Adsorption and photocatalytic degradation of methylene blue over TiO_2 films on carbon fiber prepared by atomic layer deposition

Nilay Kumar Dey[a], Myoung Joo Kim[a], Kwang-Dae Kim[a], Hyun Ook Seo[a], Dongwun Kim[a], Young Dok Kim[a,*], Dong Chan Lim[b], Kyu Hwan Lee[b]

[a] Department of Chemistry, Sungkyunkwan University, Cheoncheon-dong, Jangan-gu, Suwon 440-746, Republic of Korea
[b] Materials Processing Division, Korea Institute of Materials Science, Changwon 641-010, Republic of Korea

ARTICLE INFO

ABSTRACT

TiO_2 films were grown on carbon fiber by atomic layer deposition (ALD), and adsorption and photocatalytic decomposition of methylene blue (MB) on these TiO_2 films were studied. They showed very high adsorption capacities of MB, indicating that these films can be used as adsorbents for removing organic dyes under dark conditions. The adsorption capacities of used TiO_2 films could be regenerated by light exposure through the photocatalytic degradation of the adsorbed MB.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous photocatalysis has been proposed as a method of mineralizing various environmental organic pollutants in gases and liquids [1–7]. Semiconductors such as TiO_2 are widely used as photocatalysts as electron–hole pairs are easily induced by light exposure [6,7] which can create $O_2{}^-$ and OH radicals in air. These radicals can decompose liquid and gaseous organic pollutants [6,7]. TiO_2's wide band gap of 3.2 eV allows it to absorb only UV light, reducing its photocatalytic efficiency in sunlight [6,7]. Much effort has been made to improve its photocatalytic activity through dopants, which can allow photocatalysis with visible light irradiation [4,8–20]. Among various heterostructures consisting of TiO_2 and other materials, TiO_2/carbon nanostructures have recently attracted particular attention [8,17–20] as carbon can efficiently separate the electrons and holes in TiO_2 [17]. Incorporation of carbon increases the absorption of visible light, as it yields additional band gap states in the electronic structure of TiO_2 [1,10,19,20]. However, during application, problems arise from the use of fine TiO_2 powders: the separation of the photocatalyst from the reaction medium is difficult and particulate suspensions are not easily applicable in continuous processes. As an alternative to TiO_2 powders, TiO_2 films on fibers can be used as photocatalytic filters without suffering these problems.

In addition to photocatalysis, high surface area adsorbents can be used for removing organic pollutants from liquids and gases [21–32]. A disadvantage of removing pollutants with adsorbents is that an adsorbent is limited by its adsorption capacity. In contrast, photocatalysts can be used permanently, providing surface poisoning does not occur. Used adsorbents should be able to be efficiently regenerated. The adsorption capacities of used adsorbents can be recovered by thermal and electrochemical treatments [27–31].

Carbon based materials, such as activated carbon and carbon fibers, have been considered as potential materials for removing volatile organic compounds by adsorption, largely due to their high surface areas. Their mechanical strength and high thermal and chemical stabilities allow carbon fibers to be applied as high-temperature gas filters, electrodes and anti-static components [33].

This work studies the adsorption and photocatalytic degradation of methylene blue (MB) by bare and TiO_2-coated carbon fibers. Atomic layer deposition (ALD) was used for the homogeneous growth of TiO_2 films on the carbon fibers. TiO_2 films have very high MB adsorption capacities under dark conditions. In addition, they are photocatalytically active. Combining their high adsorption capacities and photocatalytic activities, TiO_2 films on carbon fibers can be used to adsorb organic dyes and subsequently be regenerated by light exposure under ambient conditions.

* Corresponding author. Tel.: +82 31 299 4564; fax: +82 31 290 7075.
E-mail address: ydkim91@skku.edu (Y.D. Kim).

