Self-cleaning and photocatalytic properties of TiO_2/SnO_2 thin films

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Abstract

The study measured the self-cleaning effect in terms of contact angle value and photocatalytic properties of TiO_2 and TiO_2/SnO_2 (1, 3 and 5 %mol SnO_2) thin films coated on glass substrate. The thin films were prepared by sol-gel dip coating technique and calcinations at the temperature of 600 °C for 2 hours with the heating rate of 10 °C/min. 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, self-cleaning properties of thin films were evaluated by measuring the contact angle of water droplet on the thin films with and without UV irradiation. It was found that thin films of SnO_2 doped with 1 %mol TiO_2 showed the highest of photocatalytic activity and provided the best self-cleaning properties.

Keywords: Self-cleaning, Photocatalytic, Contact angle, TiO_2/SnO_2, Thin films

1. Introduction

Titanium dioxide (TiO_2) has many applications in the environment. TiO_2 under UV irradiation exhibits photocatalytic activity that enables the oxidatiive destruction of a wide range of organic compounds and biological species, causing self-decontanmination effce. In additional, TiO_2 exposed under UV exhibits photocatalytically induced superhydrophilicity that converts the hydrophobic character of surface to hydrophilic and forms the unifrom water film, which prevents the adhesion of inorganic or organic components on its surface, with retained cleanliness (Tryba et al., 2010). The TiO_2 thin films may be deployed on the surface of various substrates, such as glass, ceramics, metals, textiles, cement, bricks or fibers to provide layer that exhibits self sterilisation and self cleaing properties, when it is exposed to the light. Many studies have been reported on doping metal oxides to TiO_2 to improve efficiency of TiO_2 photocatalyst (Sikong et al., 2010). The most popular oxide doped to TiO_2 is SnO_2 (Farbod et al., 2012; Liu et al., 2002; Ohsaki et al., 2006). Doping SnO_2 to TiO_2 thin films could also improve hydrophilicity and photocatalytic activity of composite thin films due to reduction of TiO_2 particle growth rate (Sikong et al., 2010; Liu et al., 2002).

TiO_2 thin film can be prepared by many methods such as sol–gel (Schmidt et al., 2000; Xianfeng et al., 2005), electrochemical deposition (Lokhande et al., 2005) and chemical vapor deposition (CVD) (Hongfu et al., 2008). The sol–gel method was recently developed as a general and powerful approach for preparing inorganic materials such as ceramics and glasses. In this method, a soluble precursor molecule is hydrolyzed to form a colloidal dispersion (the sol). Further reaction causes bonds to form among the sol particles, resulting in an infinite network of particles (the gel). The gel is typically heated to yield the desired material. Methods for the synthesis of inorganic materials have advantages more than conventional methods of synthesis. For example, high-purity materials can be synthesized at low temperatures (Jerzy, 1997; Tianfa et al., 2001). In addition, homogeneous multi component systems can be obtained by mixing precursor solutions, which allows for easy chemical doping of the materials prepared.

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 calcined at the temperature of 600 °C for 2 h with the 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.

2. Experimental and Details

2.1 Preparation of TiO_2/SnO_2 thin films

TiO_2/SnO_2 thin films were prepared via sol-gel method. Firstly, $SnCl_4.5H_2O$ with fixed at 0, 1, 3 and 5 mol% of TiO_2 and Titanium (IV) isoproxide (TTIP) with fixed 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 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 a clear sol was formed.

The thin films were deposited on glass substrates by dip-coating process at room temperature with the drawing speed of about 1.25 mm/s. The coated samples were dried at room temperature for 24 h and calcined at the temperature of 600 °C for 2 h with a heating rate of 10 °C/min. All samples were designated as TiO_2, $TiO_2/1SnO_2$, $TiO_2/3SnO_2$ and $TiO_2/5SnO_2$ of various mol ratios of SnO_2 to TiO_2 were 0, 1, 3 and 5 mol%, respectively.

2.2 Charaterization

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), (Sangchay et al., 2012; Sayilkan et al., 2009).

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

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 radian.

2.3 Photocatalytic activity

The photocatalytic properties were evaluated by the degradation of MB under UV irradiation using 110 W of a black lamp. Thin films with an area of 26 x 30 cm^2 was 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 (Sayilkan et al., 2009; Sangchay et al., 2012), where C_0 is the concentration of MB aqueous solution at the beginning ($1x10^{-6}$ M) and C is the concentration of MB aqueous solution after exposure to a light source.

