

Photoinduced properties of nanocrystalline TiO₂ sol–gel derived thin films

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Abstract. In this paper, nanostructure TiO₂ thin films were deposited on glass substrates by sol–gel dip coating technique. X-ray diffraction and Fourier transform infrared spectroscopy were used to determine film behaviour. The super-hydrophilicity was assessed by contact angle measurement. Photocatalytic properties of these films were evaluated by degradation of methylene blue under UV irradiation. The XRD pattern of TiO₂ powder samples confirmed the presence of polycrystalline anatase phase with a crystal size of 17 nm. The results indicated that UV light irradiation had significant effect on super-hydrophilic and photocatalytic properties of TiO₂ thin films.

Keywords. TiO₂; sol–gel; super-hydrophilicity; photocatalytic properties.

1. Introduction

Titanium dioxide (TiO₂) thin films have attracted a great deal of attention. They have many advanced functions in photocatalysis, sterilizing, solar energy cells, gas sensors, self-cleaning effect etc (Guan *et al* 2003; Guan and Yin 2005; Karuppachamy and Jeong 2005; Sharma *et al* 2006). The self-cleaning effect of TiO₂ thin films have become an interesting subject in recent years. The self-cleaning property has been known to have a mutual effect between the two photoactive characteristics properties of TiO₂ thin films: super-hydrophilicity and photocatalysis. Both the photoactive characteristics are basically the surface-relating phenomena (Mlyashita *et al* 2001; Fujishima and Zhang 2006; Euvananont *et al* 2008). The super-hydrophilic property of the TiO₂ film on surface allows water to spread completely across the surface rather than remain as droplets, thus making the surface anti-fogging and easy to wash (Wang *et al* 1997; Guan 2005). The super-hydrophilic TiO₂ films on glass substrates are widely used in various applications such as mirrors, window glasses, light bulb, windshields of automobiles, etc (Yu *et al* 2001; Hata *et al* 2002; Karuppachamy *et al* 2006). TiO₂ has attracted considerable attention for its potential applications in photocatalysis (Hodos *et al* 2004). Many organic compounds can decompose in aqueous solution in the presence of TiO₂ under UV light irradiation. For example, azo-dyes like alizarin S, crocein orange G, methyl red, congo red and methylene blue have been completely mineralized with TiO₂/UV in aqueous suspensions (Tang *et al* 2003). It has been shown that

photocatalytic properties of TiO₂ thin films are influenced by several factors such as crystal structure, surface area, porosity, surface hydroxyl group density etc (Trapalis *et al* 2003).

The preparation methods of TiO₂ thin films have a great effect on these factors and photocatalytic properties (Barakat *et al* 2004). Various deposition methods such as electron beam evaporation, ion sputtering, chemical vapour deposition and the sol–gel techniques have been utilized for obtaining TiO₂ thin films (Wen *et al* 2001). Among these methods, sol–gel processing routes have been intensively studied because of several advantages such as low processing temperature, homogeneity, possibility of coating on large area substrates, and low cost, unlike physical vapour deposition or chemical vapour deposition coating technologies (Uhlmann *et al* 1997). Furthermore, nanostructure materials are preferred over dense structures because of their larger active surface. The production of nanostructure films is nowadays an established method and TiO₂ nanoparticles and nanostructure films are among the materials routinely produced through the sol–gel chemistry processing (Cernigoj *et al* 2006). In the present study, super-hydrophilic and photocatalytic properties of the TiO₂ sol–gel derived thin films were investigated.

2. Experimental

2.1 Preparation of films

Figure 1 shows the schematic flowchart of the experimental procedure. The TiO₂ precursor sol was prepared by dissolving tetrabutyl orthotitanate (TBOT, 1 mol) in

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ethanol (EtOH, 20 mol) and acetyl acetone (0.2 mol). Then acetic acid (1.5 mol) was dissolved in deionized water (3 mol) and ethanol (20 mol), and then added to the first solution during stirring. The stirring of each solution was continued for 30 min and then the solutions were mixed ultrasonically for another 30 min. Acetyl acetone was added to slow down the speed of hydrolysis and condensation reactions and form a stable sol. Before coating, soda-lime glass ($30 \times 20 \times 1.5$ mm) substrates were ultrasonically cleaned in acetone and absolute ethanol for 5 min, respectively. Finally, they were thoroughly rinsed with water. The TiO₂ thin films were obtained by a dip coating method and the withdrawal speed was 5 mm/s. The gel films were dried at 80°C for 2 h, and then were heat-treated at 500°C for 2 h in air. The times of coating were two. Also, TiO₂ powder sample was prepared apart from the above described thin films. TiO₂ gel was prepared by drying the initial solution at 70°C in air. TiO₂ powder was prepared by annealing the gel for 2 h at 500°C (Attia *et al* 2002).

