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Contact Angle of TiO_2/SnO_2 Thin Films Coated on Glass Substrate

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Abstract

The self-cleaning effect in terms of contact angle value and photocatalytic activity of TiO_2 and TiO_2/SnO_2 thin films coated on glass substrate was measured. The thin films were prepared using a sol-gel dip coating technique and calcinated at a temperature of 500 °C for 2 h with a heating rate of 10 °C/min. The microstructures of the fabricated thin films were characterized by SEM and XRD techniques. The photocatalytic properties of the thin films were also tested via the degradation of methylene blue (MB) solution under UV irradiation. Finally, the self-cleaning properties of the thin films were evaluated by measuring the contact angle of water droplets on the thin films with and without UV irradiation. It was found that 1 %mol SnO_2/TiO_2 thin films showed the highest of photocatalytic activity and provided the most self-cleaning properties.

Keywords: Contact angle, TiO_2/SnO_2, self-cleaning, photocatalytic activity, thin films

Introduction

Self-cleaning applications using semiconducting 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 helps decompose organic substances that come into contact with the surface and thus prevent them from building up. The hydrophilicity property makes the cleaning more effective as the water spreads over the surface, rather than remaining as droplets. This helps collect the dirt better, makes the surface dry faster, and prevents undesirable water streaking or spotting on the surface [1]. TiO_2 is one of the most widely used materials in self-cleaning applications because of its thermo stability and photocatalytic properties [2].

TiO_2 thin films, prepared by different methods [3-5], have been extensively studied due to their practical applications in various industrial areas, such as production of self-cleaning and anti-fogging surfaces. These phenomena arise due to the photocatalytic and hydrophilic properties of TiO_2. By increasing the hydrophilicity and wettability characteristics of a surface, which depends on surface microstructure, surface chemical composition and surface geometry, water can spread better over the surface and improve the cleaning character of the surface. Many attempts are now made to increase the hydrophilicity of TiO_2 thin films. It seems that the hydrophilicity can be improved by SnO_2 doping of TiO_2 [2-4]. Also, TiO_2 films show higher hydrophilicity properties and photocatalytic activities under UV irradiation [4,6-9].

In this study, TiO_2/SnO_2 thin films on glass substrate were fabricated using a sol-gel dip coating technique. The thin films were calcinated at a temperature of 500 °C for 2 h with a heating rate of 10 °C/min. The microstructures of the fabricated thin films were characterized by SEM and XRD techniques. The effect of SnO_2 doping in the precursor solution on the hydrophilicity and photocatalytic activity of thin films were evaluated by measuring the contact angle for water of TiO_2/SnO_2 thin films and the photocatalytic decolorization of aqueous methylene blue (MB), respectively.

Materials and methods

Preparation of TiO_2/SnO_2 thin films

TiO_2/SnO_2 thin films were prepared via a sol-gel method. Firstly, $SnCl_4.5H_2O$ fixed at 0, 1, 3 and 5 mol% of TiO_2 and Titanium (IV) isoproxide (TTIP) with at 10 ml were mixed into 150 ml of ethanol (C_2H_5OH) and the mixture was vigorously stirred at room temperature for 15 min. The pH of the mixed solution was adjusted to about 3 - 4 by 3 ml of 2 M nitric acid (HNO_3). Finally, it was vigorously stirred at room temperature for 30 min until clear sol was formed. The thin films were deposited on glass substrates by a dip-coating process at room temperature with the drawing speed of the dip-coater at about 1.25 mm/s. The coated samples were dried at room temperature for 24 h and calcinated at temperatures of 500 °C for 2 h with a heating rate of 10 °C/min.

Characterization

The morphology and particle size of the synthesized thin films were characterized by a Scanning Electron Microscope (SEM) (Quanta 400). The phase composition was characterized using an x-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). The crystallite size was calculated by the Scherer equation, Eq. (1), [10,11].

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

where D is the average crystallite size, λ is the wavelength of the Cu K_α line (0.15406), θ is the Bragg angle and β is the full-width at half-maximum (FWHM) in radians.

Photocatalytic activity

The photocatalytic properties were evaluated by the degradation of MB under UV irradiation using 110W black lamps. Thin films with an area of 26 × 30 cm^2 were soaked in a 4 ml MB with a concentration of 1×10^{-6} M and kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After that, the supernatant solutions were measured for MB absorption at 665 nm using a UV-Vis spectrophotometer (GENESYS™10S). The degradation of the MB was calculated by C/C_0 [12], where C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-6} M) and C is the concentration of MB aqueous solution after exposure to a light source.

