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Preparation of Carbon Nanotubes/TiO_2 Composites with Multi-Walled Carbon Nanotubes and Titanium Alkoxides by Solvent Effect and Their Photocatalytic Activity

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In this present paper, multi-walled carbon nanotubes (MWCNTs) are used as the starting material to prepare CNT/TiO_2 composites with titanium alkoxides using different solvents. The composites were comprehensively characterized by BET surface area measurements, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, energy dispersive X-ray analysis and UV-vis absorption spectroscopy. The photoactivity of the prepared materials, under UV irradiation, was tested using the conversion of methylene blue from a model aqueous solution. Finally, according to the results of the methylene blue removal experiment, it can be considered that the removal of methylene blue by the CNT/TiO_2 composites is not only due to the adsorption of the MWCNTs and photocatalytic degradation of TiO_2, but also to the electron transfer between the MWCNTs and TiO_2.

Key Words: Carbon nanotubes, Titanium alkoxides, SEM, Photocatalytic decomposition.

INTRODUCTION

Titanium dioxide has been extensively employed as a photocatalytic material for solving environmental problems, especially for eliminating toxic chemicals from waste water[1-3]. The TiO_2/UV system has been widely investigated in heterogeneous photocatalytic processes, during which the UV irradiation of the semiconductor can photoactivate the TiO_2, thereby generating electron/hole couples with strong redox properties[4]. Photocatalytic oxidation is an alternative means of completely degrading azo dyes[5-8]. The mechanism described below is widely accepted for the photodegradation of organic species[9] by UV/TiO_2. Most advanced oxidation processes (AOPs) involve the generation of a very powerful and non-selective oxidizing agent, the hydroxyl radical ($OH^\bullet$), to destroy hazardous pollutants. Photogenerated holes are formed after TiO_2 particles are irradiated with UV light (eqn. 1). Hydroxyl radicals are generated mainly in the oxidation of OH^- or H_2O by these photogenerated holes (eqns. 2 and 3) and are principally responsible for the destruction of organic

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species. Oxygen is primarily used as an efficient electron trap (eqn. 4), preventing the recombination of the electrons and photogenerated holes.

$$TiO_2 + h\nu \rightarrow TiO_2\ (e_{CB}^- + h_{VB}^+) \quad (1)$$

$$TiO_2\ (h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (2)$$

$$TiO_2\ (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \quad (3)$$

$$TiO_2\ (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \quad (4)$$

Multi-walled carbon nanotubes (MWCNTs) have attracted considerable attention since their discovery[10], because they have a special structure, extraordinary mechanical and electronic properties and can be semiconducting[11]. Therefore, carbon nanotubes (CNTs) are often used as a support for the dispersion of functional materials, in order to impart additional functionalities to these materials, such as structure, surface area, activity and conductivity[12-15]. With the development of synthesis technologies, the price of MWCNTs has been significantly reduced and it is possible for them to be used on a large scale[16]. By taking advantage of their unique electronic properties, it is expected that the combination of MWCNTs with titania would induce interesting charge transfer properties and thus enhance the photocatalytic activity of titania. Recently, researchers have shown that the addition of MWCNTs as supports for TiO_2 could improve the efficiency of the photocatalytic degradation of organics[11]. Accordingly, MWCNTs can be used as a promising material for environmental cleaning. The surface area of MWCNTs is much less than that of activated carbon. Therefore, adsorption is not the only factor involved in the enhancement of the photocatalytic activity of TiO_2 by MWCNTs.

In the present paper, multi-walled carbon nanotubes (MWCNTs) and titanium alkoxides are used with different solvents to prepare CNT/TiO_2 composites. Three titanium alkoxides, *viz.*, titanium(IV) isopropoxide (TIP, $Ti\{OCH(CH_3)_2\}_4$), titanium(IV) propoxide (TPP, $Ti(OCH_2CH_2CH_3)_4$) and titanium(IV) *n*-butoxide (TNB, $Ti\{OC(CH_3)_3\}_4$) and two kinds of solvents, *viz.*, benzene and tetrahydrofuran (THF), were used. To compare their properties, the corresponding composites were characterized by BET surface area measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). The photocatalytic decomposition properties of the CNT/TiO_2 composites in the decomposition of methylene blue (MB, $C_{16}H_{18}N_3S{\cdot}Cl{\cdot}3H_2O$) in an aqueous solution under UV irradiation were also examined.

