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 subtract 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 photoactivity 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 photoactivity 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 (HNO_3, 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 TiO_2/SiO_2 composite powders

TiO_2/SiO_2 (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 HNO_3 65 wt % was magnetically stirred for 1 h at room temperature to form a SiO_2 solution. Whereas, a TiO_2 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 SiO_2 solution was then added dropwise into the TiO_2 solution. The obtained TiO_2-SiO_2 solution was heated to 80 ºC for 1h, aged at room temperature for 24 h. After that, the TiO_2-SiO_2 solution was heated at 120 ºC for 3h and then calcined in the air at 450 ºC, 550 ºC or 650 ºC for 2 h. The resulting sample was ball milled into fine powder to obtain TiO_2/SiO_2 composite powders.

In the following sections, the labeling of the synthesized samples follows the format TSx, where x represents the mole percentage of SiO_2 in samples (ranging from 0 % to 100 %). For instance, the TiO_2:SiO_2 with the molar ratio of 95:5 denoted as TS05.

2.3 Preparation of TiO_2/SiO_2 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 ºC for 10 h in an oven. The TiO_2-SiO_2 solution was prepared similarly to the synthesis method of TiO_2/SiO_2 composite powders. The dip coating condition was fixed such that uniform distribution of the TiO_2/SiO_2 solution with molar ratio of TiO_2:SiO_2 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 ºC for 30 min and then annealed at various temperatures: 450, 550, 650 ºC for 2 h.

2.4 Analytical methods

The XRD measurements were carried out by a PAN analytical Empyrean X-ray diffractometer with a scanning rate of 0.2 º/min over a range of 20 ºC - 80 ºC. 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/P_0) 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 ºC 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 TiO_2/SiO_2 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-illumined 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 λ_{MB}= 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/C_o (C is the residual MB concentration in solution and C_o 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 TiO_2 (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 SiO_2 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.

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

where D is the thickness of crystallite (nm), k is a constant depending on the crystallite shape (0.90 for this study), λ is the X-ray wavelength (nm), β is full peak width at half maximum in radians and θ is Bragg's angle of the 2θ peak.

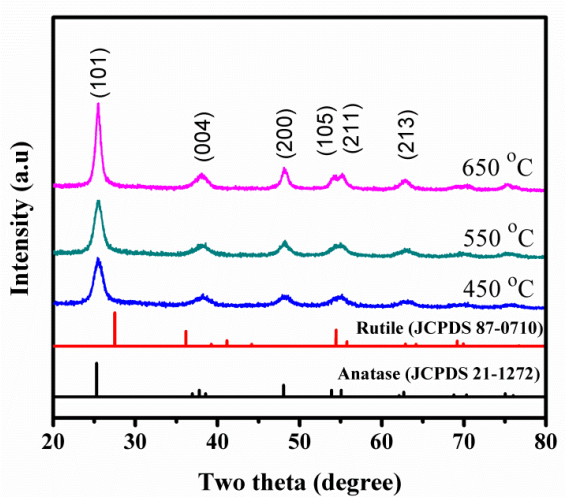

Figure 1. XRD patterns of TS15 powders with different calcined temperature.

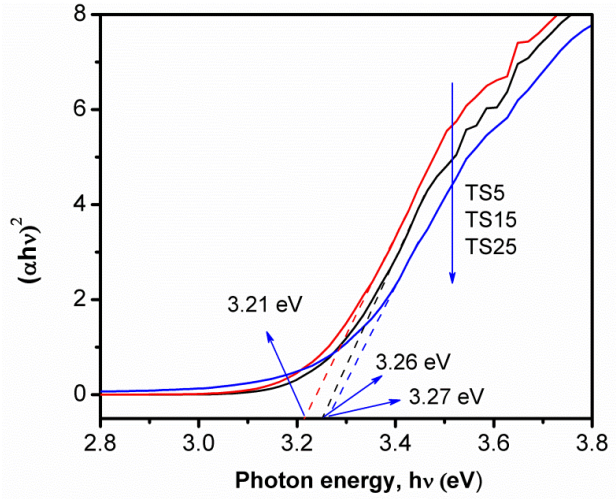

Figure 2. The band gap energy calculation of corresponding samples.

Table 1 summarizes the properties of 550 °C calcined TiO_2/SiO_2 photocatalyst in variety of TiO_2:SiO_2 molar ratio. The specific surface area of the TS05 is 78.63 m^2/g, much higher than that of the pure TiO_2 (56 m^2/g). The specific surface area increases with increasing amount of silica, reaches 100.91 m^2/g at 25 mol % of SiO_2. 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 accordance to λ= 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 TiO_2 [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 TiO_2/SiO_2 photocatalyst

Samples	Surface area (m^2/g)	Band gap (E_g)
TiO_2 (P25)	56 [8]	3.2 [9]
TS05	78.63	3.21
TS15	87.86	3.26
TS25	100.91	3.27

