Contact Angle of TiO2/SnO2 Thin Films Coated on Glass Substrate

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Received: 19 June 2013, Revised: 8 July 2013, Accepted: 16 October 2013

Abstract

The self-cleaning effect in terms of contact angle value and photocatalytic activity of TiO2 and TiO2/SnO2 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 SnO2/TiO2 thin films showed the highest of photocatalytic activity and provided the most self-cleaning properties.

Keywords: Contact angle, TiO2/SnO2, 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]. TiO2 is one of the most widely used materials in self-cleaning applications because of its thermo stability and photocatalytic properties [2].

TiO2 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 TiO2. 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 TiO2 thin films. It seems that the hydrophilicity can be improved by SnO2 doping of TiO2 [2-4]. Also, TiO2 films show higher hydrophilicity properties and photocatalytic activities under UV irradiation [4,6-9].

In this study, TiO2/SnO2 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 SnO2 doping in the precursor solution on the hydrophilicity and photocatalytic activity of thin films were evaluated by measuring the contact angle for water of TiO2/SnO2 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$_4$.$5$H$_2$O 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$_2$H$_5$OH) 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 calcined 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].

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $D$ is the average crystallite size, $\lambda$ is the wavelength of the Cu K$_\alpha$ line (0.15406), $\theta$ is the Bragg angle and $\beta$ 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 TiO₂/SnO₂ 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.

![SEM images of glass substrate.](image1)

**Figure 3** SEM images of glass substrate.

![Photocatalytic activity of TiO$_2$/SnO$_2$ thin films under UV irradiation.](image2)

**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>
<thead>
<tr>
<th>SnO$_2$ mol%</th>
<th>UV irradiation time (h)</th>
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<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>13.8</td>
</tr>
<tr>
<td>1</td>
<td>19.6</td>
</tr>
<tr>
<td>3</td>
<td>17.2</td>
</tr>
<tr>
<td>5</td>
<td>15.8</td>
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Table 1 The percent degradation of MB of TiO$_2$/SnO$_2$ thin films under UV irradiation.

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 all the samples tested for hydrophilicity 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](image_url) 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.

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<tr>
<th>SnO$_2$ mol%</th>
<th>UV irradiation time (min)</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>37.5°</td>
</tr>
<tr>
<td>1</td>
<td>23.3°</td>
</tr>
<tr>
<td>3</td>
<td>29.0°</td>
</tr>
<tr>
<td>5</td>
<td>32.5°</td>
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</table>

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

The authors would like to acknowledge the Institute of Research & Development, Songkhla Rajabhat University, and the Faculty of Industrial Technology, Songkhla Rajabhat University, Thailand for the financial support of this research.

References