Synthesis, characterization and photocatalytic activity using SiO₂-TiO₂ nanocomposites under UV light

V Thongpool1,2, A Phunpueok1,2, S Jaiyen1,2 and T Rojviroon3

1 Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand
2 Materials Physics and Instrumentation Research Unit, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand
3 Division of Environmental Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand

E-mail: voranut_t@rmutt.ac.th
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Abstract
SiO₂-TiO₂ nanocomposites were synthesized by the sol-gel method with different SiO₂ contents (0.125, 0.25, 0.50 and 0.75%wt). The characteristics of prepared samples were obtained from x-ray diffractometer (XRD), field emission scanning electron microscope (FESEM), UV–visible spectrophotometer, and Brunauer Emmett and Teller (BET) surface area analyzer. SiO₂-TiO₂ nanocomposites have higher UV absorption capability and a higher specific surface area compared to pure TiO₂, resulting in improved dye degradation by photocatalytic activity. The results show that the dye degradation efficiency of 0.5SiO₂-TiO₂ is higher than pure TiO₂. It can degrade the dye up to 96.91% within 2 h, while TiO₂ was able to degrade dye at 88.62%.

1. Introduction
Titanium dioxide (TiO₂) is a semiconductor commonly used for photocatalysis because it has excellent properties such as non-toxic, chemical stability, and cost-effectiveness [1, 2]. The photocatalytic activity of TiO₂ depends on its morphology, crystal phase crystallite size, surface area, and so on [2–6]. When TiO₂ absorbs photon energy (hv), this results in electrons (e⁻) being transferred from the valence band to the conduction band, with the generation of holes (h⁺) in the valence band. Electrons will interact to create superoxide radicals (O₂⁻) with the surrounding oxygen, and holes will interact with the surrounding water to create hydroxyl radicals (OH⁻). The superoxide radicals (O₂⁻) interact with water (H₂O) to create hydrogen peroxide (H₂O₂), which then interacts with electrons to produce hydroxyl radicals. Hydrogen Peroxide (H₂O₂) reacts with the photon energy that also creates a hydroxyl radical (OH⁺). The organic compound is decomposed into water (H₂O) and carbon dioxide (CO₂) by this hydroxyl radical (OH⁺) [7, 8].

Improving the efficiency of the photocatalytic activity of TiO₂ is a topic that many researchers are interested in. It is well known that a promising photocatalyst should have a high specific surface area for the benefit of absorbing and decomposing the pollutants. Using the support with a high surface area and pore size is a simple way to increase the absorption capacity of TiO₂ [9]. Silica (SiO₂) is often used as a support because it is chemically inert and high specific surface area.

Rice husk is an agricultural waste that is abundant in Thailand. When rice husk is burned at high temperatures, the product is rice husk ash which consists of 72.1% SiO₂, 0.3% Al₂O₃, 0.43% CaO, 0.5% Na₂O, 0.72% K₂O, 0.15% MnO, 0.05% TiO₂, 0.7% MgO, 0.06% P₂O₅ and ~24.3% weight loss on ignition [10]. Therefore, rice husk is a cheap natural source of silica. In this study, we synthesized SiO₂-TiO₂ nanocomposites using SiO₂ from rice husk ash via the sol-gel method. The prepared nanocomposites were used as the photocatalyst for Methylene blue (MB) dye degradation under UV light. The characteristics of the prepared nanocomposites were analyzed by x-ray diffractometer (XRD), field emission scanning electron microscope (FESEM), UV–visible spectrophotometer, and Brunauer Emmett and Teller (BET) surface area analyzer.
2. Experimental

2.1. Materials
All chemicals were used as received without further purification. Titanium tetraisopropoxide (TTIP) supplied by Acros organic (∼98% purity). Ethyl alcohol was purchased from Duksan. Hydrochloric acid was received from RCI Labscan company.

2.2. Preparation of SiO₂ nanoparticles from rice husk ash
Before the experiment, rice husks were washed with tap water and then dried at 60 °C in the oven. Rice husks were burned at 500 °C for 2 h to get rice husk ash. 10 g of rice husk ash was added to 100 ml of sodium hydroxide 1 M and continuously stirred with a magnetic stirrer at 200 °C for 3 h. The mixture is filtered to separate sediment. 1 M hydrochloric acid was added to the supernatant until the pH was 7, then left at room temperature for 24 h to get the gel. The gel was dried at 120 °C for 24 h and then calcined at a temperature of 500 °C for 5 h to get SiO₂ nanoparticles.

