

# Photocatalytic Degradation of Toluene in a Continuous Flow Reactor Using TiO<sub>2</sub> and UV Light

Chiu-Hsuan Lee<sup>1</sup>, Je-Lueng Shie<sup>2, +</sup>, Fang-Ru Kuo<sup>2</sup> and Ching-Yuan Chang<sup>1</sup>

<sup>1</sup> Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 10617, Taiwan

<sup>2</sup> Department of Environmental Engineering, National I-Lan University, I-Lan 26041, Taiwan

**Abstract.** This study investigated the photocatalytic degradation of volatile organic compounds (VOCs) (taking toluene as target material) from indoor pollution source using a continuous flow reactor with TiO<sub>2</sub> at ultraviolet lamp (254 nm, UVC). From the characteristic analyses, the maximum absorbance wavelength is major at 250 nm from UV/vis spectrum and it proved that UVC is that peak absorbance wavelength of TiO<sub>2</sub>. XRD patterns show that the major crystal composition is composed of about 70% anatase, and part of the rutile of 30%. From SEM spectrum, the average particle size of TiO<sub>2</sub> is between 40-50 nm. I-V curve of PECSC of TiO<sub>2</sub> also proved that there is really low photoelectrochemical effect of TiO<sub>2</sub> under the visible light source. Therefore, UVC light is the best light choice. In the continuous flow reactor, the vapor toluene was volatilized from mixing toluene liquid, and the initial concentration was decreased from 3632.81 to 358.06 ppmv with the volatilized temperature of 288 to 275 K, respectively. In the case of air flow rate of 30 mL min<sup>-1</sup> and initial concentration of 358.06 ppmv, the toluene maximum removal efficiency with UVC light was more than 72.38%. The photocatalytic degradation efficiency increased with the initial concentration decreased as expected. The removal mass of toluene increased from 44.45 to 151.31 mg g<sup>-1</sup>-TiO<sub>2</sub> as the initial concentration of 3632.81 to 358.06 ppmv, respectively. This is very useful information and design specifications for scientific researchers.

**Keywords:** Volatile organic compounds (VOCs), toluene, ultraviolet, photocatalysis, TiO<sub>2</sub>

## 1. Introduction

The removal of organic pollutants with oxidative photocatalysis from water and air has demonstrated successful performance for its environmental applications. The oxidative photocatalysis of TiO<sub>2</sub> are drove from the irradiation of ultraviolet (UV) light to excite the charge carriers (electric hole and electron) which occurs upon from valence band to the conduction band as well as forming hydroxyl radicals (•OH), furthermore, which typically reacts with molecular oxygen in the air to produce superoxide radical anions (O<sub>2</sub>•<sup>-</sup>). The radical can react with volatile organic compounds because of their oxidizing power from light source to irradiate semiconductors [1]-[7].

Photocatalysis allows the use of sunlight under the existence of photocatalyst to destruct the highly toxic molecules, synthetically useful redox transformations in specific organic compounds, various inorganic and metal ions, and even biological pathogens such as bacteria and viruses. The main drawbacks are the low quantum yields and the lack of visible-light utilization, however, they hinder their widespread acceptance as a practical remediation technology. Various approaches have been attempted to enhance the photocatalytic efficiency and visible light utilization of TiO<sub>2</sub>, which include impurity doping of various elements such as F, S, N, etc. [3]-[10], metallization [2]-[13], and sensitization [4]-[18].

Toluene is used as an target material of VOCs in this research, the reason is due to its less toxicity and less hazardous to be used in the environment [2]-[11]. The main motivation of this study is to analyse the

---

<sup>+</sup> Corresponding author. Tel.: + 886-3-9353563; fax: +886-3-9353563.  
E-mail address: jlshie@niu.edu.tw.

characteristics of TiO<sub>2</sub> and evaluate the competitiveness of toluene removal in a single pass as well as continuous flow system using ultraviolet lamp as light source at the photodegradation utilizations and efficiencies.

## 2. Materials and Methods

### 2.1. Reagents and catalyst

Toluene of purity 99.7% was purchased from Nihon Shiyaka Industries, Ind. Co., Ltd., Japan. The known volume of toluene was injected into the single pass system. The toluene was diluted to 5-25 % using ethylene, then the diluted liquid of 100 mL was put into the 500 mL tank. For the control of the input initial concentration, the 5 to 25 % liquid toluene were vaporized with a continuous flow of 30 mL min<sup>-1</sup> of air at 275 K and atmospheric pressure, the initial concentration into the reactor were detected as 3632.81 to 358.06 ppmv while the volatilization temperature of 288 to 275 K, respectively. TiO<sub>2</sub> (Degussa P-25, Germany) was used as received without any pretreatment for comparison. For coating purpose, 4 g TiO<sub>2</sub> was suspended in solutions of 40 mL D. I. water, 20 mL acetylacetone (2,4-Pentanedione, Nacalai Tesque Inc., Kyoto, Japan) and 1 mL Triton X-100 (Nacalai Tesque Inc., Kyoto, Japan). Then, the TiO<sub>2</sub> solution was uniformly coated on the supports of 350 glass sticks of 1.8 g dry coated TiO<sub>2</sub>, calcined at 623 K for 20 min.

