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Characterization and Photocatalytic Activity of Nano-TiO_2 Doped with Iron and Niobium for Turquoise Blue Dye Removal

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The nano-TiO_2 photocatalysts doped with Iron and Niobium for dye wastewater treatment were prepared by temperature-controlled sol-gel method. The effects of these dopants on the physical and chemical properties of TiO_2 were compared with the commercially available Degussa TiO_2 P25. Among these characteristics are crystalline size, the presence of absolute anatase phase, band gap energy and specific surface area. The characterization data were correlated to photocatalytic activities using Turquoise blue dye (TBD) as model pollutant. Single doping (with Nb) and co-doping (Fe and Nb) catalyst reached complete decolorization within 2.5 hours and 3 hours. In addition, their kinetic reaction rate constants of apparent first-order model are 0.0258 min^{-1} and 0.0225 min^{-1}, respectively. The presence of Nb as traps is considered to play a crucial key in enhancing the photocatalytic activity.

Keyword: Photocatalysis, Titanium Dioxide, Doping, Iron, Niobium, Turquoise Blue Dye

INTRODUCTION

The textile industry is one of the biggest consumers of water. Every kilogram of textile product needs approximately 100 – 200 L of water through the production process (Wang et al., 2004). As a result, the amount of wastewater from this industry is very considerable. Textile wastewater is well known with its high chemical oxygen demand, strong color, large amount of suspended solids, variable pH, salt content and high temperature (Körbahti and Tanyolaç, 2008). Therefore, the treatment of this polluted water is necessary due to its toxicity to our life, biota and surroundings. Recently, photocatalysis has become an effective technology in textile wastewater because of its excellent properties: capacity of complete mineralization, low cost, non-toxicity and high stability. It has great application in degrading both gaseous and liquid pollutants (Tayade et al., 2007).

However, this technology needs to be improved to reduce the recombination rate of electron-hole pairs, increase the efficiency of photoutilization (Fujishima and Zhang, 2006) and enhance the stability of active sites. This can be done by focusing on the photocatalyst preparation. Doping is an interesting method to change characteristics of catalysts. An appropriate amount of dopants of interest is inserted into the lattice of TiO_2 to generate defects in the initial basic structure. As a result, new advanced properties of doping catalysts are created to enhance activity.

Niobium-doping catalysts exhibit unique activity, selectivity and stability for many different catalytic reactions. For the reaction carried out in the liquid phase, Ziolek (2003) pointed out high stability of niobium species protects the catalysts from leaching of the active phase. Besides, researchers are paying attention to Iron-doping catalysts. This is due to the most abundance of Iron in the Earth’s crust will make photocatalytic process more practical. Furthermore, similar radius between Fe^{3+} and Ti^{4+} (Ma et al., 2003) facilitates the defects formation. But the role and mechanism of Iron in photocatalyst is controversial (Asiltürk et al., 2009)

In this study, the single doping and co-doping with Fe and Nb were done on nano-TiO_2 using temperature-controlled sol–gel process. The physical and chemical properties were correlated to photocatalytic activities using an azo dye, Turquoise blue dye (TBD), as model pollutant. This study aims to compare the activity of these catalysts in terms of decolorization removal to investigate the role of every dopant.

EXPERIMENTAL

Materials and Catalyst Preparation

Titanium tetraisopropoxide (TTIP), Ammonium niobium oxalate was purchased from Aldrich Chemical Co., USA. Ferric nitrate, Isopropyl alcohol (IPA) was purchased from Scharlau and TBD was provided by Saffron Inc, a textile mill operator in Cavite, Philippines. Degussa TiO_2 P25 was supplied by Nippon Aerosil, Japan. Distilled water was used in material preparation and experimental runs. The catalyst was prepared by temperature-controlled sol–gel method described in the literature of Estrellan et al. (2009). The amount of dopant is calculated so that the molar of Niobium or Iron element is always equal to 0.1 percentage of Titanium in TTIP in both single doping and co-doping.

Photocatalytic Activity

The batch photoreactor system is equipped with 100 W high pressure mercury lamp (Riko-Kagaku Sangyo, Japan) in the range of 312nm ~ 577 nm. At the wavelength of 365nm, light source emits most strongly. The quartz sleeve was also used for cooling the system during illumination and transmitting both UV and visible light. After inserting the cooling tube into the reactor vessel at the axial center, the effective volume is 800 ml. This system was placed on the magnetic stirrer during irradiation. The photoreactor system is shown in Figure 1.

