

# Photocatalytic Degradation of Methylene Blue by CNT/TiO<sub>2</sub> Composites Prepared from MWCNT and Titanium *n*-butoxide with Benzene

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## ABSTRACT

In this study, CNT/TiO<sub>2</sub> composites were prepared using surface modified Multiwall carbon nanotube (MWCNT) and titanium *n*-butoxide (TNB) with benzene. The composites were characterized by nitrogen adsorption isotherms, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), FT-IR spectra, and UV-vis absorption spectroscopy. The UV radiation induced photoactivity of the CNT/TiO<sub>2</sub> composites was tested using a fixed concentration of methylene blue (MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S·Cl·3H<sub>2</sub>O) in an aqueous solution. Finally, it can be considered that the MB removal effect of the CNT/TiO<sub>2</sub> composites is not only due to the adsorption effect of MWCNT and photocatalytic degradation of TiO<sub>2</sub>, but also to electron transfer between MWCNT and TiO<sub>2</sub>.

**Key words :** CNT, TNB, SEM, XRD, UV, Photocatalytic decomposition

## 1. Introduction

Multiwall carbon nanotubes (MWCNTs) could be considered as a good support for materials with photocatalytic properties. This follows from their high mechanical<sup>1)</sup> and chemical<sup>2)</sup> stability as well as their mesoporous structure, which favors diffusion of reacting species. In addition, the dispersion of TiO<sub>2</sub> on the surface of the MWCNTs could create many active sites for the already been used to coat carbon supports for specific applications. A TiO<sub>2</sub> coating on active carbon fibers via TiCl<sub>4</sub> hydrolysis of was used to obtain absorptive materials for NH<sub>3</sub>.<sup>3)</sup> TiO<sub>2</sub> has been also deposited on carbon fibers via a sol-gel method in order to increase their thermal stability.<sup>4)</sup> Electrodeposition techniques have been used to deposit a thin TiO<sub>2</sub> layer on a graphite support, which is an important component of Lead Zirconate Titanate (PZT, Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub>) solid solutions.<sup>5)</sup> In our previous work,<sup>6,7)</sup> activated carbon coated with TiO<sub>2</sub> via a CCl<sub>4</sub> solvent method demonstrated very good performance in terms of photocatalytic degradation of methylene blue.

The photocatalytic degradation of organic pollutants on TiO<sub>2</sub>-anatase surface has been proven to be the most efficient (and popular) method because the TiO<sub>2</sub> is a stable and low-cost photosensitized material.<sup>8)</sup> Effective photoexcitation of TiO<sub>2</sub> particles requires light of energy in excess of its band gap energy; consequently, the formation of electrons (e<sup>-</sup>) in the conduction band, positive holes (h<sup>+</sup>) in

the valance band, and formation of OH radicals results.<sup>9)</sup> Photogenerated electron-hole pairs often recombine. Inhibiting this recombination prolongs the lifetime of carriers and is essential for improving the efficiency of net charge transfer at the semiconductor/electrolyte interface. Hydroxyl ions (OH<sup>-</sup>) are the likely traps for holes. This trapping leads to formation of hydroxyl radicals, which are strong oxidizing agents. Similarly, adsorbed oxygen species are traps for electrons. This leads to the formation of superoxide species (O<sub>2</sub><sup>-</sup>), which are unstable.<sup>10)</sup> The reactive radical species thus generated (OH<sup>-</sup>, O<sub>2</sub><sup>-</sup>) attack organic pollutants (molecules) present in suspensions causing their hydroxylation, oxidation, and finally mineralization occur in forming to carbon dioxide and water.<sup>11,12)</sup>

Here, we report on CNT/TiO<sub>2</sub> composites prepared from MWCNTs and titanium(IV) *n*-butoxide with benzene via a *m*-chloroperbenzoic (MCPBA) oxidation method. To examine their property, the corresponding composites were characterized by BET surface area, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), and FT-IR. To determine the photocatalytic decomposition, the CNT/TiO<sub>2</sub> composites were also investigated using methylene blue (MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S·Cl·3H<sub>2</sub>O) in an aqueous solution under UV irradiation.

