Preparation of MWCNT/TiO_2 Composites by Using MWCNTs and Titanium(IV) Alkoxide Precursors in Benzene and their Photocatalytic Effect and Bactericidal Activity

Won-Chun Oh,[†,*] Feng-Jun Zhang,[†,‡] and Ming-Liang Chen[†]

[†]*Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam-do 356-706, Korea*
[*]*E-mail: wc_oh@hanseo.ac.kr*
[‡]*Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Anhui Hefei, 230022, P. R. China*
Received July 30, 2009, Accepted September 14, 2009

In this present paper, we prepared MWCNT/TiO_2 composites by using pre-oxidized multi-walled carbon nanotubes (MWCNTs) with different titanium alkoxide precursors in benzene solvent. The composites were comprehensively characterized by BET surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX) and UV-Vis absorption spectroscopy. The photoactivity of the prepared materials, under UV irradiation, was tested using methylene blue (MB) in aqueous solution. Finally, according to the results of MB removal experiment, it can be considered that the MB degradation infect mainly caused by photocatalytic effect of TiO_2. Furthermore, the bactericidal test of the composites was also determined. It was indicated that MWCNT/TiO_2 composites with sunlight had greater effectiveness for *B. cereus*, *S. aureus* and *E. coli* than any other experimental conditions.

Key Words: MWCNTs, Titanium alkoxide, TEM, Photocatalytic decomposition, Bactericidal activity

Introduction

Water pollution has become a global concern threatening the survival of human beings. Effluents discharged from textile industries, including azo dyes and phenyl matters, contain toxic organic chemicals,[1] which are resistant to decomposition by biological treatment methods.[2,3] Photocatalysis is a novel method for the treatment of air and water pollutants.[4] Many researchers have done a lot of works in this field.[5-9]

Since the discovery of photoelectrochemical water splitting over titanium dioxide (TiO_2) electrode by Fujishima and Honda in 1972,[10] titanium dioxide (TiO_2) have been acting as an important semiconductor material, which has been applied as white pigment, cosmetic, catalyst and carrier owing to its excellent physical and chemical properties.[11-15] One of its most important applications is to act as photocatalyst for some chemical reactions, especially for the decontamination of water polluted with organic pollutants.[16-20] TiO_2/UV catalytic system has been widely investigated in the heterogeneous photocatalytic process. As a good support for nanomaterials, multi-walled carbon nanotubes (MWCNTs) have been widely investigated due to their high mechanical[21] and chemical[22] stability and their mesoporous character which favors the diffusion of reacting species. On the other hand, TiO_2/MWCNT composites have also obtained many attentions which could create many active sites for the photocatalytic degradation. Different techniques have already been used to obtain TiO_2/MWCNT composites. Jitianu and his coworkers coated MWCNTs with anatase by a sol-gel method using classical alkoxides as precursors;[23] Wang *et al.* prepared TiO_2/MWCNT composites with MWCNTs embedded in TiO_2 nanoparticles by a modified sol-gel method, and investigated their activity in photodegradation of phenol under irradiation of visible light.[24] However, the conventional preparation techniques usually suffer from their inherent disadvantages. For example, the CNTs need to be treated with strong acids to introduce active function groups on their surface. So in our preview works, we prepared CNT/TiO_2 composites with MWCNTs which preoxidized with *m*-chlorperbenzoic acid (MCPBA) and different titanium alkoxide precursors, and investigated their activity in photodegradation of methylene blue (MB) solution under irradiation of UV light.[25-28]

In the present paper, we used sol-gel method to prepare the MWCNT/TiO_2 composites. Three kinds of classical alkoxides: titanium(IV) *n*-butoxide (TNB, $Ti\{OC(CH_3)_3\}_4$), titanium(IV) isopropoxide (TIP, $Ti\{OCH(CH_3)_2\}_4$) and titanium(IV) propoxide (TPP, $Ti(OCH_2CH_2CH_3)_4$) as precursors were used to form TiO_2 and MWCNTs was pre-oxidized with MCPBA, resulting in MWCNT/TiO_2 composites. The resultant MWCNT/TiO_2 composites were characterized by different techniques including Brunauer-Emmett-Teller (BET) surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). The photocatalytic activity of the as-prepared MWCNT/TiO_2 composites for methylene blue (MB, $C_{16}H_{18}N_3S{\cdot}Cl{\cdot}3H_2O$) degradation under the UV light irradiation was also investigated. Finally, the bactericidal effects of the MWCNT/TiO_2 composites against *Bacillus cereus* (*B. cereus*), *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were investigated.