2. Experimental

2.1. Preparation of TiO$_2$ films

TiO$_2$ films were deposited on carbon fibers using a flow-type atomic layer deposition (ALD) reactor, where two precursors (titanium tetraisopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$) as a metal precursor and H$_2$O as oxidizing agent), were separately introduced into the chamber. The growth was self-limiting, as only precursors chemisorbed on the surface could participate in film growth. The growth rate of TiO$_2$ is typically 0.2–0.6 Å/cycle, depending on the experimental parameters [34]. In this work, carbon papers (TPGH060, Torray) of specific area (0.4 m^2 g^{-1}, determined by BET) were used as substrate. The process used high purity N$_2$ (99.999%) as a carrier and purging gas of both precursors. For each ALD cycle, TTIP and H$_2$O pulses were injected for 60 and 5 s at working pressures of 0.1 and 1.0 Torr, respectively. During deposition, the base pressure of the ALD reactor was <5 mTorr and the temperature of the TTIP bottle was 80 °C, whereas that of H$_2$O was room temperature. Samples were maintained at 180 °C during film deposition. After preparation of TiO$_2$ thin films, the samples were annealed under vacuum at 500 °C for 3 h. The BET-measured surface area remained almost constant (± 0.1 m^2/g) regardless of the amount of TiO$_2$ deposited.

2.2. Characterization

The samples' surfaces were characterized by X-ray photo-electron spectroscopy (XPS) under ultra-high vacuum conditions with a base pressure of 3×10^{-10} Torr. All XPS spectra in this work were obtained at room temperature using a Mg Kα-source (1253.6 eV). The XPS spectra were collected in fixed-pass-energy mode using a concentric hemispherical analyzer (CHA, PHOIBOS-Hsa3500, SPECS). The aperture of the analyzer was located normal to each sample's surface, separated by 35 mm. Surface morphological images of the TiO$_2$ films were acquired by scanning electron microscopy (SEM) at 15 kV. Due to a low surface area and thickness of TiO$_2$, crystal structure of TiO$_2$ was hardly identified using X-ray Diffraction (XRD). However, TiO$_2$ thin films prepared using the same method as that of the present work on other substrates were identified to be in the anatase phase by XRD and transmission electron microscopy (TEM) independent of the substrate [35].

2.3. Adsorption, photodegradation, and cyclic adsorption experiments

Comparative studies of the catalysts' adsorptions and photocatalytic activities were performed using aqueous MB (C$_{16}$H$_{18}$N$_3$Cl, Shinyo Pure Chemicals Co. Ltd) under dark condition and UV light irradiation at room temperature, respectively. In each experiment, a 50 mg paper of bare or TiO$_2$-coated carbon fibers with an area of 6 cm^2 was placed at the bottom of a Petri-dish with 12 ml MB aqueous solution (0.5 mg L^{-1}). The amount of MB adsorbed on the samples (adsorption capacity) was determined from time-dependent measurement of MB concentration by UV/vis spectrometry (MECASIS, 2120 UV). For comparison, adsorption of MB on 50 mg of bare carbon fiber and TiO$_2$ (p-25 Daegussa, Anatase ~85%, Rutile ~15%, 0.5 mg, 55 m^2/g in BET surface area) powder were studied under the same conditions [36].

During photocatalytic degradation using the TiO$_2$ films (400 and 800 ALD cycles), UV light ($\lambda_{max} = 365$ nm, 0.27 W) was irradiated with a distance of 2 cm between sample and light source. The variation of MB concentration with illumination time was monitored by measuring the absorbance at 666 nm using a UV/vis spectrometer at 10 min intervals.

Adsorption of MB on carbon fibers coated with 800 cycles of ALD of TiO$_2$ was studied with an initial MB concentration of 2 mg L^{-1}.

After 3 h, saturation of MB adsorption was observed. The saturated sample was exposed to UV (365 nm, 0.27 W) light for 1 h, and the MB adsorption experiment subsequently repeated. These experiments studied the recovery of adsorption capacity of the used TiO$_2$/carbon fibers by the photocatalytic degradation of the adsorbed MB.

