

## Evaluation of photocatalytic activity of carbon-doped TiO<sub>2</sub> films under solar irradiation

Donghyuk Jung\*, Gysun Kim\*, Moon-Sun Kim\*\*, and Byung-Woo Kim\*,†

\*Department of Chemical Engineering, Sungkyunkwan University,

\*\*Bio/Nano-Fusion Material Research Center, Sungkyunkwan University,  
300, Cheoncheon-dong, Jangan-gu, Suwon 440-746, Korea

(Received 20 January 2011 • accepted 5 October 2011)

**Abstract**—We proposed a method to obtain carbon-doped TiO<sub>2</sub> (C-TiO<sub>2</sub>) with a higher photocatalytic activity for degradation of toluene. Solar radiation was used as a visible light source for photocatalytic oxidation. An optical fiber reactor (OFR) was used to investigate the photocatalytic oxidation of toluene in air. All C-TiO<sub>2</sub> films used as catalysts were synthesized by a modified sol-gel and combustion method using carbon nanoparticles. The performance of the OFR using C-TiO<sub>2</sub> was evaluated under various experimental conditions. The effects of solar flux, surface sensitization, inlet concentration of toluene and concentration of carbon nanopowder in C-TiO<sub>2</sub> were examined.

Key words: Photocatalyst, Carbon-doped TiO<sub>2</sub>, Toluene, Solar Irradiation

### INTRODUCTION

Volatile organic compounds (VOCs) are an important class of air pollutants found in the atmospheres of all urban and industrial areas. VOCs are likely to be harmful to human health and can cause nausea, headaches, irritation, affect the nervous and breathing systems, or initiate cancer [1]. Toluene is a common VOC emitted by many industrial processes, such as chemical manufacturing, painting and petroleum refining. Due to its noxiousness, several strategies have been identified to reduce its presence in civil and industrial emissions.

Among the methods to oxidize toluene, heterogeneous photocatalytic oxidation (PCO) is one of the most attractive due to the mild conditions under which experiments are usually carried out. During the past decade, heterogeneous PCO has been studied extensively as a promising method of removing VOCs [2]. Titanium dioxide (TiO<sub>2</sub>) is extensively used as a photocatalyst for the degradation of volatile organic compounds [3]. Therefore, the improvement and optimization of TiO<sub>2</sub> as a photocatalyst is an important task for technical applications of heterogeneous PCO. Many investigators have reported ways to enhance the activity of TiO<sub>2</sub> including surface sensitization, control of structure and particle size, cationic and anionic doping, and surface modification with noble metals [4]. In addition, many investigators have reported photocatalytic activity either in the ultraviolet or visible light ranges [5,6]. Recently, various anion-doped TiO<sub>2</sub> photocatalysts that show relatively high levels of activity under visible-light irradiation have been reported [7-11].

In this paper, we investigated the concentrations of carbon nanopowder in carbon-doped TiO<sub>2</sub> (C-TiO<sub>2</sub>) to obtain higher photocatalytic activity under visible light irradiation. Using C-TiO<sub>2</sub> with different masses of carbon nanopowder, we evaluated the removal efficiency (RE) of gaseous toluene. We also investigated the RE of toluene under various solar fluxes.

### EXPERIMENTAL SECTION

#### 1. Preparation of C-TiO<sub>2</sub> Film

C-TiO<sub>2</sub> films that were used as photocatalysts in experiments were prepared by the following procedure. After blending 15 mL of titanium tetraisopropoxide (TTIP, over 98.0% pure, Junsei, Japan) and 134.5 mL of ethyl alcohol (99.9% pure, Samchun, Korea), the mixture was stirred for 30 min. To this mixture, 0.4 g of HNO<sub>3</sub> (Daejung, Korea) and 3 mL of distilled water were added followed by stirring again for 90 min. Varying specific amounts of carbon nanopowders (Aldrich, U.S.A., average diameter <50 nm) and 3.75 g of TiO<sub>2</sub> (p-25, Degussa, Hanau, Germany) nanoparticles were added to the mixture. After stirring for 60 min, the mixture was dispersed by an ultrasonic generator for 10 min. In this procedure ultrasonic waves produce a cavitation effect resulting in localized pressure reduction. The low-pressure areas are highly localized and changing all the time (between lowest and highest pressure is typically 10 to 25 microseconds). The bubbles can exist only when the pressure is low. They are extremely unstable when at high pressure, so they collapse violently. This leads to increase the chemical reactivity, due to increased number of molecular collisions. The obtained solution was immobilized onto the external surfaces of the optical fibers (BFH37-1000, Thorlabs, U.S.A.) by a dip-coating method described in our previous report [12]. The coated TiO<sub>2</sub> film was dried at room temperature for 12 h and sintered at 550 °C for 2 h. The synthesized TiO<sub>2</sub> film was characterized by X-ray diffraction (XRD) (Philips PW 1050-3710 diffractometer with Cu K $\alpha$  radiation), scanning electron microscopy (SEM; JSM7000F, JEOL, U.S.A.).