Experimental

Materials. Crystalline MWCNTs (purity, 95.9 wt.%; diameter: ~ 20 nm; length: ~ 5 μm) powder obtained from Carbon Nano-material Technology Co., Ltd, Korea. The TNB (99%), TIP (97%) and TPP (98%) as titanium alkoxide precursors to form the TiO_2 were purchased from Acros Organics (New Jersey, USA), Kanto Chemical Company (Tokyo, Japan) and Aldrich Chemical Company, respectively. For the oxidization the surface of MWCNT, *m*-chlorperbenzoic acid (MCPBA) was chose as oxidizing agent which was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as organic solvent purchased from Samchun Pure Chemical Co., Ltd, Korea. The MB was used as analytical grade which was purchased from Dukan Pure Chemical Co., Ltd. MB has been used as such a dye because it shows less absorption at the absorption edge (~ 380 nm) of anatase TiO_2 and is relatively stable against UV irradiation without any photocatalysts.

Synthesis of MWCNT/TiO_2 composites. In this experimental, at first, for preparing the oxidizing agent, 0.96 g MCPBA was melted in 60 mL Benzene. And then 0.2 g MWCNTs was put into the oxidizing agent, refluxed at 353 K for 6 h until the solid precipitates were formed and dried at 363 K. On the other hand, titanium alkoxide precursors were dissolved in benzene separately by a ratio of 50 : 50. The solution was stirred magnetically for 30 min to obtain titanium alkoxide precursor/benzene solution. Subsequently, the pre-oxidized MWCNTs were introduced into the titanium alkoxide precursors/benzene solution. The mixtures were loosely covered and kept stirring by magnet at 343 K for 5 h, until a homogenous MWCNTs- contained gel formed. The gel was heat treated at 973 K for 1 h with a heating rate of 279 K/min to obtain MWCNT/TiO_2 composite catalyst. By changing the titanium alkoxide precurors, different samples were obtained. The preparation condition and code of samples were listed in Table 1.

Characterization. BET surface area was measured using a Quantachrome Surface Area analyzer (Monosorb, USA). SEM (JSM-5200 JOEL, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) were used to observe the surface state and structure of the MWCNT/TiO_2 composites. XRD (Shimata XD-D1, Japan) was used for crystal phase identification and estimation of the anastase-to-rutile ratio which were obtained at room temperature. EDX was used to measure the elemental analysis of the MWCNT/TiO_2 composites. UV-Vis spectra for the MB and piggery waste aqueous solution degraded by MWCNT/TiO_2 composites under UV light irradiation were recorded using a Genspec III (Hitachi, Japan) spectrometer.

Photocatalytic activities. The photocatalytic effect of MWCNT/TiO_2 composites was determined using MB decomposition in aqueous solution under an UV lamp (356 nm, 1.2 mW/cm^2). Because the characteristic dyes concentrations in wastewater from textile industry were in the range of 3.0×10^{-5} to 1.5×10^{-4} mol/L,[29] so the initial MB concentration was chosen 1.0×10^{-5} mol/L. The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. Before turning on UV lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-Vis spectrophotometer.[30] The spectra (550 - 750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

Table 1. Nomenclatures of MWCNT/TiO_2 composite samples

Samples	Nomenclatures
0.2 g MWCNT + Titanium(IV) *n*-butoxide (TNB) + benzene	CTNBB
0.2 g MWCNT + Titanium(IV) isopropoxide (TIP) + benzene	CTIPB
0.2 g MWCNT + Titanium(IV) propoxide (TPP) + benzene	CTPPB

Table 2. The BET surface area of the MWCNT/TiO_2 composites

Samples	S_{BET} (m^2/g)
CTNBB	17.52
CTIPB	27.58
CTPPB	26.64

Bactericidal tests. For the bactericidal activity, 2 kinds of method were used, the halo test and the shake flask method. Employing the halo teat proposed by the Berman method,[31] the bactericidal activity against *B. cereus*, *S. aureus* and *E. coli* were examined in a cultivated culture. For quantitative analysis of bactericidal effects, the shake flask method was employed.[32] In our previous studies,[32,33] bactericidal activity of carbon materials against *E. coli* was investigated in detail using the shake flask method. For the test, 300 mL of prepared Trypticase Soy Broth (TSB badge, *ca*. 394 K, 15 min) was first sterilized. Then, each badge strain was cultivated for 24 h under conditions of constant humidity, at a temperature of 310 K. After culturing, a phosphate buffer solution was then counted again. The MWCNT/TiO_2 composites were then dispersed into the counted strain solution, both with and without sunlight. After dispersion and irradiation, the number of bacteria was counted as a function of time. The process was carried out again after 120 min under constant humidity and temperature.

