

STUDY ON ENERGY STORAGE ABILITY OF ZnO/TiO₂ FOR PHOTOCATALYTIC DEGRADATION OF ISOPROPANOL

Ratchawan Jarumane^a, *Pramoch Rangsunvigit*^{*a,b}, *Pailin Ngaotranwiwat*^c

a The Petroleum and Petrochemical College, Chulalongkorn University

b Center of Excellence on Petrochemical and Materials Technology

c Department of Chemical Engineering, Burapha University

Keyword: Photocatalytic degradation/ Photocatalyst/ TiO₂/ Isopropanol/ Energy storage

ABSTRACT

The photocatalytic degradation of isopropanol under UV irradiation was studied by using p-n junction of ZnO/TiO₂ photocatalysts prepared by sol-gel technique. Their energy storage ability was tested with their photocatalytic activity where there was no UV illumination. That was investigated by illumination the system with UV light for 2 h and off for 2 h until 8 h. The composition and surface structure of the catalyst were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area analysis, and particle size analysis. The change in the isopropanol concentration was observed by using gas chromatography. The result showed that the degradation efficiency of the ZnO doped on TiO₂ layer films was higher than the single-TiO₂ thin film, about 74.0% and 48.0%, respectively. Moreover, acetone was found during the photocatalytic degradation process of isopropanol. The effects of isopropanol solution pH, ZnO loading, and ZnO calcination temperature were studied. ZnO calcined at 600°C and 77 mol% at unadjusted pH was suitable for both photocatalytic activity and energy storage. The photocatalytic degradation rates of isopropanol for the first and second illumination were about 21.0% and 20.8%, respectively. With no illumination, the highest degradation of isopropanol was about 14.8%.

*pramoch.r@chula.ac.th

INTRODUCTION

Isopropanol is a commonly used solvent in semiconductor industry and present at high concentrations in wastewater, which is harmful to microbes, aquatic system, and human health (Tian *et al.*, 2009). In recent era, photocatalytic oxidation/degradation process has been found as an effective and alternative way for treatment of the organic compounds. Among the photocatalysts, titanium dioxide (TiO₂) has been attracted for the degradation of environmental contaminants because of remarkable photocatalytic activity, non-toxicity, low cost, and good chemical stability (Pelaez *et al.*, 2015). However, the uses of TiO₂ as a photocatalyst have some limitations, which are the recombination of photo-generated charged carriers, and TiO₂ functions only under light irradiation. To overcome these limitations, researchers have developed photocatalysts with energy storage ability. ZnO is a p-type semiconductor, and it is considered to be a suitable semiconductor to be coupled with TiO₂ due to its high photocatalytic activity, approximative band gap energy, and similar photocatalytic mechanism of reaction as compared to TiO₂. Oxidative energy storage has been reported by p-n junction concept, which utilizes the contact between a p-type and n-type semiconductor. The oxidative energy of photocatalysts is stored in a p-type semiconductor, and it is possible to retain the removal of some toxic compounds without illumination (Takahashi and Tatsuma,

2005). Yamashita *et al.* (2001) also suggested that the contact between the n-type TiO₂ and the p-type doped TiO₂ introduced the p-n junction, which drove electrons and holes. The holes flow into the ZnO region, while the electrons moved to the TiO₂ region. As a result, the separation of electron-hole pairs was efficiently generated leading to the enhancement of photocatalytic activity. The main goal of this research was to prepare a p-n junction, which are TiO₂ as an n-type semiconductor and ZnO as a p-type semiconductor by sol-gel method. Moreover, the photodegradation of isopropanol by using ZnO/TiO₂ as the oxidative energy storage photocatalyst with and without UV illumination, and intermediate product of isopropanol photodegradation was investigated.

EXPERIMENTAL

A. Chemicals

All chemical reagents used in this work were bis(2,4-pentanedionato)-titanium (IV) oxide (reagent grade, TiO(C₅H₇O₂)₂, TCI Co., Ltd, Japan), zinc oxide (99%, ZnO, analytical grade, Ajax, Australia), isopropanol (99.7%, analytical grade, Carlo Erba Reagents, Italy), polyethylene glycol (100%, MW = 1000 g/mol, (H(OCH₂CH₂)_nOH, Wako, Japan), hydrochloric acid (37%, HCl, analytical grade, Labscan, Thailand), ethanol (99.8%, C₂H₅OH, analytical grade, Merck, Germany), nitric acid (65%, HNO₃, Merck, Germany), and cleaning solution (MICRO-90, Cole-Parmer, USA).

