The hybrid photocatalyst of TiO$_2$–SiO$_2$ thin film prepared from rice husk silica

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**A B S T R A C T**

The TiO$_2$–SiO$_2$ thin film was prepared by self-assembly method by mixing SiO$_2$ precursor with titanium precursor solution and aged to obtain a co-precipitation of silica and titanium crystals. Dip coating method was applied for thin film preparation on glass slide. The X-ray diffraction (XRD) of the self-assembly thin film had no characteristic property of SiO$_2$ and even anatase TiO$_2$ but indicated new crystal structure which was determined from the Fourier Transform Infrared Spectrophotometer (FTIR) as a hybridized Ti–O–Si bonding. The surface area and surface volume of the self-assembly sample were increased when SiO$_2$ was incorporated into the film. The self-assembly TiO$_2$–SiO$_2$ thin film exhibited the enhanced photocatalytic decolorization of methylene blue (MB) dye. The advantages of SiO$_2$ are; (1) to increase the adsorbability of the film and (2) to provide the hydroxyl radical to promote the photocatalytic reaction. The self-assembly thin film with the optimum molar ratio (SiO$_2$:TiO$_2$) as 20:80 gave the best performance for photocatalytic decolorization of MB dye with the overall efficiency of 81%.

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1. Introduction

Recently, TiO$_2$ has been widely used in the photocatalytic process due to the excellent properties such as high production of hydroxyl radicals, inexpensive, non-toxic and having physical and chemical stability [1]. However, the applications of TiO$_2$ photocatalytic process have many limitations such as the recombination of electron and holes, easy agglomeration during the synthesis and the need of activation energy in a range of ultraviolet (UV) radiation for photocatalytic reaction [2]. Nevertheless, there are many researches focusing on the improvement of TiO$_2$ qualities for photocatalytic reactivity by doping it with, such as, transition metals [3] and rare metals [4]. Although the transition metal doped TiO$_2$ showed higher photocatalytic reactivity than pure TiO$_2$, the toxicity or hazard of transition metals is a matter of environmental and health concern. Therefore, the development of TiO$_2$ photocatalyst using less toxic dopant becomes more interesting issue. It was reported that a SiO$_2$ group is able to boost photocatalytic reactivity of TiO$_2$ [5–8]. Generally, the application of SiO$_2$ with TiO$_2$ in photocatalytic process for environmental abatement is in a powder form. Therefore, the method for recycling this catalyst after completion of photocatalytic process is a matter of concern. Normally, the process for recycling catalyst is very complex and expensive. To overcome the recycling and disposal problem of TiO$_2$ powder catalyst, the process for immobilizing the catalyst on the substrate is essential. There are many processes such as sol–gel, Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) which have been proposed to immobilize the catalyst on suitable substrates as thin film [9]. Nevertheless, the sol–gel technique is most attractive for preparation of thin film because the method is simple, inexpensive and practicable for working in atmospheric conditions [10–12]. Generally, the preparation process of TiO$_2$–SiO$_2$ precursor solution before immobilizing the thin film on the substrate can be conducted by impregnation (ex situ) and co-precipitation (self-assembly) method [13]. Both of this method provides the different properties of the thin film. Generally, the ex situ thin film sustain the characteristics of the both TiO$_2$ and SiO$_2$ while, the self-assembly thin film introduce a new hybrid materials between TiO$_2$ and SiO$_2$ enhance photocatalytic reactivity [5,13].

In this study, the self-assembly method was selected for preparation of TiO$_2$–SiO$_2$ precursor solution. The SiO$_2$ precursor solution prepared from rice husk silica was dissolved in titanium solution at the initial process expecting to form a new hybrid material between SiO$_2$ and TiO$_2$ for enhancement of the photocatalytic reaction. The sol–gel dip coating technique was chosen for preparation of TiO$_2$–SiO$_2$ thin film on the glass slides. Additionally, the photocatalytic reactivity of the hybrid materials thin film was investigated by the decolorization of MB dye under UV irradiation.

2. Methodology

2.1. Chemicals

All the chemicals used were analytical grade. Titanium (IV) butoxide (TBOT), obtained from Fluka Chemical, was used as titanium source. Rice husk silica was extracted from the acid leaching process following the method of Grisdanurak et al. [14]. The extracted silica was used as a silica source. Cetyltrimethylammoniumbromide (CTAB) obtained from Aldrich chemical was used as a directing agent for a template of TiO$_2$–SiO$_2$ synthesis. Ethanol and acetylacetone provided from Merck Chemical were used as a solvent in sol–gel process.

