Enhancing the photoactivity of TiO$_2$/SiO$_2$ monolithic catalyst and its reusability for wastewater treatment

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Abstract. A series of TiO$_2$/SiO$_2$ photocatalysts were successfully synthesized by the sol-gel method. The TiO$_2$/SiO$_2$ monolith was also synthesized by dip-coating process. The crystalline structure of TiO$_2$/SiO$_2$ powders was identified as pure anatase. The photocatalytic activity of the TiO$_2$/SiO$_2$ powders was evaluated by photodegradation of 20 ppm methylene blue (MB) using a 26W lamp which has the wavelength in the visible light region under different Ti: Si molar ratios and calcination temperatures. The TiO$_2$/SiO$_2$ powders which have Ti: Si molar ratio of 85:15 (TS15) and calcined at 550°C showed the highest photodegradation yield of 84 % after 3h irradiation. Furthermore, the 550°C calcined TS15 monolith performed the MB degradation yield of 88.9 % after 3h irradiation and its photoactivity still remained after 4 recycle times. The results of this study demonstrated that the TS15 monolith photocatalyst has a reasonable efficiency in the degradation of methylene blue, it could be a promising photocatalyst for removal and degradation of organic pollutants.

1 Introduction

In recent years, titanium dioxide (TiO$_2$), a semiconductor material, is recognized as one of the potential photocatalysts to address urgent and global environmental concerns of organic pollutants in water or wastewater problems, because of its interesting properties: non–toxic, inexpensive, chemically stable in nature and high photocatalytic efficiency [1-3]. However, many recent studies show that the efficiency of the photodegradation using only pure TiO$_2$ as a catalyst is not sufficient due to the low specific surface areas and wide band gap energy. Besides reducing the band gap energy, several attempts have been adopted to enhance the surface area of TiO$_2$ particles. In which, the trend synthesizing TiO$_2$ composite with SiO$_2$ has attracted a great deal of attention because of the special intrinsic properties of SiO$_2$. The presence of the porous SiO$_2$ which has the high specific surface areas (535 m$^2$/g) in the catalyst films not only increases surface areas of the catalyst but also improves their thermal stability and mechanical strength [3, 4, 5].

Nevertheless, the use of TiO$_2$/SiO$_2$ powders are still limited in practical application due to difficulties in separation of the suspended photocatalyst particles after the treatment process. Therefore, immobilization of photocatalytic on the substrate is received more attention. Recently, monolith has been demonstrated as a potential material, because it not only can be recovered and reused more easily than powders but also has special characterizations, such as: low-pressure drop, short diffusion distances and large geometric surface area. Therefore, the monolithic photocatalyst has more and more development and uses widely. For instant, Wei Chang et al. synthesized successfully double pore structure TiO$_2$/SiO$_2$ monoliths. With special support of microchannel monolith, the highest surface area of the TiO$_2$/SiO$_2$ 400 °C calcined catalyst was enhanced up to 210.93 m$^2$/g and its photocatalytic activity reached 90 % of yield after 60 minutes irradiation by degradation of methylene blue under a 300 W Xe lamp. Besides, the reusability of 400 °C calcined TiO$_2$/SiO$_2$ catalyst was also investigated and its photoactivity still achieved nearly 80 % degradation yield after 5 reused cycles [6].

Thejaswini et al. also synthesized TiO$_2$/SiO$_2$ monolith which have the TiO$_2$-SiO$_2$ molar ratio of 7:3 and calcined at 520 °C for 5 h. The specific surface areas of this catalyst reached a value of 164.95 m$^2$/g. The photocactivity of (7:3 molar ratio) TiO$_2$/SiO$_2$ monolith was evaluated by degradation of organic textile dye (AR-85) under 16W UV light. The yield of (AR-85) degradation is nearly 97 % after 90 minutes of irradiation [7]. According to these results, coating on monolith is a potential trend to improve the activity of photocatalyst and enhance pollutant degradation yield.

