

Photocatalytic Decomposition of Toluene Vapor by Bare and TiO₂-coated Carbon Fibers

Yuan Luo, Kwang-Dae Kim, Hyun Ook Seo, Myoung Joo Kim, Wei Sheng Tai, Kyu Hwan Lee,[†] Dong Chan Lim,[†]
and Young Dok Kim*

Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea. *E-mail: ydkim91@skku.edu

[†]Materials Processing Division, Korea Institute of Materials Science, Changwon 641-010, Korea

Received March 3, 2010, Accepted March 31, 2010

The photocatalytic decomposition of toluene vapor by bare and TiO₂-coated carbon fibers was studied. Atomic layer deposition (ALD) was used to perform the TiO₂ coating. We show that, under our conditions, the photocatalytic activity of bare carbon fibers was comparable with that of TiO₂ films, which are known to be good photocatalysts. The origin of the high photocatalytic activity of bare carbon fibers is discussed.

Key Words: Carbon fiber, Toluene, Photocatalysis, TiO₂, Atomic layer deposition

Introduction

The removal of organic pollutants using photocatalysts is an important issue in environmental science.¹ In many cases, semiconductive oxide materials such as TiO₂ are widely used as photocatalysts since they can efficiently yield electron-hole pairs by interacting with UV/visible light. The electrons and holes can create O₂⁻ and OH radicals, which are strong oxidizing agents that decompose organic pollutants.¹ TiO₂ can only absorb UV light due to its wide band gap, and therefore, its photocatalytic efficiency under sunlight is low. In the past, much effort has been made to improve the photocatalytic activity of TiO₂ using dopants, which can activate photocatalysts *via* irradiation with visible light.²⁻⁷ Among the various heterostructures consisting of TiO₂ and other materials, TiO₂/carbon nanostructures have recently attracted particular attention.^{4,5,7} It has been suggested that carbon can efficiently separate the electrons and holes in TiO₂.⁴ In contrast to TiO₂/carbon heterostructures, less attention has been paid to the photocatalytic activity of pure carbon structures, even though carbon nanostructures are regarded as efficient adsorbents of organic pollutants.^{8,9} Only very recently, photochemical reactivity of graphene was addressed.¹⁰

In the present work, the photocatalytic decomposition rates of toluene by bare and TiO₂-coated carbon fibers were studied. Atomic layer deposition (ALD) was used for the homogeneous growth of TiO₂ films on top of the carbon fibers. In the ALD process, two precursors are sequentially introduced, and only chemisorbed species can participate in the chemical reactions to form thin films.¹¹ Therefore, the film-growth is self-limiting, and precise control of the film thickness is possible. Also, thin films can be evenly deposited on top of complex structures using ALD. A direct comparison of the photocatalytic activities of bare and TiO₂-coated carbon fibers as a function of TiO₂ thickness was conducted. Bare carbon fibers showed a higher toluene photodecomposition rate than that of TiO₂ films with various thicknesses, indicating that carbon fibers can be used as efficient photocatalysts for removing volatile organic compounds (VOCs) from the indoor atmosphere.

Experimental

Papers consisting of carbon fibers purchased from Torray (060, paper thickness 170 μm) were used as substrates for TiO₂ thin films. TiO₂ films were coated onto the carbon fibers using ALD, in which H₂O and TTIP (titanium tetraisopropoxide) were used as precursors. N₂ was used as a carrier gas for the injection of both TTIP and H₂O. N₂ was also used as a purging gas for both precursors. The temperature of the TTIP and H₂O bottles were 80 °C and room temperature, respectively. The injection times for the TTIP and H₂O were both 15 seconds. The base pressure of the system was 1.5 mtorr, and after each purging step, a pressure of < 2.5 mtorr was maintained. During the injection of the precursors, the working pressures were 0.1 and 1 torr for the TTIP and H₂O, respectively. The sample temperature was maintained at 180 °C during deposition, and after synthesis of the thin films, the samples were annealed under vacuum at 500 °C for 3 hrs. Using ellipsometry with a Si wafer as the substrate, the deposition rate of TiO₂ was estimated to be 0.5 Å/cycle.