3. Results and discussion

The SEM images of Fig. 1 show the morphologies of bare and TiO$_2$-coated carbon fibers with various amounts of TiO$_2$. Carbon fibers were of 6–7 μm mean thickness with their microscopic structures preserved with increasing TiO$_2$ deposition (Fig. 1a). After 800 ALD cycles, cracks associated with the TiO$_2$ films were observed, most likely caused by the strain of the curvature of carbon fibers (Fig. 1a). The samples of Fig. 1a have higher magnification SEM images in Fig. 1b. The bare carbon fiber surface was composed of flat and stepped parts. 50 cycles of ALD only deposited TiO$_2$ on the steps, implying their preferential covering by TiO$_2$. With increasing the amount of TiO$_2$ deposited, the sizes of the TiO$_2$ domains increased. After 800 ALD cycles, the carbon fiber surface was completely covered by TiO$_2$.

XPS data are shown in Fig. 2a, indicating that the surfaces of these samples contained titanium, oxygen, and carbon; all of which originated from the TiO$_2$ films and carbon fibers. Spectra of individual lines of Ti 2p and C 1s were measured at a higher resolution with the results displayed in Figs. 2b and c. With increasing number of ALD cycles, the intensity of the Ti 2p spectrum increased. The Ti 2p$_{3/2}$ peak centered at 459.1–459.6 eV suggests that Ti was totally oxidized to Ti (IV), i.e. TiO$_2$. It is noteworthy that the Ti 2p peak was shifted to higher binding energies with increasing number of ALD cycles, correlated to the increased thicknesses of the TiO$_2$ layers: the final-state charging effect becomes more pronounced with the increased thicknesses of TiO$_2$ layers, resulting in a positive core level shift [37].

The C 1s spectra of various TiO$_2$/carbon fiber surfaces were normalized with respect to the maximum intensity of each spectrum. With increasing ALD cycles, the additional state of the spectra at approximately 286–88 eV became more pronounced [38]. These additional states can be assigned to C atoms associated with TiO$_2$. A positive chemical shift of the C 1s state by TiO$_2$ can be partially explained by the charging effect as a consequence of the low conductivity of TiO$_2$. On the other hand, the C 1s state centered at ~289 eV is related to oxidized carbon (C=O), i.e. carbon atoms on TiO$_2$ are partially oxidized.

MB adsorption on bare carbon fibers and carbon fibers coated by 50, 100, 200, 400, and 800 cycles of ALD of TiO$_2$ deposition were studied under dark conditions, and the results are presented in Fig. 3. Increasing TiO$_2$ thickness led to increased adsorption capacity of MB. For the TiO$_2$ films deposited by up to 400 ALD cycles, a rapid adsorption of MB at the initial stage of each experiment was observed before slowing as reaction time reached 20–30 min. In contrast, the surface deposited by 800 cycles had an adsorption rate of MB almost unvarying with reaction time (Fig. 3). When both TiO$_2$ and carbon were exposed on the surface, i.e. for up to 400 ALD cycles (Fig. 1b), adsorption of MB was fast, most likely due to the more rapid uptake of MB by TiO$_2$/C interface sites. Terraces of TiO$_2$ domains were less reactive than the periphery sites so that MB adsorption on the flat part of the TiO$_2$ surface took place more slowly. 800 ALD cycles of TiO$_2$ completely coated the carbon surfaces, slowing MB uptake throughout the adsorption test.