EXPERIMENTAL

Crystalline MWCNT powder with a purity of 95.9 wt. % from Carbon Nanomaterial Technology Co., Ltd, Korea (diameter: *ca.* 20 nm, length: *ca.* 5 μm) was used as the starting material. The TIP (97 %), TPP (98 %) and TNB (99 %) used as titanium sources for the preparation of the CNT/TiO_2 composites were purchased from Kanto Chemical Company, Aldrich Chemical Company and Acros Organics, respectively. For the oxidation of the surface of the MWCNTs, *m*-chlorperbenzoic acid (MCPBA) purchased from Acros Organics (New Jersey, USA) was used as the oxidizing agent. Benzene (99.5 %) and THF, which were purchased from Samchun Pure Chemical Co., Ltd, Korea and Daejung Chemicals & Metals Co., Ltd, Korea, respectively, were used as the organic solvents. The methylene blue used was of analytical grade and was purchased from Dukan Pure Chemical Co., Ltd. It was selected because it can be readily decomposed under anaerobic conditions to produce potentially more hazardous aromatic amines.

Synthesis of CNT/TiO_2 composites: 0.96 g of MCPBA was melted in 60 mL of benzene and then 0.2 g of MWCNTs were put into the oxidizing agent solution, refluxed at 353 K for 6 h until solid precipitates were formed and dried at 363 K. The oxidized CNTs were put into TIP, TPP or TNB without an additional solvent and also put into a mixture solution of TIP, TPP or TNB plus benzene or THF at a ratio of 50:50. Then, these solutions were homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After stirring, the solutions were transformed into CNT/TiO_2 gels and these gels were heat treated at 973 K for 1 h. The preparation conditions and codes of the samples are listed in Table-1.

TABLE-1
NOMENCLATURES OF CNT/TiO_2 COMPOSITE SAMPLES

Samples	Nomenclatures
0.2 g MWCNT + 20 mL Titanium(IV) isopropoxide (TIP)	CTIP
0.2 g MWCNT + 20 mL Titanium(IV) propoxide (TPP)	CTPP
0.2 g MWCNT + 20 mL Titanium(IV) *n*-butoxide (TNB)	CTNB
0.2 g MWCNT + Titanium(IV) isopropoxide (TIP) + benzene	CTIPB
0.2 g MWCNT + Titanium(IV) propoxide (TPP) + benzene	CTPPB
0.2 g MWCNT + Titanium(IV) *n*-butoxide (TNB) + benzene	CTNBB
0.2 g MWCNT + Titanium(IV) isopropoxide (TIP) + THF	CTIPT
0.2 g MWCNT + Titanium(IV) propoxide (TPP) + THF	CTPPT
0.2 g MWCNT + Titanium(IV) *n*-butoxide (TNB) + THF	CTNBT

The synthesized powders were characterized by various techniques. BET surface area was measured using a Quantachrome Surface Area analyzer (Monosorb, USA). SEM (Jeol, JSM-5200, Japan) was used to observe the surface state and structure of the CNT/TiO_2 composites. TEM (Jeol, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the titanium deposits on the CNT surface of the various samples. The TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. XRD was used for crystal phase identification and estimation of the anastase-to-rutile ratio. The XRD patterns were obtained at room temperature with a Shimata XD-D1 (Japan) using CuK_α radiation. EDX was used for the elemental analysis of the CNT/TiO_2 composites. The UV-vis spectra for the methylene blue solution degraded by the CNT/TiO_2 composites under UV irradiation were recorded using a Genspec III (Hitachi, Japan) spectrometer. The flow chart in Fig. 1 provides a summary of the route to prepare the CNT/TiO_2 composites and their characterization.

