SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF VISIBLE-LIGHT TITANIA/SILICA PHOTOCATALYST

N. Sirikawinkobkul[1], C. Kalambaheti[2], S. Jiemsirilers[1,3], D. P. Kashima[1,3], and S. Jinawath [1,3*]
[1] *Reaearch unit of Advanced Ceramics, Department of Materials Science, Faculty of Science,Chulalongkorn University,Phayathai Road, Patumwan, Bangkok 10330,Thailand*
[2] *PTT Research and Technology Institute (PTT RTI), Ayutthaya 13170, Thailand.*
[3] *Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University*
**E-mail: supatra.j@chula.ac.th*

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1 Introduction

The composites of nano-TiO_2 and porous material supports such as SiO_2 with large surface area have received much attention because their adsorption can enhance photocatalytic activity. Moreover the addition of SiO_2 also enhances the thermal stability of TiO_2 particles against anatase to rutile phase transformation [1]. TiO_2 is widely accepted as one of the best photocatalysts for organic degradation in polluted water and air because of its excellent (photo) chemical stability, low cost and non-toxicity. Each crystalline structure of TiO_2 exhibits specific physical properties, band gap, surface states, etc. Anatase phase is mostly used in catalyst and photocatalytic applications. However, Anatase has wide band gap energy (3.2 eV) which means that it can absorb only 5% of solar spectrum. Moreover, TiO_2 presents a relatively high electron-hole recombination rate which reduces its photocatalytic activity [2]. Many researchers studied TiO_2 doping with transition metals (Fe^{3+}, Cu^{2+}) [3-5] to reduce band gap energy and recombination rate to shift the resulting photocatalytic activity to visible light.

The objective of this research was to study the photocatalytic activities of TiO_2/SiO_2 and metal ions (Fe^{3+}, Cu^{2+}) doped TiO_2/SiO_2 photocatalysts prepared by a controlled hydrolysis of $TiCl_3$ in presence of SiO_2 substrate.

2 Experimental

2.1 Methods

TiO_2/SiO_2 and metal ions doped TiO_2/SiO_2 photocatalysts was synthesized by preparing $TiCl_3$ (Fluka 15%) solution in HCl (10–15%) under vigorous stirring in deionized water ($[Ti^{3+}] = 0.15M$) [6], followed by the additions of $Fe(NO_3)_3 \cdot 9H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution (0-1.0mol% of Fe doped TiO_2) in the case of metal doping . The obtain solution was stirred for 30 min and then porous silica was added (TiO_2: SiO_2 = 1:1 w/w) [7] with stirring for 30 min. A blue–violet obtained solution was titrated at room temperature with sodium hydroxide (2M NaOH) solution until pH = 6. Then, the white suspension was stirred for 30 min at constant pH. The solution was hydrolysis at 60 ºC in an oven for 24 h. The solid was then filtered and washed with deionized water to remove chloride ion and dried at 60 ºC for 5 h. After that the solid was ground and calcined at 400 ºC for 2 h (heating rate of 5ºC/min).

2.2 Characterization

The obtained powders were characterized for mineral phases, particle size and specific surface area by XRD (Bruker, D8 Advance), particle sizer (Malvern Instrument 2000), and BET (Coulter SA 3100) techniques, respectively.

2.3 Photocatalytic activity

The photocatalytic activity was analyzed by measuring the absorbance in the photodegradation of methylene blue (MB) dye (using 0.005 g of each prepared catalysts in 50 ml of 0.02 mM aqueous dye solution) at 664 nm, using a UV–Vis spectrophotometer (PerkinElmer Lambda 35). The mixture was magnetic stirred in the dark for 60 min to confirm an adsorption/desorption equilibrium and then under UV-A irradiation (intensity 2 mW/cm^2) and visible light (intensity 5 mW/cm^2) for 2 h. The

supernatant liquid was taken for measurement every 10 min.

The rate constant of photocatalytic degradation was calculated up to a period of 1 h irradiation using the following equation [10]:

$$\ln \frac{c_0}{c_t} = kt \qquad (1)$$

Where C_0 and C_t represent the initial concentration of MB aqueous solution and the concentration measured at the irradiation time, t, respectively, and k represents the apparent rate constant.