For comparison, TiO$_2$ (p-25) was used for the MB adsorption experiment, in which the adsorption capacity of MB was found to be much lower than those of TiO$_2$/carbon fiber samples, i.e. the high adsorption capacity of MB is a unique characteristic of ALD-made TiO$_2$ films, which cannot be found in p-25.
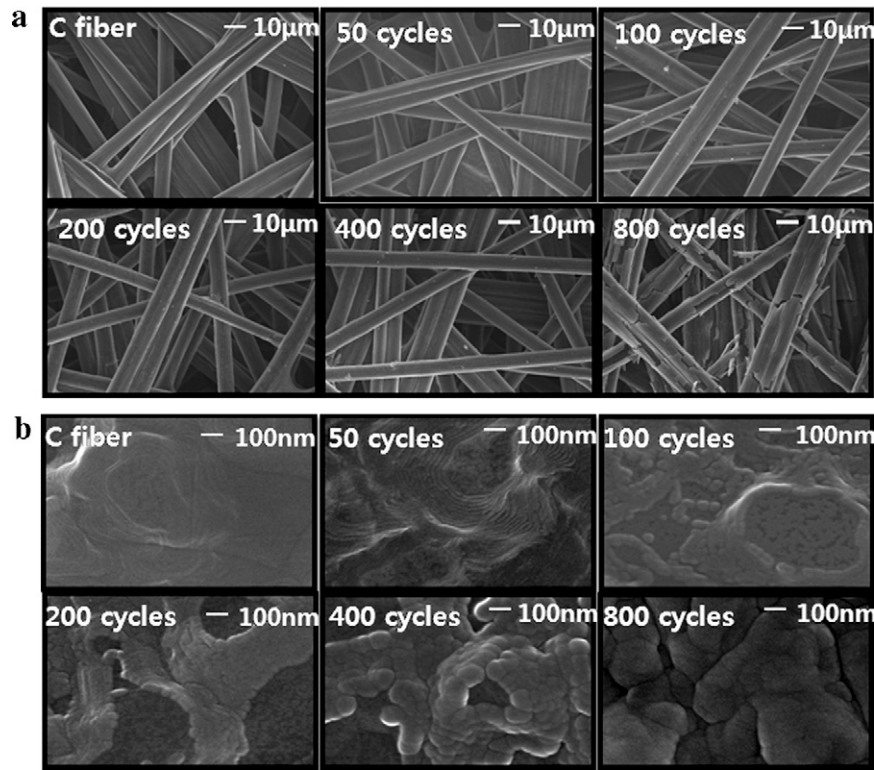
Fig. 1. SEM images of bare and various TiO_2-coated carbon fibers at magnifications of (a) ×3000 and (b) ×150,000 times. Number of ALD cycles used for preparing each sample is shown in the figure.

