrates. The glass slides were ultrasonicated in DI water, acetone, ethanol and isopropanol for 15 min each, respectively. The coated films were dried at 60 °C for 30 min and calcined at 450 °C for 4 h in air [11]. Reasonably smooth and uniform TiO_2 films were selected for characterization.

2.3. Characterization

Morphologies of the TiO_2 films were investigated using tapping mode atomic force microscopy (AFM, Seiko Instrument SPA 400) and field emission scanning electron microscopy (Hitachi S-4700 FE-SEM). The film thicknesses were measured using a Dektak 3st surface profilometer. Crystal structures of the TiO_2 films were studied using Rigaku TTRAX III X-ray diffractometer (XRD). The Cu Kα radiation was operated at 50 kV, 300 mA with a scanning speed of 2°/min at 2θ step of 0.02°. Photocatalytic activity of TiO_2 was evaluated by investigating degradation of methylene blue (MB, Riedel-deHaën), which was used to represent a pollutant. For the photodegradation investigation, the TiO_2 films on glass substrates were immersed in an aqueous solution of methylene blue (6.25×10^{-5} M) for 3 min then irradiated with UV light (long wavelength mode) for 1 h. After the radiation, degradation of the methylene blue was determined by measuring absorbance of the methylene blue of each decanted solution using UV–vis spectrophotometer (JASCO V-530) at $\lambda_{max} = 661$ nm. Finally, the hydrophilic property was evaluated by measuring contact angle of water droplet on the film under an ambient condition at 25 °C in air, before the UV radiation.

After calcinations, dip-coated TiO_2 films (withdrawing speed of the substrates 0.5 mm/s) from TiO_2 precursor solution was the most uniform and smooth among all techniques employed. We, then, compared TiO_2 film dip-coated one, two and three times to investigate the effect of number of dipping times.

3. Results and discussion

3.1. Microstructure and thickness of the films

Among all film coating techniques investigated, dip coating was the only technique that yielded homogenous TiO_2 films. Fig. 1(a)–(c) are AFM micrographs showing the surface morphologies of TiO_2 films dip-coated for one, two and three times, respectively. Fig. 1(d) shows an AFM micrograph of P25 Degussa TiO_2 film prepared by screen printing (with scale different from Fig. 1(a)–(c) due to much higher roughness).

Fig. 2 shows SEM micrographs of the one time dip-coated TiO_2 film and the one time screen printed P25 Degussa TiO_2 films. Dip coating of the TiO_2 from the prepared precursor resulted in a denser film than screen printed P25 Degussa TiO_2 film. However, it was not possible to prepare smooth films from the in-house prepared TiO_2 by screen printing due to the difference in sizes of primary particles and viscosity of the starting precursor. Increasing dip coating time of the TiO_2 film from the prepared precursor from one to three times resulted in thicker and less rough films (Table 1). The TiO_2 film screen

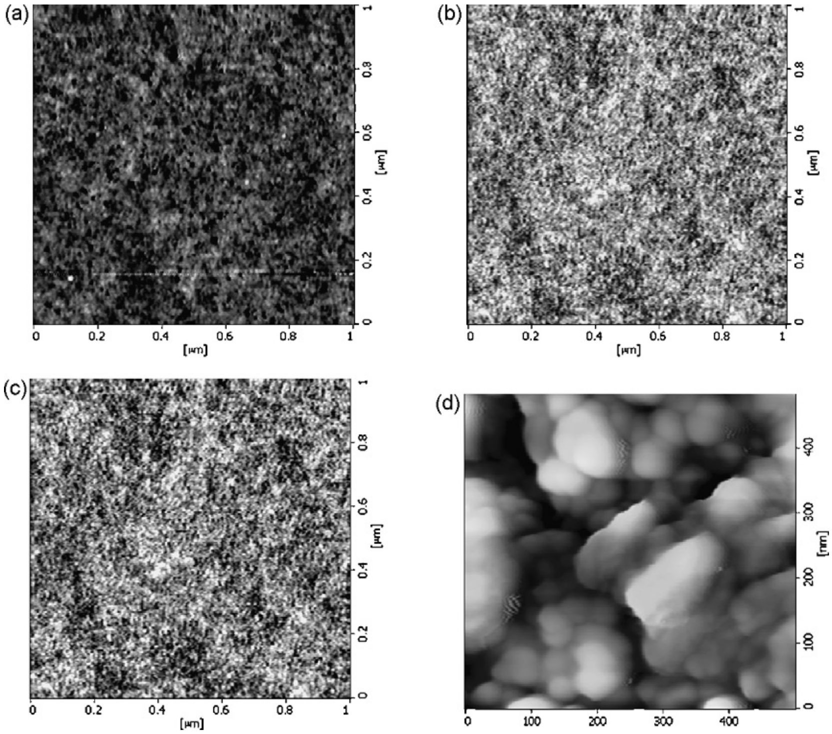

Fig. 1. AFM micrographs (1 μm × 1 μm) of the TiO_2 thin films dipped for (a) one time, (b) two times, (c) three times and (d) P25 Degussa screen printed films (500 nm × 500 nm).