Hydrophilic properties

The hydrophilic or self-cleaning property was evaluated by measuring the contact angle of water droplets on the thin film with and without UV irradiation using 110 W black lamps under an ambient condition of 25 °C. Water droplets were placed at 3 different positions for one sample and the averaged value was adopted as the contact angle.

Results and discussion

Characterization

Figure 1 shows the XRD patterns of TiO_2/SnO_2 thin films composed of various mol ratios of SnO_2 to TiO_2 were 0, 1, 3 and 5 mol%. The X-ray diffraction peak at 25.5° corresponds to the characteristic peak of the crystal plane (1 0 1) of anatase at 27.6° in thin films [11]. According to the XRD patterns, all samples were constituted of a pure anatase phase. An Sn-compound phase was not detected here due to a very small amount of SnO_2 doping.

The average crystallite size of thin films was determined from the XRD patterns, according to the Scherer equation. The average crystallite size of TiO_2/SnO_2 thin films composed of various mol ratios of SnO_2 to TiO_2 were 0, 1, 3 and 5 mol% are 20.7, 8.3, 9.2 and 14.6 nm, respectively. It was apparent that SnO_2 added in TiO_2 has a significant effect on crystallite size [2]. It was found that TiO_2 doped with 1 mol% of SnO_2 showed ($TiO_2/1SnO_2$) the smallest crystallite size.

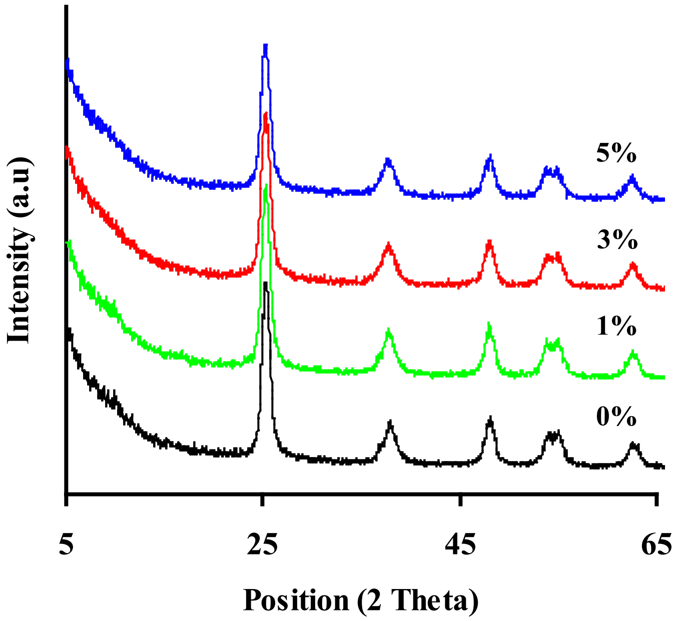
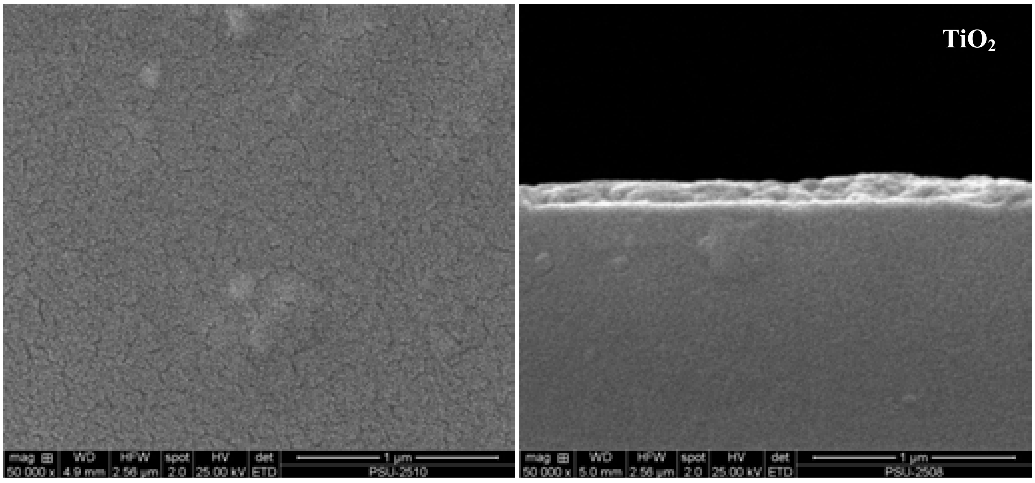


Figure 1 The XRD patterns of TiO_2/SnO_2 thin films.



