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Fabrication and performances of MWCNT/TiO_2 composites derived from MWCNTs and titanium (IV) alkoxide precursors

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Abstract. **Multi-walled carbon nanotubes (MWCNTs)/TiO_2 composites were synthesized by sol–gel technique using titanium (IV) *n*-butoxide (TNB), titanium (IV) isopropoxide (TIP) and titanium (IV) propoxide (TPP) as different titanium alkoxide precursors. The as-prepared composites were comprehensively characterized by BET surface area, SEM, XRD, EDX and UV-Vis absorption spectroscopy. The samples were evaluated for their photocatalytic activity towards the degradation of methylene blue (MB) under UV irradiation. The results indicated that the sample MPB had best excellent photocatalytic activity among the three kinds of samples. Furthermore, we also used piggery waste to determine the photocatalytic activity for the MWCNT/TiO_2 composites by using a chemical oxygen demand (COD) method. It seemed all of the samples have an excellent removal effect of COD. From the results of the bactericidal test, MWCNT/TiO_2 composites with sunlight had a greater effect on *E. coli* than any other experimental conditions.**

Keywords. **MWCNTs; TEM; photocatalytic decomposition; bactericidal effect.**

1. Introduction

Over past few decades, there have been significant advances in the development of photocatalyst based on the immobilization of the metal oxide semiconductor (Negishi *et al* 1997; Sonawane *et al* 2002; Yang *et al* 2004; Zhang *et al* 2005). Particular attention has been directed towards heterogeneous photocatalytic degradation technique, which makes use of suitable semiconductors, such as TiO_2, ZnO, ZnS,WO_3, CdS, CeO_2 and ZrO_2 (Justicia *et al* 2005; Behnajady *et al* 2007), and irradiated by a light source whose energy is higher than, or at least equal to, their band gap. Among these catalysts, TiO_2 has distinct advantages, such as high photosensitivity, large band gap, inexpensive, commercially available in various crystalline forms and particle characteristics, non-toxic and photochemical stable (Fang *et al* 2007; Papadam *et al* 2007; Pekakis *et al* 2006).

Multi-walled carbon nanotubes (MWCNTs) have attracted considerable attention since their discovery. Taking advantage of the unique electronic and physical properties of the MWCNTs, we expect that the combination of MWCNTs with TiO_2 may induce interesting charge transfer and thus enhance the photocatalytic activity of TiO_2. The application of TiO_2 photocatalysts in the presence of MWCNTs has been reported to enhance chemical reactions (Xia *et al* 2007). Although various methods for the preparation of carbon nanotubes (CNTs)/TiO_2 composites have been reported in the literature (Oh and Chen 2008; Zhang *et al* 2008), the photocatalytic properties of CNTs/TiO_2 composite photocatalysts remain largely unexplored. However, the conventional preparation techniques are usually hindered by their inherent disadvantages. For example, the CNTs need to be treated with strong acids to introduce active function groups on their surface.

We use the 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. Moreover, piggery waste was used to investigate the degradation effect of waste

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water. Finally, the bactericidal effects of the MWCNT/TiO_2 composites against *Escherichia coli* (*E. coli*) were investigated.

2. Experimental

2.1 *Materials*

Crystalline MWCNTs (purity: 95·9 wt.%; diameter: ~20 nm; length: ~5 μm) powder was 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 chosen as the oxidizing agent which was purchased from Acros Organics, New Jersey, USA. Benzene (99·5%) was used as the organic solvent purchased from Samchun Pure Chemical Co., Ltd, Korea. MB was the analytical grade solvent used, and it 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. For the effluent characterization, the work involved the treatment of aqueous piggery waste with chemical oxygen demand (COD) levels approaching 50,000 mg/l from a piggery farm. The levels can be reduced to under 600 mg/l by a physic-chemical primary treatment step (coagulation). Samples under this level were used for characterization of the prepared MWCNT/TiO_2 composites.

2.2 *Synthesis of MWCNT/TiO_2 composites*

To prepare the oxidizing agent, 0·96 g MCPBA was melted in 60 ml benzene. 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. Titanium alkoxide precursors were dissolved separately in benzene 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 catalysts. By changing the titanium alkoxide precurors, different samples were obtained. The preparation condition and code of samples are listed in table 1.

2.3 *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. Finally, the COD analyses were measured with a cell test spectrophotometer (PhotoLab S6, WTW, Germany) in accordance with standard cell teat methods (Merck, Germany).