In this study, we concentrated synthesizing and comparing the crystal structure and the photocactivity of TiO$_2$/SiO$_2$ nanoparticles and TiO$_2$/SiO$_2$ monolithic catalysts by the photocatalytic degradation of methylene blue (MB) solution under visible light. The obtained results from this study will be the premise for further researches to develop TiO$_2$/SiO$_2$ monolithic photocatalyst, which is aimed at practical application in wastewater treatment.

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2 Materials and methods

2.1 Materials and reagents

All chemical reagents were of analytical grade and were used as received without further purification. Titanium n-butoxide (TNB, ≥ 98 %), Tetraethyl orthosilicate (TEOS, ≥ 99 %), Acetyl Acetone (AcAc, ≥ 99 %), Polyethylene glycol 400 (PEG 400, 98 %), acid nitric (HNO₃, 65 %) and alcohol were purchased from Merck. Methylene Blue (MB, 100 %) was purchased from Xilong Chemical Company (China). Double distilled water was used in all experiments.

2.2 Preparation TiO₂/SiO₂ composite powders

TiO₂/SiO₂ (TS) powders were synthesized by the sol–gel method. A mixture of TEOS, 7 ml absolute ethanol, 1 ml PEG 400 and 0.5 ml HNO₃ 65 wt % was magnetically stirred for 1 h at room temperature to form a SiO₂ solution. Whereas, a TiO₂ solution was obtained by adding an appropriate amount of TNB to 11ml absolute ethanol and 1 ml AcAc under stirring continuously for 30 min. Subsequently, the SiO₂ solution was then added dropwise into the TiO₂ solution. The obtained TiO₂–SiO₂ solution was heated to 80 °C for 1 h, aged at room temperature for 24 h. After that, the TiO₂–SiO₂ solution was heated at 120 °C for 3 h and then calcined in the air at 450 °C, 550 °C or 650 °C for 2 h. The resulting sample was ball milled into fine powder to obtain TiO₂/SiO₂ composite powders.

In the following sections, the labeling of the synthesized samples follows the format TSx, where x represents the mole percentage of SiO₂ in samples (ranging from 0 % to 100 %). For instance, the TiO₂/SiO₂ with the molar ratio of 95:5 denoted as TS05.

2.3 Preparation of TiO₂/SiO₂ monolithic photocatalyst

A monolith substrate, which was purchased from Chauger Honeycomb Ceramics Co. Ltd. (New Taipei City, Taiwan), was carefully cleaned with acetone in ultrasonic bath for 30 min and dried at 100 °C for 10 h in an oven. The TiO₂–SiO₂ solution was prepared similarly to the synthesis method of TiO₂/SiO₂ composite powders. The dip coating condition was fixed such that uniform distribution of the TiO₂/SiO₂ solution with molar ratio of TiO₂:SiO₂ was 85:15 (TS15), the speed of dipping and withdrawing of 1 cm/min and soaked for 30 min. After dip-coating, the coated monolith was dried at 100 °C for 30 min and then annealed at various temperatures: 450, 550, 650 °C for 2 h.

2.4 Analytical methods

The XRD measurements were carried out by a PAN analytical Empyrex X-ray diffractometer with a scanning rate of 0.2°/min over a range of 20 °C - 80 °C. Morphologies of samples were taken by Scanning Electron Microscope (SEM) using Hitachi Fe-SEM S4800. The Brunauer–Emmett–Teller (BET) analytical technique was implemented using data over the relative pressure (P/P₀) ranging from 0.046 to 0.35 to determine the specific surface area. UV–Vis diffuse reflectance spectra (DRS) of the samples were recorded to determine the band gap energies of the samples.

2.5 Analytical methods

The photocatalytic activities were evaluated through the degradation of 200 mL MB (20 ppm) solution over 0.20 g of catalyst under simulated solar light irradiation. The suspension containing MB and photocatalytic powders was placed in dark and stirred for 2 h to achieve adsorption/desorption equilibrium. After that, the mixture was exposed to illuminating source which is a ReptiGlo 2.0 compact light source lamp with nominal capacity of 25 W at the stirring speed of 400 rpm. The temperature was maintained at 30 ± 2 °C during 3 h irradiation. At predetermined time intervals, 5 ml of the solution was extracted using syringe, and then separated the catalyst from the aliquots.