## 2. Experimental

### 2.1. Materials

Crystalline MWCNT powder of 95.9 wt% purity from Nanokarbon (Nanokarbon Co., Ltd, Korea) was used as a starting material. A titanium source (titanium *n*-butoxide,

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**Table 1.** Nomenclatures of Samples Prepared with MWCNT and TNB

Samples	Nomenclatures
MWCNT+Titanium n-butoxide (TNB) 5 mL+benzene 15 mL	CTNBB1
MWCNT+Titanium n-butoxide (TNB) 10 mL+benzene 10 mL	CTNBB2
MWCNT+Titanium n-butoxide (TNB) 15 mL+benzene 5 mL	CTNBB3

Ti(OC<sub>4</sub>H<sub>7</sub>)<sub>4</sub>) used for the preparation of CNT/TiO<sub>2</sub> composites was purchased from Acros Organics, New Jersey, USA. To oxidize the surface of the MWCNT, an oxidizing reagent (MCPBA) was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%), which was purchased from Samchun Pure Chemical Co., Ltd, Korea, was used as an organic solvent. Methylene blue (MB) purchased from Dukan Pure Chemical Co., Ltd. was used as analytical tool. It was selected because it can be easily under anaerobic conditions to produce potentially more hazardous aromatic amines.

### 2.2. Synthesis of CNT/TiO<sub>2</sub> composites

To prepare the oxidizing agent, 0.96 g MCPBA was melted in 60 mL Benzene solution. Then, 0.2 g of MWCNT was put into the oxidizing agent, refluxed for 6 h, filtered, and dried. The oxidized CNT was put into the unevenly mixed solution of benzene and TNB. In a vial, the solutions were then homogenized under reflux at 343 K for 5 h using a magnetic stirrer. After stirring, the solutions were transformed to CNT/TiO<sub>2</sub> gels. These gels were heat treated at 973 K for 1 h at a heating rate of 279 K/min. The preparation conditions and samples nomenclature are listed in Table 1.

The synthesized powders were characterized by various techniques. The Brunauer-Emmett-Teller (BET) surface area of the CNT/TiO<sub>2</sub> composites was evaluated via the N<sub>2</sub> adsorption isotherm at 77 K using a BEL SORP. MINI (BEL, Japan, INC.). SEM (JSM-5200 JOEL electron microscope, Japan), was used to observe the surface state and structure of the CNT/TiO<sub>2</sub> composites. XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. The XRD (Shimada XD-D1, Japan) patterns were obtained at room temperature using CuK $\alpha$  radiation. EDX was used for elemental analysis of the CNT/TiO<sub>2</sub> composites. FT-IR spectroscopy (FTS 3000MX, Biored Co.) was used to characterize the functional groups of CNT/TiO<sub>2</sub> composites. UV-vis spectra for the MB solution obtained from degradation by CNT/TiO<sub>2</sub> composites dispersion under UV ray irradiation were recorded using a Genspec (Hitachi, Japan) spectrometer.

### 2.3. Photocatalytic decomposition

The photocatalytic effect of the CNT/TiO<sub>2</sub> composites was determined using MB decomposition in an aqueous solution under an ultraviolet (UV) lamp (356 nm, 1.2 mW/cm<sup>2</sup>). The initial MB concentration was 1.0  $\times$  10<sup>-5</sup> mol/L. The amount of suspended composites was kept constant at 1 g/L in a 50 mL MB solution. Prior to UV irradiation, the solution-

composite mix was kept in the dark for at least 2 h thus allowing adsorption-desorption equilibrium to be reached. 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 the solution, this is hereafter considered the initial concentration (C<sub>0</sub>) after dark adsorption. Samples were then withdrawn from the reactor at 10 min intervals starting at 10 min to 1 h. They were immediately centrifuged to separate any suspended solids. The clean transparent solution was analyzed by using a UV/vis spectrophotometer (250~600 nm).<sup>7)</sup> The spectra (550~750 nm) for each sample were recorded and the absorbance at a characteristic wavelength 660 nm was then determined.