B. Physical Characterization

The morphology of ZnO/TiO₂ bilayer films was examined by scanning electron microscope (SEM, Hitachi, S-4800). The crystalline structure and crystal size was determined by X-ray diffraction measurement (XRD, Rigaku, Smartlab) with Cu-*k*_α radiation ($\lambda = 1.5406 \text{ \AA}$), 40 Kv, 30 mA in the 2 θ range of 20-80° with 3°/min scanning rate and step interval was 0.02°. And particle size diameter is analyzed by particle size analyzer (Malvern, Mastersizer X).

C. TiO₂ and ZnO/TiO₂ Bilayer Films Preparation

A glass slide plate as the substrate was ultrasonically cleaned with the cleaning solution before coating. A TiO₂ film was coated on the glass plate with the solution containing 3 g of bis(2,4-pentanedionato)-titanium(IV) oxide and 3 ml ethanol by spin coating technique at 1,500 rpm for 20 s and calcined at 400 °C for 1 h. For the second layer, ZnO layer was prepared by spin coating technique at the same conditions as above. The solution containing 4 ml TiO₂-sol with 39, 50, 77, and 89 mol% ZnO and 0.16 g polyethylene glycol was prepared. ZnO particles were obtained from the calcination temperatures at 400-600°C for 1 h. TiO₂-sol was synthesized by sol-gel technique using titanium isopropoxide (TIPP) as a precursor. Firstly, 1.4 ml of 70% HNO₃ was diluted with 200 ml deionized water then added to 16.7 ml of TIPP under vigorous stir for a couple of days until clear solution was obtained. The resulting solution was dialyzed by a membrane to obtain TiO₂ sol at a pH condition of 3.5 ± 0.1. The ZnO layer was coated on the TiO₂ layer and were calcined at 350 °C for 1 h to obtain a ZnO/TiO₂ bilayer films.

D. Photocatalytic Activity and Analysis

ZnO/TiO₂ was used as a bilayer film catalyst for the photocatalytic degradation of isopropanol (IPA). The first layer was coated by TiO₂ and then covered by the mixture

of ZnO/TiO₂ as the second layer. To control the adsorption effect that could hinder for the photocatalytic reaction, the bilayer film was immersed in the isopropanol solution for 12 h. The reactor was blocked from any disturbance from other light sources by using a black box. The conditions for the photocatalytic reaction were 30°C, 150 rpm of stirred speed, 5 lamps of UV light, 200 ml of 100 ppm isopropanol solution, and reaction time for 8 h. And the solution was tested every hour for quantitative analysis by using a gas chromatograph with flame ionization detection, (Agilent 6890N, DB-WAX column, 30 m × 0.32 mm, ID of 0.53 μm) operated at 80°C and was connected to a flame ionization detector with H₂ as the carried gas.

RESULTS AND DISCUSSION

A. Catalyst Characterization

The surfaces ZnO/TiO₂ bilayer photocatalyst films were studied from the SEM micrographs. The results are shown in Figures 1-2. Figure 1a and b show the first TiO₂ layer, which shows the uniform surface. TiO₂ solution seems to cover well over the glass plate substrate. Figure 1c and 1d show the ZnO/TiO₂ bilayer films. It can be seen that ZnO particles disperse on the TiO₂ layer and show the porous structure of ZnO particles, which may be resulted from the addition of PEG in the preparation step.

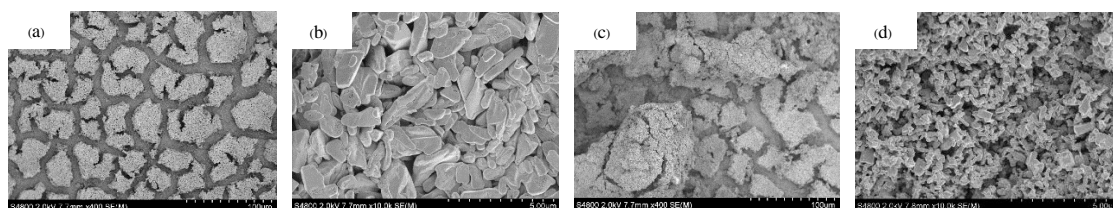


Figure 1 SEM micrographs of (a) TiO₂ at 400X, (b) TiO₂ at 10,000X, (c) ZnO/TiO₂ at 400X, and (d) ZnO/TiO₂ at 10,000X.