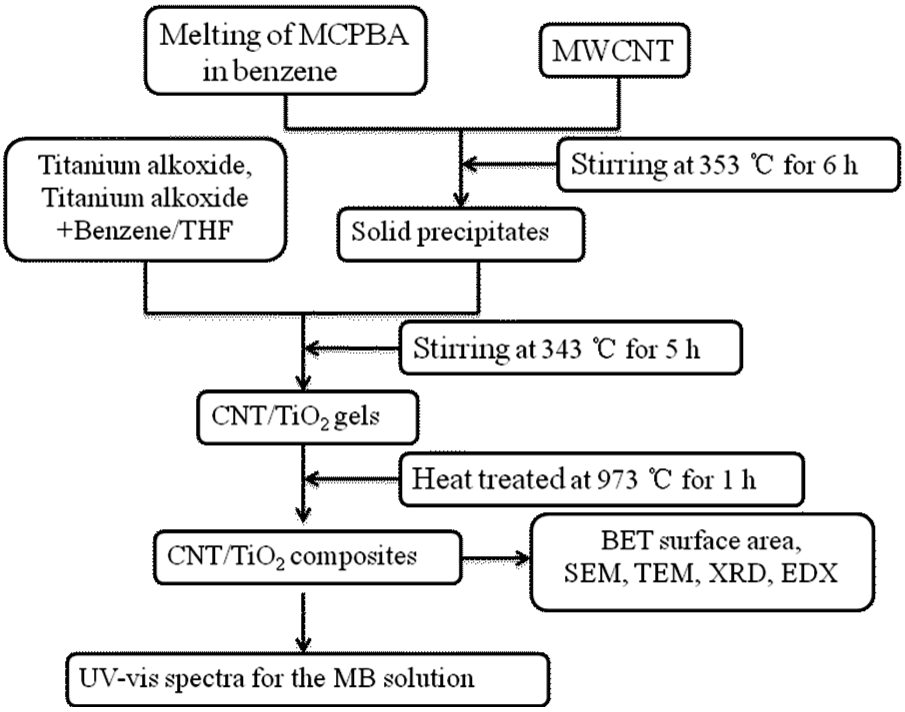


Fig. 1. Schematic diagram showing the procedure used for the preparation of the CNT/TiO_2 composites derived from titanium alkoxides with different solvents

Photocatalytic decomposition: The photocatalytic effect of the CNT/TiO_2 composites was determined using methylene blue decomposition in aqueous solution under a UV lamp (356 nm, 1.2 mW/cm^2). Because the characteristic dyes concentrations in the wastewater derived from the textile industry were in the range of 3.0×10^{-5} to 1.5×10^{-4} mol/L[17], the initial methylene blue concentration was chosen to be 1.0×10^{-5} mol/L. The amount of suspended composites was kept at 1 g/L in 50 mL of methylene blue solution. Before turning on the UV lamp, the solution mixed with the 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 light. 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 methylene blue concentration in the solution, which was hereafter considered as the initial concentration (c_0) after the dark adsorption period. Samples were then withdrawn regularly from the reactor after 10, 20, 30, 40, 50 and 60 min and immediately centrifuged to separate any suspended solids. The clean transparent solution was analyzed using a UV-vis spectrophotometer[18-20]. The spectra (550-750 nm) for each sample were recorded and the absorbance was determined at the characteristic wavelength of 660 nm for each methylene blue solution that was degraded.