The origin of this high MB adsorption capacity was studied through the O 1s spectrum of TiO_2 (p-25) and the TiO_2-coated carbon fibers fabricated by 800 ALD cycles (Fig. 4). Each O 1s spectrum consists of three chemical states of oxygen: the lattice oxygen of TiO_2 (531 eV), –OH groups on TiO_2 (532.7 eV) and C–O bonds (533.9 eV) [39]. The OH-groups on the surfaces of TiO_2 films can be attributed to the reaction of adsorbed H_2O with TiO_2 (e.g. $H_2O + Ti–O–Ti \rightarrow 2Ti–OH$). Since water was used as precursor for
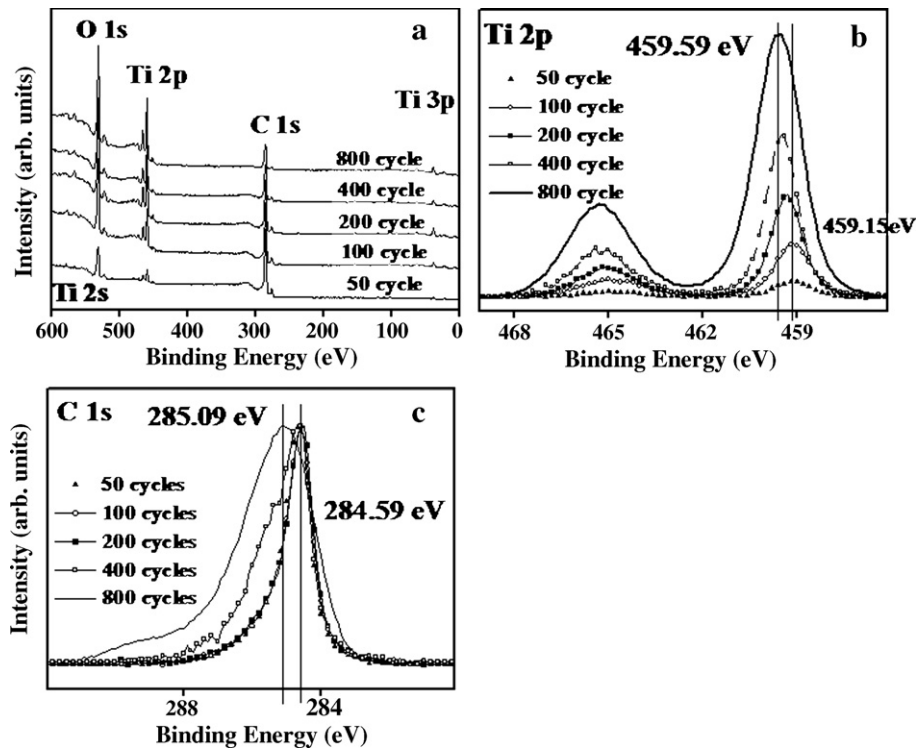
Fig. 2. (a) XPS spectra for the surfaces of various TiO_2-coated carbon fibers. Number of ALD cycles used for preparing each sample is shown in the figure. XPS spectra of individual lines of (b) Ti 2p and (c) C 1s measured at higher resolution, respectively.
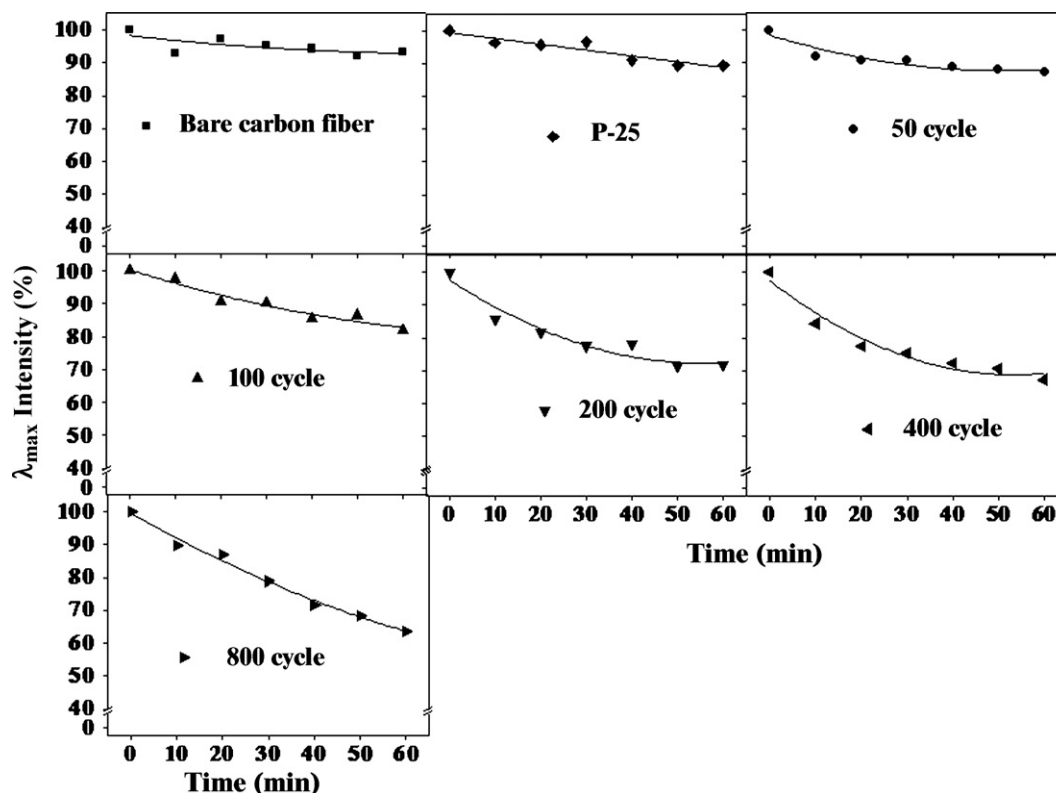
Fig. 3. Change in MB concentration with time for unlit MB adsorption using bare carbon fibers, TiO$_2$ (p-25) powder and various TiO$_2$-coated carbon fibers.

oxidizing TTIP, high concentrations of OH-groups on the TiO$_2$ thin films are expected. Fig. 4 shows more –OH groups on the surfaces of TiO$_2$ films than on p-25. It has recently been shown that a higher OH-group population on the surface of TiO$_2$ can increase its toluene adsorption capacity [39]. It can be suggested that OH-groups on the surface of TiO$_2$ can also enhance its MB adsorption capacity.