Figure 2 shows the effect of the calcinations temperature on the particle size. It can be seen that by increasing the temperature, the particle size increases. That can be ascribed by the agglomeration of the particles.

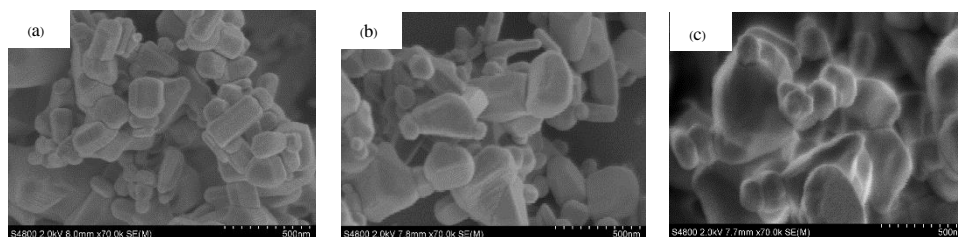


Figure 2 SEM micrographs of (a) 400ZnO (b) 500ZnO (c) 600ZnO at 70,000X magnification.

The photocatalysts were investigated by XRD technique. Figure 3a shows the XRD patterns of ZnO/TiO₂ bilayer films compared with TiO₂ and ZnO. It is clear that the intensity of the main peaks of TiO₂ and ZnO in the case of bilayer films is not different from that of pure TiO₂ and ZnO films; therefore, there is no indication of mixed compound formation. When the calcination temperature of ZnO/TiO₂ increases, the

crystallinity of catalyst increases by the increase of the diffraction peak sharpness, as shown in Figure 3b.

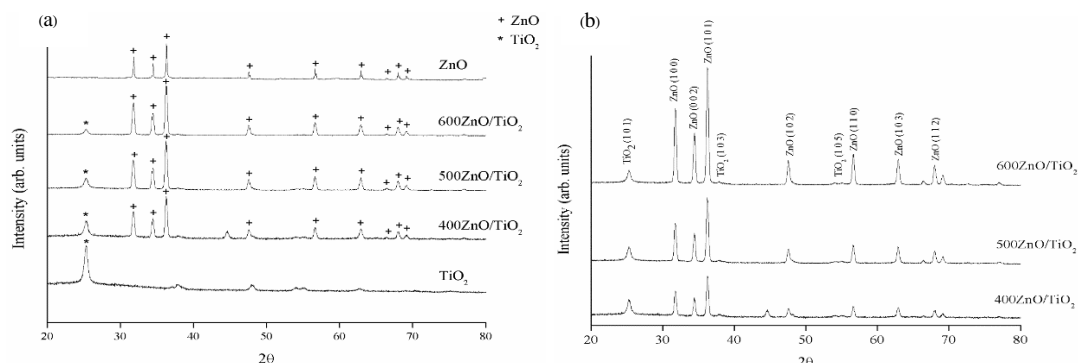


Figure 3 (a) XRD patterns of TiO_2 , ZnO and ZnO/TiO_2 bilayer films (b) XRD patterns of the 400, 500 and 600 ZnO/TiO_2 bilayer films.

B. Photocatalytic Degradation

ZnO/TiO_2 was used as a bilayer film catalyst for the photocatalytic degradation of isopropanol. The first layer was coated by TiO_2 and then covered by the mixture of ZnO/TiO_2 as the second layer. Figure 4a shows the degradation of isopropanol solution under the UV illumination for 8 h. The result shows that the degradation of isopropanol increases with the increase in the operating time. 600 ZnO/TiO_2 shows the highest photodegradation activity, 74.0%. TiO_2 and ZnO alone show 47.8% and 61.9% degradation of isopropanol, respectively. Moreover, Figure 4b shows that the concentration of acetone increases continually, while the concentration of isopropanol decreases with the long-term irradiation.

