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Original Article

Effect of doped SiO_2 and calcinations temperature on phase transformation of TiO_2 photocatalyst prepared by sol-gel method

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Abstract

The purpose of this research was to study the effect of calcinations temperature and SiO_2 addition on phase transformation, crystallite size, and photocatalytic activity of SiO_2/TiO_2 thin films by using indigo carmine as an indicator. The composite particles were prepared by sol-gel method via calcinations at a temperature range of 300-700°C for 2 h, and the composite thin films were prepared by means of spin coating. The microstructure and crystallite size of pure TiO_2 and SiO_2/TiO_2 composite powders were characterized by using XRD, SEM and DTA. It was found that anatase structures were formed at a calcinations temperature range of 300-600°C and mixed phases of anatase and rutile were observed at a temperature of 700°C. Crystallite size of pure TiO_2 tends to increase with an increase in calcinations temperature. Doped SiO_2 in the TiO_2 has an effect on crystal phases and crystallite size of the composite powders and thin films, resulting in the change of the photocatalytic activity of TiO_2.

Keywords: sol-gel method, SiO_2/TiO_2, photocatalyst, photocatalytic activity, phase transformation

1. Introduction

Titanium dioxide (TiO_2) thin-films have many applications, from environmental purification (Sun *et al.*, 1997; Amat *et al.*, 2005; Fujishima *et al.*, 2005; Hara-Kudo *et al.*, 2005; Ishiki *et al.*, 2005), over solar cells (Tai, 2001; Rodriguez *et al.*, 2004; Latour *et al.*, 2005;), and sunscreens (Serpon *et al.*, 2007), to bacteria killer, and self-cleaning surfaces (Watanabe *et al.*, 1999; Mills *et al.*, 2003; Yamashita *et al.*, 2003; Mellot *et al.*, 2005; Yuranova *et al.*, 2005;). In general, TiO_2 has three crystal forms namely, anatase, rutile and bookite. The efficient photocatalytic activity of TiO_2 deeply depends on its crystallite size, surface area, and crystal structure (Yang *et al.*, 2002). As known, anatase or the mixture phase of anatase and rutile show the highest photocatalytic activity (Nakamura *et al.*, 2005; Zhang *et al.*, 2002). Anatase with large surface area, high crystallinity and nanoscaled crystallite size exhibits a high photocatalytic activity. Many studies have focused on doping metal oxides such as Fe_2O_3 (Feng *et al.*, 2004; Ismail, 2005), SiO_2 (Yuranova *et al.*, 2005; Guan, 2005; Kyeong *et al.*, 2004; Elizabeth *et al.*, 2004; Shang *et al.*, 2004; Awate *et al.*, 2005; Wang *et al.*, 2005), V_2O_5 (Begin *et al.*, 1996), Cr_2O_3 (Zakrzewaka *et al.*, 1997), Y_2O_3 (Ismail , 2005), SnO_2 (Liu *et al.*, 2004; Sermon *et al.*, 1997; Sambrano *et al.*, 2003; Kanai *et al.*, 2004; Sarah *et al.*, 2003; Tarre *et al.*, 2001; Rickerby *et al.*, 1998), ZnO (Liu *et al.*, 2004), Nb_2O_5 (Zhang *et al.*, 2002; Zakrzewaka *et al.*, 1997), and precious metals, such as Pt and Ag (Sermon *et al.*, 1997; Mao *et al.*, 2005). The phase transformation of TiO_2 depends on the calcinations temperature and dopant (Zhang *et al.*, 2002). Among these

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doping materials SiO_2 exhibits a good hydrophilic property for cotton textiles surfaces (Yuranova *et al.*, 2005) and self-cleaning glasses (Mellot *et al.*, 2005; Watanabe *et al.*, 1999; Yamashita *et al.*, 2003). In this study, the effect of SiO_2 loading of SiO_2 coupled TiO_2 photocatalyst and the calcinations temperature on phase transformation of TiO_2 and the photocatalytic reaction of TiO_2/SiO_2 films coated on glass substrate were investigated. Sol-gel technique widely used for the manufacturing of nanophase of TiO_2 was applied to prepare Si^{4+} ion doping TiO_2 nanoparticles and films of TiO_2/SiO_2 coated on a glass substrate. Because of the synthesis from atomic or molecular precursors, sol-gel technique can give a better control of particle size and homogeneity in the particle distribution (Liqun *et al.*, 2005).