2.4 Hydrophilic properties

The hydrophilic property or self-cleaning was evaluated by measuring the contact angle of water droplet on the thin film with and without UV irradiation using 110 W of black lamps under an ambient condition at 25 °C. Water droplets were placed at 3 different positions for one sample and the average value was adopted as the contact angle (Sangchay et al., 2013).

3. Results and Discussion

3.1 Characterization

Figure 1 shows the XRD patterns of TiO_2/SnO_2 thin films with various mol ratios of SnO_2 to TiO_2. X-ray diffraction peak at 25.5° corresponds to characteristic peak of crystal plane (1 0 1) of anatase (TiO_2) in thin films (Kaleji et al., 2012). According to the XRD patterns, all sample constituted of pure anatase phase. 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 Scherer equation. The average crystallite sizes of the anatase phase of TiO_2/SnO_2 thin films are shown in Table 1. It was apparent that SnO_2 added in TiO_2 has significantly effect on crystallite size (Sikong et al., 2010). It was found that TiO_2 doped with 1 mol% of SnO_2 show ($TiO_2/1SnO_2$) the smallest crystallite size.

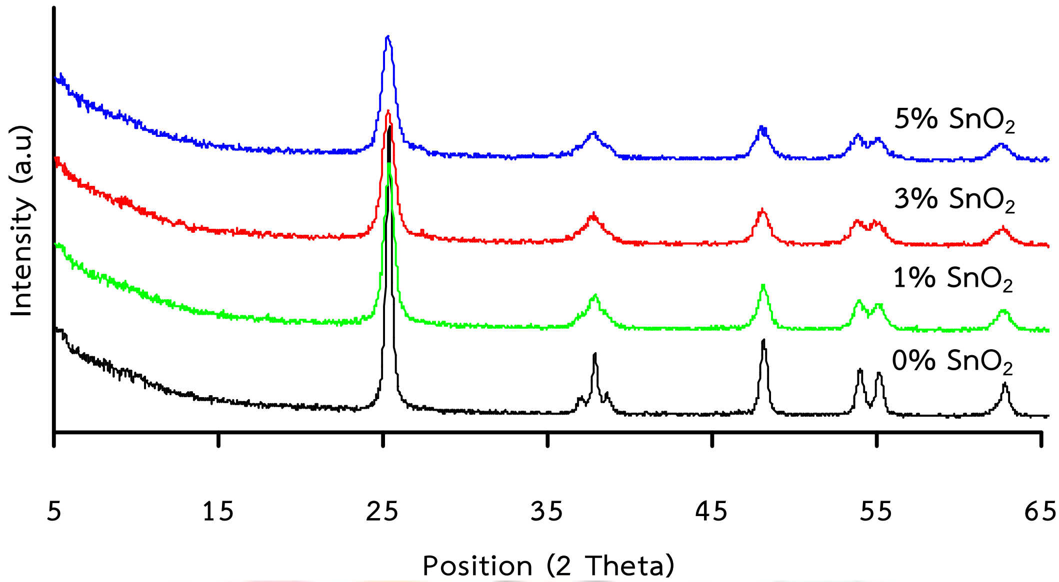

Figure 1 The XRD patterns of TiO_2/SnO_2 thin films

Table 1 The average crystallite size of the anatase phase found in the thin films

Sample	Crystallite size (nm)
TiO_2	40.6
$TiO_2/1SnO_2$	15.0
$TiO_2/3SnO_2$	23.6
$TiO_2/5SnO_2$	33.1

The surface morphology was observed with SEM at a magnification of 50,000X. Figure 2 shows cross-sectional morphologies of TiO_2/SnO_2 thin films coate0d on the glass substrates. It was found that the thicknesses of thin films were in the range of 0.25 to 0.50 μm. Their surfaces are dense and very smooth.