#### 2. Photo Reactor and Operation Conditions

A schematic diagram of the photo reactor and the operation conditions are shown in Fig. 1 and Table 1, respectively. In the photo reactor, air was supplied to the mixing tank at a constant rate of 10 L min<sup>-1</sup> by an air pump (MCD6062Z, Fuji Electric Co. Ltd., Japan). Liquid toluene was spurred into the mixing tank at 0.2 mL h<sup>-1</sup> using a syringe pump. When the toluene was introduced into the mixing tank, it vaporized and was carried away in the air stream. The diluted

†To whom correspondence should be addressed.  
E-mail: bwkim@skku.edu

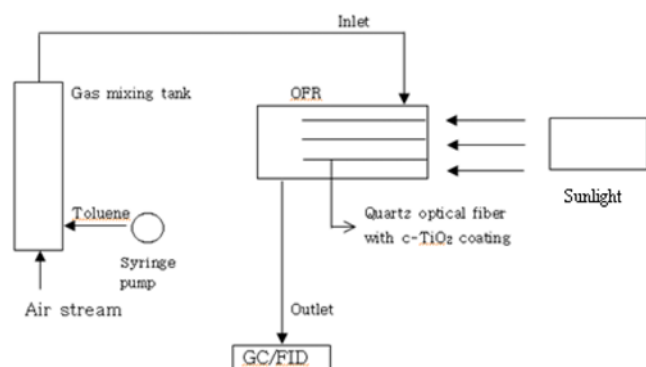


Fig. 1. Schematic diagram of the optical fiber reactor (OFR) system.

Table 1. Operation conditions of the OFR system

OFR reactor	Internal diameter (cm)	6
	Height (cm)	35
	Reactor volume (L)	1
Environmental conditions	Temperature (°C)	20-27
	Relative humidity (%)	70-95
	Empty bed retention time (s)	20
	Inlet concentration of toluene (ppm)	~200
	Light source	Sun
Optical fibers	Diameter (mm)	1
	Length (cm)	25

gaseous toluene was discharged to the photo reactor at 210-230 ppm, 25 °C. The photo reactor volume is a 1 L cylinder, which contains optical fibers. PCO was performed in the reactor with a TiO<sub>2</sub> film and solar irradiation, which was used as the visible light source. To determine the influence of sunlight intensity on toluene removal, removal efficiency of toluene was measured for different light intensities. The concentrations of the outlet toluene and the byproducts from the reactor through the PCO were analyzed by a gas chromatography-mass spectrometer (HP 6890, Hewlett Packard Co., CA, U.S.A.) with an HP-5MS column (model 19091S-143, Hewlett Packard Co., CA, U.S.A.). The RE (%) of gaseous toluene was evaluated as shown in Eq. (1) [13], and the concentration of VOC in the gas mixture can be calculated from ideal gas equations, i.e., (2) and (3).

$$Re = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

$$C_{(mg/m^3)} = \left( \frac{\rho R_1}{R} \right) \left( \frac{273}{T} \right) \left( \frac{P}{760} \right) \times 10^6 \quad (2)$$

$$C_{ppm} = 22.4 \times 10^6 \left( \frac{\rho R_1}{MR} \right) \left( \frac{273}{T} \right) \left( \frac{P}{760} \right) \quad (3)$$

Where  $C_i$  and  $C_f$  in the gas phase are defined as the initial and final concentrations of toluene (ppm), respectively,  $\rho$  is the specific gravity (g mL<sup>-1</sup>),  $M$  is the molecular weight (g mol<sup>-1</sup>),  $R$  and  $R_1$  are the flow rates of supplied air (L h<sup>-1</sup>) and of injected toluene (mL h<sup>-1</sup>), respectively,  $T$  is the temperature (K), and  $P$  is the pressure (Torr).