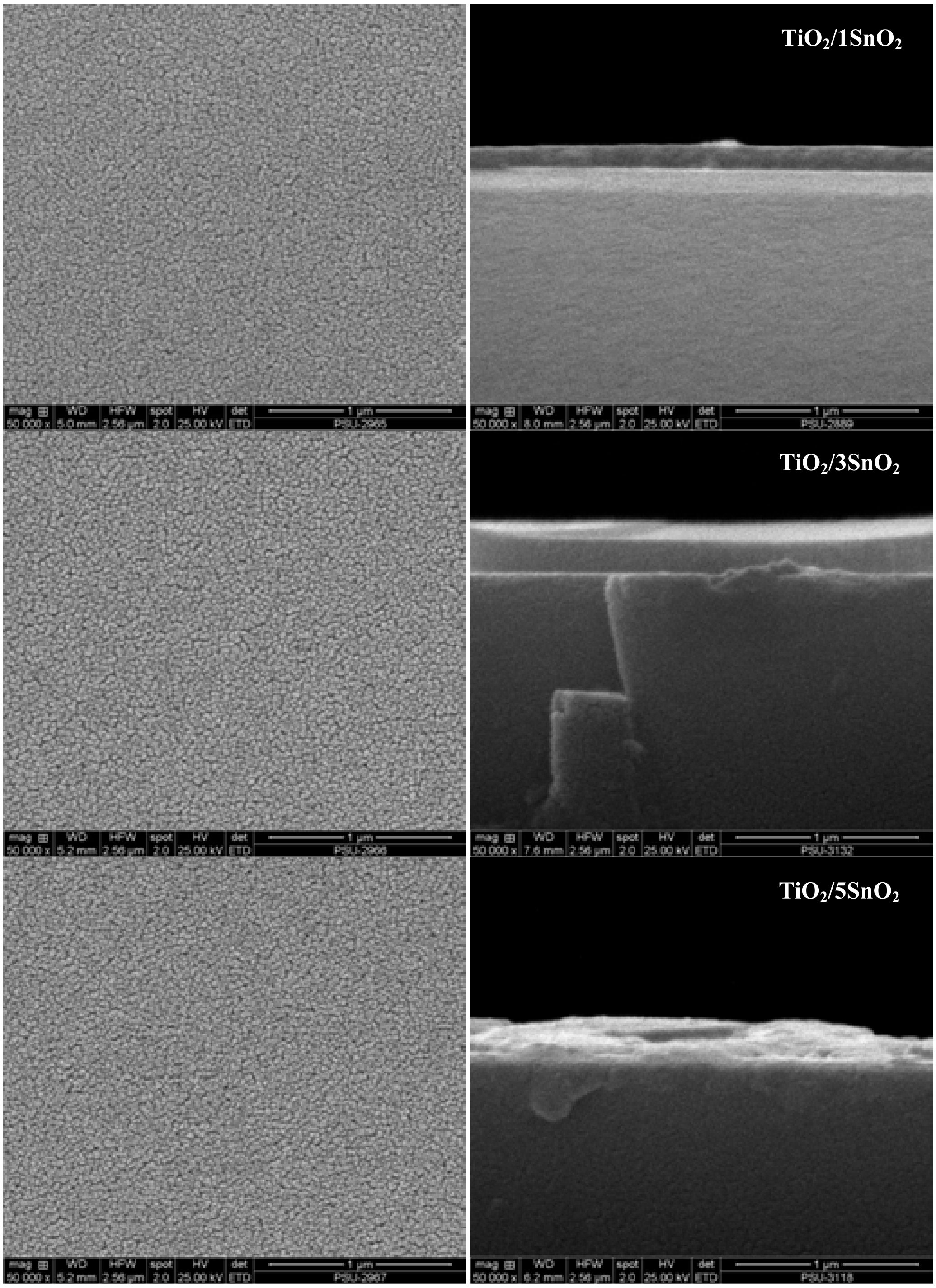


Figure 2 SEM images of TiO_2/SnO_2 thin films.