Results and Discussion

BET surface area analysis. Table 2 shows the BET surface area of the MWCNT/TiO_2 composites. The BET surface area of CTNBB, CTIPB and CTPPB are 17.52, 27.58 and 26.64 m^2/g, respectively. It is noted that the surface area of the composite catalysts is very lower than that of neat TiO_2 (123 m^2/g) and MWCNTs (299 m^2/g). It seems that the amount of Ti content is much more than the amount of C content in all of the composite catalysts, and TiO_2 embedded into MWCNT particles with the TiO_2 particles agglomerated together, thus the surface area of composites was decreased much more. This result is also supported by EDX data, SEM and TEM observations.

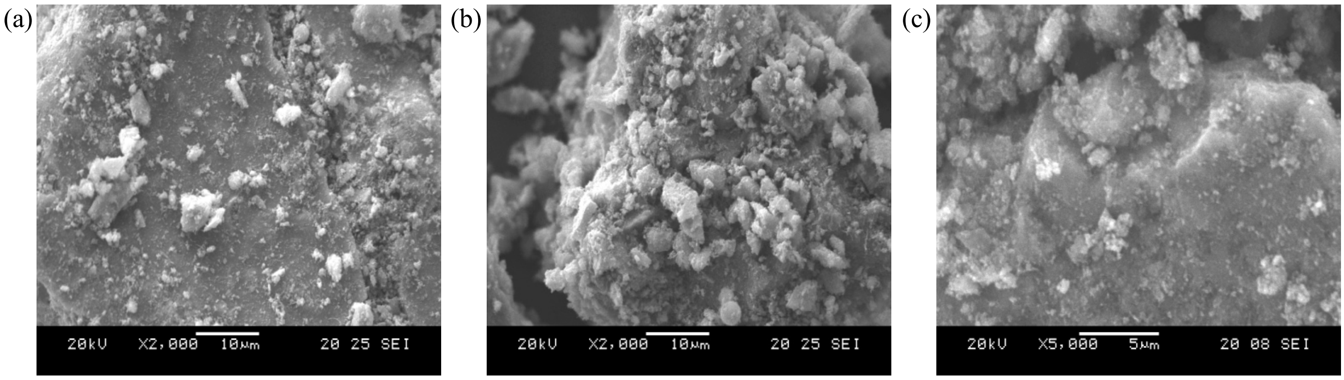

Figure 1. SEM images of the MWCNT/TiO_2 composites; (a) CTNBB, (b) CTIPB and (c) CTPPB.

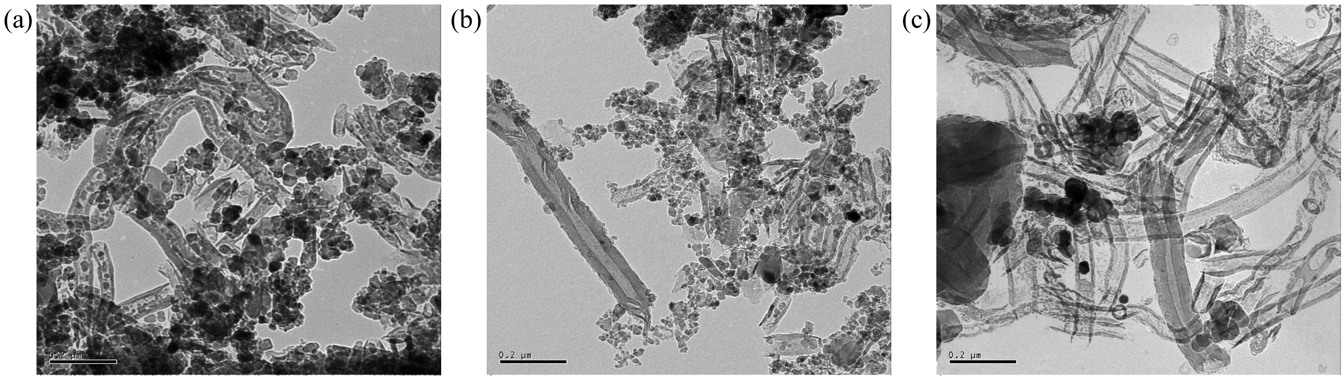

Figure 2. TEM images of the MWCNT/TiO_2 composites; (a) CTNBB, (b) CTIPB and (c) CTPPB.