2.2. Synthesis of TiO$_2$–SiO$_2$ thin film by self-assembly method

The preparation of TiO$_2$–SiO$_2$ thin film was started by dissolving TBOT in the mixed solvents (ethanol and acetylacetone) [15]. Simultaneously, the SiO$_2$ precursor solution was prepared by mixing rice husk silica and CTAB with ethanol solution. After that, the two precursor solutions were mixed together under vigorous stirring at 80 °C for 96 h. The molar ratios of SiO$_2$:TiO$_2$ were varied from 0:100, 20:80, 50:50 and 80:20, respectively. Then preparation of the TiO$_2$–SiO$_2$ thin film on glass substrates was conducted by sol–gel dip coating technique. Before coating process, the substrates were cleaned with piranha solution (an oxidizing agent consisting of sulfuric acid and hydrogen peroxide)
at 80 °C for 0.5 h and rinsed with deionized water and acetone. After that, the substrate was dipped into the TiO$_2$–SiO$_2$ precursor solution at constant withdrawn speed of 10 cm min$^{-1}$. Then, the coated substrates were calcined at 550 °C for 5 h under an air flow in an electrical furnace. After dipping, the residual solution was collected by evaporation of solvents at room temperature until the solution turned into slurry. Then, the slurry was dried at 103 °C for 1 h in an oven before calcination at 550 °C for 5 h to obtain TiO$_2$–SiO$_2$ powder.

### 2.3. Thin film characterizations

The physical and chemical properties of TiO$_2$–SiO$_2$ thin film and powder were characterized by various instruments. The crystal structure of the thin film was characterized by XRD (Rigaku Model D/MAX III with CuK$_\alpha$ radiation in angular range (2θ) from 1° to 60° with 15 mA and 30 kV). FE-SEM (Hitachi S-4800) was used to reveal the surface morphology, smoothness and thickness of the thin film. The UV–Visible absorption pattern of the thin film was examined by UV–Visible spectrophotometer (Shimadzu ISR-2200). The functional groups of TiO$_2$–SiO$_2$ powder were investigated by FTIR (Perkin Elmer Spectrum One). Finally, the porosity of TiO$_2$–SiO$_2$ powder such as specific surface area, specific volume and pore size diameter were examined by nitrogen adsorption analyzer (Micromeritics ASAP 2010) following Brunauer Emmett Teller (BET) technique.

### 2.4. Photocatalytic decolorization of MB dye

This experiment was designed for investigating the photocatalytic reactivity of the prepared TiO$_2$–SiO$_2$ thin film. The TiO$_2$–SiO$_2$ thin film was put into 20 ml of 10$^{-5}$ M MB solution. The determination of adsorption of thin film was carried out in the dark by measuring the reduction of absorbance intensity of methylene blue solution at 663 nm, which is the $\lambda_{\text{max}}$ of MB. The 3 ml of MB solution was taken every 20 min and return to the reservoir after finishing a measurement of the changed wavelength absorption intensity by using UV–Visible spectrophotometer. After the adsorption equilibrium, the samples were irradiated with 20 W mercury lamps; the UV intensity of 0.6 W cm$^{-2}$ with $\lambda_{\text{max}}$ at 330 nm. The photocatalytic reactivity was determined by monitoring the reduction of absorbance intensity of MB every 20 min. The rate of photocatalytic decolorization of MB solution was calculated by the equation below based on the assumption that the photocatalytic decolorization of MB is the first order reaction.

$$\ln\left(\frac{A_0}{A}\right) = kt$$

where $A_0$ and $A$ are the initial absorbance and the absorbance after irradiation of MB solution, $t$ is an irradiation time and $k$ is the first-order rate constant.

### 3. Results and discussion

#### 3.1. Thin film characterization

The crystalline phase characterized by XRD of bare TiO$_2$ (SiO$_2$:TiO$_2 = 0:100$) thin film showed the anatase phase at 2θ equal to 25°, 38° and 48°. Whiles, the TiO$_2$–SiO$_2$ thin film prepared from self-assembly method demonstrated the new crystalline peak at 2θ equal to 31° and 45° (Fig. 1). It is possible that the inter lattice between Ti, O and Si are formed during the self-assembly process when the two precursor solution are mixed before crystal precipitation takes place. This result is different from the study of TiO$_2$–SiO$_2$ thin film prepared by the ex situ method, which reported from other results for preparation of TiO$_2$–SiO$_2$ [1,2,5,16]. To identify these new observed peaks, the FTIR technique was employed to confirm the existing of Ti–O–Si bonding which will be discussed later. If the hybridized bonding exists, it is interesting to figure out whether this band has significant effects on the photocatalytic reactivity of the film.
The FE-SEM images of TiO₂–SiO₂ thin film revealed the homogeneous phase between the TiO₂ and SiO₂ particles (Fig. 2). The surface morphology of these thin films showed porosity, which increased as SiO₂ was increased. Similarly the thickness of the thin film increases corresponding with an increase of SiO₂ contents. The thickness of the thin film (1 cycle) stayed in a range of nano-thin film. For the molar ratio of SiO₂:TiO₂ equal to 0:100, 20:80, 50:50 and 80:20, the thickness was observed to be 57, 62, 79 and 87 nm, respectively (Fig. 3).