2.3. Preparation of SiO₂-TiO₂ nanocomposites
SiO₂-TiO₂ nanocomposites were prepared via the sol-gel method. First, 8.9 ml of TTIP was dissolved in 100 ml of ethanol, and the SiO₂ nanoparticles (0.125, 0.25, 0.50, 0.75%w/v) were added into the mixture and continuously stirred with a magnetic stirrer at room temperature for 15 min. Then, 1.62 ml of distilled water was added into the mixture, and the stirring was maintained for 45 min. After that, HCl 1 M was slowly added into the mixture until the pH was 3 and left at room temperature for 24 h to get the gel. The gel was dried at 120 °C for 24 h and then calcined at a temperature of 500 °C for 5 h to get SiO₂-TiO₂ nanocomposites.

2.4. Characterization of SiO₂-TiO₂ nanocomposites
The crystalline phase of SiO₂-TiO₂ nanoparticles was analyzed by an x-ray diffractometer (XRD, BruckerAxs D800 Advance, Germany) with Cu K radiation (λ = 0.15406 nm). A field emission scanning electron microscope (FESEM, Hitachi SU8200, Japan) was used to investigate the morphology of prepared nanocomposites. The absorbance spectra were obtained by UV–vis spectrophotometer (UV–vis, Thermoscientific evolution 600, USA). Brunauer Emmett and Teller (BET) surface area analyzer was used to determine the specific area of prepared samples.

2.5. Photocatalytic study
Photocatalytic activities of photocatalyst were studied by observing the degradation of methylene blue (MB) dye under UV light. 60 ml of methylene blue dyes (12.5 ppm) was added with 180 mg photocatalyst and then placed in a dark place for 30 min to ensure the establishment of an adsorption/desorption equilibrium among the photocatalyst and methylene blue dyes. After that, the solution was irradiated with a 10 W UV lamp while bubbling with synthetic airflow. The distance between reactance and the UV lamp was 10 cm. About 2 ml of aliquots were removed from the solution at a regular interval of 15 min and centrifuged at 6,000 rpm for 10 min to remove the photocatalyst. The concentration of MB dye was measured by a UV–vis spectrophotometer at λmax = 663 nm.

\[
\eta = \frac{|C_0 - C|}{C_0} \times 100 = \frac{|A_0 - A|}{A_0} \times 100
\]

where C₀ is the initial, and C is the final MB dye concentration an A₀ and A are the absorbance values of the MB solutions at 663 nm at the initial and final time, respectively [11].

3. Results and discussion

3.1. Characterization of prepared samples
The crystalline structures of the prepared photocatalysts were analyzed by XRD technique. The XRD patterns of the prepared photocatalysts are shown in figure 1. The XRD pattern shows that TiO₂ has an anatase phase, with diffraction peaks at 2θ of 25.4°, 37.8°, 48.1°, 54.0° and 55.2°, consistent with JCPDS no. 894921. SiO₂ nanoparticles prepared from rice husk ash shows the diffraction peak at 2θ of 31.7°, 45°, 57.1° and 74.1°, corresponding to JCPDS no. 802148. In the XRD pattern of SiO₂/TiO₂ nanocomposites, all peaks are a good index to both phases of TiO₂ and SiO₂. The crystallite size of prepared samples was calculated from XRD peaks using the Scherer:
Where $D$ is crystallite size, $\lambda$ is the wavelength of the x-ray radiation ($\text{CuK} \alpha = 0.15406 \text{ nm}$), $k$ is a shape factor constant (typically $k \sim 0.94$ for spherical crystallites), and $\beta$ is the full width of half-maximum height peak, and $\theta$ is the Bragg diffraction angle in which peak was observed \cite{12}.

After analyzing the crystalline structure and crystalline size, FESEM was performed to determine the morphology of the prepared samples. Figure 2(a) shows the FESEM image of TiO$_2$ nanoparticles. The particles are uniform and spherical in shape, approximately 20 nm in diameter. The morphology of SiO$_2$ nanoparticles is shown in figure 2(b). The spherical aggregated shape is observed. Figure 3 shows the morphology of SiO$_2$-TiO$_2$ nanocomposites. From figure 3 and table 1, it is found that the particles have a spherical shape and are smaller in size compared to TiO$_2$ and SiO$_2$ nanoparticles. The decrease in particle size caused by the Si–O net generated by SiO$_2$ restricts the formation of anatase crystalline and grain growth \cite{13}.