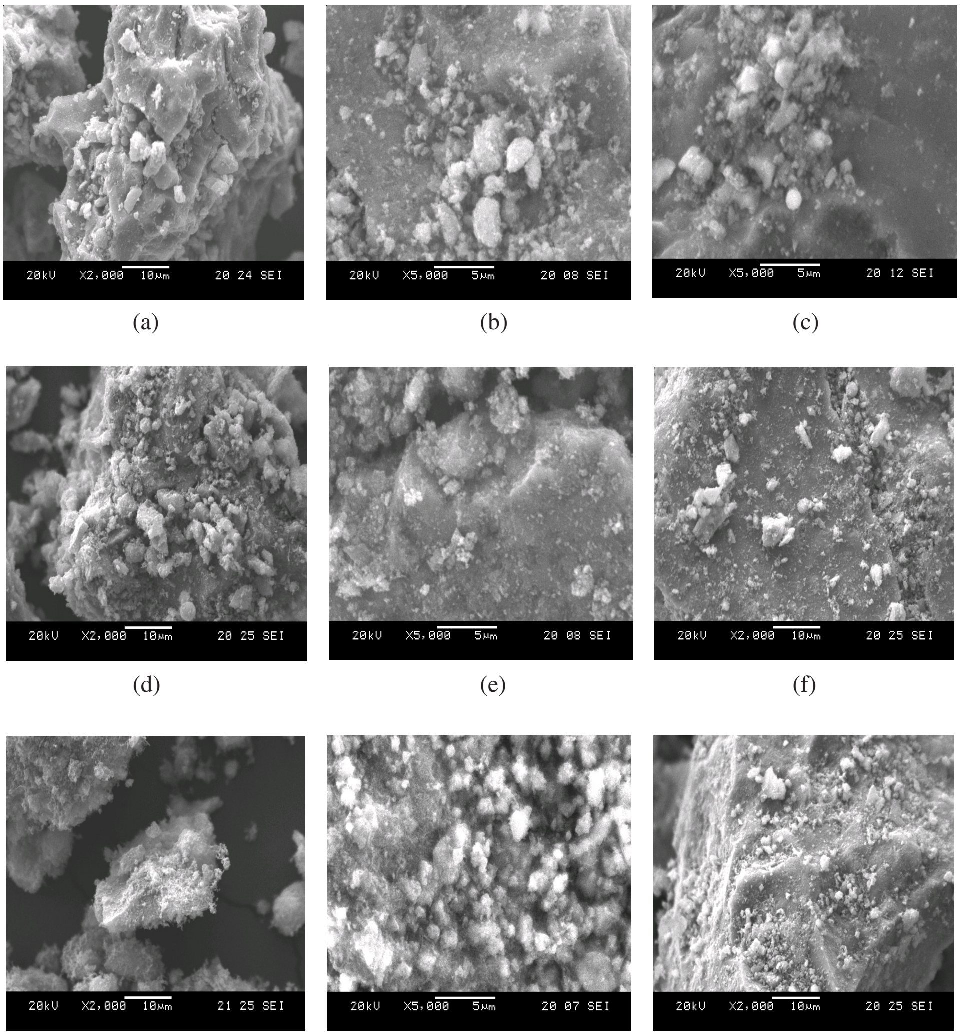
RESULTS AND DISCUSSION

Characteristics of CNT/TiO_2 composites: The BET surface areas of the CNT/TiO_2 composites are shown in Table-2. From these results, it can be seen that the BET surface area of the composite samples is much less than that of the pristine MWCNTs (232.17 m^2/g) and that of the sample, CTPP, is only 3.9 m^2/g. However, the BET surface area of the samples CTIPT and CTNBT reached 129.26 m^2/g and 54.05 m^2/g, respectively. It is also noticed that the BET surface areas of the samples which used TIP as titanium source are larger than other samples which used TNB and TPP as titanium source. Wang *et al.*[21] reported that the introduction of MWCNTs into the TiO_2 matrix can prevent the TiO_2 particles from agglomerating. Therefore, in this paper, it can be considered that the samples prepared from MWCNTs with TIP would show much better efficacy in preventing the TiO_2 particles from agglomerating.

TABLE-2
BET SURFACE AREA OF CNT/TiO_2 COMPOSITES

Samples	S_{BET} (m^2/g)	Samples	S_{BET} (m^2/g)
Pristine MWCNT	232.170	CTPPB	26.64
CTIP	84.061	CTNBB	17.52
CTPP	3.901	CTIPT	129.26
CTNB	21.788	CTPPT	16.06
CTIPB	27.580	CTNBT	54.05

The morphology and microstructure of the CNT/TiO_2 composites prepared from MWCNTs and titanium alkoxides with different solvents were examined by SEM. The changes in the morphology for the MWCNT based composites obtained under unique experimental conditions are shown in Fig. 2. From these figures, it can be clearly seen that the MWCNTs were homogenously decorated with well-dispersed particles, with a few TiO_2 aggregates being formed. These materials were shown microscopically to have a compact and uniform distribution and the aggregates linked the MWCNTs, resulting in a dense material. The good dispersion of the small MWCNT particles in the TiO_2 aggregates would be expected to lead to the existence of more reactive sites, because the major portion of TiO_2 would be enclosed in the three-dimensional matrix[22]. Accordingly, a high photocatalytic yield was expected for the composites having a homogenous distribution of small MWCNTs particles in the TiO_2 aggregates. To explain this in more detail, the TEM image for the sample CTNBT is also presented in Fig. 3. This image clearly shows the existence of a homogeneous sample with few TiO_2 aggregates and that the TiO_2 particles are not only coated on the surface of the MWCNTs, but also introduced inside their tubes. This result is very different from that reported in other studies[23,24], where only the nanotube surface was covered with TiO_2 particles.



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Fig. 2. SEM images of CNT/TiO_2 composites prepared from MWCNT and titanium alkoxides with different solvents; (a) CTIP, (b) CTPP, (c) CTNB, (d) CTIPB, (e) CTPPB, (f) CTNBB, (g) CTIPT, (h) CTPPT and (i) CTNBT

The X-Ray diffractograms of the CNT/TiO_2 composites prepared from CNT and titanium alkoxides with different solvents after heat treatment at 973 K for 1 h are presented in Fig. 4. According to a previous study[25], the anatase phase formed below 773 K starts to transform into a rutile-type structure above 873 K and into a single phase of rutile at 973-1173 K. However, in the present case, the patterns of all of the samples indicate that both anatase and rutile structures were present when they were annealed at 973 K. This is in agreement with the results of previous works[26,27] which reported that CNT/TiO_2 composites had a mixed structure of anatase