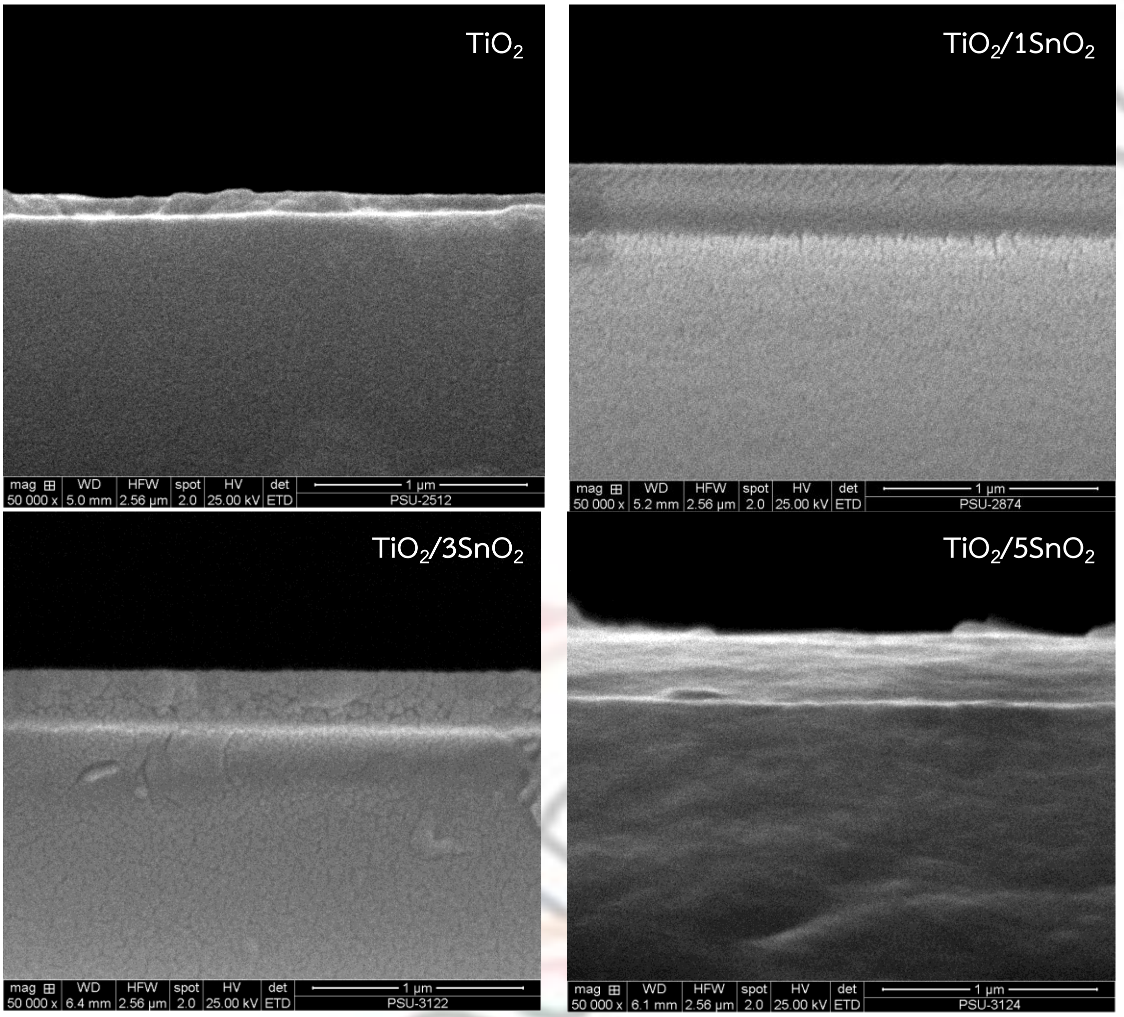

Figure 2 SEM images of TiO_2/SnO_2 thin films (magnification of 50,000X)

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using TiO_2/SnO_2 thin films under UV irradiation is show in Figure 3. It was apparent that addition of SnO_2 to TiO_2 had a significantly effect on photocatalytic reaction under UV irradiation as compared with the undoped SnO_2. For TiO_2 doped with SnO_2 thin films, it was found that the photocatalytic activity decreases with increases SnO_2 doping. The MB degradation percentage of thin films under UV irradiation is shown in Table 2. It was found that MB degradation percentage of thin films under UV irradiation for 6 h are 27.7, 39.5, 37.0 and 35.0% for 0, 1, 3 and 5 mol% of SnO_2 doping, respectively. It was found that $TiO_2/1SnO_2$ thin films showed the best photocatalytic activity.