### 2.2. Apparatus

In this study, a cylindrical pyrex glass reactor of 1500 mL capacity was used as a reaction vessel in which a UVC light source was inserted. The light source was surrounded by a quartz glass tube to protect it and to prevent direct contact with the toluene. The top cover and bottom plates of the reactor were made from stainless steel 316. The glass sticks (diameter: 1.5 mm, length: 25 cm, half illuminated area of total 350 glass sticks: 4123.35 cm<sup>2</sup>), outside surface coated TiO<sub>2</sub>, were inserted into the reactor. The flow rate of toluene with 1 mL min<sup>-1</sup> was vaporized and mixed with additional dry air of 29 mL min<sup>-1</sup> to obtain a toluene concentration of 3632.81 to 358.06 ppmv. After the complete mixing with stirrer, the mixing air flowed into the balance tank, then it was injected into the reaction reactor. It corresponded to a gas velocity of 0.38 cm min<sup>-1</sup> and a residence time of 50 min. Before the photocatalytic reaction, the catalyst was first exposed to the polluted air stream with no illumination until dark-adsorption equilibrium was reached, and afterwards UVC illumination (UV lamp,  $\lambda = 254$  nm, Philips TUV, 16 W, Japan) was switched on. The chromatographic column of the GC-MS (Focus GC and DSQ, USA) is a Rtx-1 capillary GC column (26 m long, 0.53 mm i. d., 3  $\mu$ m film thickness). The operating conditions of the GC-MS were set as follows: injector temperature 473 K, detector temperature 473 K, column temperature (following the sampling injection) being increased from 333 to 373 by program, helium carrier gas flow rate 1 mL min<sup>-1</sup>, helium make-up gas 50 mL min<sup>-1</sup>, and sample volume 150  $\mu$ L. Quantitative analysis of gaseous products was conducted using the linear calibration response equations of standards. The equation was generated for each compound of gas standard using a minimum of five different concentrations with three replicates at each concentration. All correlation coefficients ( $r^2$ ) of linear calibration response curves exceed 99.5%.

### 2.3. Catalyst characteristic analyses

Scanning electron microscope (SEM) (Hitachi Tabletop TM-3000, Japan), X-ray single crystal diffractometer (XRD) (Rigaku TTRAX III, Japan) and ultraviolet-visible (UV/vis) (EVOLVTION-220, Thermo., USA) spectroscopy were used for the characteristic analyses of TiO<sub>2</sub>. The photoelectrochemical effects of TiO<sub>2</sub> was also detected through using photoelectrochemical solar cells (PECSC). For the preparation of PECSC, TiO<sub>2</sub> was suspended in solutions of acetylacetone (2,4-Pentanedione, Nacalai Tesque Inc., Kyoto, Japan) and Triton X-100 (Nacalai Tesque Inc., Kyoto, Japan). The photocatalyst was then uniformly coated on the indium-doping tin oxide (ITO) surface. The ITO film was then calcined at 723 K for 20 min and the coated catalyst was 0.02 g. The ITO film, wetted with a film of the catalyst coating, was dried at 378 K in an oven and denoted as negative electrode. The positive electrode was prepared by coating pure carbon film. The electrolyte was chosen as KI<sub>3</sub> solution. The solar cell prepared from catalyst of TiO<sub>2</sub> was denoted as TiO<sub>2</sub> solar cell (TSC). The PECSC characteristics were analyzed by Cyclic Voltammetry (5600 Electrochemical Workstation, Jichan, Taiwan). The cyclic voltammetry measurements were carried out using a conventional three-electrode assembly (working electrode (WE), counter platinum electrode (CE) and

saturated calomel reference electrode saturated calomel electrode (SCE)). The open-circuited output voltage ( $V_{oc}$ ), short-circuit output current ( $I_{sc}$ ), fill factor (FF), maximum power ( $P_m$ ) and I-V curves of TSC under the irradiation of visible light lamp (VLL, 400-800 nm, T1 Pro 8W/840, Philips, Japan) were measured, and the light intensity is 10515.16 Lux.