To evaluate the photocatalytic activity of TiO₂/SiO₂ monolith, the MB solution (20 ppm) was fed into the internal-illuminated monolithic photo-reactor and circulated by using YW21 - SP2 pump with flow rate of 70 ml/ min. The optical fibers (Shiner Fiber Optics, Taiwan) with 1 mm in diameter were inserted into every channel of the coated monolith to transmit and prolong the light-illuminated throughout the length of monolith.

The residual MB concentration was analyzed by using a Hitachi UV-Vis spectrophotometer equipped with an Optics ISS-UV/VIS light source with a wavelength range of 500-700 nm. The absorbance of MB was detected at the wavelength of λMB= 664 nm. Blank test sample was also carried out in this study for comparison purpose. The photocatalytic degradation efficiency was calculated by the expression of C/C₀ (C is the residual MB concentration in solution and C₀ is the concentration of MB at the time start to irradiating).

3 Results and discussion

3.1 Catalyst characterization

Fig. 1 shows the XRD patterns of TS15 powder calcined at various temperatures. All peaks on the patterns are assigned to the pure anatase phase TiO₂ (JCPDS 21-1272) at characteristic peaks 2θ = 25.2° (101), 36.9° (004), 48.24° (200), 54.86° (211) and 63.01° (213). Besides, the peaks associated with silica phase are completely missed which indicates SiO₂ is the amorphous phase. The XRD patterns also show that when the calcining temperature increased from 450 to 650 °C, the XRD peaks become sharper and the intensity increases indicating the formation of larger anatase crystallites and the enhancement of crystallization. According to Scherrer’s equation (Eq. 1) the crystallite sizes which are calculated at (101) peak was calculated
to be 5.97, 6.65 and 9.77 Å for calcinating temperature of TS15 at 450, 550, 650 °C respectively.

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

where D is the thickness of crystallite (nm), k is a constant depending on the crystallite shape (0.90 for this study), \( \lambda \) is the X-ray wavelength (nm), \( \beta \) is full peak width at half maximum in radians and \( \theta \) is Bragg’s angle of the 20 peak.

Figure 1. XRD patterns of TS15 powders with different calcined temperature.

Figure 2. The band gap energy calculation of corresponding samples.

Table 1 summarizes the properties of 550 °C calcined TiO₂/SiO₂ photocatalyst in variety of TiO₂/SiO₂ molar ratio. The specific surface area of the TS05 is 78.63 m²/g, much higher than that of the pure TiO₂ (56 m²/g). The specific surface area increases with increasing amount of silica, reaches 100.91 m²/g at 25 mol % of SiO₂. The increasing of specific surface area is due to the intrinsic porous properties of silica which has a high specific surface area. The increasing amount of silica also leads to increase of the band gap energy (from 3.21 eV to 3.27 eV) as shown in Fig. 2. This made the absorption wavelength of catalyst shifts slightly to the UV region (3.21, 3.26, 3.27 eV according to \( \lambda = 383, 380, 377 \) nm, respectively). It can be explained by the formation of Ti-O-Si linkage owning to the fact that this linkage changes electrical structure of Ti molecular in composite material, leads to expanding the band gap energy of the samples [9]. On the other hand, the formation of Ti-O-Si linkage also have some advantages as make the surface area of the catalyst higher, helps the material more stable in both thermal and mechanical than that of pure TiO₂ [10].

To study morphologies of coated monolith the SEM images were conducted on the bare and TS15 coated monolith. It can be seen in Fig. 3b, the monolithic surface significantly improves after coating the TS15 catalysts and following calcinating at 550 °C for 2h: more smoothly, more uniform and fewer holes compared to bare monolithic surface (Fig. 3a). This proves that the catalytic particles hold tightly and covered well on the monolithic surface. Thus, the catalytic coating on the surface of the monolith promises to enhance the efficiency of photodegradation of MB.