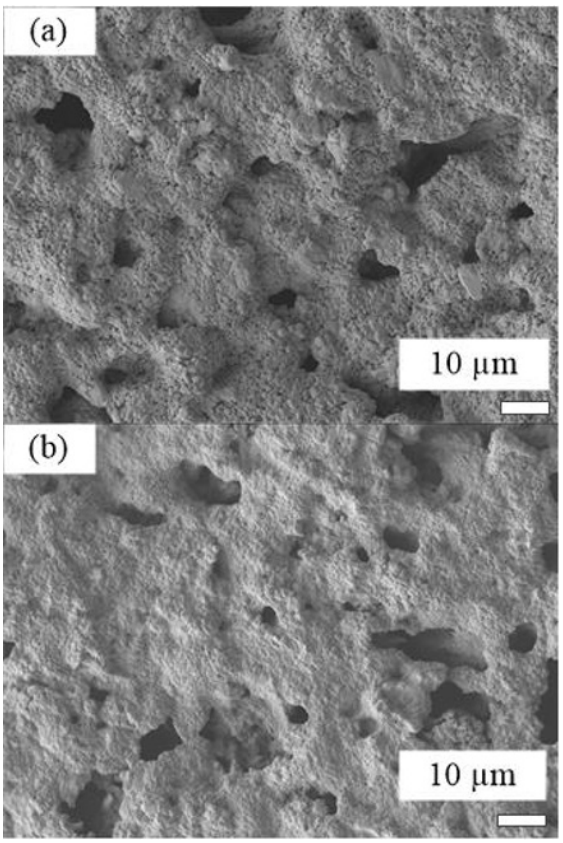

Figure 3. SEM micrographs of channel surface of (a) bare monolith and (b) TiO_2/SiO_2 monolith.

3.2 Photocatalytic activities

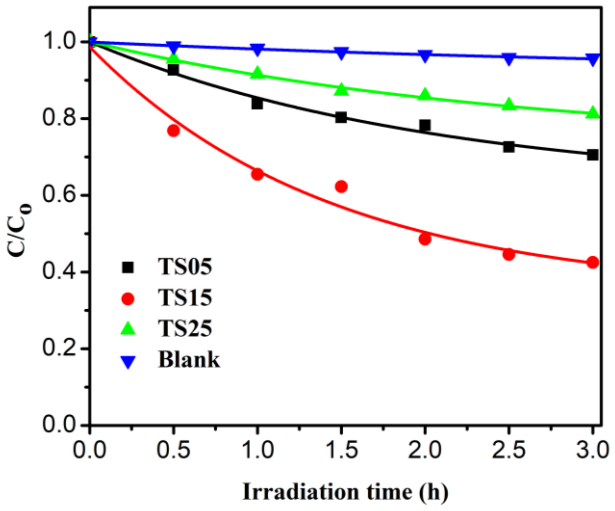

Figure 4. Degradation of 20 ppm MB over 550°C calcined TiO_2-SiO_2 powders.

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.

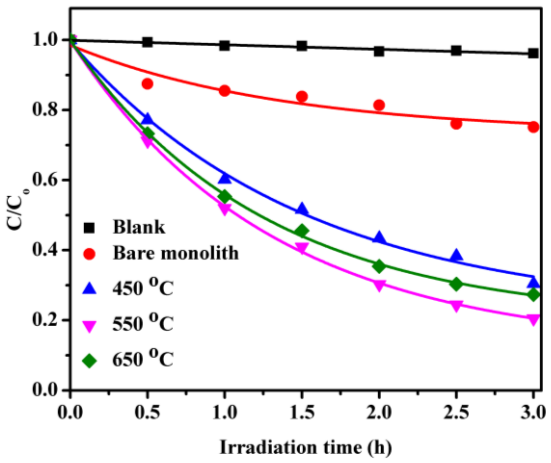

Figure 5. MB degradation over TS15 monolithic catalyst calcined at various temperatures.

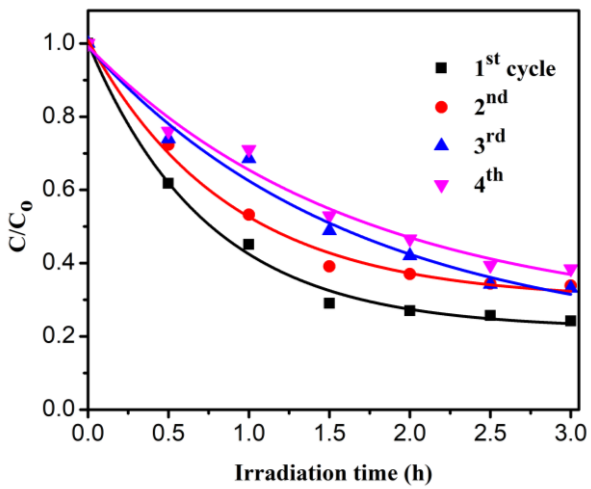

Figure 6. Reusability of the TS15 calcined at 550 °C monolithic catalyst.

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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