The initial concentration of TBD was 30

ppm. Catalyst loading 0.5 g/l was added in all the experimental runs. Air was bubbled into the solution and the irradiation was started. The samples were taken out in the specific intervals. On the other hand, the dark absorption test was conducted to examine the possibility of TBD adsorbed on the catalyst surface. In these tests, the procedure was carried out as mentioned above in the dark. The initial pH was approximately 5.2 and there was not any attempt to adjust the pH during the process.

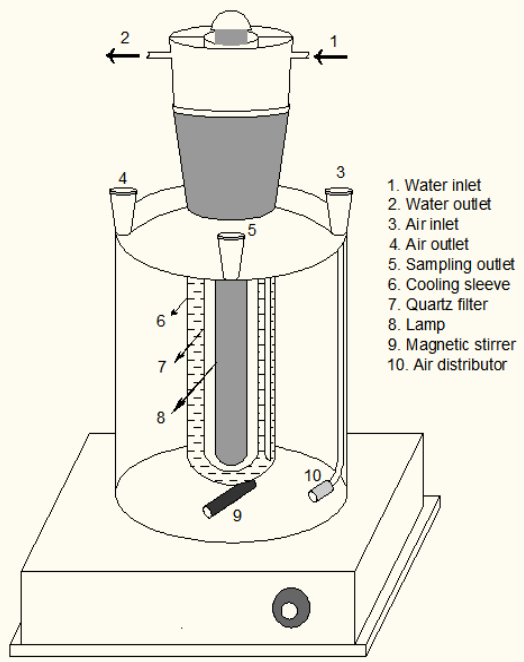

Fig. 1: Schematic diagram of batch photoreactor system

Analytical Procedures

Band gap energy (E_{bg}) was determined using UV-VIS spectrophotometer 1700 (Shimadzu, Japan) combined with making thin film of catalysts on the one side of cuvette (Figure 2.). Suspended solution (10 g/L) of catalysts was prepared in IPA. The one side of cuvette was immersed into this solution. After 15 minutes, the cuvette was dried at 80°C for evaporating the solvent to make the thin film. $BaSO_4$ thin film as a reference was done similarly. The spectrum was recorded in the range of 250-600 nm. E_{bg} was calculated using equation $E_{bg} = hc/\lambda$ (Tayade et al., 2007). The wavelength λ of band gap was extrapolated based on the UV-VIS spectrum.

The surface area was determined by 3-point BET method using Autosorb-1 Analyzer (Quantachrome, USA). The crystalline size was analyzed by JEM-2010F TEM (JEOL Ltd., Japan). X-ray diffraction patterns were obtained with MultiFlex XRD (Rigaku Corp., Japan) using Copper K alpha radiation. The concentration of TBD was measured with spectrophotometer at a wavelength of 604 nm. This can be done because there is no appearance of new absorption band in the UV and visible region during irradiation time (Gallo et al., 2011)

Catalyst $BaSO_4$

Fig. 2: Thin film on the active side of cuvette

RESULTS AND DISCUSSION

Adsorption Test

The possibility of adsorption is usually the initial step to investigate the potential performance of photocatalyst. The dark adsorption results are shown in Figure 3. The state of equilibrium of all photocatalysts was approximately established after 50 minutes. Through dark adsorption, bare TiO_2 showed the lowest percentage (40%) of decolorization and the highest result belonged to 0.1% Fe:Nb-TiO_2 with 53%. This observation is consistent with the results of specific surface area (Table 1). The strong adsorption may be explained in terms of electrostatic interaction. The point of zero charge (pzc) is the condition electrical charge density on surface is zero. The pzc of TiO_2 is widely reported at 6.25–6.90 (Sun et al., 2008). At initial pH ~ 5.2, the surface of TiO_2 is positively charged. While in aqueous media, TBD is dissociated into the positive ion Na^+ and negative ion dye containing SO_3^- (dye-SO_3^-). Therefore, the negative charge dye-SO_3^- is adsorbed on the surface of TiO_2.

Photocatalytic activity

0.1% Nb-TiO_2 and 0.1% Fe:Nb-TiO_2 completely degraded the TBD within 2.5 hours and 3 hours, respectively. 0.1% Nb-TiO_2 showed the highest activity. Degussa P25 was not able to completely degrade after 3 hours and kept constant of degradation after 2 hours. Photolysis showed the inconsiderable result with TBD removal (4.11% within 3 hours). The activity results are shown in Figure 4. The apparent first-order model is usually used as the kinetic model of azo dyes degradation process (Silva and Faria, 2003; Sajjad et al., 2010). 0.1% Nb-TiO_2 and 0.1% Fe:Nb-TiO_2 showed the highest reaction rate constant with 0.0258 min^{-1} and 0.0225 min^{-1}, respectively. The good correlation coefficients (R^2) showed suitability of the model. All the physical and chemical properties of photocatalyst are shown in Table 1.