For characterization of the catalysts, Brunauer-Emmett-Teller (BET) measurements, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were used. The surface areas of the samples were determined using BET. The surfaces of the samples were characterized by XPS under ultra-high vacuum (UHV) conditions with a base pressure of 3 × 10⁻¹⁰ torr. For the XPS analysis, an Mg Kα source (1253.6 eV) was used, and XPS spectra were collected in the fixed-pass-energy mode using a concentric hemispherical analyzer (CHA). To determine the toluene adsorption reactivities of various samples and their photocatalytic activities, the experimental set-up described in Fig. 1 was used. The base pressure of the system was less than 1 × 10⁻⁴ torr. After evacuation of the system by a rotary pump and turbo pump *via* a leak valve, the gate valve between the two chambers was closed. Then, the first chamber (without a sample) was filled with toluene (5 mtorr), O₂ (20 mtorr), and N₂ (80 mtorr). As a function of the time passed after the gate valve was open, the changes in the partial pressures of toluene and O₂ with respect to that of N₂ were monitored by leaking a

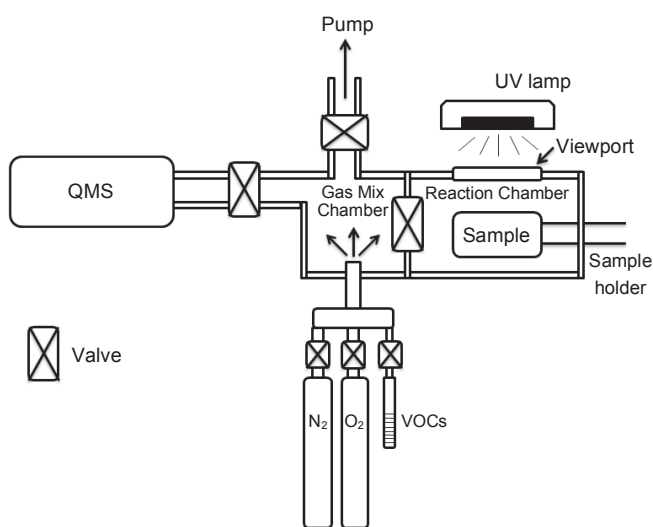


Figure 1. Experimental set-up used for measuring the photocatalytic decomposition rate of toluene. More detailed explanation about the experimental set-up can be found in the text.

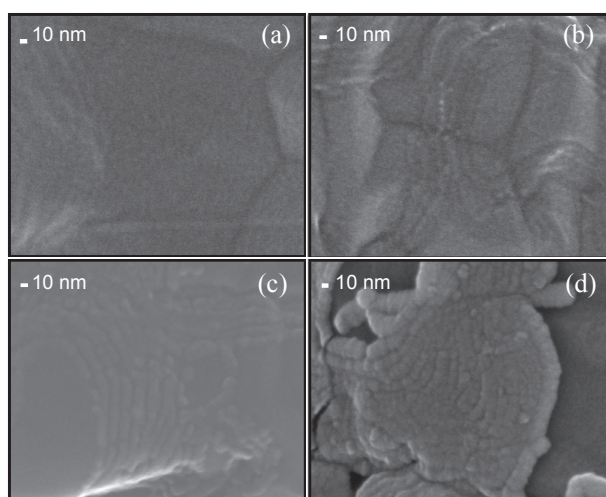


Figure 2. SEM images of bare (a) and TiO₂-coated (b-d) carbon fibers. For TiO₂ coating, the different numbers of ALD cycles (45, 180 and 500 cycles) were used, respectively. The white bar of each figure corresponds to 10 nanometers (nm).

small amount of gas from the reactor chamber into the high-vacuum chamber equipped with a quadrupole mass-spectrometer (QMS). For the first 30 minutes, the experiments were conducted in the dark, and in these experiments, no changes in the partial pressures of the reactants could be found. Then, the UV lamp (365 nm) was switched on to measure the photocatalytic activities of various samples for the decomposition of toluene. Only the changes in the partial pressures of the reactants in the presence of the UV irradiation were displayed in the present work.

Carbon fibers were also treated by high-energy e-beams from a linear electron accelerator under ambient conditions. The e-beam energy was 1.0 MeV, and the total exposure was varied from 5 to 15 kGy (Gy = J/Kg).

