

Contact Angle of Glass Substrate Coated with TiO₂/SiO₂ Thin Film

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ABSTRACT

The self-cleaning effect in terms of contact angle value and photocatalytic activity of SiO₂/TiO₂ thin films coated on glass substrate was measured. The composite thin films were prepared by means of spin coating and calcinations at the temperature 500°C for 2 h. The microstructure of pure TiO₂ and SiO₂/TiO₂ composite film were characterized by using AFM. It was found that 5 mol% SiO₂/TiO₂ film shows the highest of photocatalytic reaction while 15 mol% SiO₂/TiO₂ film provides the most hydrophilic effect.

Key words: Contact angle, SiO₂/TiO₂, Self cleaning, Photocatalytic activity

INTRODUCTION

In recent year, TiO₂ nano thin film is applied for treatment of environment. They are many advanced function and feature including antifogging and coated on the materials for self-cleaning such as glass building, glass ware, mirrors, windshields of automobiles, etc. (Guan, 2005). Self cleaning glass is applied to automotive industry (Hata et al., 2000). When expose to UV light, TiO₂ thin film can break down organic compound and it has hydrophilic properties. It was found that a certain percentage of SiO₂ doped to TiO₂ thin film can enhance the super-hydrophilic effect after UV irradiation. Activation of TiO₂ electron to the excited state by UV irradiation, the hole. In the process, oxygen atoms are ejected, and oxygen vacancies are created in the ground state is taken place. These holes can oxidize the O₂ anions. Water molecules can then occupy these oxygen vacancies to produced adsorbed OH groups, which tend to make the hydrophilic surface. The greater the duration that the surface is illuminated with UV light, the smaller the contact angle for water becomes. Finally, under a moderate intensity of UV light (after 30 min), the contact angle approaches to zero, meaning that water has a tendency to spread perfectly across the surface. (Hong et al., 2006). Mixed oxides have been widely produced by sol-gel process to improve photocatalytic reaction

(Feng et al., 2004). In this study SiO_2 , having a hydrophilic property in nature colorless appearance was selected to dope in TiO_2 thin film coated on glass in order to investigate the effect of doping on the photocatalytic activity and hydrophilicity or hydrophobicity fraction.

MATERIALS AND METHODS

Preparations of $\text{TiO}_2/\text{SiO}_2$ composite thin films

A conventional sol-gel method was employed for preparing of TiO_2 and SiO_2 (5, 20, 15, 20 % mol). Titanium (IV) isopropoxide (TTIP, 99.95%, Fluka Sigma-Aldrich) and Tetraethylorthosilicate (TEOS, 98%, Fluka Sigma-Aldrich) were used as starting materials. Ethanol (99.9%; Merck Germany) was used as a solvent. Firstly, TTIP was dissolved in ethanol mixed TEOS, stirred 30 min at a room temperature and followed by the dropping reaction with the addition of 2 M HCl to the solution until $\text{pH} = 3.5$. Distilled water was finally added to the solution and further stirred for 30 min, keeping the solution for hydrolysis reaction for 8 h, after that $\text{TiO}_2/\text{SiO}_2$ sol solutions were coated on the glass substrate ($20 \times 20 \times 0.3 \text{ cm}^3$) by spinning at room temperature. Before coating, the glass substrates were cleaned with ultrasonic for 15 min, then washed with distilled water and dried at 60°C for 2 h. The spinning speed used was fixed at 1700 rpm. The coated substrates were dried at 60°C for 30 min. heated at the temperature of 500°C for 2 h at heating rate of $20^\circ\text{C}/\text{min}$. The surface morphology and thickness of films were investigated atomic force microscopy (AFM) with scan area of $1 \times 1 \mu\text{m}^2$.