The TEM images of the self-assembly TiO₂–SiO₂ powder showed the homogeneous crystal phase between TiO₂ and SiO₂. The image (Fig. 4) revealed the homogeneous crystallinity of TiO₂–SiO₂ particles. The results indicated that adding SiO₂ contents caused decreasing in the crystal size of the photocatalyst from 20 nm to 10 nm. However, this hypothesis will be confirmed by the FTIR instrument during characterization of the functional group of the substance.

Fig. 1. XRD patterns of TiO₂–MCM-41 thin films at various molar ratios.

Fig. 2. FE-SEM images (1000×) of TiO₂–MCM-41 thin film (A) MCM-41:TiO₂ = 20:80, (B) MCM41:TiO₂ = 50:50 and (C) MCM-41:TiO₂ = 80:20.
The FTIR spectra of TiO$_2$–SiO$_2$ powder prepared from self-assembly method showed the noticeable absorption feature around 910 and 1200 cm$^{-1}$, which belong to the absorption band of Ti–O–Si and Si–O–Si (Fig. 5) [17]. Additionally, the spectra intensity of Ti–O–Si band is dominant when TiO$_2$ content increases. The spectra of Si–O–Si increased when SiO$_2$ content was increased. According to the FTIR
results the sample containing SiO₂:TiO₂ equal to 20:80 obviously shows the presence of Ti–O–Si bonding. This result corresponds with the other results, which revealed the increasing of spectral intensity of Ti–O–Si band with increasing molar ratio of TiO₂ [18]. The proposed mechanism for Ti–O–Si bond formation can be explained as the following reactions.

\[
\text{Ti(OC₄H₉)}₂ + C₂H₅OH \rightarrow \text{Ti—OH (Hydrolysis reaction)}
\]

\[
\text{SiO}_2 + C₂H₅OH \rightarrow \text{Si—OH}
\]

\[
\text{Ti—OH} + \text{Ti—OH} \rightarrow \text{Ti—O—Ti (Condensation without Si)}
\]

\[
\text{Si—OH} + \text{Si—OH} \rightarrow \text{Si—O—Si (Condensation without Ti)}
\]

\[
\text{Ti—OH} + \text{Si—OH} \rightarrow \text{Ti—O—Si (Condensation with the combination of Ti and Si)}
\]

The hydrolysis reaction of TBOT and SiO₂ in ethanol produces Ti–OH and Si–OH. After that, the condensation reaction between two precursors such as Ti–OH and Ti–OH or between Si–OH and Si–OH and the combination of Ti–OH and Si–OH occur depending on the molar ratio of Si and Ti.

Table 1 shows the improvement of porosity properties such as specific surface area, specific volume and pore size diameter of TiO₂ powder after incorporating with SiO₂. The results from BET analyzer of TiO₂–SiO₂ powder showed the increase of specific surface area, specific volume and the decrease of pore size diameter than the pure TiO₂ thin film. These results are corresponding with many reports, which explained the phenomena of increased surface area, increased specific volume and reduced pore size diameter of TiO₂ when SiO₂ was added [19–21]. The larger surface area is supposed to enhance the photocatalytic reactivity of TiO₂–SiO₂ thin film especially in the initial stage in which the adsorption plays a significant role.

<table>
<thead>
<tr>
<th>Molar ratio (SiO₂:TiO₂)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Specific volume (cm³ g⁻¹)</th>
<th>Pore size diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:100</td>
<td>48</td>
<td>11.13</td>
<td>3.782</td>
</tr>
<tr>
<td>20:80</td>
<td>120</td>
<td>27.31</td>
<td>3.749</td>
</tr>
<tr>
<td>50:50</td>
<td>292</td>
<td>65.49</td>
<td>3.234</td>
</tr>
<tr>
<td>80:100</td>
<td>487</td>
<td>110.92</td>
<td>2.238</td>
</tr>
</tbody>
</table>
Before studying the photocatalytic reactivity of TiO$_2$–SiO$_2$ thin film, the UV–Visible absorption pattern of the thin films was determined in order to select the optimum wavelength of the light source for the experiment. The absorption pattern of the film (cut off the interference of glass substrate) was obtained using UV–Visible spectrophotometer. The broad absorption band was found and it peaked at 320 nm for pure TiO$_2$. When SiO$_2$ content was increased, the blue shift of absorption was observed. The highest UV absorption was obtained for the sample SiO$_2$:TiO$_2$ (80:20) having peak at approximately 297 nm which is less than that of pure TiO$_2$ (Fig. 6). This phenomenon can be explained in terms of the change in band gap energy of TiO$_2$ due to SiO$_2$. Many reports concluded that SiO$_2$ causes the blue shift of TiO$_2$ by two mechanism; (i) reduced particle size of TiO$_2$ due to siliceous framework (quantum size effect) and (ii) forming Ti–O–Si bonds leading to the modification of the electronic structure [17,22,23]. Similar to those reports, increase of the BET surface area of the catalyst and the presence of Ti–O–Si observed in FTIR characterization study also provide the evidences that there is a decrease in particles size of TiO$_2$ in our thin film. Thus, incorporating SiO$_2$ into TiO$_2$ framework should influence the performance of TiO$_2$–SiO$_2$ thin film in photocatalytic process. According to the UV absorption, the UV light with 330 nm was used for the photocatalytic experiment.