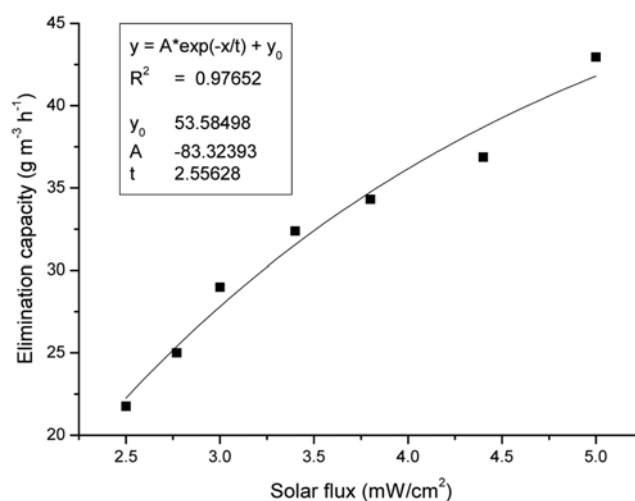


Fig. 2. Relationship between elimination capacity and solar flux (solar flux: 2.5-5.0 mW/cm<sup>2</sup>).

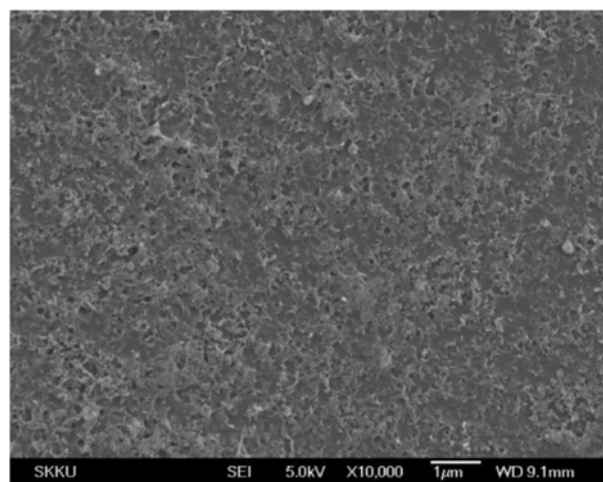


Fig. 3. SEM images of C-TiO<sub>2</sub> (carbon: 1.307 mg/ml of sol-gel solution).

## RESULTS AND DISCUSSION

### 1. Factors for Photocatalytic Activity Enhancement

C-TiO<sub>2</sub> photocatalytic activity was evaluated by the decomposition of gaseous toluene under visible light irradiation. All photocatalytic experiments were carried out on sunny days between 11 am to 3 pm in the months of May-June, 2010. Fig. 2 shows the relationship between elimination capacity and solar flux, which was 2.5-5.0 mW/cm<sup>2</sup> and depends on changes in sunlight with time. This solar flux is better than previously reported [7]. This result corresponded to that of a previous report regarding the relationship between toluene RE and light intensity [14]. The control of structure and particle size of the titania was reported by a factor of photocatalytic activity enhancement [15,16]. The synthesized carbon-doped TiO<sub>2</sub> corresponded to characteristic peaks of crystal anatase TiO<sub>2</sub> at 25.2°, 37.8° and 47.9° of 2θ as shown in Fig. 4. Compared with carbon-undoped TiO<sub>2</sub> film, the carbon-doped sample has an increased intensity due to its higher crystallinity [17]. As shown in Fig. 4, the

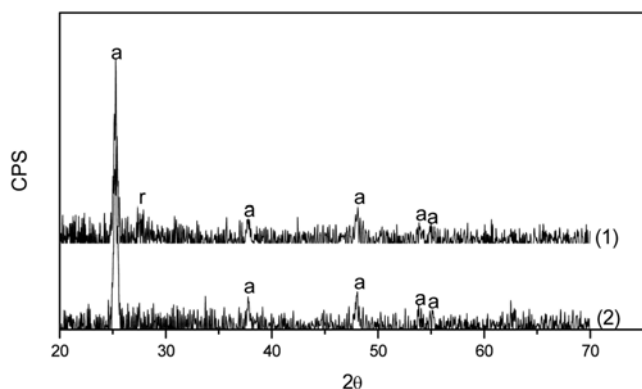


Fig. 4. XRD patterns of (1) carbon-undoped TiO<sub>2</sub> and (2) carbon-doped TiO<sub>2</sub> (a: anatase; r: rutile).