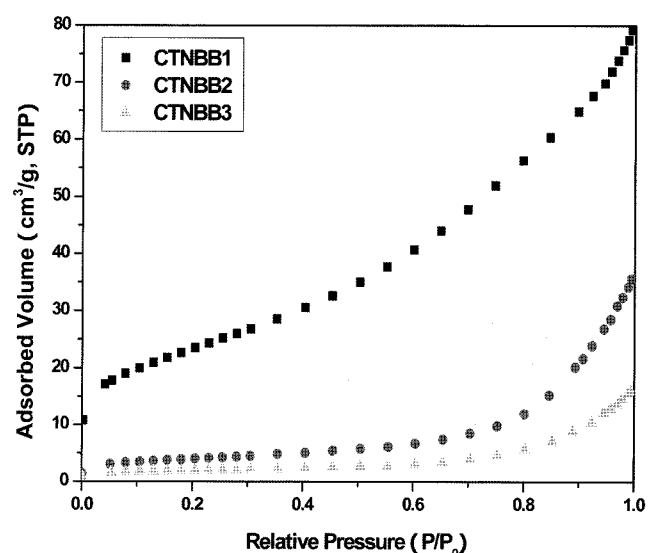
## 3. Results and Discussion

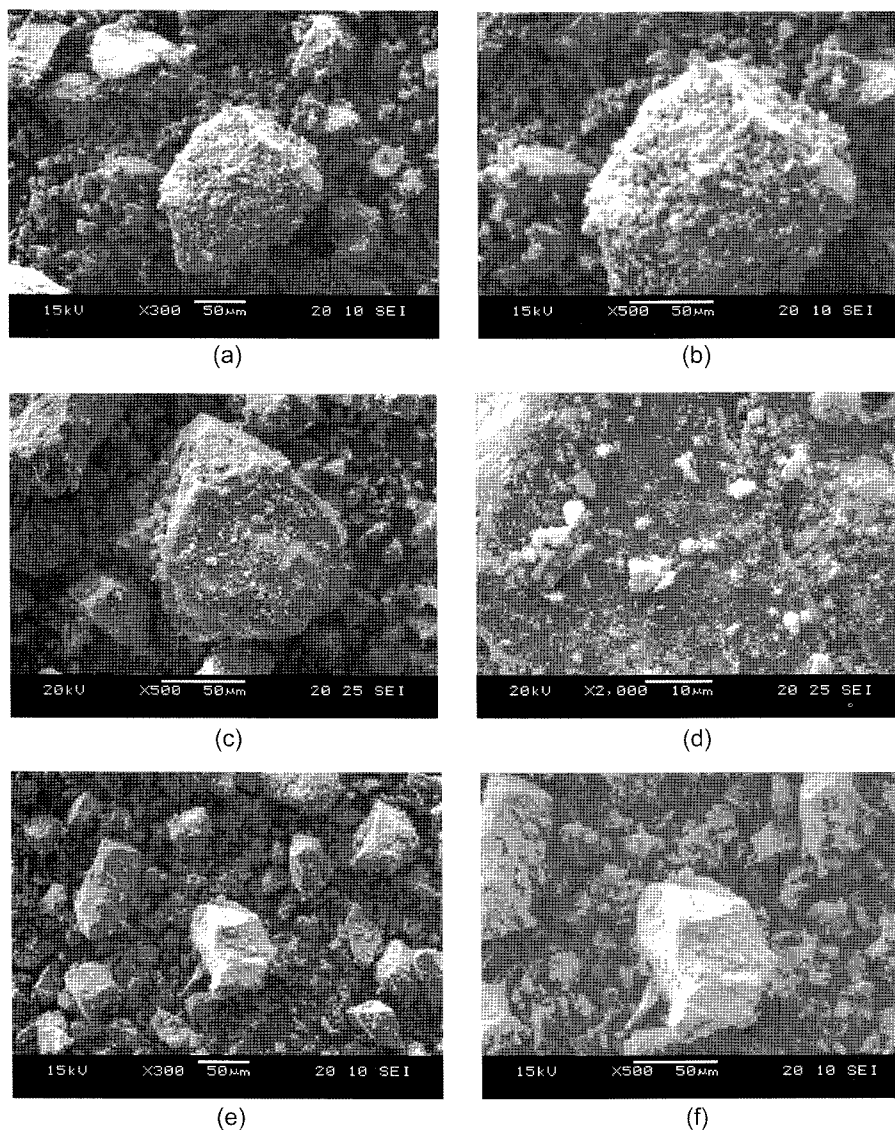
### 3.1. Characteristics of CNT/TiO<sub>2</sub> composites