SEM and TEM analysis. The morphology of the MWCNT/TiO_2 composites prepared with the MWCNTs and different titanium alkoxide precursors were examined by SEM and TEM. Fig. 1 showed the SEM images of MWCNT/TiO_2 composites, and could be affirmed the MWCNTs were dispersed on the surface of TiO_2 particles with same TiO_2 aggregations. It was indicated that MWCNT/TiO_2 composites were obtained under our experimental conditions. More detailed TEM images of the MWCNT/TiO_2 composites were also taken out and shown in Fig. 2. From the TEM images, it was cleanly seen that TiO_2 particles were coated on the surface of MWCNTs and the MWCNT particles were dispersed homogenous with apparent agglomeration of the TiO_2 particles. Sol-gel method usually leads to a heterogeneous, non-uniform coating of MWCNTs by TiO_2, showing bare MWCNTs and random aggregation of TiO_2 onto CNTs surface.[34-36] This result was agreement with present work. However, it was noted that some of TiO_2 particles were embedded into the tube of MWCNTs in the present work. Accordingly, a high photocatalytic yield would be expected for this special structure.

XRD analysis. The XRD patterns of MWCNT/TiO_2 composites were shown in Fig. 3. As we known,[30,37] the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature, and the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200) and (204) planes of anatase, the peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. In our case, all of the composites were heat-treated at 973 K for 1 h. The sample CTIPB had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase without any other peaks, indicating the CTIPB only existed in anatase state with very strong intensity. However, the samples CTNBB and CTPPB not only had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 indicating the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, but also had peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile, indicating the CTNBB and CTPPB existed a mixture structure anatase and rutile. And we could also observe that the sample CTNBB had stronger intensity of anatase and relatively weaker intensity of rutile, but the sample CTPPB had stronger intensity of rutile and relatively weaker intensity of anatase. Due to the three kinds of titanium sources had different structures, when they was heat treated at 973 K for 1 h, these titanium sources would form to TiO_2 with different crystal structures. On the other hand, the characteristic peaks of MWCNTs can hardly been identified from the XRD patterns of MWCNT/TiO_2 composites. It could be consider that the small amount of C content in the composites and the absence of MWCNTs aggregated pores were supported by the disappearance of MWCNTs characteristic peaks in XRD patterns.

EDX analysis. The EDX spectra of MWCNT/TiO_2 composites prepared with MWCNTs and different titanium alkoxide precursors were shown in Fig. 4. From the spectra, all of the

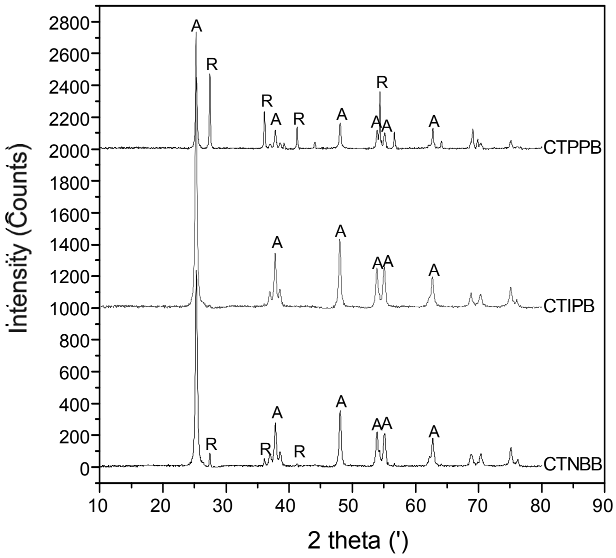

Figure 3. XRD patterns of the MWCNT/TiO_2 composites.