SiO₂ layer was pre-coated on the glass substrate by a sol-gel method. Precursor solutions for SiO₂ thin films were prepared according to the following procedure. Tetraethylorthosilicate (TEOS, 1 mol) was dissolved in an absolute ethanol solution (20 mol) and deionized water (3 mol). Then, an additional hydrochloric acid catalyst (0.5 mol) was added to the above TEOS precursor. Refluxing at 80°C for 1 h hydrolyzed this mixture, and then the mixture was aged for 24 h, resulting in the SiO₂ sol. The SiO₂ films formed on soda-lime glass were prepared from the above SiO₂ sol solution by dip coating (withdrawal of 5 mm/s). Films were dried at 100°C for 30 min and then heat-treated at 500°C for 1 h. The coating was done once (Yu *et al* 2001).

2.2 Characterization

The powder samples were characterized using X-ray diffraction (XRD, CuK α irradiation, $\lambda = 1.54184$ Å). TiO₂

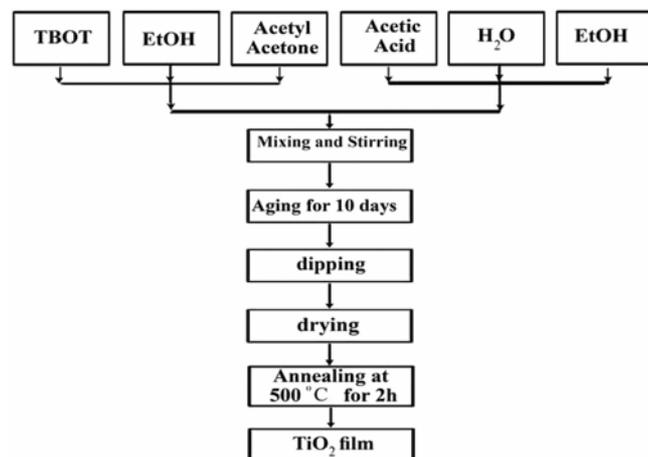


Figure 1. Sol-gel process of TiO₂ thin film preparation.

thin films were characterized using Fourier transform infrared spectroscopy (FTIR). Super-hydrophilic properties of films under UV irradiation were evaluated by measuring the contact angle of a water droplet on the films with an experimental error of $\pm 1^\circ$. A droplet was injected on to the surface using a 1 μ L micro-injector. Assuming that the geometry of the drop was a spherical section, the contact angle can be estimated directly from the diameter of the contact circle measured by an optical microscope. The water contact angle was averaged from five times of measurements. UV was irradiated to the surface of the sample by 20 W ultraviolet light and UV intensity was about 0.8 mWcm⁻².

Photocatalytic activity of TiO₂ films was evaluated by investigating degradation of methylene blue (MB). For the photodegradation experiment, the TiO₂ films on glass substrates were immersed in an aqueous solution of methylene blue (6.25×10^{-5} M) for 5 min, then irradiated with UV light for 90 min. 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 at $\lambda_{\text{max}} = 664$ nm.

3. Results and discussion

3.1 Thickness of TiO₂ films

According to the density, square and weight of the deposited film, the average thickness of each dipping can be calculated. The average thickness of films in the two dipping cycles ranges between 190 and 200 nm.

3.2 XRD study

XRD patterns which were obtained from powder of the same composition as the TiO₂ thin film has been shown in figure 2. This figure confirms the presence of polycrystalline anatase phase in the powder sample. The crystallite size of TiO₂ powder can be calculated from the Debye Scherrer equation (Doss and Zallen 1993). Using the (101) peak

$$t = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where t , K , λ , β and θ are the grain size, constant (0.94), wavelength of X-ray (CuK α -1.54184 Å), the true half-peak width and the half diffraction angle in degree, respectively. The crystallite size was estimated as ~ 17 nm.

3.3 FTIR spectra

The characterization of functional groups on the film was important to understand the photoinduced super-hydro-

philicity on the surface. An FTIR spectrum obtained from the surface of film has been shown in figure 3.

Adsorption band at about 3400 cm⁻¹ is assigned to the stretching modes of O–H bonds and is related to surface absorbed water. The adsorption band at 1600 cm⁻¹ is attributed to the bending vibration of H–O–H bonds, which is assigned to the chemisorbed water. The adsorption band at about 440 cm⁻¹ is due to the stretching vibrations of Ti–O–Ti and Ti–O bonds (Yu *et al* 2001).