### 3. Results and Discussion

#### 3.1. Characteristic analyses of $TiO_2$

Figure 1 shows that the maximum absorbance wavelength is major at 250 nm from UV/vis spectrum and it proved that UVC is that peak absorbance wavelength of  $TiO_2$ . It needs to note that the absorbance intensity is approaching to zero while the wavelength higher than 400 nm, therefore, it means that the visible light cannot excite  $TiO_2$  at the wavelength ( $\lambda$ ) of 400-760 nm. From Figure 2 of XRD patterns of  $TiO_2$ , the major crystal composition is composed of about 70% anatase, and part of the rutile of 30% as compared with the database of Joint Committee on Powder Diffraction Standards (JCPDS). The SEM spectrum was taken for the pure photocatalyst sample and is illustrated in Figure 3. The average particle size of  $TiO_2$  is between 40-50 nm. Figure 4 shows the I-V curve of PECSC of  $TiO_2$  at VLL. The values in Figure 4 are the original ones and do not evaluate the used mass of catalysts. From Figure 4,  $V_{oc}$ ,  $I_{sc}$ , FF and  $P_m$  are 0.25 V, 0.009 mA, 0.37 and 0.84  $\mu W$ , respectively. It is the evidence of that there is really low photoelectrochemical effect of  $TiO_2$  under the visible light source. And from the reference [2], the BET surface area of  $TiO_2$  is 51.85  $m^2 g^{-1}$ .

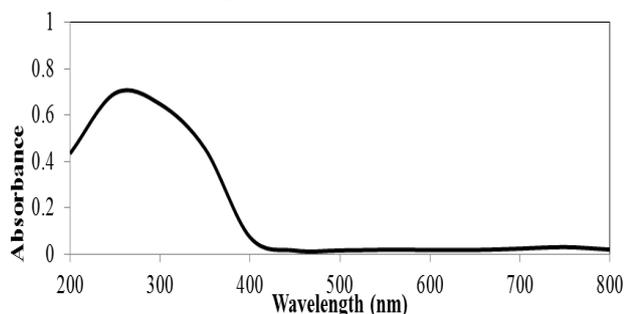


Fig. 1 UV-visible spectrum of  $TiO_2$ .

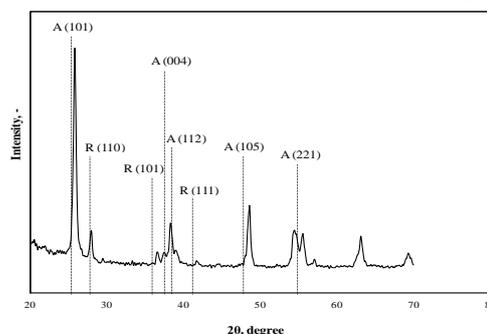


Fig. 2 XRD patterns of  $TiO_2$ .

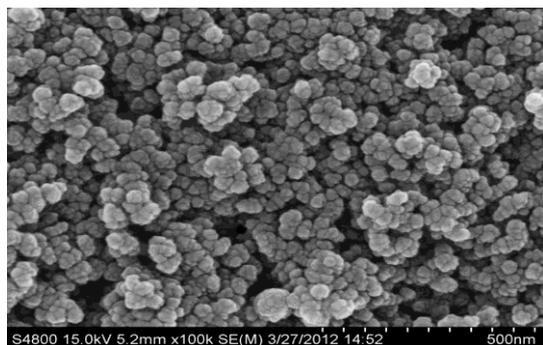


Fig. 3 SEM Photo of  $TiO_2$  (100,000 x).

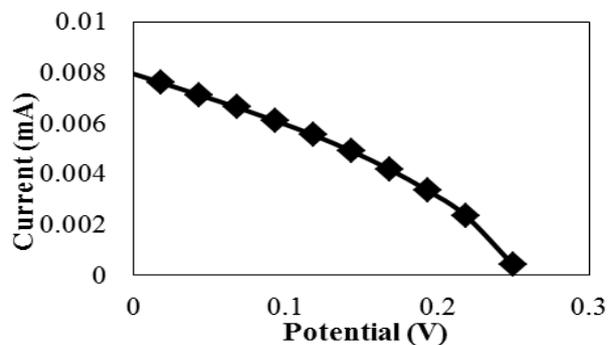


Fig. 4 I-V curve of TSC at the irradiation of VLL. Catalyst mass=0.02 g.