The TiO$_2$ thin films created here not only showed high adsorption capacities of MB, but also photocatalytic activity. Changes in MB concentration under UV irradiation were measured for the two most heavily coated carbon fibers, and the results are compared with those of a similar test without illumination for the same samples in Fig. 5. UV light greatly affected how MB concentra-

tion progressed with time. For the sample with 400 cycles of ALD without illumination, MB concentration initially rapidly decreased, attributable to a fast uptake of MB at TiO$_2$/C periphery sites, as aforementioned However, in the presence of UV light the initial fast adsorption of MB was suppressed, most likely by UV (or thermally)-induced desorption of MB from the surface. The decrease of MB concentration with time was linear in the presence of UV light, and after 60 min, the amount of MB removed under UV irradiation was 10% greater than that without illumination. The sample with 800 cycles of ALD for TiO$_2$ deposition also decreased MB concentration in the presence of UV light significantly more quickly than in its absence. This implies that under UV light, MB was decomposed by photocatalytic reactions, i.e. that these TiO$_2$ films were photocatalytically active.

The sample with carbon fibers coated with 800 cycles of ALD of TiO$_2$ was studied by XPS before and after reaction with MB in the presence and absence of UV light (Fig. 6). The results in Fig. 6 show that S could be identified on the TiO$_2$ film's surface after dark condition experiments, indicating that MB adsorbed on to TiO$_2$ thin film. However, S was not found after experiments under UV light irradiation, indicating that the decrease of MB concentration with UV is not related to the adsorption of MB on the surface, but to its photocatalytic decomposition. In the presence of UV light, MB adsorption was suppressed, and its photocatalytic decomposition observed.

Combining the high MB adsorption capacities and photocatalytic reactivities of these TiO$_2$ thin films, adsorption of MB under dark conditions was attempted, followed by the photocatalytic regeneration of the film's adsorption capacity. The sample of carbon fibers coated by 800 cycles of ALD of TiO$_2$ was used for this test. After 3 hrs, adsorption of MB on the surface was saturated (Fig. 7), and further immersion in fresh MB solution resulted in no further adsorption. When this saturated TiO$_2$ film was exposed to UV light under ambient conditions for 1 hr, and then immersed in fresh MB
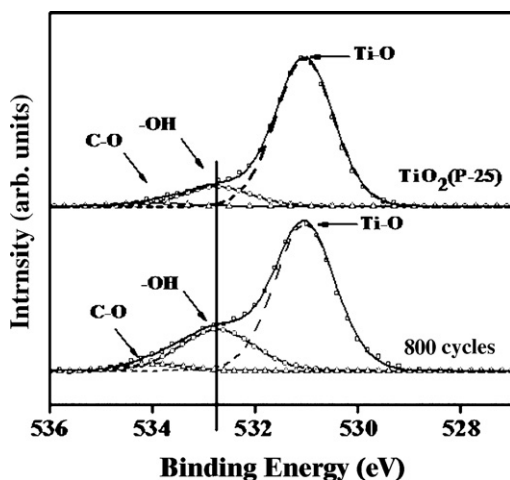