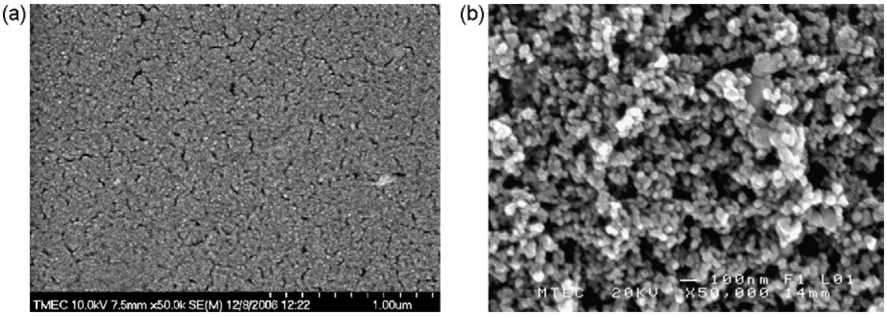

Fig. 2. SEM micrographs taken at 50,000× of TiO_2 thin films dipped one time (a) and P25 Degussa screen printed one time (b).

printed from P25 Degussa was found to be much thicker than the films prepared by dip coating. The roughness of P25 Degussa film is three orders of magnitude higher than that of the dip-coated films.

Fig. 3 shows the XRD pattern of TiO_2 films prepared from TiO_2 precursor and dip-coated one to three times, compared with the screen printed P25 Degussa. For the dip-coated films, XRD peaks indicated pure anatase phase with a tetragonal structure ($a = 3.783$ Å, $c = 9.512$ Å). Moreover, all dip-coated TiO_2 films show preferred orientation along {1 0 1} planes which is in agreement with Legrand-Buscema et al. [10]. Using Scherrer's equation to calculate the crystallite size, it was found that the crystallite sizes of TiO_2 films prepared by dip coating the prepared TiO_2 precursor three times and by screen printing of P25 Degussa were approximately the same (~20 nm). However, both anatase and rutile phases were observed for P25 Degussa TiO_2 film (Fig. 3).

3.2. Photocatalytic activity

Fig. 4 shows that all of the TiO_2 films prepared from the precursor exhibited inferior photocatalytic activities to the TiO_2 films from P25 Degussa. The differences in photocatalytic activity could be contributed from the differences in phases present, particle and surface morphology, and surface areas. From the AFM results in Fig. 2, films produced from the TiO_2 sol was found to be much smoother which means less surface area for absorption leading to lower catalytic activity when compared to the P25 film. Moreover, for sample fabricated from P25, it was found that there exist a combination of the two phases, anatase and rutile. It has been reported that a combination of the anatase and rutile phase could provide a more efficient electron–hole separation leading to a higher photocatalytic activity [12].

Table 1
Thickness and roughness of the TiO_2 films prepared by one to three dipping times and screen printing

	Thickness (nm)	Roughness (nm)
Number of dipping times		
One	116.5	0.451
Two	252.5	0.2337
Three	360	0.1952
P25 screen printing	980	20.402

When comparing the effect of number of times of dip coating, it was found that the film dip-coated three times exhibits a higher photocatalytic activity than the samples coated for one and two times. Investigation on the XRD results (Fig. 3) has shown that as the number of dip coating time increases, the XRD peak got sharper. Sharper XRD peak indicates a larger particle size or a more well-ordered crystallites. The more ordered structure which is directly associate with the lower

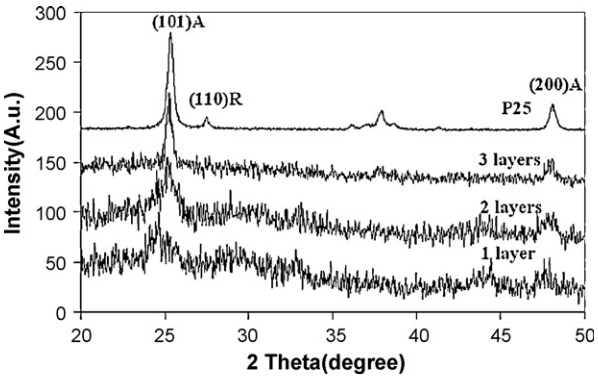

Fig. 3. XRD patterns, from top, P25 Degussa TiO_2 film and TiO_2 films dip-coated three, two and one times from a prepared TiO_2 precursor (A = anatase, R = rutile).