3 Results

3.1 Characterization of the photocatalysts

The result of phase analysis by XRD of TiO_2 (Lab- TiO_2 (BET surface area 174.6 m^2/g), prepared the same way as TiO_2/SiO_2 but without SiO_2) and TiO_2/SiO_2 powders (average particle size of 35µm) are presented in Fig 1. TiO_2/SiO_2 photocatalysts exhibited only anatase phase of TiO_2 while three main phases of TiO_2 namely anatase, brookite and rutile are detected in Lab-TiO_2. Thus it indicates that the addition of SiO_2 enhances the thermal stability of TiO_2 crystals against anatase to rutile phase transformation.

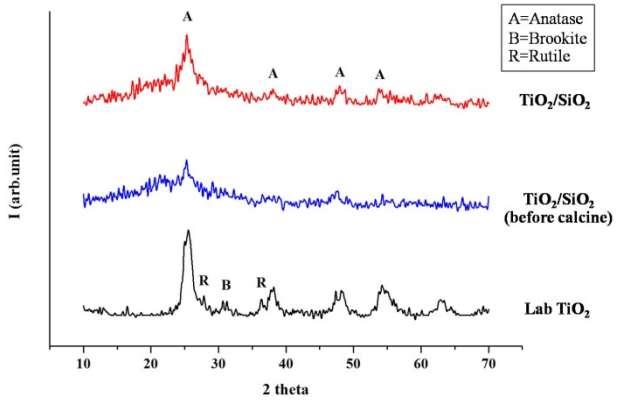

Fig.1. XRD patterns of Lab-TiO_2, and TiO_2/SiO_2 composites before and after calcining.

3.2 Photocatalytic activity

From Fig 2, The adsorptions of dye in the dark by TiO_2-P25, Lab-TiO_2 and SiO_2 reach equilibrium in 10 min and those of TiO_2/SiO_2, $Cu/TiO_2/SiO_2$ and $Fe/TiO_2/SiO_2$ powders are rapid during the first 10 min and reach equilibrium in 60 min with about 85 % of dye is adsorbed. Under UV irradiation with TiO_2-P25, the concentration of the dye rapidly decreases in the first 20 min and continues with a slower rate (Table 1). Lab-TiO_2 also shows the same trend but with a much slower rate.

The photodegradation rates of the dye by the composite catalysts, TiO_2/SiO_2, $Cu/TiO_2/SiO_2$ and $Fe/TiO_2/SiO_2$ are not significantly different but proceed much slower than those of the TiO_2 powders. However, their large adsorption of the dye in the dark is able to compensate for the discrepancy, hence almost the same concentration of the dye as TiO_2-P25 is attained at 2h. Therefore the composites exhibit a potentially adsorption-assisted photocatalysis.

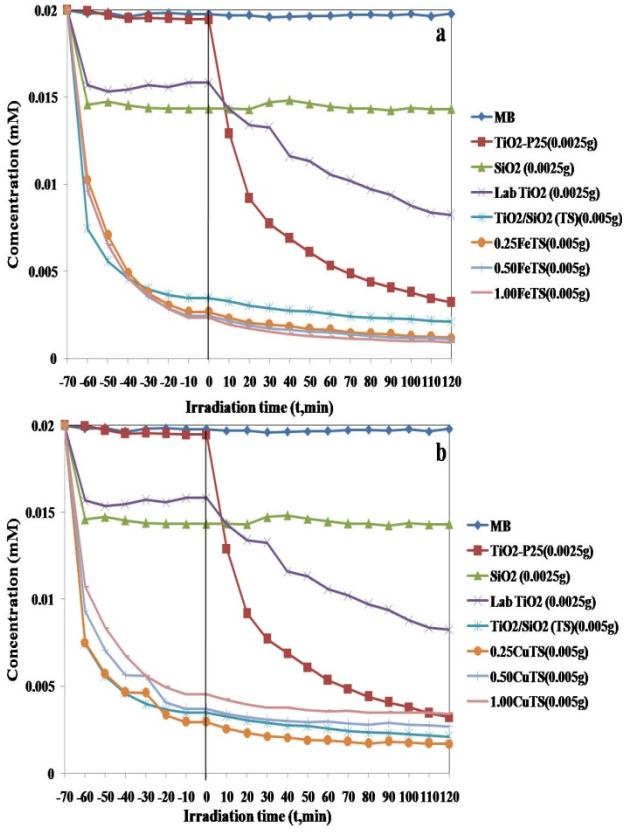

Fig.2. Concentration of methylene blue by a) $Fe/TiO_2/SiO_2$ composites and b) $Cu/TiO_2/SiO_2$ composites compared with TiO_2-P25 and the Lab-TiO_2 under UV-A irradiation.