3.4 Super-hydrophilic properties

Figure 4 shows the super-hydrophilic properties of TiO₂ films on glass substrates. The contact angle for water droplets on film surface reaches to 52° at initial step, but decreases with UV irradiation time. After 60 min UV illumination, contact angle becomes lower than 5°. Therefore, TiO₂ coated glass after enough UV illumination shows super-hydrophilic and antifogging effect.

TiO₂ is a semiconductor with a bandgap energy of 3.2 eV. According to Planck's equation

$$\lambda = \frac{hc}{E_g}, \quad (2)$$

where h , c and E_g are the Planck's constant, the speed of light and the semiconductor bandgap energy, respectively.

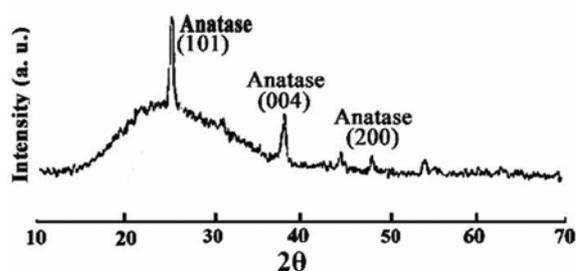


Figure 2. XRD pattern of TiO₂ powder.

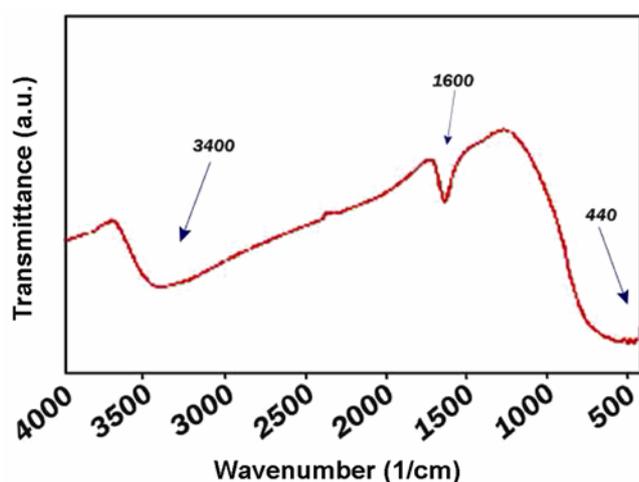


Figure 3. FTIR spectra of TiO₂ film.

When titanium oxide is irradiated with UV light ($\lambda < 380$ nm), the electrons and holes are produced in conduction band and valence band, respectively. Reaction (3) describes the mentioned phenomenon.



In following, Ti⁺⁴ on the TiO₂ crystal surface is reduced by a surface trapped electron



And the holes oxidize the O⁻² anions. In the process, oxygen atoms are ejected and oxygen vacancies are created according to this reaction



Then, water molecules can occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic (Takata *et al* 2003; Kontos *et al* 2007).

Hydroxyl groups existing in the films are attributed to the chemically adsorbed water molecules and also some water molecules are physically adsorbed on the surface of TiO₂. It can be explained that some adsorbed water molecules react with TiO₂ and forms Ti–OH groups. Generally, with the increasing of chemically absorbed –OH on the surface of TiO₂ films, van der Waals forces and hydrogen bonds interactions between H₂O and –OH will be increased. Consequently, water can be easily spread across the surface and the super-hydrophilic property gets enhanced (Fujishima *et al* 2000; Karuppachamy *et al* 2006).

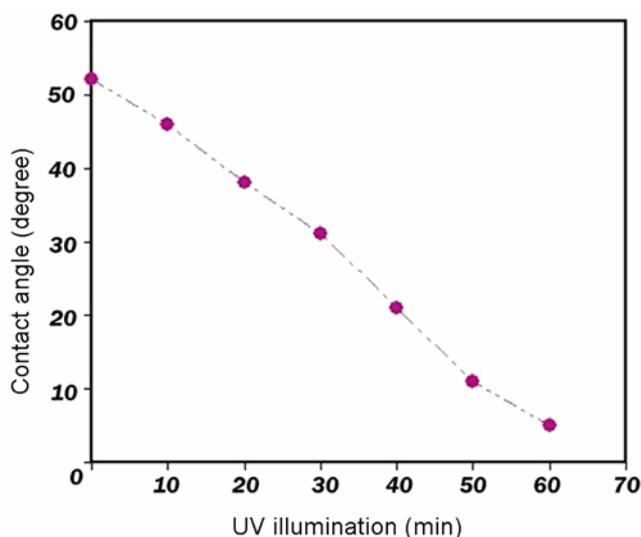


Figure 4. Contact angle of TiO₂ films under UV irradiation.