It is well known that nanomaterial is a material with a high specific surface area. The BET specific area of prepared samples is reported in table 2. From the table, it can be seen that an increasing amount of SiO$_2$ causes the specific surface area of prepared samples to increase but the surface area of 0.75SiO$_2$-TiO$_2$.

The UV-vis absorption spectra of prepared samples are shown in figure 4. It is apparent that the SiO$_2$ will greatly increase the absorption of TiO$_2$ in the field of UV light. This increased absorbance suggests the potential enhancement of the photocatalytic activity of TiO$_2$ illuminated by UV light.
3.2. Photocatalytic activity

The photocatalytic activity of the prepared samples in the degradation of MB dye was investigated. Before irradiation, the suspension of the photocatalyst in the MB dye solution was stirred in the dark for 30 min to create an adsorption-desorption equilibrium. Figure 5 shows the photocatalytic activity of various prepared photocatalysts on the degradation of 25 mg/l MB. It is seen that the 0.50SiO$_2$-TiO$_2$ and 0.75SiO$_2$-TiO$_2$ show improved photocatalytic performance, and 0.50SiO$_2$-TiO$_2$ is the best photocatalyst. The percentage of degradation achieved after an interval of 90 min is around 96.91%.

### Table 1. Crystallite sizes of the prepared samples.

| Prepared samples      | Crystallite size (nm) |
|-----------------------|-----------------------|
| TiO$_2$               | 17.56                 |
| SiO$_2$               | 43.26                 |
| 0.125SiO$_2$-TiO$_2$  | 13.68                 |
| 0.25SiO$_2$-TiO$_2$   | 12.76                 |
| 0.50SiO$_2$-TiO$_2$   | 9.94                  |
| 0.75SiO$_2$-TiO$_2$   | 8.00                  |

### Table 2. BET specific surface area of prepared samples.

| Prepared samples      | BET specific surface area (m$^2$ g$^{-1}$) |
|-----------------------|---------------------------------------------|
| TiO$_2$               | 42.22                                       |
| SiO$_2$               | 30.58                                       |
| 0.125SiO$_2$-TiO$_2$  | 51.11                                       |
| 0.25SiO$_2$-TiO$_2$   | 56.77                                       |
| 0.50SiO$_2$-TiO$_2$   | 94.10                                       |
| 0.75SiO$_2$-TiO$_2$   | 70.70                                       |

**Figure 3.** SEM images of (a) 0.125SiO$_2$-TiO$_2$, (b) 0.25SiO$_2$-TiO$_2$, (c) 0.50SiO$_2$-TiO$_2$ and (d) 0.75SiO$_2$-TiO$_2$.
The increased photocatalytic performance of SiO2–TiO2 occurs because of the increase in the light absorption and the surface area, especially 0.50SiO2–TiO2 that can absorb the visible light, and the surface area is higher than other photocatalysts.

The effect of the photocatalyst loading on photocatalytic degradation of MB using the amount of 0.50SiO2–TiO2 photocatalyst of 120 mg, 140 mg, 160 mg, 180 mg, and 200 mg is shown in figure 6. The experimental results suggest that the photocatalytic degradation of MB efficiency varies with the photocatalyst loading. However, the loading of excess photocatalysts leads to a decrease in the photocatalytic degradation of MB activity due to the agglomeration of the photocatalysts.

4. Conclusions

In this study, SiO2–TiO2 nanocomposites were synthesized using the sol-gel method. The FESEM images showed that the prepared samples were consisting of nanostructured particle agglomerates. The prepared samples have a very high specific surface area. MB was used as an indicator for the study of photocatalytic activity. SiO2 affects the specific surface area of the prepared samples and increases the efficiency of dye
degradation. $0.50\text{SiO}_2-\text{TiO}_2$ has the highest efficiency of dye degradation by photocatalytic activity under UV light with the optimum photocatalyst content of 180 mg per 60 ml of MB dye solution.

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ORCID iDs

V Thongpool © https://orcid.org/0000-0002-9734-8403

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Figure 6. Photocatalytic degradation of MB under various photocatalysts loading.