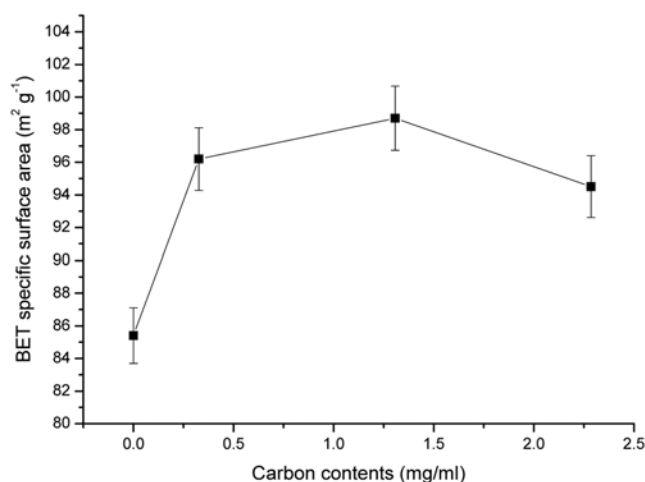


Fig. 5. Distribution of BET specific surface area of samples.

surface of the C-TiO<sub>2</sub> film was much coarser and there were many pores in the surface, due to the carbon nanopowders. The superior porosity of absorbent was helpful to improve the adsorption of gaseous toluene on the surfaces of the optical fibers. Among the procedure of preparation of porous C-TiO<sub>2</sub>, ultrasonic waves lead to increasing the chemical reactivity. The particles are aggregated like nano clusters, due to the enhanced chemical reactivity. The nano clusters in C-TiO<sub>2</sub> create nanostructured pores of various dimensions within the surface. As shown in Fig. 5, the BET specific surface area of C-TiO<sub>2</sub> (1.307 mg/ml sol-gel solution: 98.7 m<sup>2</sup> g<sup>-1</sup>) is higher than pure TiO<sub>2</sub> (85.4 m<sup>2</sup> g<sup>-1</sup>). Increase of BET specific surface area can absorb greater number of toluene molecules on the catalyst surface. This will improve the performance of the photocatalytic activity. Therefore, the carbon nanopowder was used not only as a carbon source for C-TiO<sub>2</sub>, but also to improve the performance of the photocatalyst. Thus, determining the optimum carbon mass is very important, due to its strong impact on the photocatalytic activity of TiO<sub>2</sub> and the surface adsorption to toluene.

## 2. Optimum Carbon Concentrations of C-TiO<sub>2</sub> Films

C-TiO<sub>2</sub> is a good photocatalyst in the visible light region. Irie et al. investigated the carbon states in the photocatalyst and found that there are two peaks of carbon related to binding energy [7]. One

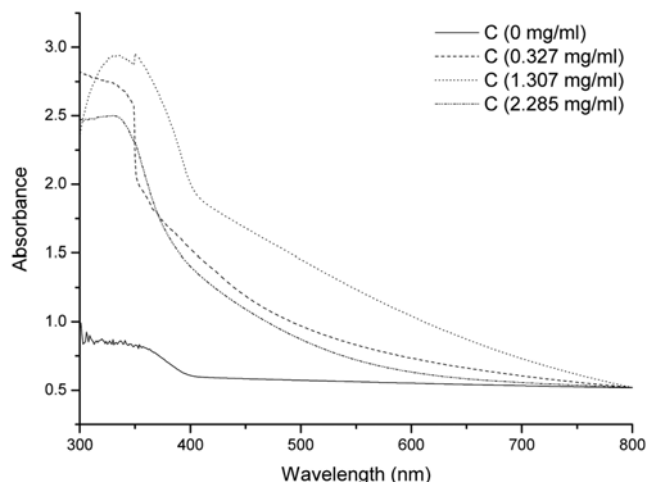


Fig. 6. UV-vis absorption spectra of C-TiO<sub>2</sub> film with various carbon nanopowders (carbon: 0.307 mg/ml, 1.307 mg/ml, 2.285 mg/ml of sol-gel solution).