The N<sub>2</sub> adsorption isotherms for the CNT/TiO<sub>2</sub> composites indicate that total sorption uptake decreases with an increasing ratio of TNB with benzene (Fig 1). All of the

**Table 2.** The BET Surface Area of CNT/TiO<sub>2</sub> Composites

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)
CTNBB1	84.06
CTNBB2	14.25
CTNBB3	6.622

**Fig. 1.** Adsorption isotherm of N<sub>2</sub> at 77 K on the CNT/TiO<sub>2</sub> composites.



**Fig. 2.** SEM images of CNT/TiO<sub>2</sub> composites; CTNBB1: (a) and (b); CTNBB2: (c) and (d); CTNBB3: (e) and (f).

isotherms can be ascribed to type II, which suggests micro- and mesoporous texture. The BET surface areas of CNT/TiO<sub>2</sub> composites results indicate that there is a marked decrease of BET surface area with an increasing ratio of TNB with benzene (Table 1). Wang *et al.*<sup>13</sup> reported that MWCNT introduced into a TiO<sub>2</sub> matrix can prevent the TiO<sub>2</sub> particles from agglomerating, and increasing the amount of MWCNT would increase the surface area. In this work, we prepared CNT/TiO<sub>2</sub> composites using a constant amount of MWCNT and an increasing ratio of TNB with benzene. So, in this case, the TiO<sub>2</sub> particles agglomerated with relative ease, thus decreasing surface area.

Morphology of the CNT/TiO<sub>2</sub> composites prepared with surface oxidized MWCNT and TNB with benzene was borne out by SEM micrographs. The synthesized powder consisted of an irregular aggregate of particles including a large amount of TiO<sub>2</sub> particles and a small amount of CNT particles (Fig. 2). A large amount of TiO<sub>2</sub> particle aggregates

were observed in the SEM images; the MWCNTs were embedded into these aggregates. We can conjecture that the TNB (as a titanium dioxide sources) was completely converted to TiO<sub>2</sub> under the experimental conditions considered in this work.

The influence of different ratios of TNB and benzene on the transformation of anatase to rutile phases at heat-treated temperatures was determined by XRD method. Fig. 3 shows typical XRD patterns obtained from the samples prepared with surface modified MWCNT and TNB with benzene. The samples were heat-treated at 973 K for 1 h. As is well-known, the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changes into a single phase of rutile at 973~1173 K.<sup>14</sup> However, in this study, the patterns (Fig. 3) indicate that the samples contained both anatase and rutile structures when annealed at 973 K. We have previously demonstrated that crystallization phenomena in C/TiO<sub>2</sub> composites heat-