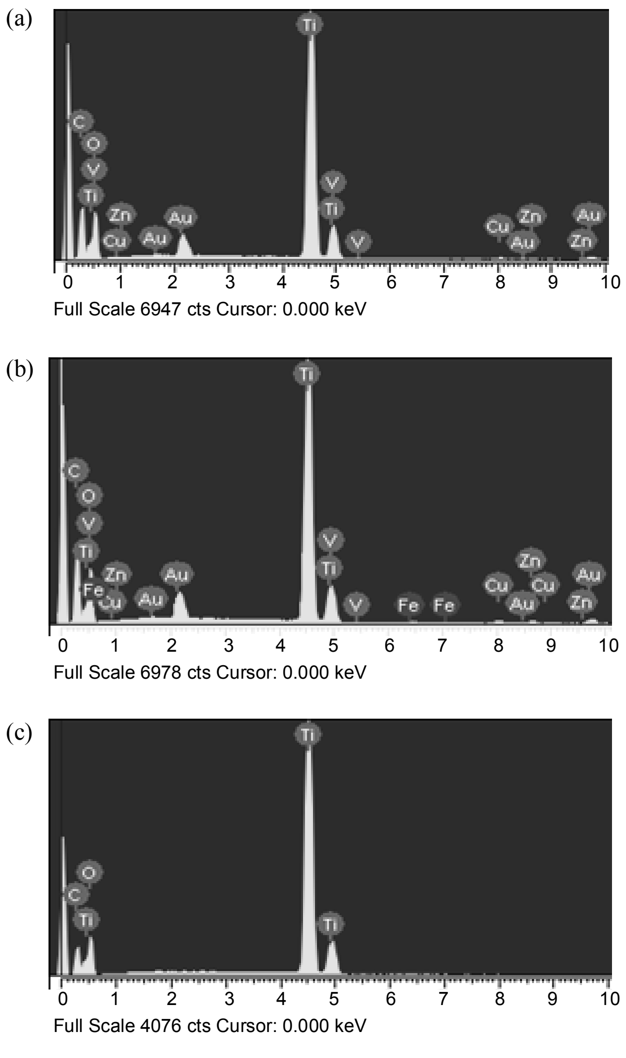

Figure 4. EDX microanalyses of the MWCNT/TiO_2 composites; (a) CTNBB, (b) CTIPB and (c) CTPPB.

Table 3. EDX elemental microanalysis (wt.%) and relative amount of TiO_2 (wt.%) of MWCNT/TiO_2 composites

Samples	Elements				TiO_2
	C	O	Ti	Others	
CTNBB	19.66	37.17	40.32	2.85	67.2
CTIPB	11.46	31.09	53.87	3.57	89.78
CTPPB	12.28	38.20	49.52	-	82.53

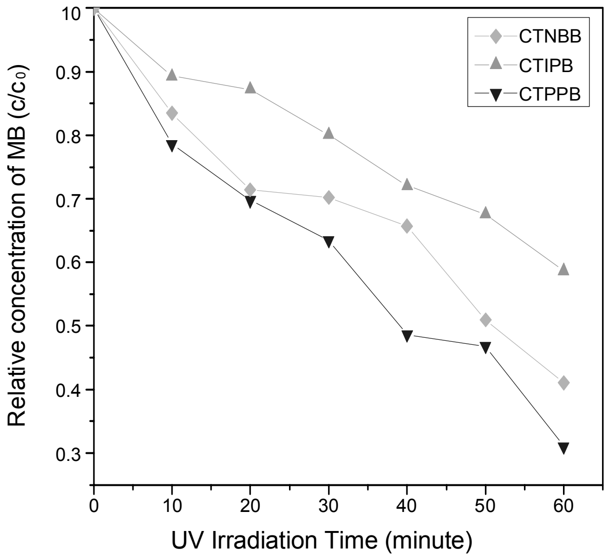

Figure 5. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the MWCNT/TiO_2 composites; the concentration of MB solution: 1.0×10^{-5} mol/L.

MWCNT/TiO_2 composites showed the peak of O and Ti, though some impure elements such as Fe, Zn, Cu, Au and V were existed (which may be introduced from experimental procedure) in the samples CTNBB and CTIPB. So it could be attested that the MWCNT/TiO_2 composites were formed. The EDX elemental microanalysis (wt.%) and the relative amount of TiO_2 (wt.%) of MWCNT/TiO_2 composites was listed in Table 3. From the data, we could also see that all of the samples had three kinds of major elements, just were C, T and O. And all of the samples were rich in O and Ti elements with a relative poor in C element. It could be explained the appearance from their SEM observations as mentioned above. Moreover, from the data of EDX elemental microanalysis (wt.%), it could calculate the relative amount (wt.%) of TiO_2 was 67.2%, 89.78% and 82.53% in samples CTNBB, CTIPB and CTPPB, respectively.