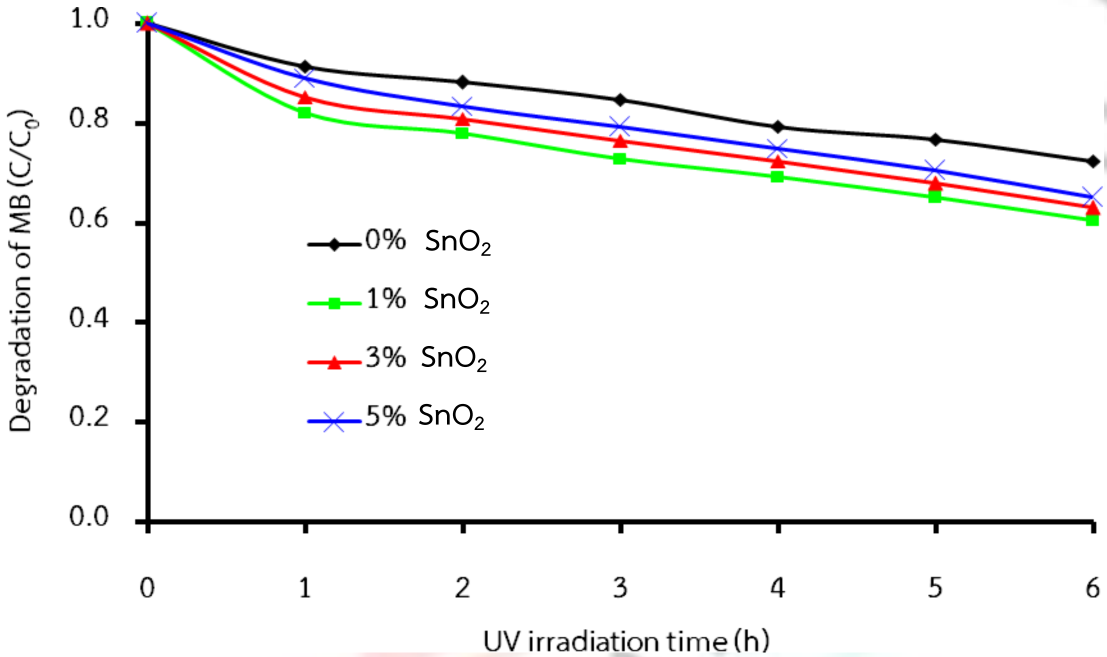

Figure 3 The photocatalytic activity of TiO_2/SnO_2 thin films under UV irradiation

Table 2 The % degradation of MB of TiO_2/SnO_2 thin films under UV irradiation for different times

Samples	%degradation under UV irradiation					
	1 h	2 h	3 h	4 h	5 h	6 h
TiO_2	8.61	11.77	15.33	20.77	23.24	27.70
$TiO_2/1SnO_2$	17.80	22.06	27.20	30.66	35.01	39.47
$TiO_2/3SnO_2$	14.74	19.19	23.54	27.70	32.15	36.99
$TiO_2/5SnO_2$	10.88	16.52	20.77	25.02	29.57	34.92

3.3 Hydrophilic properties

Self-cleaning properties of thin films based on hydrophilic phenomenon can be considered in terms of contact angle of water droplets on the thin films. The contact angles of water droplets TiO_2/SnO_2 thin films coating on the glass substrate measured under UV irradiation for 0, 10, 30 and 60 min are shown in Table 3 and Figure 4. It was apparent that SnO_2 added in TiO_2 has significantly effect on hydrophilic properties under UV irradiation (Farbod et al., 2012), with the hydrophilic properties increases with increases SnO_2 doping. It should be note here that the all samples tested for hydrophilicity for were placed for 60 min under UV irradiation prior to measurement. It found that the contact angle for water is 22.3° for the TiO_2

thin films, and 11.7°, 14.05°, 17.4° for the TiO_2/SnO_2 thin films with SnO_2 doping 1, 3 and 5 mol%, respectively.

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 group in the composite thin films (Farbod et al., 2012). The image of water droplet contact angle of TiO_2/SnO_2 thin films measured during 0, 10, 30 and 60 min UV irradiation are illustrated in Figure 5.

Table 3 The contact angles of water droplets on TiO_2/SnO_2 thin films after UV irradiation

Samples	Contact angle after UV irradiation			
	0 min	10 min	30 min	60 min
TiO_2	44.69	35.07	30.43	22.32
$TiO_2/1SnO_2$	26.13	20.08	14.53	11.56
$TiO_2/3SnO_2$	32.49	26.61	18.42	14.05
$TiO_2/5SnO_2$	34.22	30.90	23.76	17.43