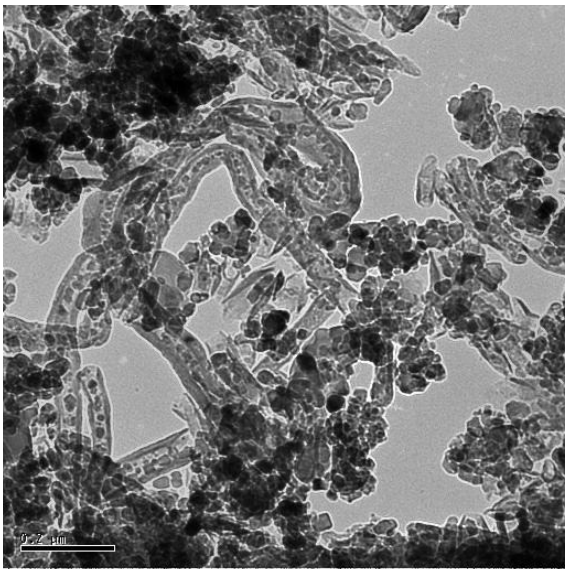


Fig. 3. TEM image of sample CTNBT

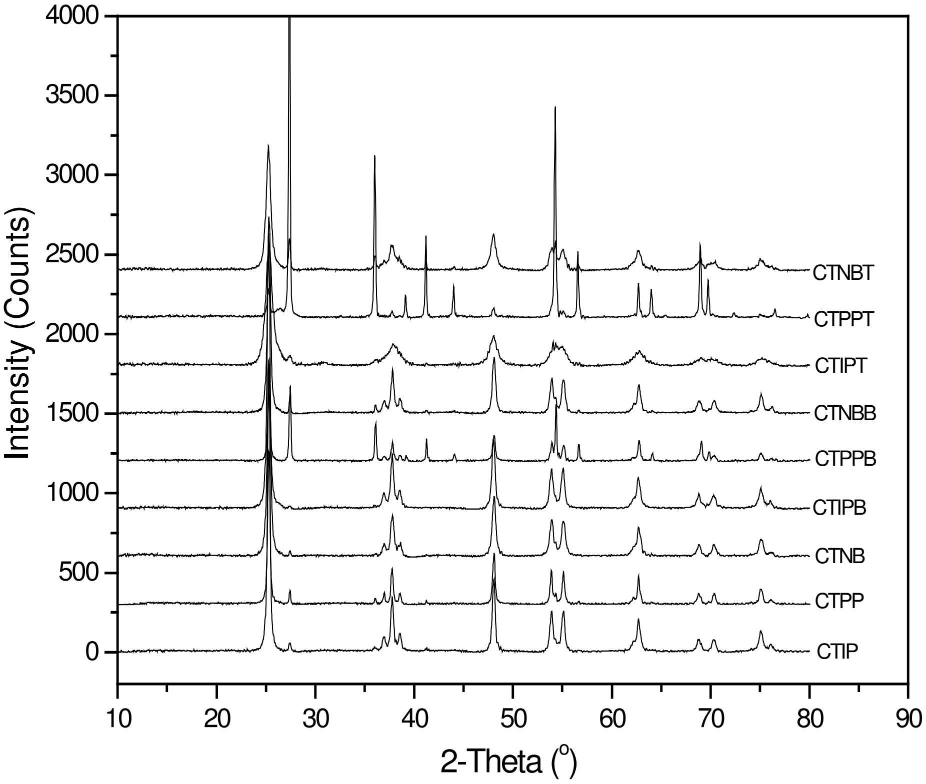


Fig. 4. XRD patterns of the CNT/TiO_2 composites prepared from titanium alkoxides with different solvents after heat treatment at 973 K for 1 h

and rutile crystals formed by crystallization when the temperature reached 973 K and that the carbon coating suppressed the phase transformation from anatase to rutile. In this study, it is worth noting that all of the samples have lots of particles with the anatase structure and a few with the rutile structure, except for samples CTPPB and CTPPT, which have peaks with a stronger intensity for the rutile structures than for the anatase structure. It is also worth noting that the characteristic peaks of the MWCNTs can hardly be identified in any of the patterns of the composite catalysts. It is considered that the peak widths broaden slightly and gradually with decreasing peak intensity of the MWCNTs for the composites.

The EDX spectra of the CNT/TiO_2 composites prepared from the MWCNTs and titanium alkoxides with different solvents are shown in Fig. 5. All of the CNT/TiO_2 composites show the peaks of O and Ti, although some impurity elements such as Fe, Zn, Cu, Au and V also exist (which may be introduced during the experimental procedure). Therefore, it can be attested that the CNT/TiO_2 composites were indeed formed. The results of the EDX elemental microanalysis (wt. %) of the CNT/TiO_2 composites are listed in Table-3. From the data, we can also see that all of the samples are rich in O and Ti elements and relatively poor in C element. This explains their appearance referred to in the SEM observations, as mentioned above.