2.4 *Photocatalytic activities*

The photocatalytic effect of MWCNT/TiO_2 composites was determined using MB decomposition in aqueous solution under a UV lamp (356 nm, 1·2 mW/cm^2). Because the characteristic dye concentration in wastewater from textile industry was in the range of $3{\cdot}0 \times 10^{-5}$ to $1{\cdot}5 \times 10^{-4}$ mol/l (Zhang *et al* 2008), the initial MB concentration was chosen $1{\cdot}0 \times 10^{-5}$ mol/l. The amount of suspended composites was kept at 1 g/l in 50 ml MB solution. Before turning on the 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 henceforth considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor in the following order: 10, 20, 30, 40, 50 and 60 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-Vis spectrophotometer (Oh and Chen 2008). The spectra (550–750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for each MB solution degraded. On the other hand, we also used the piggery waste as a dye to determine the photocatalytic effect of MWCNT/TiO_2 composites by the same method as that of the MB solution. Moreover, the clean transparent solutions were tested with a COD cell test photometer.

2.5 *Bactericidal tests*

For the bactericidal activity, two kinds of methods were used: the halo test and the shake flask method. Employing

Table 1. Nomenclatures of MWCNT/TiO_2 composite samples.

Samples	Nomenclatures
0·2 g MWCNT + titanium (IV) *n*-butoxide (TNB) + benzene	MNB
0·2 g MWCNT + titanium (IV) isopropoxide (TIP) + benzene	MIB
0·2 g MWCNT + titanium (IV) propoxide (TPP) + benzene	MPB

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

Samples	S_{BET} (m^2/g)
MNB	17·52
MIB	27·58
MPB	26·64

the halo teat proposed by the Berman method (Berman 1980), the bactericidal activity against *E. coli* were examined in a cultivated culture. For quantitative analysis of bactericidal effects, the shake flask method was employed (Oh and Jang 2003). In our previous studies (Oh and Jang 2003; Oh 2004), 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.

3. Results and discussion

3.1 *Surface characterization of the MWCNT/TiO_2 composites*

Table 2 shows the BET surface area of the MWCNT/TiO_2 composites. The BET surface area of MNB, MIB and MPB are 17·52, 27·58 and 26·64 m^2/g, respectively. It is noted that the surface area of the composite catalysts is much 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 further decreased. This result is also supported by EDX data, SEM and TEM observations.

The morphology of the MWCNT/TiO_2 composites prepared with the MWCNTs and different titanium alkoxide precursors were examined by SEM and TEM. Figure 1 shows the SEM images of the MWCNT/TiO_2 composites, and it was indicated that MWCNT/TiO_2 composites were obtained under our experimental conditions. SEM images of MNB (figure 1a), MIB (figure 1b) and MPB (figure 1c) affirmed the MWCNTs were dispersed on the surface of TiO_2 particles with the same TiO_2 aggregations. Figure 2 showed the TEM images of the MWCNT/TiO_2 composites. 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 the CNTs surface (Hernadi *et al* 2003; Sun *et al* 2004; Wang *et al* 2005). This result was in agreement with present work. However, it was interesting to note that some of TiO_2 particles were embedded into the tube of MWCNTs in this present work. Accordingly, a high photocatalytic yield would be expected for this special structure.

3.2 *Structure characterization of the MWCNT/TiO_2 composites*

The XRD patterns of MWCNT/TiO_2 composites were shown in figure 3. As we know (Chen and Oh 2008; Chen *et al* 2008a, b), 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 MIB 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 MIB only existed in an anatase state with very strong intensity. However, the samples MNB and MPB not only 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, 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 MNB and MPB included a mixture structure of anatase and rutile. We also observed that the sample MNB had stronger intensity of anatase and