#### 3.2. Photodegradation efficiency of toluene

In the continuous flow reactor, the vapor toluene was volatilized from mixing toluene liquid, and the initial concentration was decreased from 3632.81 to 358.06 ppmv with the volatilized temperature of 288 to 275 K, respectively. Figure 5 shows the photodegradation efficiency of toluene in a single pass reaction over  $TiO_2$  for the initial concentration of 3632.81 to 358.06 ppmv using UVC. From the figure, the removal efficiency increased from 21.26 to 72.38 % as the initial concentrations decreased from 3632.81 to 358.06 ppmv, respectively. Therefore, in the case of air flow rate of 30  $mL min^{-1}$  and initial concentration of 358.06 ppmv, the toluene maximum removal efficiency was more than 72.38%, as shown in Figure 6 after 80 minutes of adsorption equilibrium and then the UVC light was turned on, the concentration stable decreased

from 358.06 to 98.9 ppmv after 180 min. The photocatalytic degradation efficiency increased with the initial concentration decreased as expected. Comparison with the unit removal mass from Table 1, the unit mass of toluene per TiO<sub>2</sub> increased from 44.45 to 151.31 mg g<sup>-1</sup>-TiO<sub>2</sub> as the initial concentration of 3632.81 decreased to 358.06 ppmv, respectively. Therefore, it illustrated that the initial concentration has a great influence on the toluene removal efficiency. Furthermore, improvement to decrease of initial concentration, for example, 50 to 100 ppmv of the standard limitations of some countries, the removal efficiency will be expected to reach more 90%.

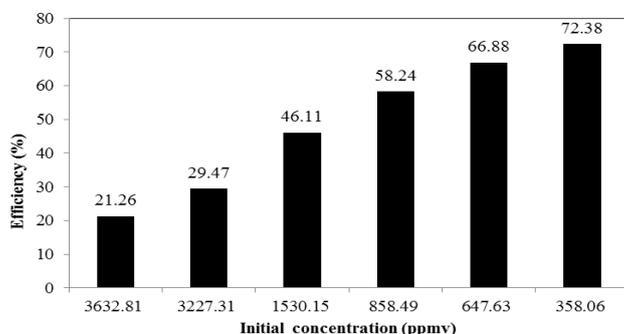


Fig. 5: The removal efficiency of different initial concentration of toluene under UVC light.

Table 1: The removal efficiency and unit mass of toluene per TiO<sub>2</sub> at different initial concentration of toluene

Initial concentration (ppmv)	Diluted times (%)	Efficiency (%)	Removal mass (mg)	Removal unit mass (mg g <sup>-1</sup> -TiO <sub>2</sub> )
3632.81	25	21.26	80.01	44.45
3227.31	25	29.47	110.90	61.61
1530.15	10	46.11	173.51	96.39
858.49	8	58.24	219.13	121.74
647.63	5	66.88	251.65	139.81
358.06	5	72.38	272.35	151.31

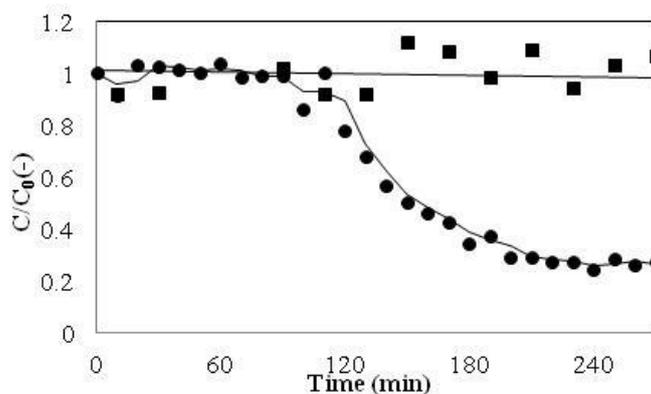


Fig. 6: Time variation of  $C/C_0$  for the photocatalytic decomposition of toluene using light source of UVC and TiO<sub>2</sub>. ■: background ; ●: under UVC turn on at 80 min. Total reaction times: 200 min, reaction temperature: 298 K, Initial concentrations: 358 ppmv.

## 4. Conclusion

This study proved that VOC of toluene can be obviously degraded in the single pass flow reactor using TiO<sub>2</sub> coating. The catalyst of TiO<sub>2</sub> is cheaper than other catalyst. In the case of air flow rate of 30 mL min<sup>-1</sup> and initial concentration of 358.06 ppmv, the toluene maximum removal efficiency with UVC light was more than 72.38%. And the removal efficiency is significant affected by the initial toluene concentration. This is a very useful information and design specifications for scientific researchers.