3.5 Photocatalytic activity

Figure 5 shows the variation of the photocatalytic activity vs UV irradiation time. It is found that the photocatalytic activity of TiO₂ films increase with increasing UV irradiation time. According to figure 5, it was found that film with pre-coated SiO₂ layer exhibits a higher photocatalytic activity than ones without SiO₂ layer. The fact that the most enhanced photocatalytic activity of multilayer films was observed in TiO₂ films with silica under-layer, is an interesting phenomenon. To achieve enough photocatalytic effect, TiO₂ are supposed to need to form a charge space layer on the surface, which is thought to separate a pair of photoelectron and hole away, and decrease the rate of recombination of the pairs. In film without silica under-layer, alkali ions can be diffused from the glass substrate to TiO₂ film which provided recombination centres for electron-hole pairs. This phenomenon could be the reason for higher photocatalytic activity observed in TiO₂/SiO₂ films. In conclusion, the enhanced photocatalytic activity of films can be assigned to synergetic effect of the prevention of the alkali ions migration from glass substrate during firing (Watanabe *et al* 1999).

Apart from the super-hydrophilic properties, TiO₂ films exhibit photocatalytic properties, after UV illumination. As in the case of super-hydrophilicity, in photocatalysis, electrons and holes are still produced, but they react in a different way.

These electron-hole pairs have an oxidizing potential which is enough to oxidize most pollutants present in aqueous systems. The photogenerated electrons then react with molecular oxygen (O₂) to produce superoxide radical anions (O₂^{•-}), and the photogenerated holes react with water to produce hydroxyl (OH) radicals (figure 6). These highly reactive species are able to decompose a

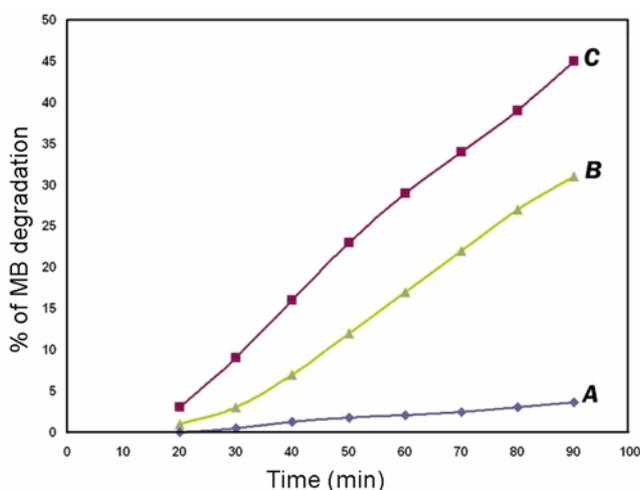
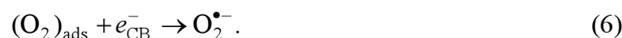


Figure 5. Photo degradation of MB: A. without films, B. TiO₂ films and C. TiO₂/SiO₂ films.

variety of organic compounds (Liu and Zhao 2000; Carneiro *et al* 2007; Parida and Sahu 2008).

The presumed mechanism of photocatalysis follows the following steps (Houas *et al* 2001). Formation of superoxide radicals: (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to -1/2),



Neutralization of OH⁻ groups by photoholes which produces OH[•] radicals:



Neutralization of O₂^{•-} by protons:



Transient hydrogen peroxide formation and dismutation of oxygen:



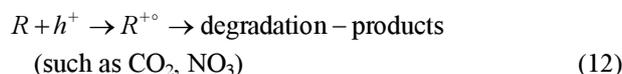
Decomposition of H₂O₂ and second reduction of oxygen:



Oxidation of the organic reactant (R) via successive attacks by OH[•] radicals:



Direct oxidation by reaction with holes:



Therefore, photodegradation reaction of methylene blue (MB) on nanocrystalline TiO₂ film surface can be written as follows



4. Conclusions

In summary, nanostructure of TiO₂ thin films were prepared by sol-gel process and dip coating methods. XRD

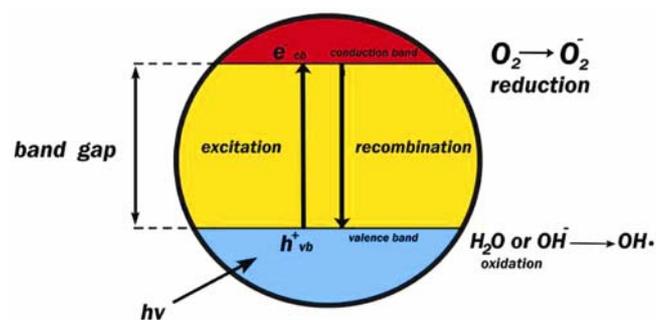


Figure 6. Primary steps in the photocatalysis mechanism of TiO₂.