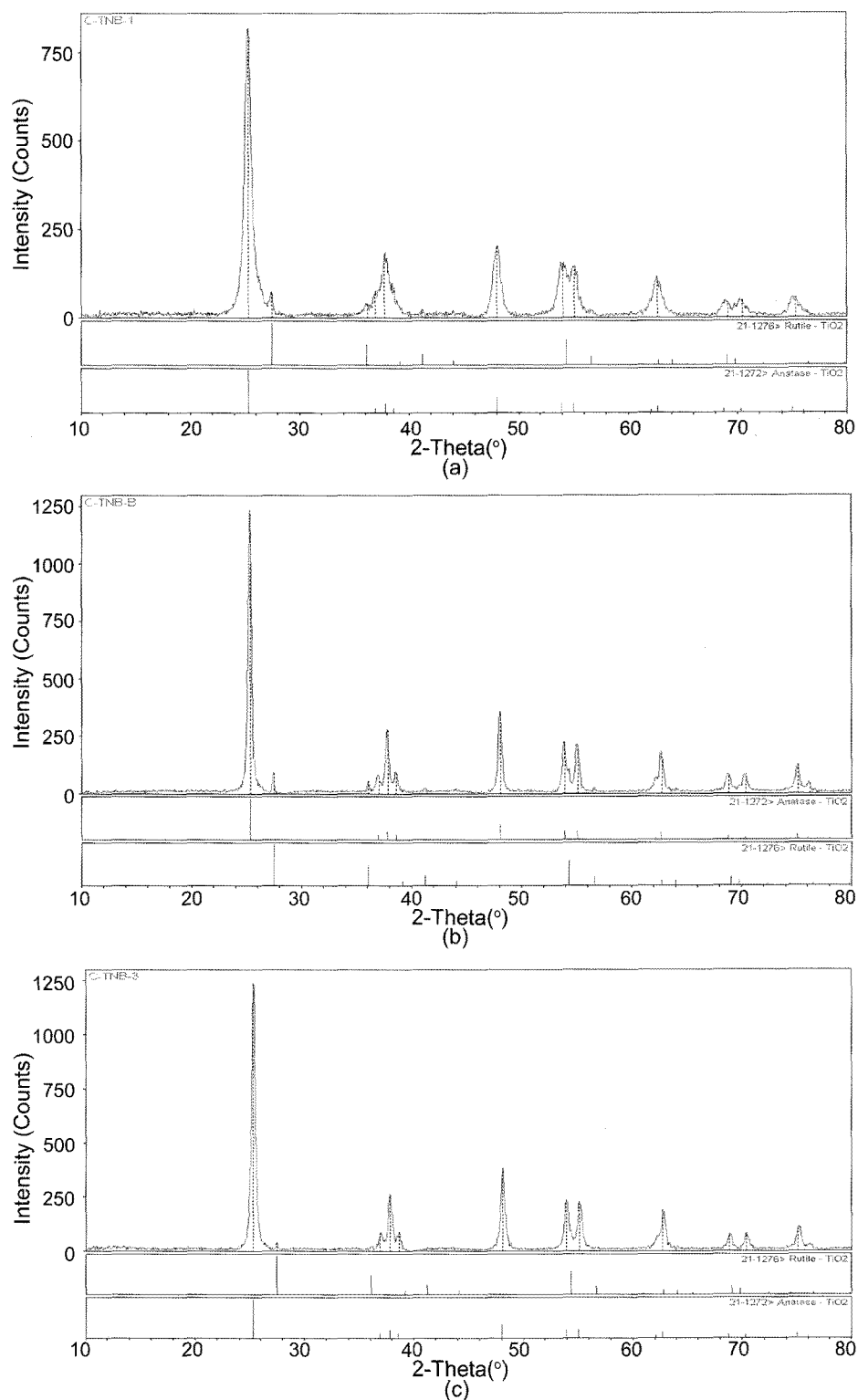


Fig. 3. The XRD patterns of CNT/TiO<sub>2</sub> composites which were heat treated at 973 K. (a) CTNBB1, (b) CTNBB2, and (c) CTNBB3.

treated at 973 K results in a mixed anatase-rutile structure.<sup>7,15)</sup> Thus, the XRD results obtained here are reasonable.