2. Experimental

2.1 Preparation of titania - silica composite powder

A conventional sol-gel method (Figure 1) was employed for preparing of TiO_2 and SiO_2 (5, 10, 15, 20 mol %). Titanium (IV) isoproxide (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 pH = 3.5. Distilled water was finally added and the solution was further stirred for 30 min. The solution was dried at 105^{o}C for 24 h and then calcined the powders at a temperature range between 300-700^{o}C. These synthesized powders were characterized in terms of phase compositions and crystallite size by using X-ray diffraction (XRD) (Philips E'pert MPD, Cu-K*á*), SEM and differential thermal analysis (DTA). These results can be used to elucidate the phase of the film coated on the glass substrate that calcined at the same conditions.

2.2 Thin film coating preparation

TiO_2/SiO_2 thin films were formed on soda lime glass substrate (10×10×0.3 cm) by spinning the sol solutions at room temperature. Before coating, the substrates were cleaned with ultrasonic for 15 min, then washed with distilled water, and dried at 60^{o}C for 2 h. The spinning speed used was fixed at 2,200 rpm. The coated substrates were dried at 60^{o}C for 30 min. heated at the temperature range of 300-500^{o}C for 2 h with a heating rate of 10^{o}C/min. The phases of thin films were characterized by using data of composite powder calcined at the same conditions.

2.3 Photocatalytic reaction test

The photocatalytic activity of the titania -silica thin film coated on glass substrates was tested by using an aqueous solution of indigo carmine having an initial concentra-

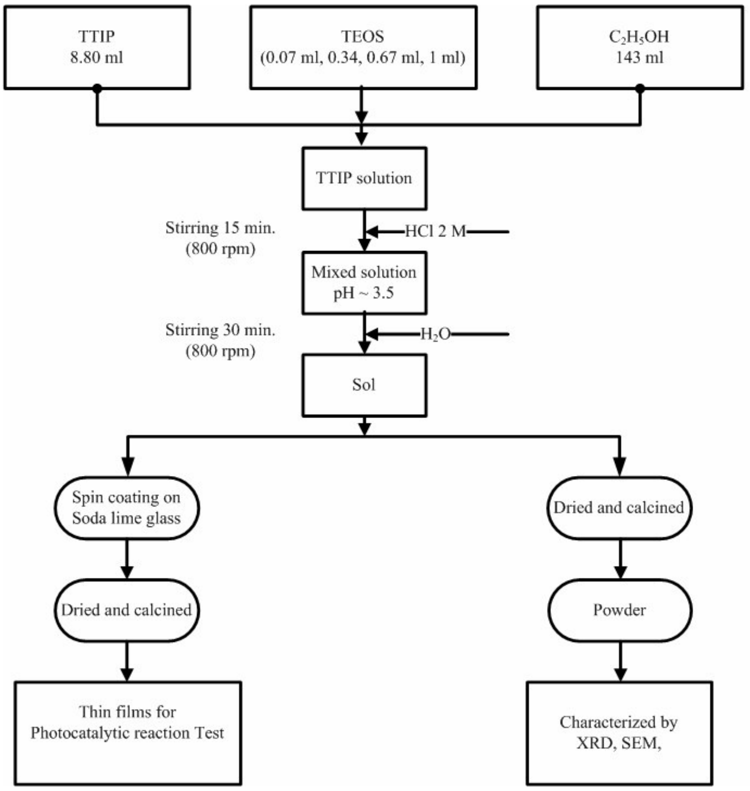

Figure 1. Illustration of SiO_2 doped TiO_2 preparation procedure using sol-gel method.

tion of 2 mg/l as an indicator under the UV-lamp (black light) of 20 W power. The intensity irradiated to the thin film surface is about 1.5 mW/cm^2 at 310-400 nm wavelengths. The distance between the testing substrate and the light source was 32 cm. The photocatalytic reaction test was done in a dark chamber by UV light irradiated at various times, 45, 90, 135, and 180 min. After that the photocatalytic degradation of indigo carmine was determined by an UV-VIS spectrometer.