TABLE-3
EDX ELEMENTAL MICROANALYSIS (wt%) of CNT/TiO_2 COMPOSITES

Samples	Elements			
	C	O	Ti	Others
CTIP	5.35	43.02	50.85	0.78
CTPP	6.21	43.93	49.86	-
CTNB	5.44	42.72	51.84	-
CTIPB	11.46	31.09	53.87	3.57
CTPPB	12.28	38.20	49.52	-
CTNBB	19.66	37.17	40.32	2.85
CTIPT	17.01	42.14	39.15	1.70
CTPPT	16.71	24.11	56.53	2.65
CTNBT	19.89	35.61	39.61	5.24

Photocatalytic activity of CNT/TiO_2 composites: The absorption spectra of methylene blue recorded with a UV-vis spectrophotometer for the determination of the concentration of the dye can be done in the wavelength range from 550 to 750 nm. In the present case, the absorbance of the methylene blue solution was measured at 660 nm. Fig. 6(a) shows the variation in the relative concentration (c/c_0) of methylene blue in the aqueous solution with the UV irradiation time for the CNT/TiO_2 composites prepared from TIP and different solvents. After 1 h of UV irradiation, it can be observed that the sample CTIPT shows the highest level of degradation of methylene blue solution, which was almost 71 % removed. The levels of methylene blue degradation of samples CTIP and CTIPB after 1 h of UV irradiation were 63 and 41 %,

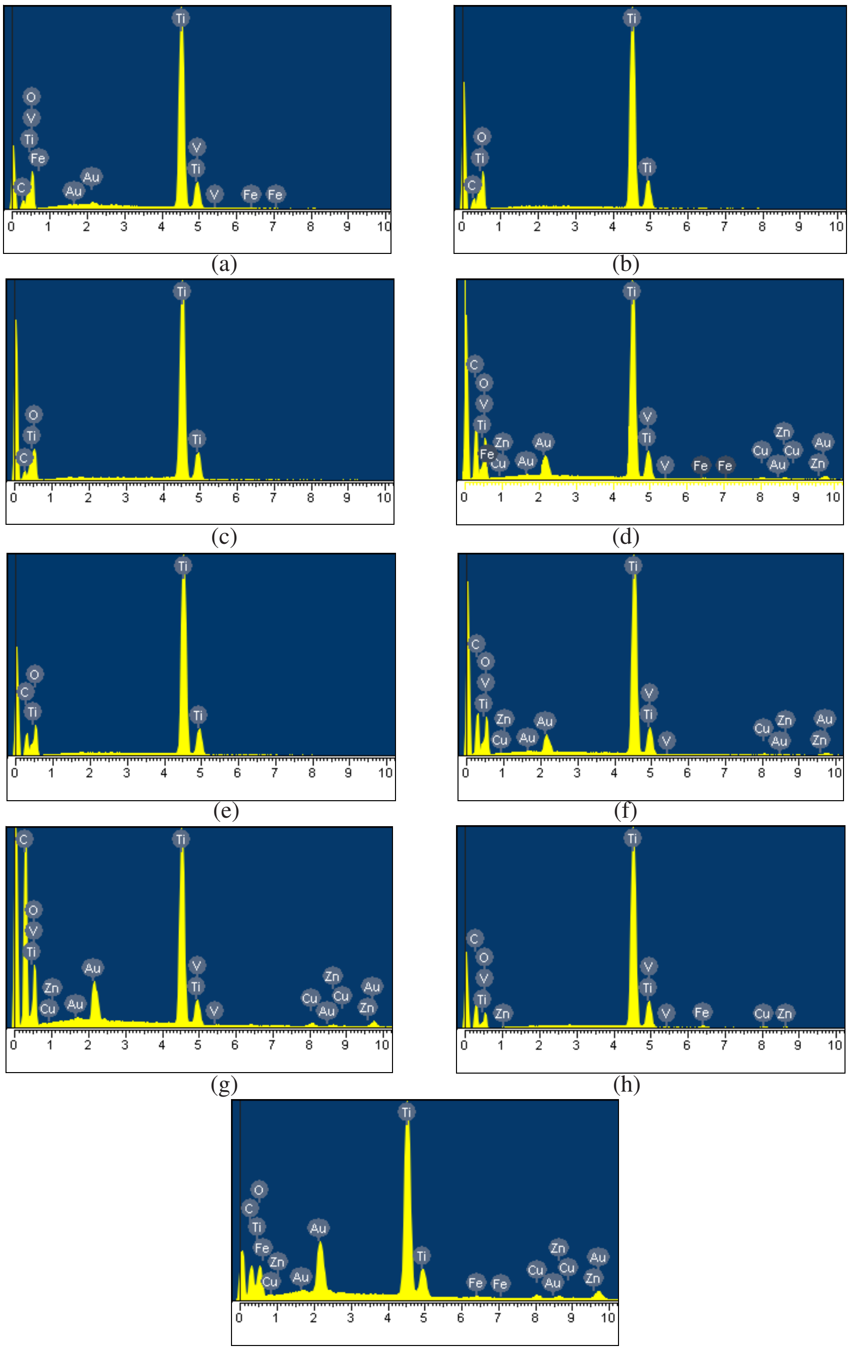
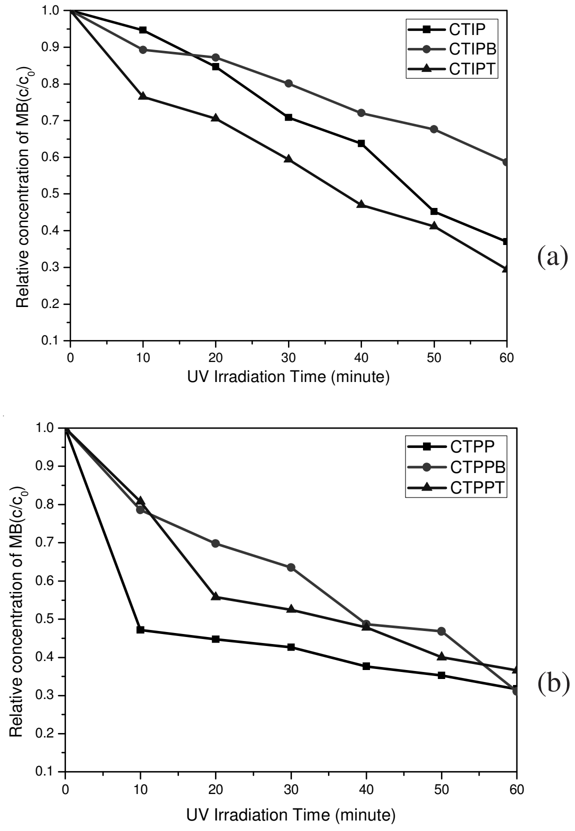