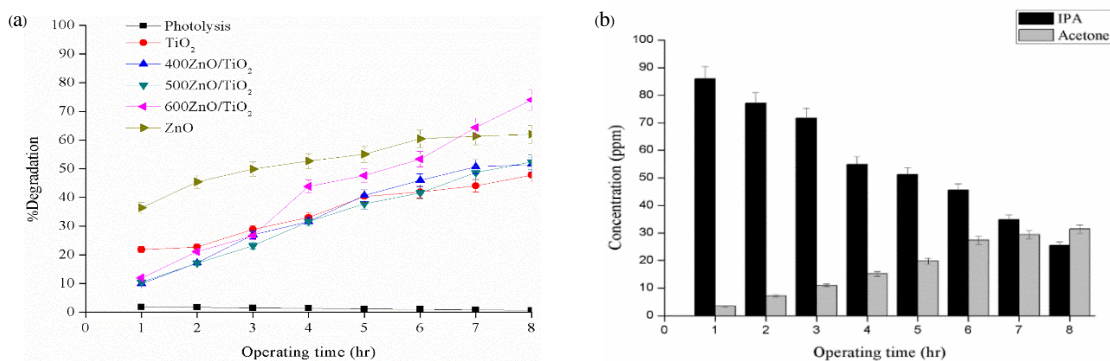


Figure 4 (a) Photocatalytic degradation of isopropanol in unadjusted pH as a function of operating time with the UV illumination for 8 h (b) Changes of isopropanol concentration and acetone from isopropanol degradation as a function of operating time.

C. Energy Storage of Single- TiO_2 and ZnO Film and ZnO/TiO_2 Bilayer Films

Figure 5a shows that the photocatalytic degradation of isopropanol by TiO_2 alone without illumination does not happen because it cannot form the p-n catalyst. On the other hand, in Figure 5b, the bilayer films with illumination show photocatalytic activity. That is because electron-hole pairs are generated, the holes flow into the

negative field p-ZnO, and the electrons flow into the positive field n-TiO₂. The holes are transported into the p-ZnO for the oxidative energy storage. From this reason, the p-n junction of ZnO/TiO₂ can store energy (Takahashi and Tatsuma, 2005).

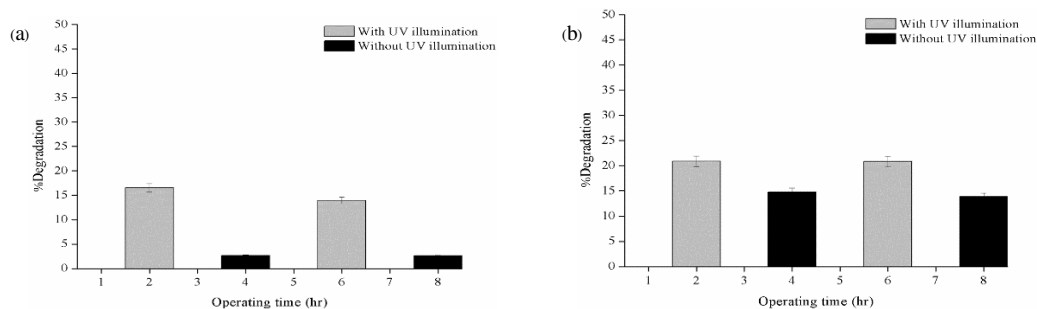


Figure 5 Photocatalytic degradation of isopropanol by (a) TiO₂ and (b) ZnO/TiO₂ bilayer films with and without UV illumination.

D. Effects of Isopropanol Solution pH

ZnO/TiO₂ bilayer films were used as a photocatalyst to study the effect of oxidation energy storage on the photocatalytic activity with and without UV illumination. From Figure 6, isopropanol solution was adjusted to pH 3.0 by HCl. The result indicates that the degradation rate of isopropanol solution at unadjusted pH shows the highest rate; therefore, at unadjusted pH can improve the reaction site more than at pH 3.0, the photocorrosion may be occur.