The surface morphology was observed with SEM at a magnification of 50,000×. **Figure 2** shows surface and cross-sectional morphologies of TiO_2/SnO_2 thin films with coating on the glass substrate. It was found that the thicknesses of thin films have a range of 0.25 to 0.50 µm compared with glass substrate (**Figure 3**). Their surfaces are dense and very smooth.

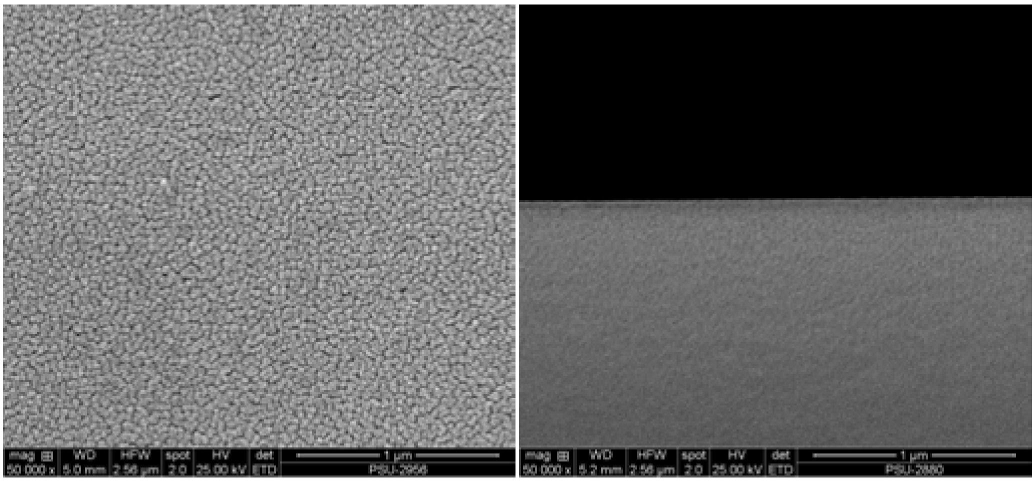


Figure 3 SEM images of glass substrate.

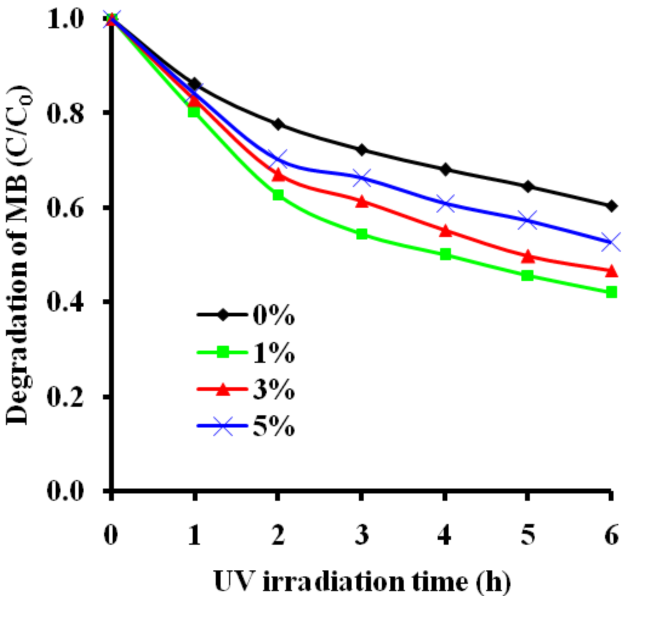


Figure 4 The photocatalytic activity of TiO_2/SnO_2 thin films under UV irradiation.

Photocatalytic activity

The photocatalytic degradation of MB by using TiO_2/SnO_2 thin films under UV irradiation is shown in **Figure 4**. It was apparent that SnO_2 added in TiO_2 has a significant effect on photocatalytic reaction under UV irradiation compared with undoped SnO_2. For TiO_2 doped with SnO_2 thin films, it was found that the photocatalytic activity decreases with an increase in SnO_2 doping. The MB degradation percentage of thin films under UV irradiation is shown in **Table 1**. It was found that MB degradation percentage of thin films under UV irradiation for 6 h are 39.6, 58.1, 53.3 and 47.5 % for 0, 1, 3 and 5 mol% of SnO_2 doping, respectively. It was found that $TiO_2/1SnO_2$ thin films show the best photocatalytic activity.

Table 1 The percent degradation of MB of TiO_2/SnO_2 thin films under UV irradiation.