Photocatalytic reaction and self cleaning test

The photocatalytic activity of the titania-silica thin film coated on glass substrates was tested by using an aqueous solution of methylene blue having an initial concentration of $1 \times 10^{-5} \text{ M}$ as an indicator under the UV-lamp (black light) of 50 W power and intensity irradiated to the thin film surface is about $3.89 \text{ mW}/\text{cm}^2$ with 320-400 nm wavelength. The distance between the testing substrate and light source was 32 cm. The photocatalytic reaction test was done in a dark chamber by UV light irradiated at the various times of 0-6 h and after that the photocatalytic degradation of methylene blue was determined by UV-VIS spectrometer. Hydrophilic properties of film were investigated by measuring the contact angle using a CAM-PLUS Tanteq company apparatus in the black box with UV irradiation from 36 W light source.

RESULTS AND DISCUSSION

The morphology of coated surface of $\text{TiO}_2/\text{SiO}_2$ composite film heated at 500°C was observed by AFM (Figure 1) It can be seen that the crystals nucleated from the thin film are homogeneous. The 5% mol $\text{SiO}_2/\text{TiO}_2$ film has a smoother surface than that of a pure TiO_2 film because its particle size of 5%mol of SiO_2 addition on TiO_2 was smaller than that of pure TiO_2 film. The average crystallite size is 20-30 nm and film thickness is about 53.66-237.91 nm for 1-3 cycles coating (Table 1).

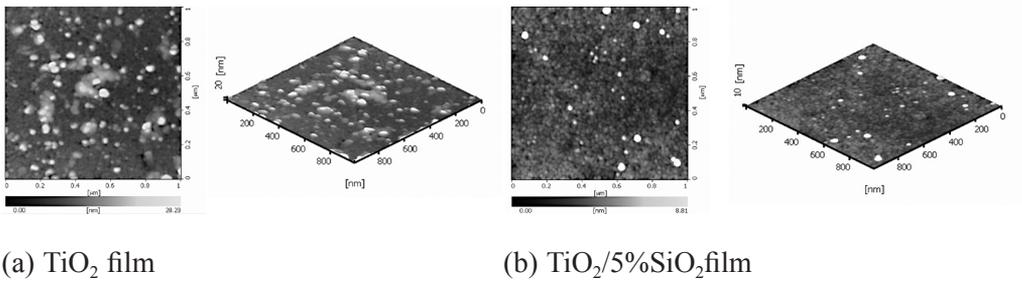


Figure 1. AFM image with scan area of $1 \times 1 \mu\text{m}^2$ of the films calcined at 500°C

Table 1. Thickness of TiO_2 films determined by AFM.

Number of Coating cycles	Thickness (nm)
1 cycle coating	53.66
2 cycles coating	124.80
3 cycles coating	237.91

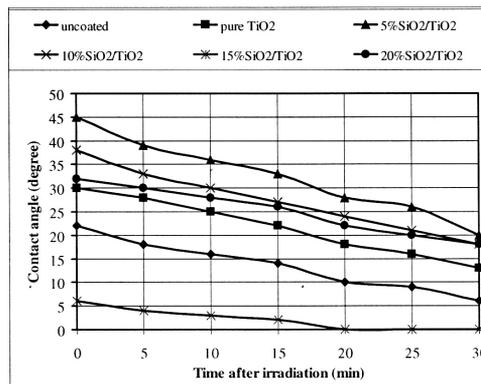


Figure 2. Water contact angle of composite thin film after irradiation UV light heated at 500°C .

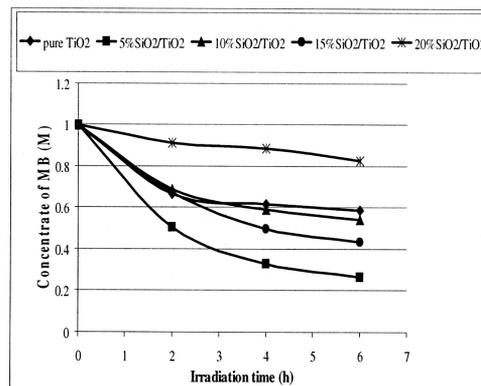


Figure 3. Photocatalytic decoloration of Methylene blue (MB), \blacklozenge Pure TiO_2 , \blacksquare $5\% \text{SiO}_2/\text{TiO}_2$, \blacktriangle $20\% \text{SiO}_2/\text{TiO}_2$, \bullet $15\% \text{SiO}_2/\text{TiO}_2$, $*$ $20\% \text{SiO}_2/\text{TiO}_2$.