The CNT/TiO<sub>2</sub> composites prepared with surface modified MWCNT and TNB with benzene were characterized by

EDX. From the spectra thus obtained (Fig. 4), we can see that the main elements such as C, O, and Ti are present. Note, however, that though impurities such as Fe, Zn, Cu, Au, and V are also present. Their presence may be derived from the titanium alkoxide precursors (TNB). From the

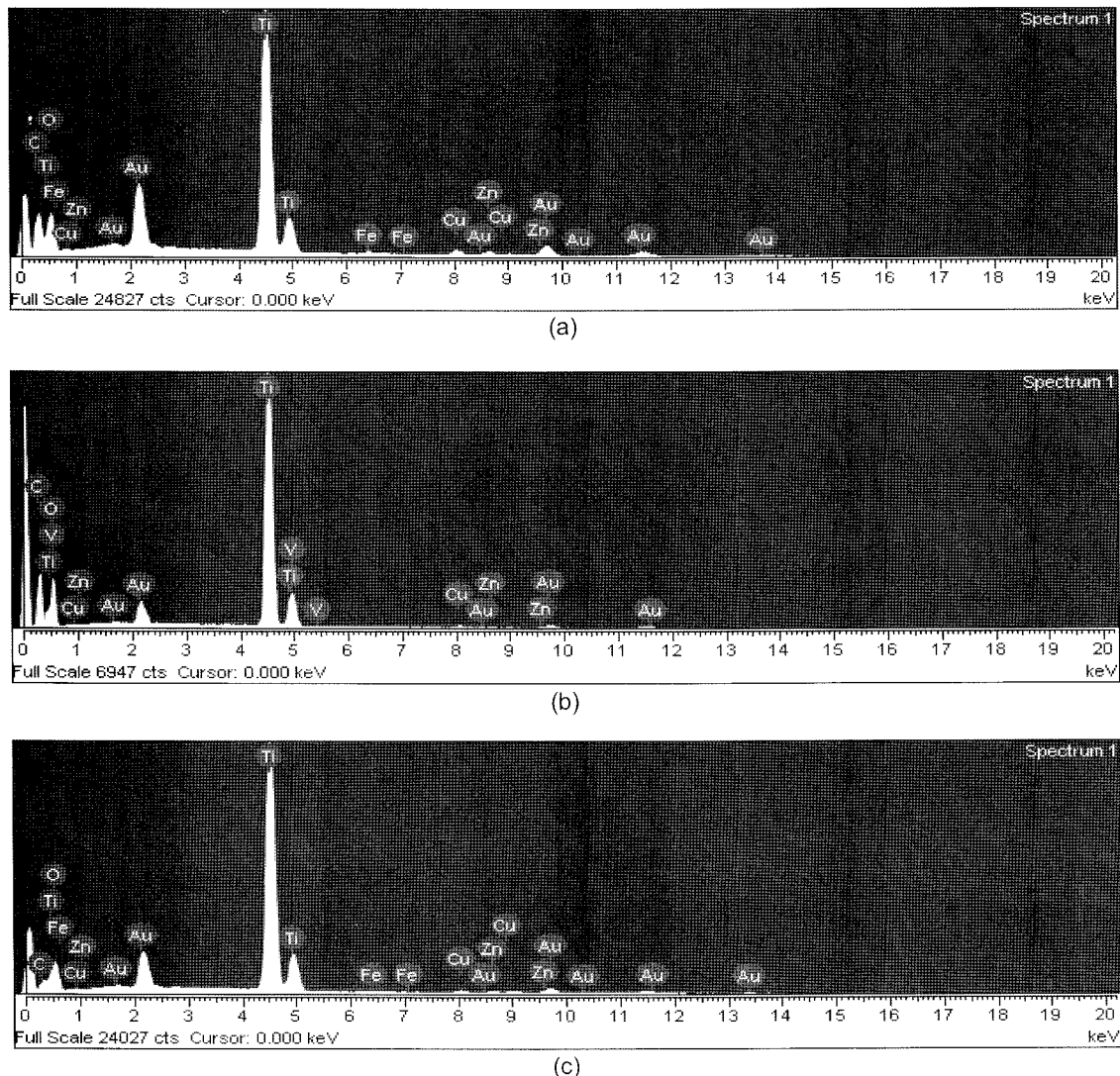


Fig. 4. EDX elemental microanalysis of CNT/TiO<sub>2</sub> composites; (a) CTNBB1, (b) CTNBB2, and (c) CTNBB3.