3. Results and Discussion

3.1 The effect of calcinations temperature and doped SiO_2

XRD was used to investigate the phase structure of the prepared SiO_2-doped and undoped TiO_2. Figure 2 shows the effect of temperature on the phase structures of the TiO_2 powders prepared by sol-gel method. It was found that TiO_2 powders exhibit a phase transformation from amorphous to anatase (see the peaks at $2\theta = 37.5^\circ, 47.5^\circ, 53^\circ, 55^\circ, 62^\circ, 75^\circ$ and 83°) or from anatase to rutile as the calcinations temperature increases (600°C~ 700°C). A single phase of anatase can be seen in temperature range of 300-600°C and both anatase and rutile phases were formed at the temperature of 700°C (Figure 2 and Table 1) since anatase phase is not stable at such a high temperature. The phase ratio of anatase to rutile at this temperature is about 66:34.

The crystallite size was determined from XRD peaks using the Scherer equation (Bakardjieva *et al.*, 2005),

$$D = 0.9\lambda\ \beta \cos\theta_B \qquad (1)$$

Where D is crystallite size; λ is the wavelength of the X-ray radiation ($CuK_\alpha = 0.15406$ nm), and β is the angle width at half-maximum height, and θ_B is the half diffraction angle of the centroid of the peak in degree. The peaks of anatase (101) and rutile (110) occurred at $2\theta = 25.3^\circ$ and 27.4°, respectively. The calculated crystallite sizes of anatase or rutile are listed in Table 1. It is seen that the crystallite size of TiO_2 powder depends on the TiO_2/SiO_2 ratio. For pure TiO_2, the crystallite size of anatase phase increases with increasing calcinations temperature from 300°C to 700°C. It is due to the grain growth induced by an increased temperature as illustrated in Figure 3. The crystallite size of single phase anatase increases from 8.3 nm to 33 nm when calcinations temperature is raised from 300°C to 600°C. It is noted that the anatase phase is transformed to rutile phase at the temperature of between 600-700°C as the crystallite size of more than 33 nm. Calcinations at a temperature of 700°C give the crystallite size of the anatase and rutile phases of 41 nm.

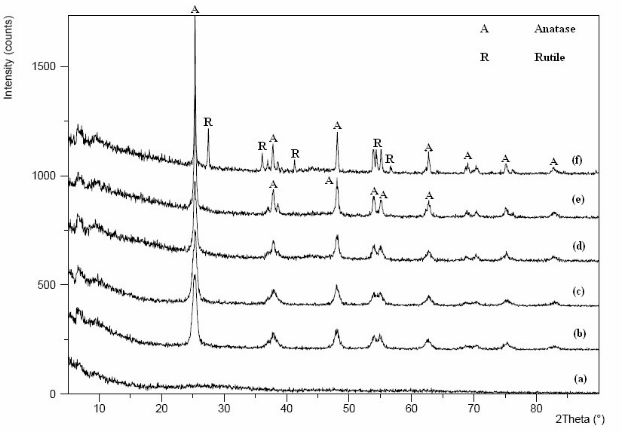

Figure 2. XRD patterns of pure TiO_2 powders prepared by sol-gel method, with (a) no calcinations, and calcined at temperatures of (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, and (f) 700°C.