SnO_2 mol%	UV irradiation time (h)					
	1	2	3	4	5	6
0	13.8	22.3	27.6	31.9	35.4	39.6
1	19.6	37.2	45.5	50.0	54.3	58.1
3	17.2	32.9	38.5	44.7	50.2	53.3
5	15.8	29.9	33.6	39.0	42.8	47.5

Hydrophilic properties

The self-cleaning properties of thin films based on hydrophilic phenomenon can be considered in terms of the contact angle of water droplets on the thin films. The contact angles of water droplets on TiO_2 thin films with SnO_2 coating on the glass substrate measured under UV irradiation for 0, 10, 30 and 60 min are shown in **Table 2** and **Figure 5**. It was apparent that SnO_2 added in TiO_2 has a significant effect on hydrophilic properties under UV irradiation [4], with the hydrophilic properties increasing with increased SnO_2 doping. It should be noted here that the all samples tested for hydrophilicity for were placed for 60 min under UV irradiation prior to measurement. It was found that the contact angle for water is 16.2° for pure TiO_2 thin films, and 6.4, 7.8, 12.6° for the TiO_2/SnO_2 thin films with SnO_2 doping 1, 3 and 5 mol%, respectively.

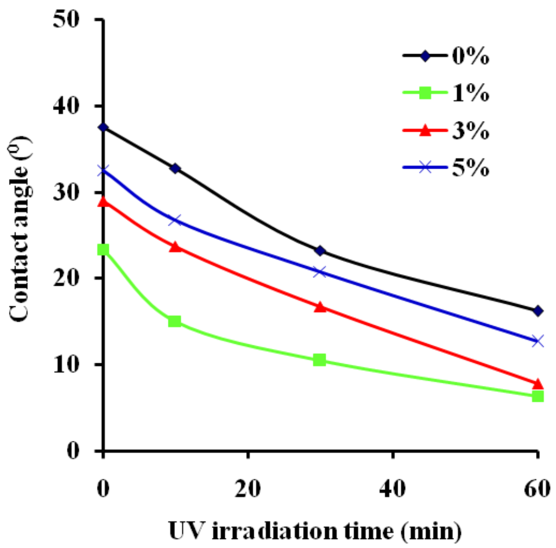


Figure 5 The contact angles of water droplets TiO_2/SnO_2 thin films measured after UV irradiation.

Table 2 The contact angles of water droplets on TiO_2/SnO_2 thin films after UV irradiation.

SnO_2 mol%	UV irradiation time (min)			
	0	**10**	**30**	**60**
0	37.5	32.8	23.2	16.2
1	23.3	15.0	10.4	6.4
3	29.0	23.7	16.7	7.8
5	32.5	26.7	20.7	12.6

The result indicated that low doping of SnO_2 can improve the hydrophilicity of the TiO_2 thin films, most probably due to the increase of hydroxyl in the composite thin films [7]. The images of water droplet contact angles of thin films measured during 0 and 60 min UV irradiation are illustrated in **Figures 6 - 9** for SnO_2 doping 0, 1, 3 and 5 mol%, respectively.

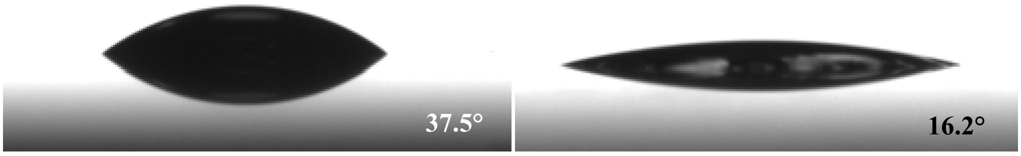


Figure 6 The image of water droplet contact angles after 0 and 60 min UV irradiation of TiO_2 thin films.

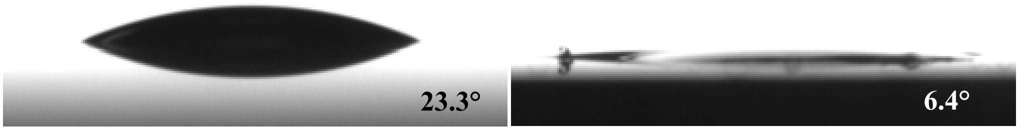


Figure 7 The image of water droplet contact angles after 0 and 60 min UV irradiation of $TiO_2/1SnO_2$ thin films.