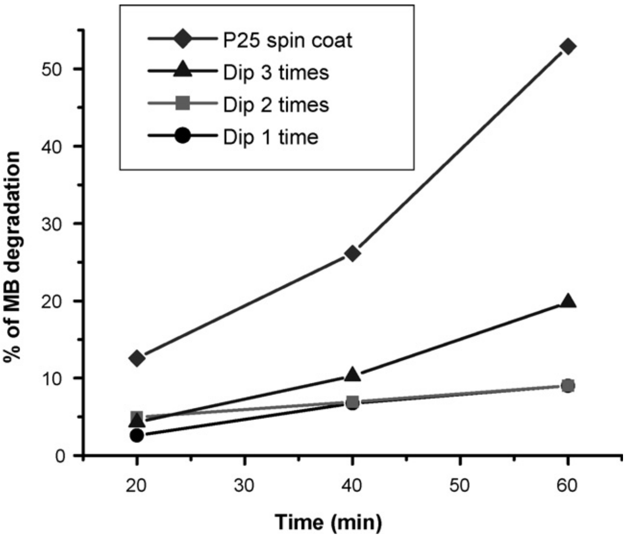

Fig. 4. A comparison of photocatalytic activities of TiO_2 prepared by dipping coating: (a) one time, (b) two times, (c) three times and (d) screen printed P25 Degussa.

Table 2
Contact angle of water on the TiO_2 films prepared by one to three dipping times and screen printing

	Contact angle (deg.)
Number of dipping times	
One	8
Two	Almost 0
Three	Almost 0
P25 screen printing	Almost 0

concentration of defects would make the recombination of electrons and holes less favored [13] and thus could be the reason for higher photocatalytic activity observed for the sample dip-coated for three times.

3.3. Hydrophilicity

TiO_2 films dip-coated two and three times showed superhydrophilic nature, comparable to screen printed one layer of P25 Degussa (Table 2). For the P25 Degussa screen printed TiO_2 film, superhydrophilic property may be caused by its porous structure (Figs. 1(d) and 2(b)) that enables fast water absorption [14]. Moreover, in the case of the dip-coated TiO_2 films, calcinations temperature at 450 °C was reported to be the best for pure anatase phase in the TiO_2 films as it is believed to be responsible for the superhydrophilicity of the TiO_2 films [3]. The hydrophilicity is also believed to relate to the density of surface hydroxyl of the TiO_2 films. The surface hydroxyl can combine with water molecules to form hydrogen bond, resulting in good wettability. Mass density of the film is also known to affect the superhydrophilicity. Morover, the dip-coated TiO_2 films have {1 0 1} preferred orientation which has been reported to be in favor of hydrophilicity [6]. The dip-coated anatase TiO_2 films in this study seem to have all the properties required for superhydrophilicity. As self-cleaning is a mutual effect of hydrophilicity and photocatalysis, the three times dip-coated TiO_2 films gives the most promising results. Table 2 lists contact angle of water on differently prepared TiO_2 films.

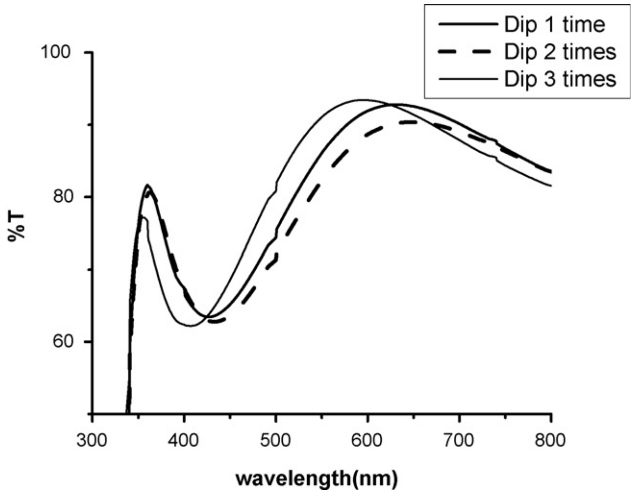

Fig. 5. UV–vis spectra of TiO_2 dip-coated films one to three layers.

3.4. Optical quality of the films

UV–vis transmission spectra of dip-coated films are shown in Fig. 5. Results indicated that all films prepared by dip coating allow a good transmission of light in the visible region.

4. Conclusions

TiO_2 optical layers coated from titanium isopropoxide, dissolved in isopropanol, in presence of acetylacetone as a chelating agent and acetic acid. Among dip coating, spin coating and screen printing techniques, dip coating was the only technique that resulted in smooth films. Dip coating the TiO_2 optical layers two and three times resulted in superhydrophilic surfaces. The superhydrophilicity of the prepared dip-coated TiO_2 films were due to pure anatase TiO_2 with preferred {1 0 1} orientation. An increase in number of dipping times was found to increase the photocatalytic activity. The best self-cleaning TiO_2 film was obtained by dip coating the prepared TiO_2 precursor three times on glass slide substrates.

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