Fig. 5. EDX elemental microanalysis of CNT/TiO$_2$ composites prepared from titanium alkoxides with different solvents; (a) CTIP, (b) CTPP, (c) CTNB, (d) CTIPB, (e) CTPPB, (f) CTNBB, (g) CTIPT, (h) CTPPT and (i) CTNBT

respectively. The variation in the relative concentration (c/c_0) of methylene blue in the aqueous solution with the UV irradiation time for the CNT/TiO_2 composites prepared from TPP and different solvents is shown in Fig. 6(b). The samples CTPP and CTPPB have the same levels of methylene blue degradation of 69 %, while that of the sample CTPPT was 63 %. Fig. 6(c) shows the changes in the relative concentration (c/c_0) of methylene blue in the aqueous solution with the UV irradiation time for the CNT/TiO_2 composites prepared from TNB and different solvents. It can be observed that the levels of methylene blue degradation of the samples CTNB, CTNBB and CTNBT were 63, 59 and 79 %, respectively. From these results, it can be inferred that the methylene blue removal effect of the CNT/TiO_2 composites which prepared by using THF as solvent is much better than that of the CNT/TiO_2 composites which prepared by using benzene as solvent. On the other hand, as indicated above, the TiO_2 particles with an anatase structure have better photocatalytic activity[28,29]. However, the XRD results showed that the sample CTNBT with the best degradation effect on the methylene blue solution had a mixture structure containing anatase and rutile. This observation is in agreement with the work of Ohno *et al.*[30] who reported that the co-existence of anatase and rutile structures leads to a synergistic effect.



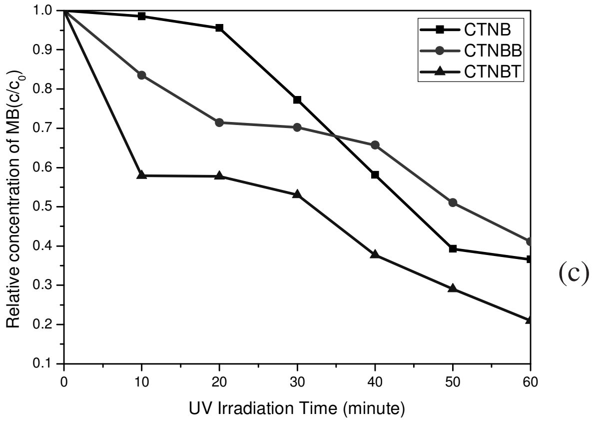


Fig. 6. Dependence of relative concentration of methylene blue (MB) in the aqueous solution c/c$_0$ on UV irradiation time for the CNT/TiO$_2$ composites prepared from titanium alkoxide, TNB, with different solvents; methylene blue (MB): 1.0×10^{-5} mol/L; (a) CTIP, CTIPB and CTIPT; (b) CTPP, CTPPB and CTPPT; and (c) CTNB, CTNBB and CTNBT