The Nb-containing (Nb-TiO_2 and Fe:Nb-TiO_2) catalysts showed the better activity compared with others. Niobium plays a crucial key in enhancing the activity. The most stable state of Niobium is Nb^{+5} while Titanium is Ti^{+4}. Nb^{+5} may substitute Ti^{4+} to create the cation vacancies. Therefore, these cation vacancies and Nb^{+5} itself may

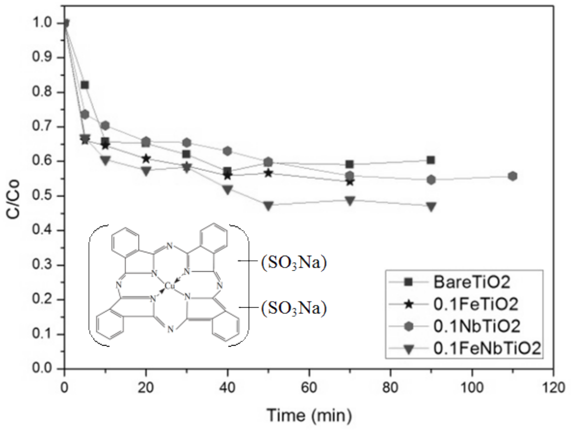

Fig. 3: Dark adsorption test and molecular structure of TBD

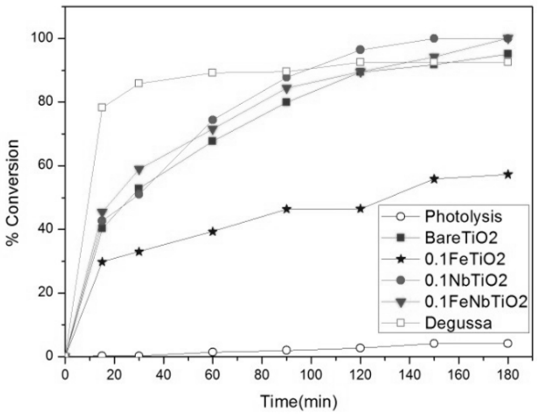

Fig. 4: Photocatalytic activity of catalysts.

Table 1. Physical and chemical properties of photocatalyst

Photocatalysts	Surface Area (m^2/g)	Crystal Size (nm)	Band Gap Energy (eV)	k (min^{-1})	R^2	TBD Conversion (after 2.5h)
Bare TiO_2	72.07	16.5	3.21	0.0164	0.9907	91.8%
0.1% Fe – TiO_2	75.50	15.0	3.12	0.0039	0.8757	55.8%
0.1% Nb – TiO_2	79.90	17.0	3.14	0.0258	0.9767	100%
0.1% Fe:Nb – TiO_2	83.69	16.2	3.15	0.0225	0.9460	94.1%
Degussa P25	56.13	21.8	3.22	-	-	92.5%
Photolysis				0.0003	0.9740	4.11%

play role as traps with electrons and reduce the recombination of photoexcited electrons and the holes. Moreover, Nb with the extra d electron appears to contribute to stronger metal-metal bonding in the bulk metals (Nowak and Ziolek, 1999) may make these traps more stable. As a result, active sites in these catalysts are more efficient than others. Nb addition is also considered to retard the anatase to rutile transformation (Hirano and Ichihashi, 2009). The presence of anatase phase usually gives better activity than rutile phase (Tayade et al., 2007). The high surface area of Nb-TiO_2 (79.90 m^2/g) and Fe:Nb-TiO_2 (83.69 m^2/g) assists their advantages.

The role of Fe^{3+} depends on the dosage of Iron loading. At low dosage, Fe^{3+} traps photogenerated holes to form Fe^{4+}. These Fe^{4+} cations react OH^- on the surface to produce hydroxyl radicals resulting in the increase of activity (Zhang et al., 2008). But in the case of 0.1% Fe-TiO_2, the lower activity (55.8% TBD conversion within 2.5 hours) than bare TiO_2 may be caused by the high doping concentration of Fe^{3+} ions. This may act as recombination sites resulting in the decrease of activity (Zhang et al., 2008).