3.2. Photocatalytic decolorization of MB dye

To understand the influence of SiO$_2$ on the photocatalytic reaction, the experiment was designed as dark and UV irradiation phase. In dark phase, the adsorption of MB dye on the thin film occurred. After the adsorption equilibrium, the UV light was turn on and the photocatalytic reaction was performed. The adsorption capacity of these thin films was determined during the dark reaction and it increased as SiO$_2$ content was increased. The adsorption equilibriums of TiO$_2$–SiO$_2$ thin film at the molar ratio of SiO$_2$:TiO$_2$ equal to 0:100, 20:80, 50:50 and 80:20 were 80, 120, 140 and 160 min, respectively (Fig 7). This effect can be explained by the role of SiO$_2$, which enhances the specific surface area and increases active sites (hydroxyl group) on the surface of the photocatalyst [19,24]. However, it is noticeable that the sample containing SiO$_2$:TiO$_2$ equal to 20:80 and 50:50 have the highest adsorbability. This might be because of the limitation of amount of Si incorporating into Ti–O bonding. In case of the sample at the SiO$_2$:TiO$_2$ equal to 20:80, the excess silica probably leaches out from the thin film causing the reduction in adsorption capacity. During the UV irradiation phase, all of the molar ratios of the thin film were able to decolorize MB dye. But for the sample at molar ratio of SiO$_2$:TiO$_2$ equal to 20:80, the rate of photocatalytic decolorization of MB dye was higher than that of pure TiO$_2$ (Fig 8). The calculated rate constants of TiO$_2$–SiO$_2$ thin film for the molar ratio of SiO$_2$:TiO$_2$ equal to 0:100, 20:80, 50:50 and 80:20 were 0.0028, 0.0034, 0.0022 and 0.0026 min$^{-1}$, respectively. This phenomenon can be explained by two mechanisms of photocatalytic process; (i) the adsorption process and (ii) irradiation process. Firstly, the molecules of MB dye is adsorbed on the surface of the catalyst. The ability of this process relies on the specific surface area of the photocatalyst. The irradiation process establishes
the redox reactions for degradation of MB dye on the surface. The overall efficiency of photocatalytic process depends not only on the adsorption capacity of the photocatalyst but also on the chemical bonding of the photocatalyst. The results of photocatalytic decolorization of MB dye indicated that in the part of adsorption phase the rate of reaction was influenced by the specific surface area of the photocatalyst, which facilitates the attraction of the molecules of MB dye onto the photocatalytic sites. After that, the rate of reaction could be controlled by the UV responsive chemical structure Ti–O–Si bonding of the photocatalyst. The improvement of overall photocatalytic reactivity is resulted from the combination of these factors (increased specific surface area and Ti–O–Si bonding). This result corresponded with the results of other researches [25,26], which showed the increasing of photocatalytic decolorization of MB dyes by the synergic effect between SiO$_2$ and TiO$_2$ when adding zeolite into TiO$_2$. The samples with SiO$_2$:TiO$_2$ equal to 20:80 was proved to be the best photocatalyst among others even
comparing to pure TiO₂. The overall efficiency for photocatalytic decolorization of the hybrid thin films containing SiO₂:TiO₂ equal to 0:100, 20:80, 50:50 and 80:20 were 72%, 81%, 79% and 75%, respectively.

4. Conclusion

The TiO₂–SiO₂ thin film prepared by the self-assembly method demonstrated the homogeneous thin film. This thin film hybrid photocatalyst demonstrated a new characteristic feature in it which occurred from chemical reaction between SiO₂ and TiO₂. The SiO₂ enhanced the TiO₂ photocatalytic decolorization of MB dye by increasing the specific surface area and established a chemical bonding with TiO₂. The photocatalytic reactivity of the thin film for decolorization of MB dye relied on the increasing specific surface area and chemical structure of the photocatalyst.

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