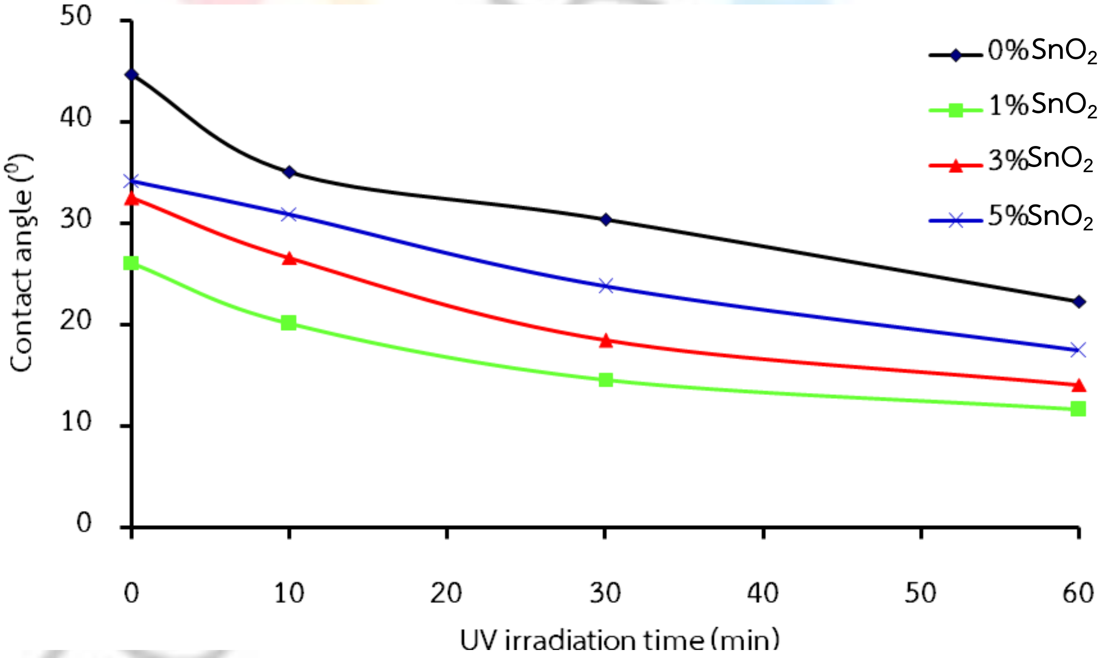

Figure 4 The contact angles of water droplets TiO_2/SnO_2 thin films

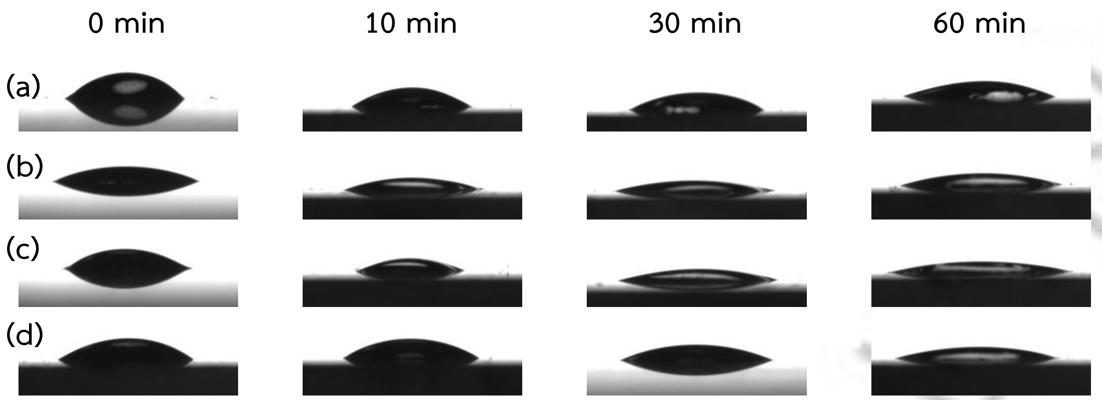

Figure 5 The image of water droplet contact angle of (a) TiO_2, (b) TiO_2/1SnO_2, (c) TiO_2/3SnO_2 and (d) TiO_2/5SnO_2 thin films

4. Conclusion

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

1. Only anatase phase was found on the TiO_2/SnO_2 thin films by using an XRD technique.

2. It was found that glass substrate coated with SnO_2 to added TiO_2 thin films enhances the photocatalytic activity and hydrophilic property.

3. TiO_2/SnO_2 thin films with doping SnO_2 1 mol% were found to exhibit the best photocatalytic activity and hydrophilic or self-cleaning properties.

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6. Refernces

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