Fig. 4. XPS O 1s spectra of carbon fibers coated with 800 cycles of ALD of TiO$_2$ and TiO$_2$ (p-25) powder surfaces. Each spectrum was decomposed into three components consisting of Lorentzian and Gaussian functions.
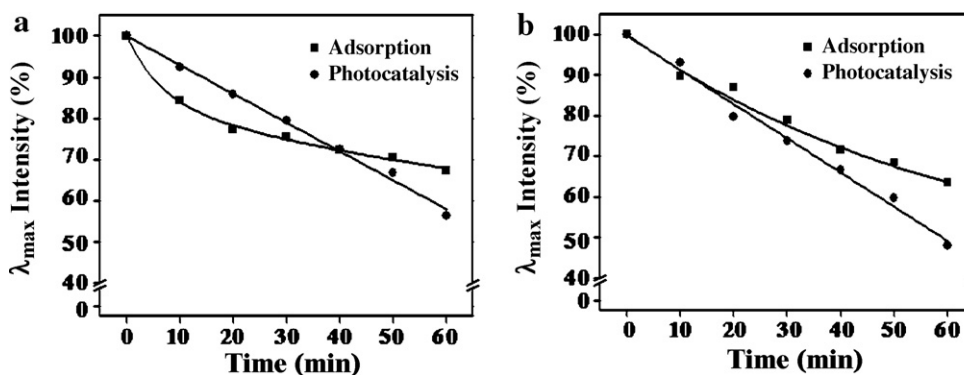
Fig. 5. Changes in MB concentration caused by unlit adsorption and photocatalytic degradation of MB (by UV 365 nm) using carbon fibers coated with 400 (a) and 800 (b) cycles of ALD of TiO₂ deposition.
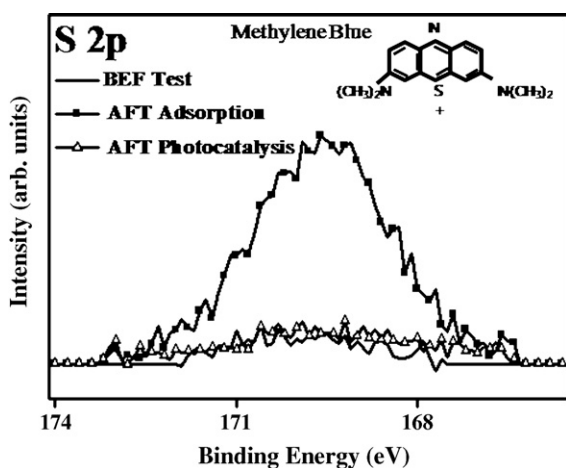

Fig. 6. S 2p spectra of carbon fibers coated with 800 cycles of ALD of TiO₂. The spectrum of the as-prepared sample, that taken after adsorption of MB under dark conditions, and that taken after photocatalysis under UV light, are compared.
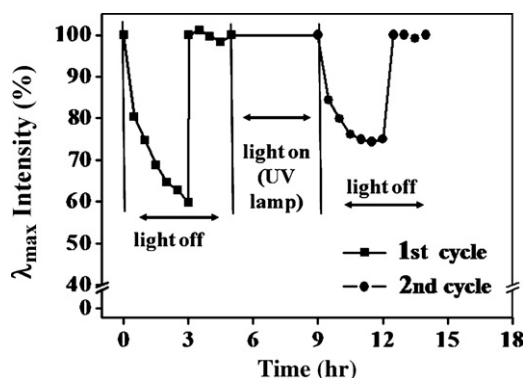

Fig. 7. Cyclic adsorption performance of carbon fibers coated with 800 cycles of ALD of TiO₂.

solution, further adsorption of MB was observed. This implies that these TiO₂ films can remove MB from liquid by adsorption, and that their adsorption capacities can be recovered by photocatalytic decomposition of MB in air.

4. Conclusions

Various TiO₂ films deposited on carbon fiber by ALD, in which TTIP and water were used as precursors, showed both high adsorption capacities of MB and photocatalytic activities to decompose MB under UV light. Using such films, MB was removed from aque-

ous solution under dark conditions by adsorption, and subsequent UV light irradiation photocatalytically regenerated their adsorption capacities.