Photocatalytic activity of MWCNT/TiO_2 composites. The photocatalytic removal of MB aqueous solutions was investigated using UV light irradiation source. Fig. 5 shown the changes in relative concentration (c/c_0) of MB in the aqueous solution of UV irradiation time for the MWCNT/TiO_2 composites prepared with MWCNTs and different titanium alkoxide precursors. It had been indicated that MWCNTs had no photocatalytic removal of dye solution.[38-39] So in this study, we did not test the photocatalytic removal effect for MWCNTs. After 60

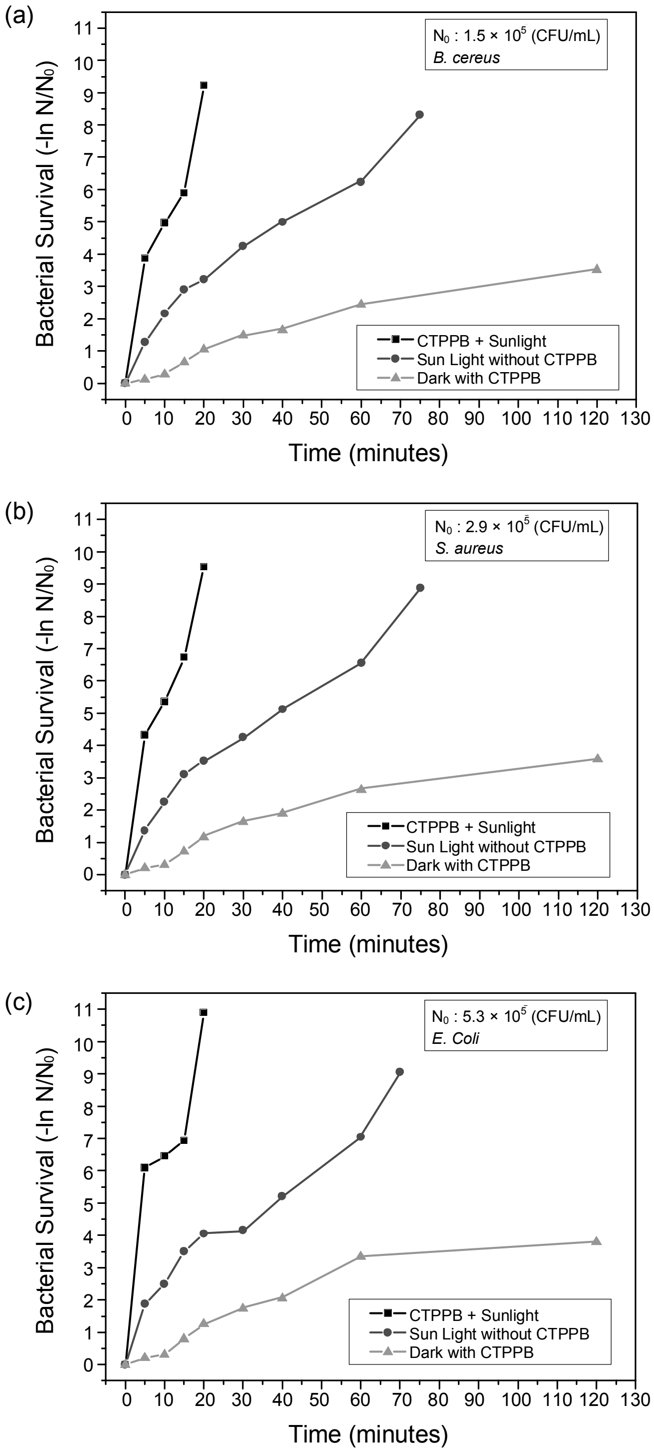

Figure 6. Effect of CTPPB composite on different bacteria survival with or without sunlight as a function time; (a) *B. cereus*, (b) *S. aureus* and (c) *E. coli*.

min of UV irradiation, it could be observed that the sample CTPPB has the highest degradation of MB solution which was almost removed 70%. And the MB degradation of samples CTNBB and CTIPB were also achieved at 60% and 40%, respectively. From the data of the BET surface area, we could be known that the composites would have low adsorption ability because they had very low surface area. So we can consider that the MB degradation infect mainly caused by photocatalytic effect of TiO_2. On the other hand, as we known, the TiO_2 particles with anatase structure have a better photocatalytic activity.[40-41] However, the present results shown that the samples CTNBB and CTPPB contained both anatase and rutile structures and only sample CTIPB had a single structure anatase. However, the MB degradation of the samples CTNBB and CTPPB were better than that of CTIPB. This observation matched the work of Ohno *et al.*[42] that the co-existence of anatase and rutile structures leads to a synergistic effect.