## 5. Acknowledgements

We express our sincere thanks to the National Science Council of Taiwan for their generous financial support, under the contract No. NSC 98-2221-E-197-003-MY2 and NSC NSC 100-2221-E-197 -005 -MY3.

## 6. References

- [1] K. Nakata, and A. Fujishima. TiO<sub>2</sub> photocatalysis: Design and applications. *J. Photochem. Photobiol., C: Photochem. Rev.* 2012, **13**(3): 169–189.
- [2] J. L. Shie, and C.Y. Pai. Photodegradation kinetics of toluene in indoor air at different humidity using UVA, UVC and UVLED light sources in the presence of silver titanium dioxide. *Indoor Built Environ.* 2010, **19**(5): 503–512.
- [3] J. L. Shie, C.Y. Chang, C.S. Chiou, Y.H. Chen, C.H. Lee, and C.C. Chang. Characteristics of N-doped titanium oxide and photodegradation of formaldehyde using visible light lamp and light emitting diode. *Sustain. Environ. Res.* 2012, **22**(2): 69-76.
- [4] Y. Cho, W. Choi, , C.H. Lee, T. Hyeon, and H.I. Lee. Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO<sub>2</sub>. *Environ. Sci. Technol.* 2001, **35**(5): 966–970.
- [5] E. Bae, and W. Choi. Highly enhanced photoreductive degradation of perchlorinated compounds on dye-sensitized metal/TiO<sub>2</sub> under visible light. *Environ. Sci. Technol.* 2003, **37**(1): 147–152.
- [6] M.V. Alexander, and J.J. Rosentreter. Photocatalytic oxidation of aqueous trichloroethylene using dye sensitized buoyant photocatalyst monitored via micro-headspace solid-phase microextraction gas chromatography/electron capture detection and mass spectrometry. *Microchem. J.* 2008, **88**(1): 38–44.
- [7] W. Zhao, Y. Sun, and F.N. Castellano. Visible-light induced water detoxification catalyzed by PtII dye sensitized titania. *J. Am. Chem. Soc.* 2008, **130**(38): 12566–12567.
- [8] T. Umebayashi, T. Yamaki, S. Yamamoto, A. Miyashita, S. Tanaka, T. Sumita, and K. Asaia. Sulfur-doping of rutile-titanium dioxide by ion implantation: Photocurrent spectroscopy and first-principles band calculation studies. *J. Appl. Phys.* 2003, **93**(9): 5156 – 5160.
- [9] Z.M. Wang, G. Yang, P. Biswas, W. Bresser, and P. Boolchand. Processing of iron-doped titania powders in flame aerosol reactors. *Powder Technol.* 2001, **114**(1-3): 197–204.
- [10] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 2001, **293**(5528): 269–271.
- [11] J.L. Shie, C.H. Lee, C.S. Chiou, C.T. Chang, C.C. Chang, and C.Y. Chang. Photodegradation kinetics of formaldehyde using light sources of UVA, UVC and UVLED in the presence of composed silver titanium oxide photocatalyst. *J. Hazard. Mater.* 2008, **155**(1-2): 164–172.
- [12] H. Einaga, S. Futamura, and T. Ibusuki. Complete oxidation of benzene in gas phase by platinumized titania photocatalysts. *Environ. Sci. Technol.* 2001, **35**(9): 1880–1884.
- [13] V. Subramanian, E. Wolf, and P.V. Kamat. Semiconductor-metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO<sub>2</sub> films? *J. Phys. Chem. B.* 2001, **105**(46): 11439–11446.
- [14] B. O'Regan, and M. Grätzel. A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature*.1991, **353**(24): 737–740.
- [15] A. Hagfeldt, and M. Grätzel. Light-induced redox reactions in nanocrystalline systems. *Chem. Rev.* 1995, **95**(1): 49–68.
- [16] R.W. Fessenden, and P.V. Kamat. Rate constants for charge injection from excited sensitizer into SnO<sub>2</sub>, ZnO, and TiO<sub>2</sub> semiconductor nanocrystallites. *J. Phys. Chem.* 1995, **99**(34): 12902–12906.
- [17] J. M. Stipkala, F.N. Castellano, T.A. Heimer, C.A. Kelly, K.J.T. Livi, and G. Meyer. Light-induced charge separation at sensitized sol-gel processed semiconductors. *J. Chem. Mater.* 1997, **9**(11): 2341–2353.
- [18] J. P. Ghosh, C.H. Langford, and G. Achari. Characterization of an LED based photoreactor to degrade 4-Chlorophenol in an aqueous medium using Coumarin (C-343) sensitized TiO<sub>2</sub>. *J. Phys. Chem. A.* 2008, **112**(41): 10310–10314.