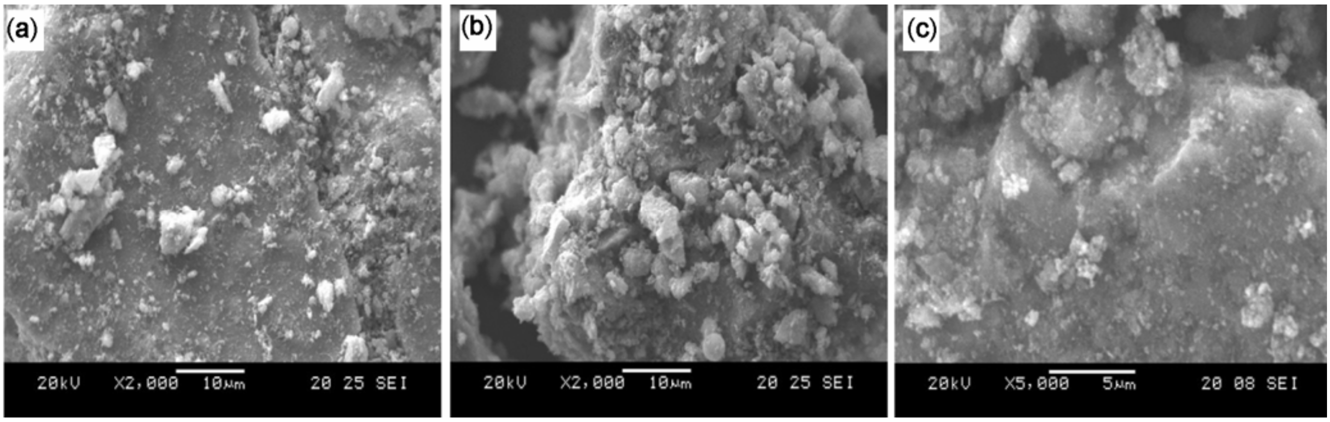

Figure 1. SEM images of the MWCNT/TiO_2 composites: (**a**) MNB, (**b**) MIB and (c) MPB.

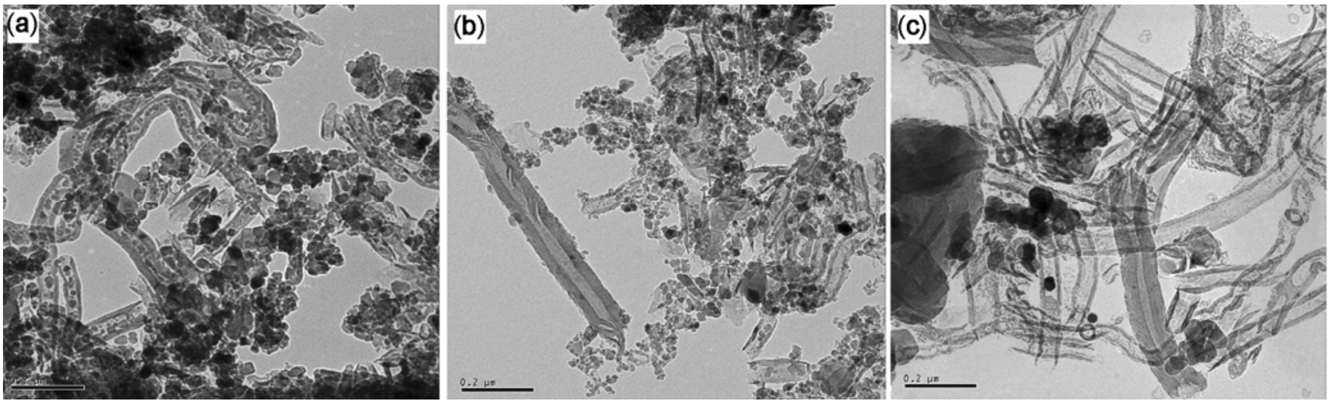

Figure 2. TEM images of the MWCNT/TiO_2 composites: (**a**) MNB, (**b**) MIB and (**c**) MPB.

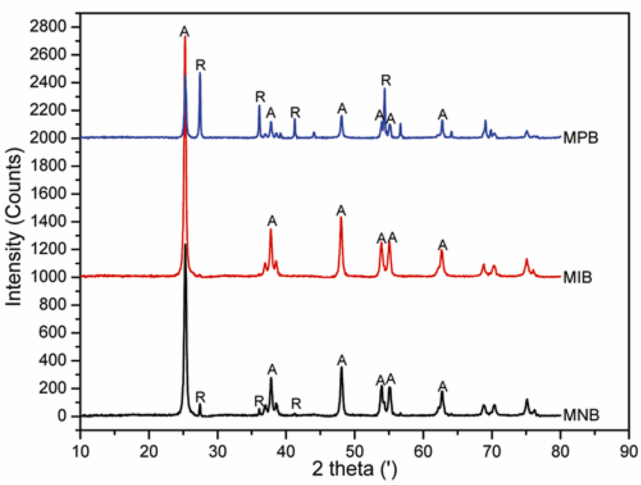

Figure 3. XRD patterns of the MWCNT/TiO_2 composites.

relatively weaker intensity of rutile, but the sample MPB had stronger intensity of rutile and relatively weaker intensity of anatase. Because the three kinds of titanium sources had different structures, when it 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 could hardly be identified from the XRD patterns of MWCNT/TiO_2 composites. It was thought 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.