Characterization Data

X-ray Diffraction

X-ray patterns (Figure 5.) show that the structure of all the prepared catalysts is anatase. The broadening of X-ray peaks and the shift of diffraction angle are observed compared with bare TiO_2. There are no typical peaks for the presence of Iron and Niobium or their oxides. This implies that these elements are incorporated with crystallinity of TiO_2 and their oxides are very small and highly dispersed (Wu and Chen, 2004). The similar radius of Nb^{5+}, Ti^{4+} and Fe^{3+} (Ma et al., 2003; Carvalho et al., 2009) may facilitate the penetration of these elements into the bulk. The crystalline size (Table 1.) is calculated using Scherrer equation (Tayade el al., 2007)

Transmission Electron Microscopy (TEM)

The five crystals in TEM analysis (Figure 6) were chosen to calculate average size. The crystalline size of 0.1% Nb–TiO_2 and 0.1% Fe:Nb–TiO_2 is 14 nm and 16.3 nm, respectively. These values are very close to the results based on XRD pattern shown in Table 1.

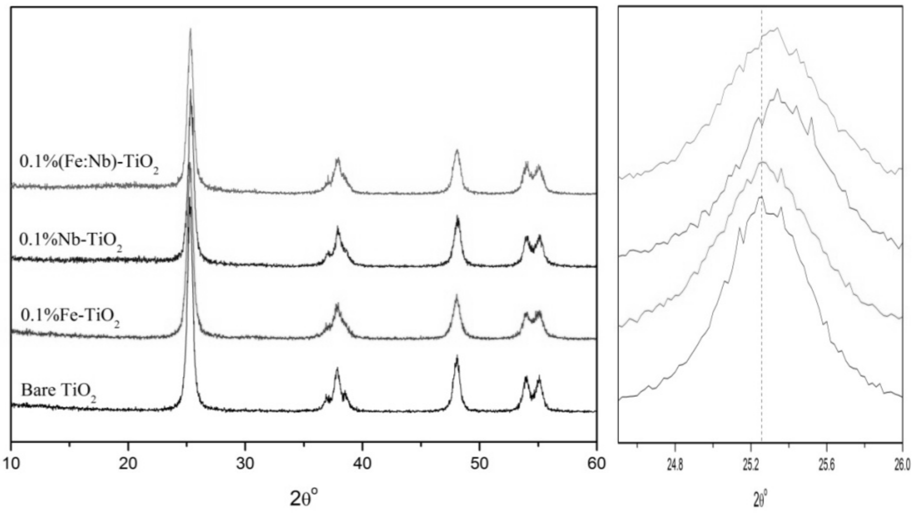

Fig. 5: X-ray patterns for catalysts

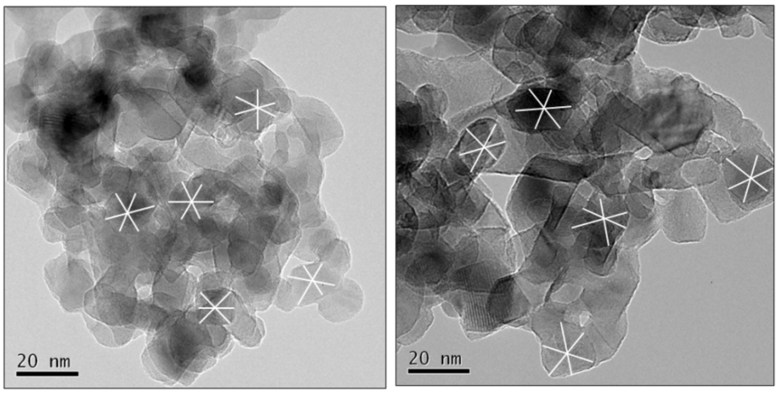

Fig. 6: TEM analysis: (a) 0.1% Nb – TiO_2 (b) 0.1% Fe:Nb – TiO_2

Band Gap Energy

The band gap energy of doping catalysts (Table 1) shows slight decrease compared with bare TiO_2 and Degussa. The role of Nb and Fe in the decrease of band gap energy (redshift) has been reported. This is due to the charge-transfer transition between the d electrons of the transition metals and the conduction band or valence band of TiO_2 (Asiltürk et al., 2009, Hirano and Ichihashi, 2009). This redshift is very meaningful in terms of photoutilization.

CONCLUSIONS

The photocatalytic activity of prepared doping catalysts was done. Nb-containing catalysts showed the highest activity. The presence of Nb as a stabilizer for traps is considered to play a crucial key in improving the efficiency of TBD removal. Fe addition reduces the band gap energy but significantly decreases the TBD conversion. This may be due to the excess concentration of Fe acts as recombination centers. Further research may be carried out to find the optimum doping concentration for photocatalytic activity.

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