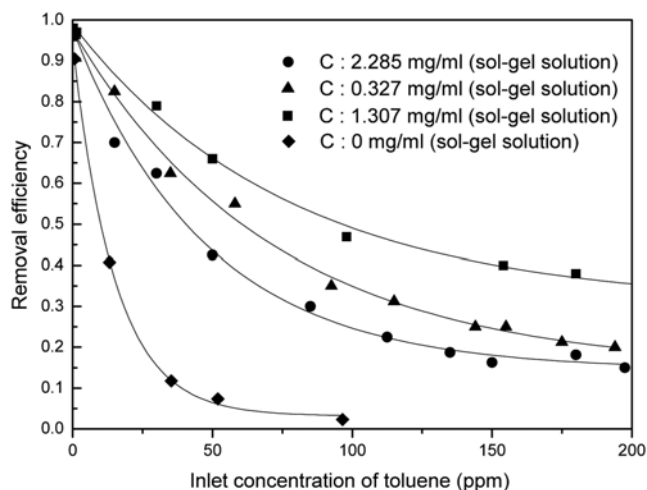


Fig. 7. The effects of C-TiO<sub>2</sub> synthesized by different carbon mass on photocatalytic degradation of toluene (flowrate=3 L/min, RH=40%, EBRT=20 s, T=24 °C).

peak is at 285 eV and another peak is at 276 eV, both of which correspond to carbon sources [18]. Therefore, the two peaks absorb visible light wavelengths. Compared with pure TiO<sub>2</sub>, it reveals that the new powerful absorption at 400-800 nm is related to the carbon content [19]. To investigate the optimum concentration of carbon nanopowder in C-TiO<sub>2</sub> films, various masses of carbon nanopowders were added to the TiO<sub>2</sub> sol-gel solution, i.e., 0.327 mg/ml, 1.307 mg/ml and 2.285 mg/ml. UV/Vis spectroscopy was used to analyze the absorbance of each C-TiO<sub>2</sub> film, as shown in Fig. 6. The C-TiO<sub>2</sub> synthesized by 1.307 mg/ml (sol-gel solution) showed the highest absorbance in the visible light region. In Fig. 7, we illustrate the effects of C-TiO<sub>2</sub> synthesized by different carbon masses on the degradation of toluene. The toluene inlet concentration ranges from 0 to 200 ppmv, and the C-TiO<sub>2</sub> synthesized using the 1.307 mg/ml sol-gel solution showed the best photocatalytic activity for the degradation of toluene. When the carbon mass was 0 mg/ml, photocatalytic activity showed worse toluene degradation efficiency.

## CONCLUSIONS

C-TiO<sub>2</sub> photocatalyst with a high photocatalytic activity was successfully synthesized by a sol-gel and combustion method using carbon nanopowders. The performance of an OFR was evaluated under experimental conditions for the photocatalytic degradation of toluene using C-TiO<sub>2</sub> catalysts. The factors for photocatalytic activity enhancement were evaluated, including solar flux and the morphological properties of C-TiO<sub>2</sub>. These results corresponded to those of previous reports. Absorbance according to various masses of carbon nanopowders was evaluated to obtain an optimum concentration of carbon in the C-TiO<sub>2</sub> films. The C-TiO<sub>2</sub> that was synthesized using the 1.307 mg/ml sol-gel solution showed better absorbance than other formulations in the visible light region. The toluene inlet concentration ranges from 0 to 200 ppm, and the C-TiO<sub>2</sub> synthesized by 1.307 mg/ml sol-gel solution showed the best photocatalytic degradation of toluene.

## ACKNOWLEDGEMENTS

This research was supported by the Ministry of Land, Transportation and Maritime Affairs (project no. 08-CTIP-B01), Republic of Korea.

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