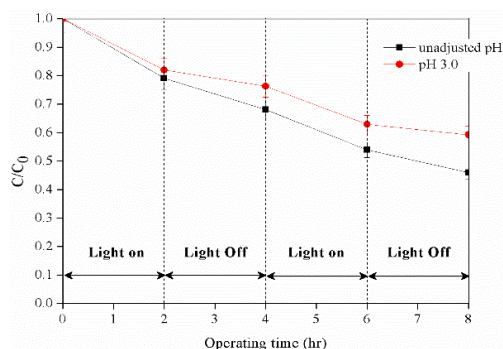


Figure 6 Concentration of isopropanol at various time compared with isopropanol initial concentration by the ZnO/TiO₂ bilayer films with different pH.

E. Effects of ZnO Loading

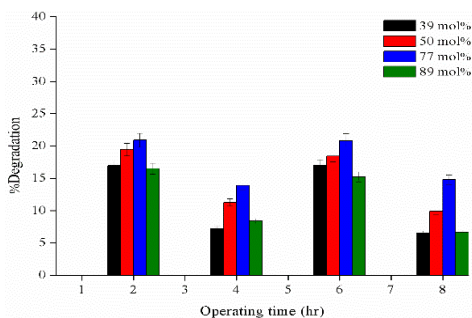


Figure 7 Effect of ZnO loading on the photocatalytic degradation of isopropanol.

Figure 7 shows the effect of ZnO loading with 39, 50, 77, and 89 mol% on the ZnO/TiO₂ bilayer films. The results indicate that the degradation rate with and without illumination also decreases with the increase in the ZnO loading. With higher loading, the dispersion of ZnO particles on TiO₂ may decrease and decrease in the penetration of UV light and hence the photoactivated electron-hole pairs decreases (Bansal *et al*, 2009).

F. Effects of ZnO Calcined Temperature

To investigate the optimum oxidation energy storage, ZnO particles were calcined at 400, 500, and 600°C. And the bilayer films were prepared at 77 mol%. Table 1 shows the photocatalytic degradation of isopropanol with the tested catalysts. The results show that 600ZnO/TiO₂ has the highest photodegradation efficiency that may be because it has the highest crystallinity, as shown in Figure 3b. Xu *et al.* (2009) reported that the higher crystallinity may provide direct path for the transfer of electron and decrease the charge recombination, thus increasing the efficiency.

Table 1 Effect of ZnO calcined temperature to photocatalytic degradation of isopropanol

Photocatalysts	Photocatalytic degradation (%)			
	2 h	4 h	6 h	8 h
400ZnO/TiO ₂	15.4	7.9	14.4	5.4
500ZnO/TiO ₂	16.5	10.2	14.8	7.3
600ZnO/TiO ₂	20.9	14.8	18.8	13.9

CONCLUSIONS

ZnO/TiO₂ bilayer films were prepared by spin coating method to test the photocatalytic degradation of isopropanol. ZnO/TiO₂ showed the highest degradation rate of isopropanol about 74.0%. From the investigated of bilayer films, 77 mol% 600ZnO/TiO₂ was found to be optimum and exhibited the best activity in degradation of isopropanol solution at unadjusted pH in the dark condition.

ACKNOWLEDGEMENTS

The author would like to sincerely thank The 90th Anniversary of Chulalongkorn University Fund and Grant for International Integration; Chula Research Scholar, Rachadaphiseksomphot Endowment Fund, Chulalongkorn University, Thailand; The Petroleum and Petrochemical College, Chulalongkorn University, Thailand; Center of Excellence on Petrochemical and Materials Technology, Thailand; and Department of Chemical Engineering, Burapha University, Thailand.

REFERENCES

- Bansal, P., Bhullar, N., and Sud, D.** (2009) *Water Treatment*, 12, 108-113.
- Pelaez, G.M., Tomas, S.A., Morales-Luna, M., Arvizu, M.A., and Tellez-Cruz, M.M.** (2015) *Thin Solid Films*, 594, 304-309.
- Takahashi, Y., and Tatsuma, T.** (2005) *Langmuir*, 21 (26), 12357-12361.
- Tian, B., Li, C., Hu, Y., and Zhang, J.** (2009) *Chemical Engineering*, 151, 220-227.
- Xu, L., Hu Y.-L., and Pelligra C.** (2009) *Chemistry of Materials*, 21 (13), 2875–2885.
- Yamashita, H., Harada, M., and Misaka J.** (2001) *Synchrotron Rad*, 8, 569-571.
- Yasomane, J.P. and Bandara, J.** (2008) *Solar Energy Materials*, 92, 348-352.