Bactericidal activity. According to the results of photocatalytic effect for MB, we choose the sample CTPPB which had best photocatalytic activity for determining the antibacterial activity. Three kinds of bacteria *B. cereus*, *S. aureus* and *E. coli*, which had bacterial survival number of 1.5×10^5 CFU/mL, 2.9×10^5 CFU/mL and 5.3×10^5 CFU/mL, were used to carry out the bactericidal test. Fig. 6 showed the effect of CTPPB composite on the three kinds of different bacteria with or without sunlight as a function of time. The total time of bacterial abatement was shorter under the condition of composite and sunlight than under other conditions. Based on the bacterial survival number, the graph of the $-\ln(N/N_0)$ versus time should give a straight line, where: N represents the bacterial survival number at time (t); N_0, the initial number of bacteria; and t, the contact time. From the Fig. 5, it can be seen that inactivation of all of the bacteria was much more effective for the CTPPB sample, in sunlight, than in any other experimental conditions. After 20 min, the residual amount of *B. cereus*, *S. aureus* and *E. coli* showed a constant value of 14.8 CFU/mL, 21 CFU/mL and 9.8 CFU/mL, respectively. However, the amount of bacterial survival number under the dark conditions with CTPPB, and sunlight without CTPPB, was much higher than that under sunlight with CTPPB after 20 min. As confirmed by bactericidal tests and previous work,[43] it could be considered that MWCNT/TiO_2 composite showed microbicidal effects and strong antibacterial activity against all of three kinds of bacteria. Solar disinfection with MWCNT/TiO_2 composite is a consequence of both the direct action of the light on the microorganisms and the photocatalytic action of the photo-induced electron (e^-) accepted by the MWCNT from the sunlight. It was regarded that the electrons in the MWCNT transfer into the conduction bands of the TiO_2 particles. Conversely, the photocatalytic effect has been explained as an attack of the radicals photogenerated at the surface of the MWCNT/TiO_2 composite, such as O_2^- (superoxide radical ion) and OH· (hydroxyl radical), both possessing bactericidal characteristics, with the hydroxyl radical being the most potent. Therefore, the recombination of photo-induced charge carriers can be effectively inhibited, which could greatly enhance the activity of the photocatalysts to enable the degradation of the surrounding bacteria.

Conclusion

In this study, we present the synthesis and characterization of MWCNT/TiO_2 composites prepared with pre-treated MWCNTs and different titanium alkoxide precursors in benzene solvent. The BET surface area and surface properties, as well as the structural and chemical composition, were investigated in terms of the synthesis of the MWCNT/TiO_2 composites. Very small BET surface area was obtained in our case for all of the composites. The SEM and TEM images showed the MWCNT particles were dispersed homogenous with apparent agglomeration of the TiO_2 particles. The XRD patterns vary with strong peaks of the anatase in sample CTIPB, and with a mixture structure of the anatase and rutile in samples CTNBB and CTPPB. The EDX spectra showed the three kinds of major elements of C, Ti and O with small amount of impure elements. Finally, the photoactivity of the prepared materials, under UV irradiation, was tested using the conversion of MB from model aqueous solution. According to the results it could be suggested all of samples had a good photocatalytic activity for the MB degradation, especially the sample CTPPB. And it could considered that the MB degradation infect mainly caused by photocatalytic effect of TiO_2. Furthermore, from the bactericidal effects, MWCNT/TiO_2 composites with sunlight had greater effectiveness for *B. cereus*, *S. aureus* and *E. coli* than any other experimental conditions.