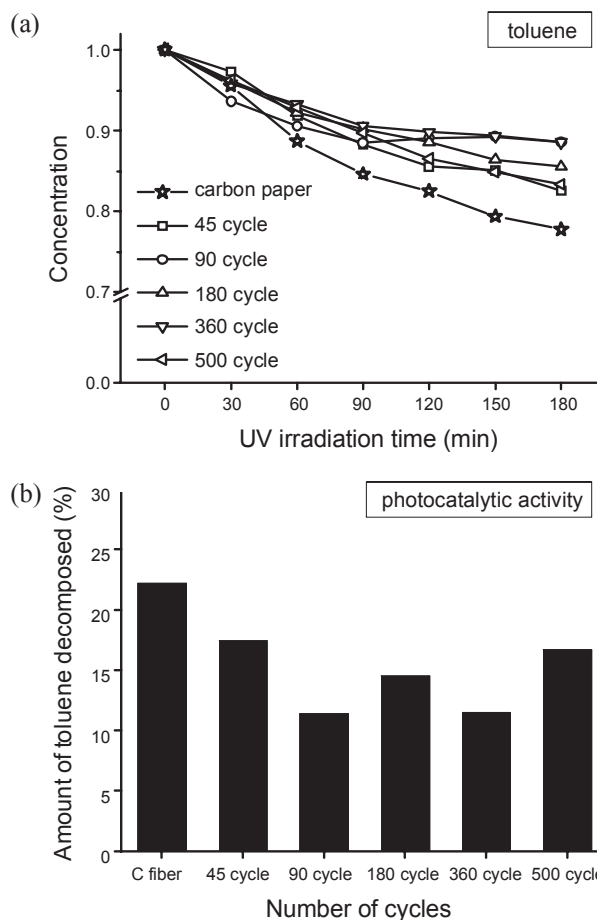


Figure 3. a) The activities of bare and TiO₂-coated carbon fibers for photocatalytic decomposition of toluene are compared. Number of ALD cycles used for the preparation of each sample is given in the figure. For each sample, change in the toluene/N₂ intensity ratio as a function of the UV irradiation time (3 hrs) was measured, and the result of each sample is displayed in a). The amounts of toluene decomposed for 3 hrs under UV irradiation using bare and TiO₂-coated carbon fibers as catalysts are compared.

Results and Discussion

Figure 2 shows SEM images of TiO₂-coated carbon fibers in which the diameter of the carbon fiber was estimated to be about 6 - 7 μm. A close inspection of the structure of various TiO₂/C surfaces using SEM reveals that TiO₂ particles selectively formed at steps of the carbon fiber. In contrast, flat terraces of the carbon fiber surface remained uncovered by TiO₂. When 180 ALD-cycles were used for the deposition of TiO₂, small nanoparticles of TiO₂ with an elongated shape were found. For the TiO₂ film deposited with 500 ALD-cycles, large domains of TiO₂ could be identified on the carbon. In the side view of the cut sample prepared with 500 ALD-cycles, the thickness of the TiO₂ coating was ~25 nm (data not shown). The surface area of each sample was estimated to be 0.4 ± 0.05 m²/g using BET, that is, no significant change in the surface area could be found upon deposition of TiO₂ onto carbon fibers using ALD. Using XPS, pronounced peak in the Ti 2p level spectra corresponding to the Ti (IV) state was identified, confirming formation of TiO₂ by the ALD process (data not shown).

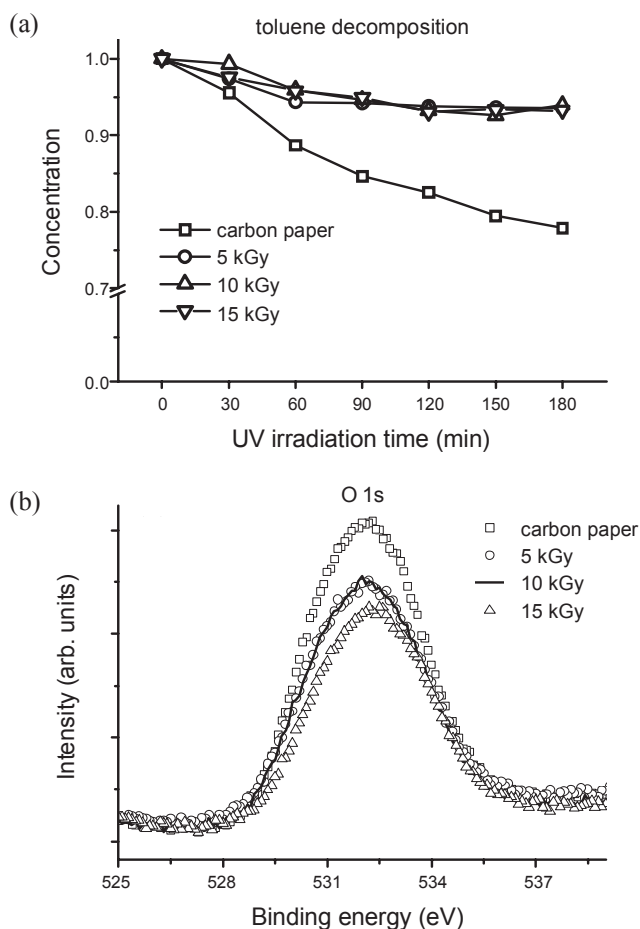


Figure 4. a) Photocatalytic activities of bare carbon fibers with various e-beam treatments (5, 10, and 15 kGy) for toluene decomposition. For samples with various e-beam treatments of catalysts, change in the toluene/ N_2 intensity ratio as a function of the UV irradiation time (3 hrs) was measured b) XPS results (O 1s spectra) of carbon fibers before and after e-beam irradiations (5, 10, and 15 kGy).