Table 1. Phases and crystallite sizes of the synthesized powders

Calcinations Temperatures (°C)	Crystallite size (nm)		Content of phase (%)	
	Anatase	Rutile	Anatase	Rutile
300	8.27	-	100	0
400	33.10	-	100	0
500	23.64	-	100	0
600	33.10	-	100	0
700	41.38	41.56	66	34

Figure 4 illustrated the XRD peaks of SiO_2-doped TiO_2 powders calcined at the temperature of 700°C for 2 h. It shows that the mole percentage of 5-20% SiO_2 added seems to have an effect on the XRD patterns of the composite powders. For calcinations temperatures of 300-400°C it was found that the height of the $2\theta = 25.3^\circ$ peak becomes lower and broader for SiO_2-doped TiO_2 powders than for undoped ones (Figure 2), At an SiO_2 mole percentage of SiO_2 range from 5 to 20 mol% (Figure 4). Because the Si-O nets produced by SiO_2 prevent the formation of anatase crystalline and grain growth. However, at higher temperatures between 500-700°C, such phenomenon was not found due to the influence of the temperature. It was also apparent that the anatase phase could withstand at a temperature of 700°C. It means that the anatase phase exhibits to be more stable at a higher temperature when SiO_2 is doped to TiO_2. Because the SiO_2 phase inhibits the growth of anatase particles (Lee *et al.*, 2005) it is leading to the formation of nanocrystallite size of TiO_2/SiO_2 powders. It is evident from Figure 4 that doped SiO_2 has a significant effect on the crystallite size of SiO_2 doped anatase. Figure 5 shows that the crystallite size of TiO_2/SiO_2, prepared by the sol-gel technique and calcined at a temperature of 500°C, drastically decreases (from 23.6 nm to 7-8 nm) as the small amount of SiO_2 (such as 5-10 mol%) is added to TiO_2.With an increase in SiO_2 addition (10-20 mol%), the crystallite size shows almost no change, remaining in the 8-9 nm range. Although the addition of SiO_2 has an effect on the decrease in crystallite size or on the other hand an increase in surface area, it cannot enhance the

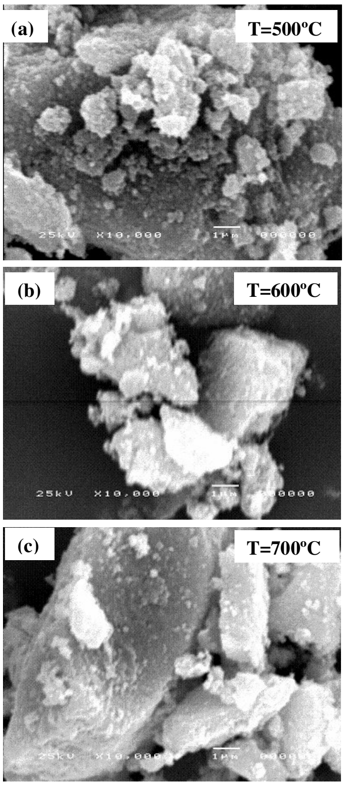

Figure 3. SEM images of pure TiO_2 powders prepared by sol-gel process via calcinations at temperatures of (a) 500°C, (b) 600°C and (c) 700°C.

photocatalytic activity. It is due to a decrease in crystallinity of the anatase structure as SiO_2 is an insulator having no photocatalytic activity. The addition of SiO_2 can inhibit the amorphous-anatase transformation as well as the subsequent anatase-rutile transformation (Muralidharan *et al.*, 1997). The amorphous-to-anatase and anatase to- rutile transformation temperatures are higher as the SiO_2 content increases. This finding confirms the similar work of Yu *et al.* (2002) and co-workers even though the SiO_2/TiO_2 thin films of their work were prepared by sol-gel technique of different starting precursors and dip coating method was used.

3.2 Photocatalytic reaction

Figure 6 gives the photocatalytic degradation curves of indigo carmine in an aqueous solution treated by using undoped TiO_2 and doped SiO_2/TiO_2 coated on glass substrates as the photocatalysts calcined at a temperature of 500°C. Doped SiO_2 about 5 mol% exhibits the highest rate of degradation of indigo carmine, while those of about 10~20 mol% tend to have no effect on the photocatalytic reaction after irradiation with UV light in a dark chamber for 3 h. It is well known that the photocatalytic activity of TiO_2 is greatly influenced by its crystallinity, grain size, surface areas and surface hydroxyl content (Yu and Yu, 2002).