References

[1] A. Hagfeldt, M. Graetzel, Chem. Rev. 95 (1995) 49–68.
[2] A.L. Linsebigler, L. Guangquan, J.T. Yates, Chem. Rev. 95 (1995) 735–758.
[3] D.S. Bhatkhande, V.G. Pangarkar, A. Beenackers, J. Chem. Technol. Biotechnol. 77 (2002) 102–116.
[4] X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.
[5] A. Fujishima, K. Honda, Nature 238 (1972) 37–38.
[6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemannt, Chem. Rev. 95 (1995) 69–96.
[7] J.T. Yates, Surf. Sci. 603 (2009) 1605–1612.
[8] K. Woan, G. Pyrgiotakis, W. Sigmund, Adv. Mater. 21 (2009) 2233–2239.
[9] X. Chen, C. Burda, J. Am. Chem. Soc. 130 (2008) 5018–5019.
[10] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269–271.
[11] G. Colon, M.C. Hidalgo, J.A. Navio, A. Kubacka, M. Fernandez-Garcia, Appl. Catal. B: Environ. 90 (2009) 633–641.
[12] G. Colon, M. Maicu, M.C. Hidalgo, J.A. Navio, A. Kubacka, M. Fernandez-Garcia, J. Mol. Catal. A: Chem. 320 (2010) 14–18.
[13] A. Kubacka, G. Colon, M. Fernandez-Garcia, Appl. Catal. B: Environ. 95 (2010) 238–244.
[14] S. Tojo, T. Tachikawa, M. Fujitsuka, T. Majima, J. Phys. Chem. C 112 (2008) 14948–14954.
[15] T. Morikawa, T. Ohwaki, K.I. Suzuki, S. Moribe, S. Tero-Kubota, Appl. Catal. B: Environ. 83 (2008) 56–62.
[16] F. Fresno, M.D. Hernandez-Alonso, D. Tudela, J.M. Coronado, J. Soria, Appl. Catal. B: Environ. 84 (2008) 598–606.
[17] L.-W. Zhang, H.-B. Fu, Y.-F. Zhu, Adv. Funct. Mater. 18 (2008) 2180–2189.
[18] Y.Z. Long, Y. Lu, Y. Huang, Y.C. Peng, Y.J. Lu, S.Z. Kang, J. Mu, J. Phys. Chem. C 113 (2009) 13899–13905.
[19] C.S. Kuo, Y.H. Tseng, C.H. Huang, Y.Y. Li, J. Mol. Catal. A: Chem. 270 (2007) 93–100.
[20] S.-H. Wang, T.-K. Chen, K.K. Rao, M.-S. Wong, Appl. Catal. B: Environ. 76 (2007) 328–334.
[21] G.-Y. Oh, Y.-W. Ju, H.-R. Jung, W.-J. Lee, J. Anal. Appl. Pyrol. 81 (2008) 211–217.
[22] F.-Y. Yi, X.-D. Lin, S.-X. Chen, X.-Q. Wei, J. Porous Mater. 16 (2009) 521–526.
[23] N. Mohan, G.K. Kannan, S. Upendra, R. Subha, N.S. Kumar, J. Hazard. Mater. 168 (2009) 777–781.
[24] Y.-C. Chiang, P.-C. Chiang, C.-P. Huang, Carbon 39 (2001) 523–534.
[25] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, Appl. Catal. B: Environ. 46 (2003) 453–462.
[26] G. Crini, Prog. Polym. Sci. 30 (2005) 38–70.
[27] A. Bagreev, H. Rahman, T.J. Bandosz, Carbon 39 (2001) 1319–1326.
[28] N.W. Brown, E.P.L. Roberts, A.A. Garforth, R.A.W. Dryfe, Electrochim. Acta 49 (2004) 3269–3281.
[29] C.-H. Weng, M.-C. Hsu, Sep. Pur. Technol. 64 (2008) 227–236.
[30] J. Carratalá-Abril, M.A. Lillo-Ródenas, A. Linares-Solano, D. Cazorla-Amorós, Chem. Eng. Sci. 65 (2010) 2190–2198.
[31] Y. Han, X. Quan, X. Ruan, W. Zhang, Sep. Pur. Technol. 59 (2008) 43–49.

[32] E.A. El-Sharkawy, A.Y. Soliman, K.M. Al-Amer, J. Colloid Interface Sci. 310 (2007) 498–508.

[33] H. Matsumoto, Membrane 35 (2010) 113–118.

[34] D.M. King, X. Liang, Y. Zhou, C.S. Carney, L.F. Hakim, P. Li, A.W. Weimer, Powder Technol. 183 (2008) 356–363.

[35] K.-D. Kim, N.K. Dey, Y.D. Kim, in preparation.

[36] M. Kim, K.-D. Kim, W. Tai, H. Seo, Y. Luo, Y. Kim, B. Lee, O. Park, Catal. Lett. 135 (2010) 57–61.

[37] W.F. Egelhoff, Surf. Sci. Rep. 6 (1987) 253–415.

[38] S.F.S.J.F. Moulder, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc., Minnesota, 1995.

[39] Y. Luo, W.S. Tai, H.O. Seo, K.-D. Kim, M.J. Kim, N.K. Dey, Y.D. Kim, K.H. Choi, D.C. Lim, Catal. Lett. 138 (2010) 76–81.