Table 1. Properties of 550 °C calcined TiO₂/SiO₂ photocatalyst

| Samples   | Surface area (m²/g) | Band gap (E₉) |
|-----------|---------------------|---------------|
| TiO₂ (P25)| 56 [8]              | 3.2 [9]       |
| TS05      | 78.63               | 3.21          |
| TS15      | 87.86               | 3.26          |
| TS25      | 100.91              | 3.27          |

Figure 3. SEM micrographs of channel surface of (a) bare monolith and (b) TiO₂/SiO₂ monolith.
3.2 Photocatalytic activities

![Figure 4](image)

Figure 4. Degradation of 20 ppm MB over 550°C calcined TiO$_2$-SiO$_2$ powders.

Fig. 4 illustrates the effect of SiO$_2$ content in composite to the photocatalytic activity evaluated through the degradation of 20 ppm MB solution under the simulated solar irradiation. After 3h irradiation, the yield of both absorption and degradation of the TS15 sample reaches 84.0 %, higher than that of TS05 sample (55.2 %) or TS25 sample (only 36.7 %). This can be explained that the increasing amount of silica leads to increase of the surface area, the efficiency of MB photodegradation over TS15 hence is higher than that of TS5. However, when the amount of silica increased to 25 %, it could make the amount of active site-titanium decreases, SiO$_2$ can form the Si-O net in the TiO$_2$/SiO$_2$ and prevent the formation of the anatase, leading to weak activity [11]. Therefore, the MB degradation yield of the TS25 lower than that of TS05 and TS15.

To immobilize catalyst, which is the important factor of catalyst for practical application, the TS15 catalyst is chosen for coating on monolith’s surface channels. Fig. 5 shows photocatalytic activity of various calcined temperature monolithic photocatalyst. Clearly, after irradiation for 3 h, the degradation rates of MB solution catalyzed by 450, 550 and 650 °C calcined monolithic catalyst are 80.4 %, 88.9 %, 84.1 %, respectively. This result can be attributed to the growth in crystallinity with the calcining temperature. However, at 650 °C calcined temperature, the crystallite size is larger, the specific surface area decreases, the band gap increases so the photocatalytic activities of the monolithic catalyst decrease. Therefore, it requires an appropriate calcined temperature in order for forming complete crystals and optimizing the specific surface area.

Besides evaluating the activity of the catalyst, the durability of monolithic catalyst is also an important factor for practical application. In this investigation, the recycling experiments were conducted in the same condition. The used monolithic photocatalyst after the first cycle of the degradation process was rinsed by deionized water and heat treated at 300 °C for 2 h to remove totally MB contaminant for the next cycle. As shown in Figure 6, the monolithic catalyst still maintains photocatalytic activity after four cycles. The decomposition of the MB solution is 88.9 % in the first cycle after 3 h irradiation, slightly decreases about 6-8 % after each cycle and finally obtains 70.1 % in the fourth cycle. This result can be compared to previous research which indicated the reduction was about 18 % after 5 cycles [6]. It believes that the synthesized monolithic photocatalyst has great potential in practical application to remove organic pollutants.

![Figure 5](image)

Figure 5. MB degradation over TS15 monolithic catalyst calcined at various temperatures.

![Figure 6](image)

Figure 6. Reusability of the TS15 calcined at 550 °C monolithic catalyst.

4 Conclusion

This study deals with the synthesis and evaluation of TiO$_2$/SiO$_2$ powders and TiO$_2$/SiO$_2$ monolithic photocatalyst for water treatment. The 550°C calcined TiO$_2$/SiO$_2$ monolithic photocatalyst with the 85:15 molar ratio of TiO$_2$-SiO$_2$ performed the MB high degradation yield of 88.9 % after 3h irradiation, whereas the highest yield of powders is 84 %. In addition, the photocatalytic
activity of monolithic catalyst decreased insignificantly after each reused time. It believes that monolithic photocatalyst has many potentials to apply in practice, especially in environmental treatment. This research is the premise for further research to develop the photocatalyst to enhance their activity, durability and reusability.

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