The EDX spectra of MWCNT/TiO_2 composites prepared with MWCNTs and different titanium alkoxide precursors were shown in figure 4. From the spectra, all of the MWCNT/TiO_2 composites showed the peak of O and Ti, though some impure elements such as Fe, Zn, Cu, Au and V existed (which may be introduced from experimental procedure) in the samples MNB and MIB. So it could be attested that the MWCNT/TiO_2 composites were formed. The EDX elemental microanalysis (wt.%) of MWCNT/TiO_2 composites is listed in table 3. From the data, we could also see that all the samples had three kinds of major elements: C, T and O. All the samples were rich in O and Ti elements but relatively poor in C element. This can explain the appearance of their SEM observations as mentioned above.

3.2 *Photocatalytic activity of MWCNT/TiO_2 composites*

The effect of irradiation time on the photocatalytic degradation of MB from its aqueous solution was investigated from 0 to 60 min, at 1×10^{-5} mol/l MB concentration, 1 g/l catalyst concentration. The results are shown in figure 5. The results clearly show that the sample MPB can achieve almost 70% MB removal for 60 min, and the sample MNB can also achieve 60% MB removal for 60 min while sample MIB achieved only 40% MB removal for the same irradiation time. For all of samples, the photodegradation efficiency increases with time, up to 60 min. From the data of the BET surface area, we knew that the composites would have low adsorption ability because they had very low surface area. As a result, we can consider that the MB degradation infect was mainly caused by the photocatalytic effect of TiO_2. In addition, as we know, the TiO_2 particles with anatase structure have a better photocatalytic activity (Barakat *et al* 2004; Barakat *et al* 2005). However, the present results show

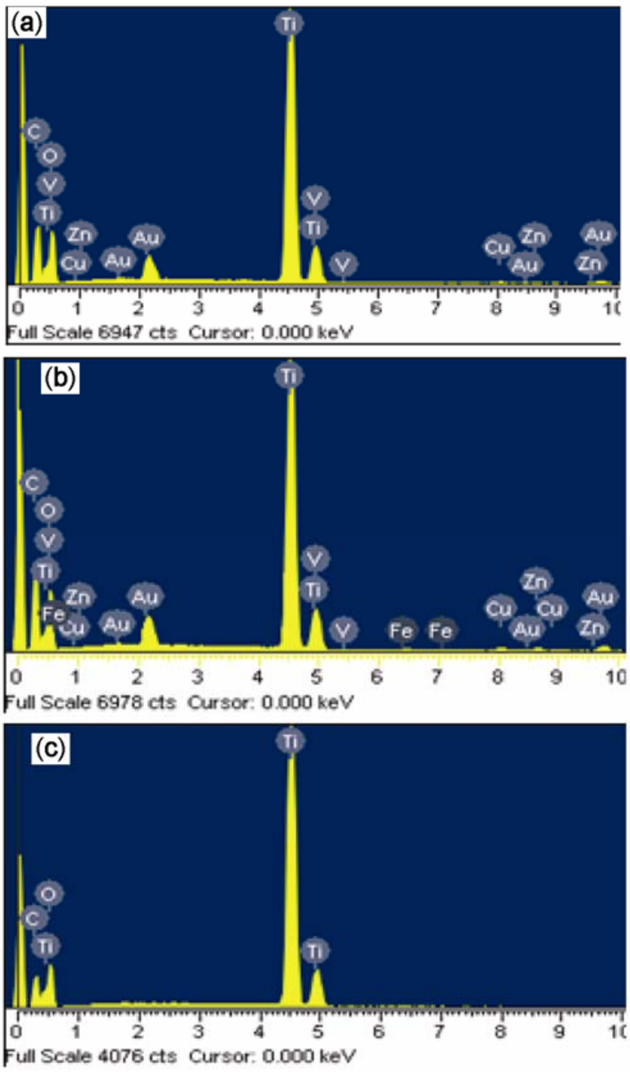

Figure 4. EDX microanalyses of the MWCNT/TiO_2 composites: (**a**) MNB, (**b**) MIB and (**c**) MPB.