Guan (2005) reported that the addition of SiO_2 in TiO_2 film can enhance the acidity of Si-O-Ti bonds at the $\text{SiO}_2\text{-TiO}_2$ interfaces, which would induce a greater amount of hydroxyl groups at the film (Permpoon et al., 2007). The enhancement of acidity of the film can improve the photocatalytic and hydrophilicity. The surface of a coated film can absorb more the OH radicals. Figure 2 shows hydrophilic properties of $\text{SiO}_2/\text{TiO}_2$ composite film compared with TiO_2 film and uncoated glass substrate, under UV light irradiation for 30 min. The contact angle of uncoated glass is about 60 and that of 15 mol% $\text{SiO}_2/\text{TiO}_2$ is 0o. The 15mol% $\text{SiO}_2/\text{TiO}_2$ composite film exhibits a super-hydrophilicity due to the effect of SiO_2 addition and photocatalyst, TiO_2 . The contact angle seems to decrease with increasing irradiation time.

Figure 3 The photocatalytic reactions of the composite films were also investigated by using methylene blue as an indicator under UV irradiated in order to observe the correlation between contact angle and photocatalytic reaction. A certain percentage of SiO_2 doped to TiO_2 films shows a higher activity than pure TiO_2 . When the addition of SiO_2 is 5mol%, the photocatalytic reaction rate tends to increase with an increase in irradiation time. The addition of SiO_2 5mol% seems to exhibit a highest efficiency for degradation of MB about 73% for 6 h UV exposure due to its larger surface area. The contact angle seems to depend not only on photocatalytic activity of the film but also on surface roughness. Smooth surface seems to show a higher hydrophilic effect. The photocatalytic properties of the thin films are dependent on many factors (Mei et al., 2006), such as crystalline phase, grain size, specific surface area, surface morphology and surface state (surface OH). However, the photocatalytic reaction decreases with an increase in SiO_2 content to 20-20% because of the increase in amorphous TiO_2 phase (Figure4). The crystallite series of SiO_2 doped TiO_2 seems to decrease with an increase in SiO_2 content which leads to the film smoothness.

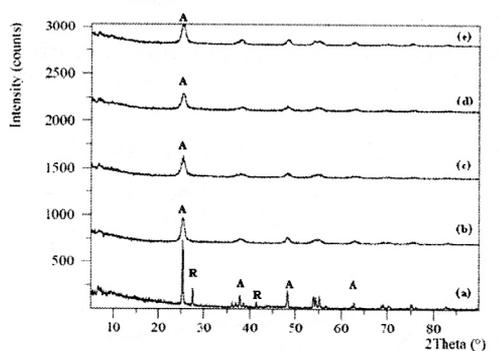


Figure 4. XRD patterns of $\text{TiO}_2/\text{SiO}_2$ powder prepared by sol-gel method and calcinations at the temperature of 700°C for (a) pure TiO_2 , (b) 5mol% $\text{SiO}_2/\text{TiO}_2$, (c) 20 mol% $\text{SiO}_2/\text{TiO}_2$, (d) 15mol% $\text{SiO}_2/\text{TiO}_2$ and (e) 20 mol% $\text{SiO}_2/\text{TiO}_2$.

CONCLUSION

It was found that glass substrate coated with a certain amount of SiO₂ to added SiO₂/TiO₂ film enhances the photocatalytic reaction and the hydrophilic property. Too much SiO₂ addition exhibits the reverse effect because of the more amorphous phase of TiO₂ film.

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