According to previous studies[22,31], it is reasonable to attribute the effect of the MWCNTs acting as an electron sensitizer and donator in the composite photocatalysts. A schematic mechanism of the photocatalytic activity of the CNT/TiO$_2$ composites is shown in Fig. 7 and the equations given below. Due to their semiconducting properties, the MWCNTs may accept the electron (e^-) photo-induced by UV irradiation. It is considered that the electrons in the MWCNTs are transferred into the conduction band in the TiO$_2$ particles (eqn. 1). At this time, these electrons in the conduction band of TiO$_2$ may react with O$_2$, which can be trigger the formation

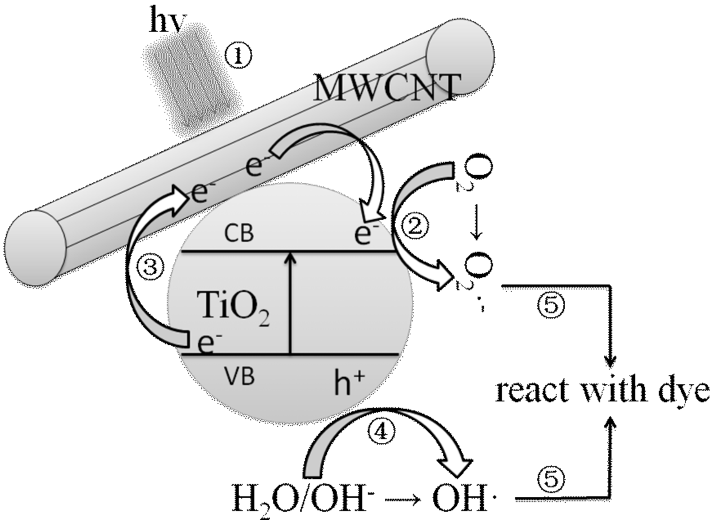


Fig. 7. Mechanism for the dye degradation effect of the CNT/TiO$_2$ composites

of the very reactive superoxide radical ion ($O_2^{\bullet-}$). Simultaneously, a positively charged hole (h^+) might be formed due to the electron transfer from the valence bond in TiO_2 to the MWCNTs. This positively charged hole (h^+) may react with OH^- derived from H_2O, which can trigger the formation of the hydroxyl radical ($OH^\bullet$). Consequently, these two important species, *viz.*, the superoxide radical ion $O_2^{\bullet-}$ and hydroxyl radical $OH^\bullet$, are responsible for the decomposition of the organic compounds.

(1) $MWCNT/TiO_2 \xrightarrow{h\nu} MWCNT^+/TiO_2^-$

(2) $MWCNT^+/TiO_2^- + O_2 \longrightarrow MWCNT^+/TiO_2 + O_2^{\bullet-}$

(3) $MWCNT^+/TiO_2 \longrightarrow MWCNT/TiO_2^+$

(4) $MWCNT/TiO_2^+ + (H_2O/OH^-) \longrightarrow MWCNT/TiO_2 + OH^\bullet$

(5) $O_2^{\bullet-}$ or $OH^\bullet$ + Methylene blue $\longrightarrow$ degradation

Conclusion

CNT/TiO_2 composites were prepared using MWCNTs and titanium alkoxides with different solvents. The surface morphologies, structures and elemental compositions of nine kinds of CNT/TiO_2 composites were investigated. The BET surface area of the composite samples is much less than that of the pristine MWCNTs. From the SEM results, it was found that the samples prepared from the MWCNTs and titanium alkoxides with different solvents showed a homogenous structure in which the individual MWCNTs were covered with TiO_2 and few TiO_2 aggregates were formed between the CNTs and TiO_2. From TEM images, it was clearly shown that the TiO_2 particles not only coated the surface of the MWCNTs, but were also introduced inside their tubes. In the XRD patterns, all of the samples were observed to consist of a mixed phase of anatase and rutile when they were heat treated at 973 K. All of the samples showed lots of (particles with the) anatase structure and a few with the rutile structure, except for the samples CTPPB and CTPPT, for which the peaks for the rutile structure had a stronger intensity than those for the anatase structure. From the EDX data, it was inferred that the main elements, *viz.* C, O and Ti, existed in all of the samples. Finally, the photoactivity of the prepared materials, under UV irradiation was tested using the conversion of methylene blue in a model aqueous solution. According to the results, a plausible photocatalytic mechanism between the MWCNTs and TiO_2 was proposed.

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