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

	Elements			
Samples	C	O	Ti	Others
MNB	19·66	37·17	40·32	2·85
MIB	11·46	31·09	53·87	3·57
MPB	12·28	38·20	49·52	–

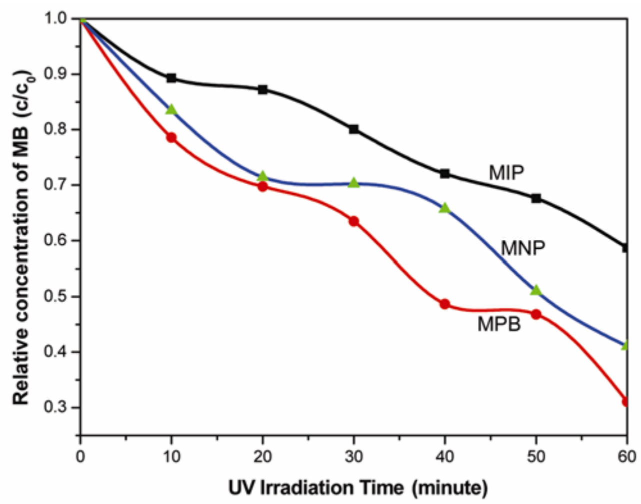

Figure 5. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the MWCNT/TiO_2 composites; the concentration of MB solution: $1{\cdot}0 \times 10^{-5}$ mol/l.

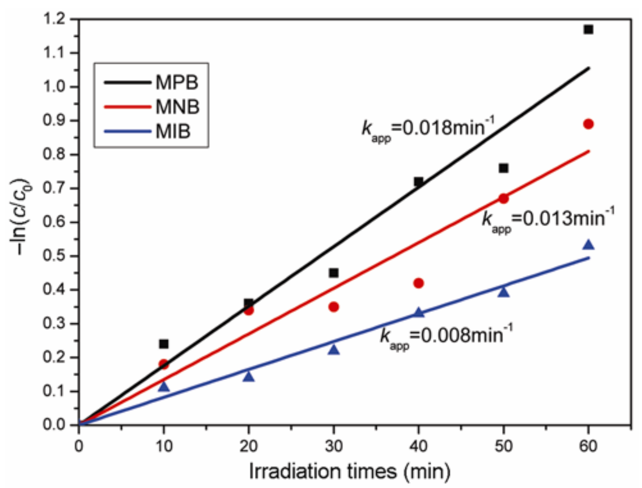

Figure 6. Apparent first-order linear transform $-\ln(c/c_0)$ vs t of MB degradation kinetic plots on MWCNT/TiO_2 composites prepared from MWCNT with different titanium sources in benzene solution under UV irradiation.

that the MNB and MPB samples contained both anatase and rutile structures, and only MIB sample had a single structure anatase. However, the MB degradation of the samples MNB and MPB were better than that of MIB. This observation matched the work of Ohno *et al* (2001) that the co-existence of anatase and rutile structures leads to a synergistic effect. Photocatalytic reactions on the TiO_2 surface can be expressed by the Langmuir–Hinshelwood model (Li *et al* 2006). The photocatalytic degradation of MB containing MWCNT/TiO_2 composites catalyst obeys pseudo-first-order kinetics with respect to the concentration of MB

$$-dc/dt = k_{app}c. \quad (1)$$

Integration of (1) (with the restriction of $c = c_0$ at $t = 0$, with c_0 being the initial concentration in the bulk solution after dark adsorption and t the reaction time) will lead to the following expected relation

$$-\ln(c/c_0) = k_{app}t, \quad (2)$$

where c and c_0 are the reactant concentration at time $t = t$ and $t = 0$, respectively, k_{app} and t are the apparent reaction rate constant and time, respectively. According to (2), a plot of $-\ln(c/c_0)$ vs t will yield a slope of k_{app}. The results are displayed in figure 6. The linearity of plots suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetics with k_{app} from 0·018 to 0·008 min^{-1} in the MB concentration of 1×10^{-5} mol/l. The apparent reaction rate constant decreased with an order of MPB, MNB and MIB. This result can also be indicated that sample MPB had more excellent photocatalytic activity than samples MNB and MIB.

Furthermore, we also used the piggery waste to determine the photocatalytic activity for the MWCNT/TiO_2 composites by using the chemical oxygen demand (COD) method. Analytical results of primitive piggery waste are described in the literature (Oh and Park 2005). The average value of the initial COD of raw waste exceeded 50,000 mg/l. The average COD values of the waste in the first chemical coagulation and physical air blowing treatment were distributed between 535–514 mg/l. Figure 7 shows the removal efficiency as a function of irradiation time. After treatment with MWCNT/TiO_2 composite catalysts, these piggery waste values dropped to less than 420 mg/l. It seemed all of the samples have an excellent removal effect of COD, especially the samples MIB and MPB, the piggery waste values almost dropped to 350 mg/l.