Figure 3 shows the photocatalytic activities of bare and TiO_2 -coated carbon fibers under irradiation of UV light. TiO_2 can photocatalytically decompose VOCs such as toluene, and, in line with the previous results, the photocatalytic decomposition of toluene by the TiO_2/C samples was observed.^{12,13} No significant change in the photocatalytic decomposition rate of toluene as a function of the TiO_2 thickness could be identified. Interestingly, the bare carbon fibers showed an even higher photocatalytic activity toward toluene decomposition than did those of the TiO_2 -coated fibers. During the reactivity measurement, evolution of the CO_2 and reduction of the partial pressure of O_2 was found. However, similar changes in the CO_2 and O_2 signals as a function of reaction time evolution were also found in the samples without toluene. The upper limit of the amount of CO_2 produced was less than 10% of the value expected based on the total oxidation of toluene, indicating that most of the toluene was only partially oxidized, and most likely the products of the partial oxidation (e.g., benzaldehyde, benzoic acid and other intermediates) would remain on the surfaces of the catalyst and the reactor wall.¹²⁻¹⁴ We have recently found using *in situ* XPS that carbonate species form on the surface of TiO_2 in the pre-

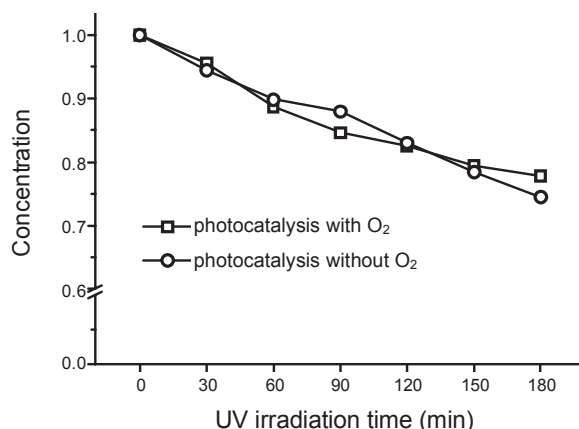


Figure 5. Photocatalytic removal of toluene during 3 hrs by carbon fibers in the presence and absence of O_2 are displayed.

sence of O_2 as a consequence of photo-induced oxidation of carbon on the surface, which could be responsible for the poisoning of the TiO_2 catalyst surfaces.¹⁵ In the case of graphene surfaces, photo-induced formation of the covalent bonds between organic molecules and graphene surfaces was identified.¹⁰

To shed light on the origin of the photocatalytic decomposition of toluene on bare carbon fibers, the photocatalytic activities of carbon fibers with various e-beam treatments were studied (Fig. 4). With increasing e-beam exposure, the photocatalytic activity decreased. In the XPS spectra, a decrease in the intensity of the O 1s peak could be found with increasing e-beam exposure (Fig. 4). No significant change in the C 1s spectrum was identified by the e-beam treatment.

Two different mechanisms can be suggested regarding the photocatalytic activity of bare carbon fibers. Based on the result of Fig. 4, oxygen impurities on the carbon fiber surfaces can be suggested to act as color centers, since decrease in oxygen concentration on the surface reduced the photocatalytic activity. Alternatively, defect sites of carbon fibers (most likely radicals with sp^3 hybridization of carbon) would be the reaction centers, which were cured by the e-beam treatment, resulting in the reduced photocatalytic activity by e-beam treatment.

It is worth mentioning that we have recently performed experiments on toluene adsorption and photo-decomposition on various carbon nanostructures including nanodiamond.¹⁵ Nanodiamond with sp^3 hybridization of carbon was found to be highly reactive for toluene adsorption at room temperature; however, no photocatalytic decomposition of toluene by nanodiamonds was identified. This result implies that defects of carbon network could act as adsorption sites of toluene, but not as an active center of photocatalytic decomposition of toluene. It is more likely that the oxygen impurities rather than carbon defect sites on carbon fibers could act as color centers, photocatalytically activating reactants (toluene) for decomposition. Further studies are needed for the identification of the structure of photocatalytically active site on carbon fiber surfaces.