Under visible light, Fig 3, as expected, due to about 5% UV radiation in the solar light TiO_2-P25 is still

able to degrade the dye, but at a much slower rate than that under UV-light. The metal ions doped TiO_2/SiO_2 further reduce the concentration of the dye below that of TiO_2/SiO_2. Therefore it can be said that the composite catalysts, TiO_2/SiO_2 and metal ions doped TiO_2/SiO_2 enhance the degradation of the dye both under UV and visible lights. They are competitive to TiO_2-P25 under UV-light but better under visible light.

Table 1 The apparent rate constants for photocatalytic activity of MB by the differrent photocatalysts under UV-A and visible lights.

Photocatalyst	**k** (min^{-1})	R^2
Under UV-A		
TiO_2-P25(0.0025g)	0.022	0.926
Lab-TiO_2 (0.0025g)	0.007	0.950
TiO_2/SiO_2 (TS) (0.005g)	0.005	0.933
0.25Fe-TS (0.005g)	0.009	0.933
0.5Fe-TS (0.005g)	0.010	0.944
1.00Fe-TS (0.005g)	0.013	0.958
0.25Cu-TS (0.005g)	0.009	0.925
0.5Cu-TS (0.005g)	0.005	0.913
1.00Cu-TS(0.005g)	0.005	0.888
Under visible		
TiO_2-P25(0.0025g)	0.001	0.935
Lab-TiO_2 (0.0025g)	0.000	0.749
TiO_2/SiO_2 (TS) (0.005g)	0.001	0.847
0.25Fe-TS (0.005g)	0.006	0.95
0.5Fe-TS (0.005g)	0.007	0.943
1.00Fe-TS (0.005g)	0.011	0.999
0.25Cu-TS (0.005g)	0.003	0.833
0.5Cu-TS (0.005g)	0.003	0.864
1.00Cu-TS(0.005g)	0.007	0.956

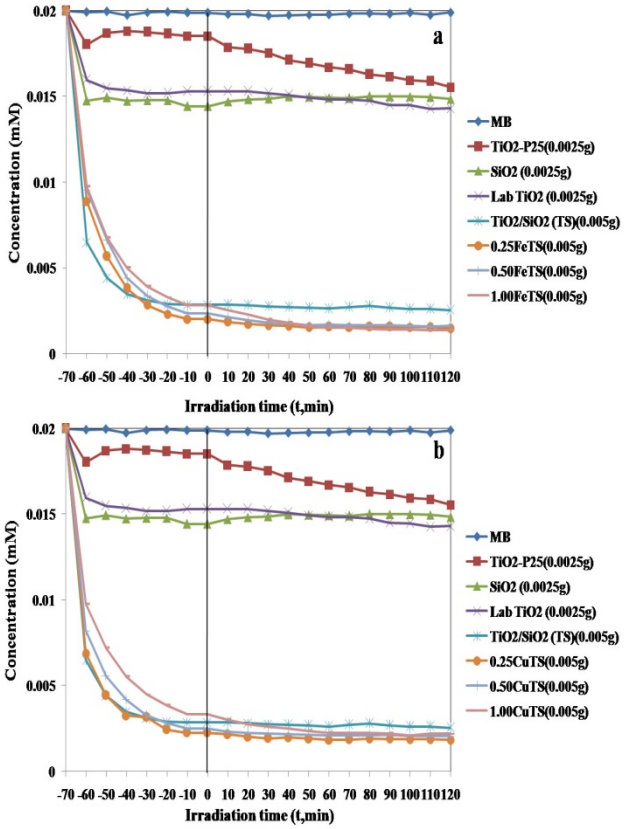

Fig.3. Concentration of methylene blue by a) $Fe/TiO_2/SiO_2$ composites and b) $Cu/TiO_2/SiO_2$ composites compared with TiO_2-P25 and the Lab-TiO_2 under visible light.

4 Conclusions

Despite the small enhancement in the degradation rate of the dye under UV-light when compared to TiO_2-P25, the large adsorption of the composite photocatalysts, TiO_2/SiO_2, $Cu/TiO_2/SiO_2$ and $Fe/TiO_2/SiO_2$ are very interesting to further development in adsorption-assisted photocatalysts under both UV and visible lights.

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