References

1. Venkatachalam, N.; Palanichamy, M.; Murugesan, V. *J. Mol. Catal. A* **2007**, *273*, 177.
2. Sobana, N.; Swaminathan, M. *Sep. Purif. Technol.* **2007**, *56*, 101.
3. Habibi, M. H.; Vosooghian, H. *J. Photochem. Photobiol. A* **2005**, *174*, 45.
4. Andronic, L.; Duta, A. *Thin Solid Films* **2007**, *515*, 6294.
5. Evans, P.; Mantke, S.; Mills, A.; Robinson, A.; Sheel, D. W. *J. Photochem. Photobiol. A* **2007**, *188*, 387.
6. El-Sharkawy, E. A.; Solimanb, A. Y.; Al-Amer, K. M. *J. Colloid Interface Sci.* **2007**, *310*, 498.
7. Orlov, A.; Jefferson, D. A.; Tikhov, M.; Lambert, R. M. *Catal. Commun.* **2007**, *8*, 821.
8. Bejarano-Perez, N. J.; Suarez-Herrera, M. F. *Ultrason. Sonochem.* **2007**, *14*, 589.
9. Patil, P. S.; Mujawar, S. H.; Inamdar, A. I.; Shinde, P. S. *Appl. Surf. Sci.* **2005**, *252*, 1643.
10. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
11. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*. In; John Wiley Sons: New York, 1988; p 654.
12. Fujishima, A.; Rao, T. N.; Tryk, D. A. *Electrochim. Acta* **2000**, *45*, 4683.
13. Kawai, T.; Sakata, T. *Nature* **1980**, *286*, 474.
14. O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
15. Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V. *et al*. *J. Am. Ceram. Soc.* **1997**, *80*, 3157.
16. Mills, A.; LeHunte, S. *J. Photochem. Photobiol. A* **1997**, *108*, 1.
17. Motos, J.; Laine, J.; Hermann, J. M. *J. Catal.* **2001**, *200*, 10.
18. Dagan, G.; Tomkiewicz, M. *J. Phys. Chem.* **1993**, *97*, 12651.
19. Dagan, G.; Tomkiewicz, M. *J. Non-Cryst. Solids.* **1994**, *175*, 294.
20. Robert, D.; Parra, S.; Pulgarin, C.; Krzton, A.; Weber, J. V. *Appl. Surf. Sci.* **2000**, *167*, 51.
21. Salvetat-Delmontte, J. P.; Rubio, A. *Carbon* **2000**, *40*, 1729.
22. Saito, T.; Matsushige, K.; Tanaka, K. *Physica B* **2002**, *323*, 280.
23. Jitianu, A.; Cacciaguerra, T.; Benoit, R.; Delpeux, S.; Beguin, F.; Bonnamy, S. *Carbon* **2004**, *42*, 1147.
24. Wang, W. D.; Serp, P.; Kalck, P.; Faria, J. L. *J. Mol. Catal. A: Chem.* **2005**, *235*, 194.
25. Oh, W. C.; Chen, M. L. *Bull. Korean Chem. Soc.* **2008**, *29*, 159.
26. Chen, M. L.; Oh, W. C. *Analytical Science & Technology* **2008**, *21*, 229.
27. Chen, M. L.; Zhang, F. J.; Oh, W. C. *Journal of the Korean Ceramic Society* **2008**, *45*, 651.
28. Chen, M. L.; Zhang, F. J.; Oh, W. C. *Analytical Science & Technology* **2008**, *21*, 553.
29. Zhang, Z. H.; Yuan, Y.; Liang, L. H.; Fang, Y. J.; Cheng, Y. X.; Ding, H. C. *et al*. *Ultrason. Sonochem.* **2008**, *15*, 370.
30. Chen, M. L.; Bae, J. S.; Oh, W. C. *Analytical Science & Technology* **2006**, *19*, 460.
31. Berman, E. *Heyden and Son, London* **1980**, 116.
32. Oh, W. C.; Jang, W. C. *Carbon* **2003**, *41*, 1737.
33. Oh, W. C. *Bull. Korean Chem. Soc.* **2004**, *25*, 639.
34. Hernadi, K.; Ljubovic, E.; Seo, J. W.; Forro, L. *Acta Materialia* **2003**, *51*, 1447.
35. Wang, W.; Serp, P.; Kalck, P.; Faria, J. L. *Appl. Catal. B Env.* **2005**, *56*, 305.
36. Sun, J.; Gao, L.; Iwasa, M. *Chem. Comm.* **2004**, *7*, 832.
37. Inagaki, M.; Hirose, Y.; Matsunaga, T.; Tsumura, T.; Toyoda, M. *Carbon* **2003**, *41*, 2619
38. Wang, S.; Shi, X. L.; Shao, G. Q.; Duan, X. L.; Yang, H.; Wang, T. G. *J. Phys. Chem. Solids* **2008**, *69*, 2396.
39. Yu, Y.; Yu, J. C.; Chan, C. Y.; Che, Y. K.; Zhao, J. C.; Ding, L.; Ge, W. K.; Wong, P. K. *Appl. Catal. B Env.* **2005**, *61*, 1.
40. Barakat, M. A.; Schaeffer, H.; Hayes, G.; Ismat-Shah, S. *Appl. Catal. B: Environ.* **2005**, *57*, 23.
41. Barakat, M. A.; Chen, Y. T.; Huang, C. P. *Appl. Catal. B: Environ.* **2004**, *53*, 13.
42. Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. *J. Catal.* **2001**, *203*, 82.
43. Oh, W. C.; Park T. S. *J. Ind. Eng. Chem.* **2005**, *11*, 671.