It is also remarkable that the decomposition rate of toluene by carbon fibers in the absence of O_2 was comparable to that in the presence of 20 mtorr O_2 (Fig. 5). In contrast, when using

TiO₂, O₂ was required for the photocatalytic decomposition of toluene, most likely because the formation of O₂ under UV irradiation is important for the decomposition of toluene.^{1,4} The photocatalytic reaction mechanisms of TiO₂ and carbon fibers should be dissimilar, and further studies for elucidating the mechanism of the photocatalytic activity of carbon fibers are needed.

It is worth mentioning that we performed a similar reactivity experiment using commercially available TiO₂ P-25 samples from Degussa, and the photocatalytic decomposition rate of toluene on the P-25 samples normalized by surface area was comparable to those of the bare and TiO₂-coated carbon fibers found in the present work. We used 20 mtorr toluene, 40 mtorr O₂, and 160 mtorr N₂ when the P-25 was used as the photocatalyst. For the preparation of the catalysts, an aqueous suspension of TiO₂ powder was deposited onto glass and was oven-annealed for 1 hr at 120 °C. The numbers of toluene molecules decomposed for 3 hrs under UV light irradiation were 4.0×10^{13} and 7.0×10^{13} molecules/cm² for P-25 and bare carbon fibers, respectively. For the P-25 samples, the photodecomposition experiment was performed using 3 torr of O₂ instead of 40 mtorr, and a similar photodecomposition rate of toluene was found, indicating that in this O₂ partial pressure range, the photocatalytic activity is not very sensitive to the O₂ partial pressure. A direct comparison between the photocatalytic activities of P-25 and carbon fiber paper is difficult since the area of each sample directly exposed to UV light and the degree of UV penetration through the catalysts could be different due to the structural dissimilarity of the samples. However, these results, together with the comparison between the photocatalytic activity of the bare carbon fibers and those of the TiO₂-coated carbon fibers, suggest that photocatalytic activity of bare carbon fibers was significantly higher.

Conclusion

In summary, we found that bare carbon fibers can show

photocatalytic activity for the decomposition of toluene comparable to the activity of TiO₂ thin films. This result implies that bare carbon fibers can be used as photocatalysts for removing organic pollutants.

Acknowledgments. This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References

1. Hoffman, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
2. Awazu, K.; Fujimaki, M.; Rockstuhl, C.; Tominaga, J.; Murakami, H.; Ohki, Y.; Yoshida, N.; Watanabe, T. *J. Am. Chem. Soc.* **2008**, *130*, 1676.
3. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
4. Zhang, L.-W.; Fu, H.-B.; Zhu, Y.-F. *Adv. Funct. Mater.* **2008**, *18*, 2180.
5. Woan, K.; Pyrgiotakis, G.; Sigmund, W. *Adv. Mater.* **2009**, *21*, 2233.
6. Chen, X.; Burda, C. *J. Am. Chem. Soc.* **2008**, *130*, 5018.
7. Fu, P.; Luan, Y.; Dai, S. *J. Mol. Catal. A: Chemical.* **2004**, *221*, 81.
8. Yi, F.-Y.; Lin, X.-D.; Chen, S.-X.; Wei, X.-Q. *J. Porous Mater.* **2009**, *16*, 521.
9. Chiang, Y.-C.; Chiang, P.-C.; Huang, C.-P. *Carbon.* **2009**, *39*, 523.
10. Liu, H.; Ryu, S.; Chen, Z.; Steigerwald, L.; Nuckolls, C.; Brus, L. E. *J. Am. Chem. Soc.* **2009**, *131*, 17099.
11. Ritala, M.; Leskela, M. in *Handbook of Thin Film Materials*; Nalwa, H. S., Ed.; Academic Press: San Diego, U.S.A., 2002; Vol. 6, pp 103-153.
12. Guo, T.; Bai, Z.; Wu, C.; Zhu, T. *Appl. Catal. B: Environmental* **2008**, *79*, 171.
13. Maira, A. J.; Yeung, K. L.; Soria, J.; Coronado, J. M.; Belver, C.; Lee, C. Y.; Augugliaro, V. *Appl. Catal. B: Environmental* **2001**, *29*, 327.
14. Sleiman, M.; Conchon, P.; Ferronato, C.; Chovenlon, J.-M. *Appl. Catal. B: Environmental* **2009**, *86*, 159.
15. Seo, H. O.; Kim, Y. D. unpublished results. **2010**.