peaks confirmed the presence of polycrystalline anatase phase in the films with no rutile phase. Also, TiO₂ films showed excellent super-hydrophilicity and photocatalytic properties after UV radiation. It can be concluded that chemical properties of surface and passivation layer are important factors for super-hydrophilic and photocatalytic activities. Therefore, we suggest that TiO₂ sol-gel derived thin films would be very useful in exhibiting super-hydrophilicity and photocatalytic properties (self-cleaning property) under solar radiation for automobile and building applications.

References

- Attia S M, Wang J, Wu G, Shen J and Ma J 2002 *J. Mater. Sci. Technol.* **18** 31
- Barakat M A, Schaeffer H, Hayes G and Ismat Shah S 2004 *Appl. Catal. B: Environ.* **57** 23
- Carneiro J O, Teixeira V, Portinha A, Magalhaes A, Coutinho P, Tavares J and Newton R 2007 *Mater. Sci. & Eng.* **B138** 144
- Cernigoj U, Stangar U L, Trebse P and Ribic P R 2006 *Acta Chim. Slov.* **53** 29
- Doss C J and Zallen R 1993 *Phys. Rev. B: Condens. Matter* **48** 15626
- Euvananont C, Junin C, Inpor K, Limthongkul P and Thanachayanont C 2008 *Ceram. Int.* **34** 1067
- Fujishima A and Zhang X T 2006 *C.R. Chim.* **9** 750
- Fujishima A, Rao T N and Tryk D A 2000 *J. Photochem. & Photobiol. C: Photochem. Rev.* **1** 1
- Guan K 2005 *Surf. & Coat. Sci. Technol.* **19** 155
- Guan K and Yin Y 2005 *Mater. Chem. & Phys.* **92** 10
- Guan K, Lu B and Yin Y 2003 *Surf. & Coat. Technol.* **173** 219
- Hata S, Kai Y, Yamanaka I, Oosaki H, Hirota K and Yamazaki S 2002 *JSAE Rev.* **21** 97
- Hodos M, Horvath E, Haspel H, Kukovecz A, Konya Z and Kiricsi I 2004 *Chem. Phys. Lett.* **399** 512
- Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C and Herrmann J M 2001 *Appl. Catal. B: Environ.* **31** 145
- Karuppuchamy S and Jeong J M 2005 *Mater. Chem. Phys.* **93** 251
- Karuppuchamy S, Jeong J M, Amalnerkar D P and Minour H 2006 *Vacuum* **80** 494
- Kontos A I, Kontos A G, Tsoukleris D S, Vlachos G D and Falaras P 2007 *Thin Solid Films* **515** 7370
- Liu G M and Zhao J C 2000 *New J. Chem.* **24** 411
- Mlyashita K, Kuroda S, Ubukata T, Zawa T and Kubota H 2001 *J. Mater. Sci.* **36** 3877
- Parida K M and Sahu N 2008 *J. Mol. Catal. A: Chem.* **287** 149
- Sharma S D, Singh D, Saini K K, Kant C, Sharma V, Jain S C and Sharma C 2006 *Appl. Catal.* **A314** 40
- Takata Y, Hidaka S, Masuda M and Ito T 2003 *Int. J. Energy Res.* **27** 111
- Tang J, Zou Z, Yin J and Ye J 2003 *Chem. Phys. Lett.* **382** 175
- Trapalis C C, Keivanidis P, Kordas G, Zaharescu M, Crisan M, Szatvanyi A and Gartner M 2003 *Thin Solid Films* **433** 186
- Uhlmann D R, Suratwala T, Davidson K, Boulton J M and Teowee G 1997 *J. Non-Cryst. Solids* **218** 113
- Wang R, Hashimoto K and Fujishima A 1997 *Nature* **388** 431
- Watanabe T, Nakajima A, Wangs R, Minabe M, Koizumi S, Fujishima A and Hashimoto K 1999 *Thin Solid Films* **351** 260
- Wen T, Gao J and Shen J 2001 *J. Mater. Sci.* **36** 5923
- Yu J, Zhao X, Yu J, Zhong G, Han J and Zhao Q 2001 *J. Mater. Sci. Lett.* **20** 1745
- Yu Y, Zhou M, Yu H and Zhang J 2006 *Mater. Chem. & Phys.* **95** 193