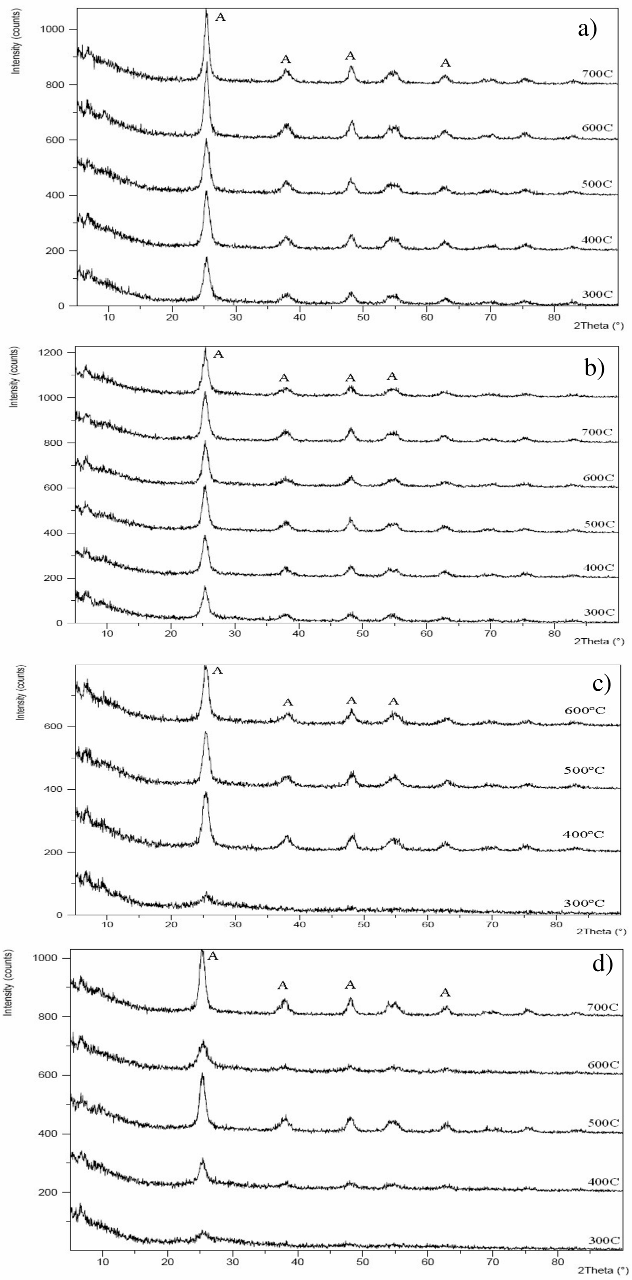

Figure 4. XRD patterns of TiO_2/SiO_2 powders prepared by sol-gel method and calcined at temperatures of 300-700°C with (a) 5mol%, (b) 10 mol%, (c) 15mol% and (d) 20 mol% SiO_2/TiO_2.

When SiO_2 is introduced to TiO_2 thin films, the composite thin films formed are different from pure TiO_2 thin film in both physical and chemical characteristics, such as phase types (Figure 4), surface areas, surface hydroxyl groups, grain size (Figure 5), and chemical compositions. A certain percentage of SiO_2 doped TiO_2 films shows higher activity than pure TiO_2. When the addition of SiO_2 is 5 mol%, the photocatalytic reaction rate tends to increase with an increase in the irradiation time. Small amounts of added SiO_2 result in a decrease in the crystallite size, which may have a larger driving force for charge transfer existing in a quantum sized TiO_2 in composite thin film. Zhang and Reller (2002) mentioned that a small amount of SiO_2 in the composite thin