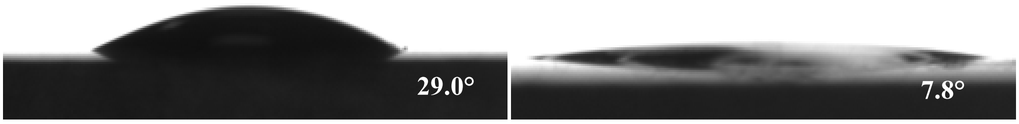


Figure 8 The image of water droplet contact angles after 0 and 60 min UV irradiation of $TiO_2/3SnO_2$ thin films.

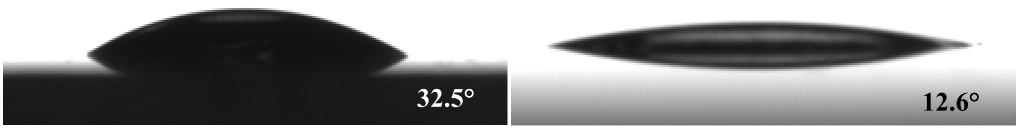


Figure 9 The image of water droplet contact angles after 0 and 60 min UV irradiation of $TiO_2/5SnO_2$ thin films.

Conclusions

In this work, TiO_2/SnO_2 thin films were prepared by a sol-gel dip coating technique. The phase transformation, surface morphology, photocatalytic activity and hydrophilic or self-cleaning properties of thin films were investigated and concluded as per the following:

1. Only anatase phase was found on the TiO_2/SnO_2 thin films.
2. It was found that glass substrate coated with SnO_2 added to TiO_2 thin films enhances the photocatalytic activity and hydrophilic property.
3. It can be noted that TiO_2 thin films doped with 1 % SnO_2 exhibit higher photocatalytic activity and hydrophilic or self-cleaning properties under UV irradiation.

Acknowledgements

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References

[1] C Euvananont, C Junin, K Inpor, P Limthongkul and C Thanahayanont. TiO_2 optical coating layers for self-cleaning applications. *Ceram. Int*. 2008; **34**, 1067-71.
[2] L Sikong, K Kooptarnond, S Niyomwas and J Damchan. Photocativity and hydrophilic property of SiO_2 and SnO_2 co-doped TiO_2 nano-composites thin films. *Songklanakarin J. Sci. Technol.* 2010; **32**, 413-8.
[3] HY Lee, YH Park and KH Ko. Correlation between surface morphology and hydrophilic/hydrophobic conversion of MOCVD-TiO_2 films. *Langmuir* 2000; **16**, 7289-93.
[4] M Farbod and S Rezaian. An investigation of super-hydrophilic properties of TiO_2/SnO_2 nano composite thin films. *Thin Solid Films* 2012; **520**, 1954-8.
[5] H Ohsaki, N Kanai, Y Fukunaga, M Suzuki, T Watanabe and K Hashimoto. Photocatalytic properties of SnO_2/TiO_2 multilayer. *Thin Solid Films* 2006; **502**, 138-42.
[6] J Damchan, L Sikong, K Kooptarnond and S Niyomwas. Contact angle of glass substrate coated with TiO_2/SiO_2 thin films. *CMU. J. Nat. Sci.* 2008; **7**, 19-23.
[7] Q Liu, X Wu, B Wang and Q Liu. Preparation and super-hydrophilic properties of TiO_2/SnO_2 composites thin films. *Mater. Res. Bull.* 2002; **37**, 2255-62.
[8] H Ching-Lee and H Weng-Sing. Substrate effects on the oxygen gas sensing properties of SnO_2/TiO_2 thin films. *Appl. Surf. Sci.* 2006; **253**, 1889-97.
[9] YC Lee, YP Hong, HY Lee, H Kim, YJ Jung, KH Ko, HS Jung and KS Hong. Photocatalysis and hydrophilicity of doped TiO_2 thin films. *J. Colloid Interface Sci*. 2003; **267**, 127-31.
[10] BK Kaleji and RS Mamoory. Nanocrystalline sol-gel TiO_2-SnO_2 coating: preparation, characterization and photo-catalytic performance. *Mater. Res. Bull.* 2012; **47**, 362-9.
[11] F Sayilkan, M Asilturk, N Kiraz and E Burunkaya. Photocatalytic antibacterial performance of Sn^{4+}-doped TiO_2 thin films on glass substrate. *J. Hazard. Mater.* 2009; **162**, 1309-16.
[12] W Sangchay, L Sikong and K Kooptarnond. Comparison of photocatalytic reaction of commercial P25 and synthetic TiO_2-AgCl nanoparticles. *Procedia Eng*. 2012; **32**, 590-6.