3.3 *Bactericidal activity*

After considering the results of the photocatalytic effect for MB and piggery waste, we choose the MPB sample which had best photocatalytic activity for determining the antibacterial activity. *E. coli* which had bacterial survival number of $5{\cdot}3 \times 10^5$ CFU/ml was used to carry out the bactericidal test. Figure 8 shows the effect of MPB composite on the *E. coli* with or without sunlight as a function of time. The total time of bacterial abatement was shorter under the composite and sunlight condition than under other conditions. Based on the bacterial survival number, the graph of the $-\ln(N/N_0)$ vs 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 figure 8, it can be seen that inactivation of *E. coli* was much more effective for the MPB sample, in sunlight, than in any other experimental condition. After 20 min, the residual amount of *E. coli* showed a constant value of 9·8 CFU/ml. However, the amount of bacterial survival under the dark conditions with MPB, and sunlight without MPB, was much higher

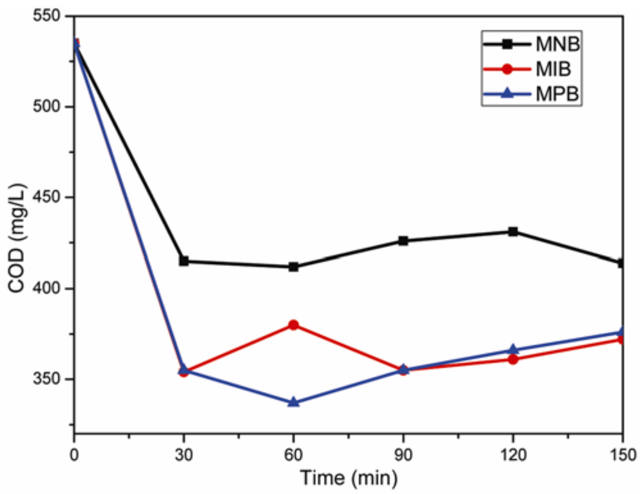

Figure 7. Results of COD removal efficiencies by the MWCNT/TiO_2 composites for the piggery waste.

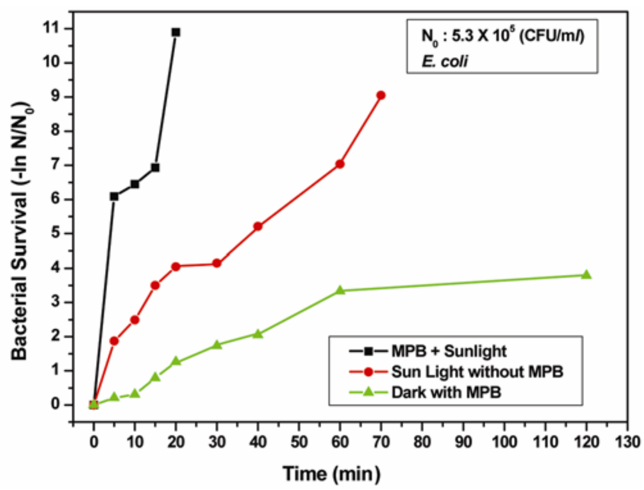

Figure 8. Effect of sample MPB composite on *E. coli* with or without sunlight as a function time.

than that under sunlight with MPB after 20 min. As confirmed by bactericidal tests and previous work (Oh and Park 2005), it could be considered that the MWCNT/TiO_2 composites showed microbicidal effects and strong antibacterial activity against *E. coli.* 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 composites, 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 photoinduced charge carriers can be effectively inhibited, which could greatly enhance the activity of the photocatalysts to enable the degradation of the surrounding bacteria.

4. Conclusions

In this study, we present the synthesis and characterization of MWCNT/TiO_2 composites prepared with pretreated 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 MIB, and with a mixture of anatase and rutile in samples MNB and MPB. The EDX spectra showed the three kinds of major elements of C, Ti and O with a 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 the samples had a good photocatalytic activity for the MB degradation, especially the sample MPB. In addition, it could be considered that the MB degradation infect was mainly caused by photocatalytic effect of TiO_2. Furthermore, we also used the piggery waste to determine the photocatalytic activity for the MWCNT/TiO_2 composites by using the chemical oxygen demand (COD) method. It seemed all of the samples have an excellent removal effect of COD. From the bactericidal effects, MWCNT/TiO_2 composites with sunlight had greater effectiveness for *E. coli* than any other experimental conditions.

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