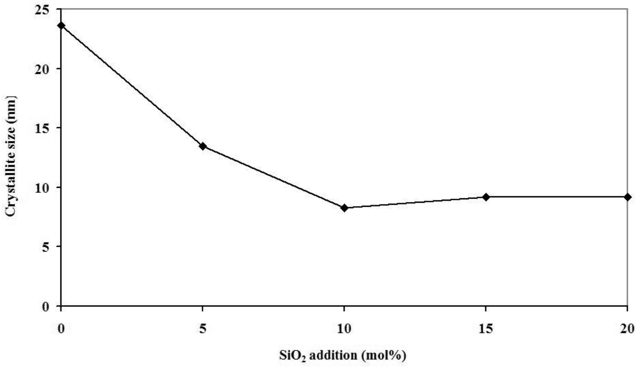

Figure 5. Crystallite size of TiO_2/SiO_2 powder prepared by the sol-gel technique and calcined at a temperature of 500°C.

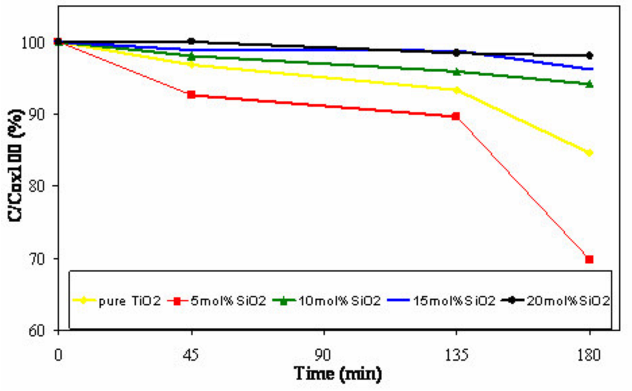

Figure 6. Photocatalytic decomposition of indigo carmine solution by using pure TiO_2 and SiO_2 doped TiO_2 catalysts calcined at a temperature of 500°C.

films did not play a significant role in determining their photocatalytic activity, because SiO_2 is an insulator and has no photocatalytic activity. Therefore, with 10-20 mol% SiO_2 addition, the photocatalytic activity is lower than of pure TiO_2. Another reason is due to the larger band gap energy of SiO_2 (11.7 eV) compared to that of TiO_2 (3.2 eV), which led to a decrease in its quantum yield of SiO_2/TiO_2 films. This may explain why the samples have relatively poor photo activity when the amount of added SiO_2 is over 10 mol% (Yu and Yu., 2002).

4. Conclusions

This study focused on the effect of calcinations temperature and the amount of added SiO_2 on phase transformation, crystallite size, and photocatalytic activity of SiO_2/TiO_2 thin films by using indigo carmine as an indicator. The composite particles were prepared from precursor solutions by sol-gel method via calcinations at a temperature range of 300~700°C and the composite thin films were then prepared by means of spin coating. It was shown that the crystal phases and crystallite sizes of SiO_2/TiO_2 synthesized powders largely depend on the calcinations temperature. Crystalline anatase single phase was found at a calcinations temperature range of 300~600°C and mixed phases of anatase and rutile were formed at a temperature of about 700°C. Crystallite size of pure TiO_2 tends to increase with an increase in the calcinations temperature. Doped SiO_2 in the TiO_2 has an effect on the crystal phases of the composite powders and thin films. Photocatalytic activity of TiO_2 is greatly influenced by its crystallinity, grain size, surface areas and surface hydroxyl content. SiO_2 inhibits the growth of crystallite size of anatase and the amorphous-anatase transformation as well as the subsequent anatase-rutile transformation. The higher amount of SiO_2 added the more amorphous phase of anatase observed at low calcinations temperatures of 300-400°C. However, at higher temperatures of 500-700°C, such phenomenon was not found due to the effect of temperature. The addition of 5 mol% SiO_2 seems to exhibit a higher photocatalytic activity than pure TiO_2, because of a large surface area effect. However, when a higher amount of SiO_2 was added, the non-active phase, such as SiO_2 covered on the TiO_2 surface has a significant influence on the decrease in the photocatalytic activity. It was also found that an increase in irradiation time could enhance the degradation of the indigo carmine concentration.

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