EDX elemental microanalysis (wt%) of CNT/TiO<sub>2</sub> composites (Table 3), we can also see that all of the composites are richer in C, O, and Ti metals than any other elements. This same result is obtained from the EDX spectra. The amount of C metal is decreased and the amount of Ti and O increase with an increasing ratio of the volume of TNB in the benzene.

FT-IR spectroscopy was used to identify the chemical structure of the CNT/TiO<sub>2</sub> composites. Fig. 5 shows the FT-IR spectra of CNT/TiO<sub>2</sub> composites as a function of the different volume of TNB and benzene. As the MWCNTs in

all of the composites were oxidized at the same experimental conditions, the three samples all show similar spectra. The 1000~1200 cm<sup>-1</sup> region demonstrates the presence of C-O groups. The 1370 cm<sup>-1</sup> peaks are attributed to the bend vibration of -CH<sub>2</sub> or -CH<sub>3</sub> groups. The characteristic band of C=O in carbonyl groups at 1726 cm<sup>-1</sup> is evident. The characteristic peaks of all samples at 2360 cm<sup>-1</sup> disappear completely. Noteworthy is the relative strength of the 1200, 1370, 1726, and 2360 cm<sup>-1</sup> peaks in the CTNBB1 sample compared to the CTNBB2 and CTNBB3 samples. It can be concluded that the CTNBB1 sample has

Table 3. EDX Elemental Microanalysis (wt%) of CNT/TiO<sub>2</sub> Composites

Samples	Elements			
	C	O	Ti	Others
CTNBB1	19.89	35.61	39.26	5.24
CTNBB2	19.66	37.17	40.32	2.85
CTNBB3	6.92	38.69	51.44	5.95

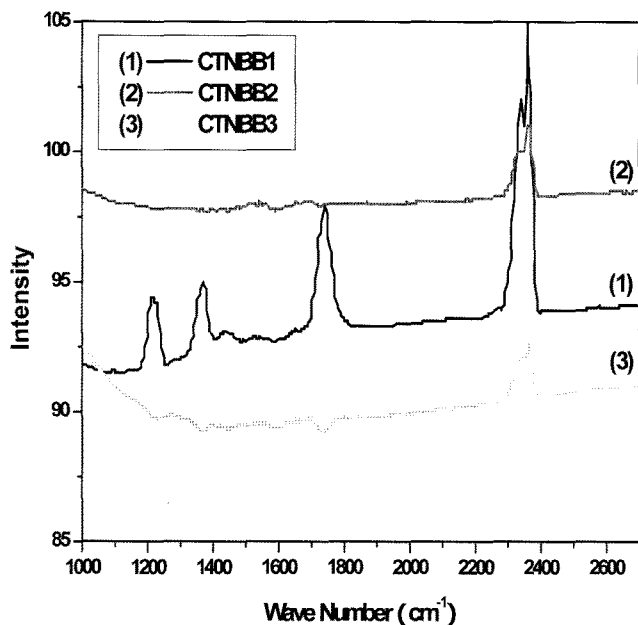


Fig. 5. FT-IR spectra of CNT/TiO<sub>2</sub> composites.

a larger number of oxygen-containing groups on the MWCNT surface. We can thus also predict that CTNBB1 will have better photocatalytic degradation of an MB solution than the other two samples. Regrettably, it is difficult to provide a definitive answer for these facts. Experiments are being performed to further elucidate this aspect of the work.

### 3.2. Photocatalytic activity of CNT/TiO<sub>2</sub> composites

The changes in relative concentration ( $C/C_0$ ) of MB in the aqueous solution upon UV irradiation of the CNT/TiO<sub>2</sub> composites were also determined (Fig. 6). The highest degradation was achieved for the CTNBB1 and CTNBB2 samples, which were almost removed 60% of the concentration of MB solution. However, the degradation of CTNBB3 sample was only 30%. According to the BET surface area data, the surface area of the CTNBB1 and CTNBB2 samples is 84.06 m<sup>2</sup>/g and 14.25 m<sup>2</sup>/g, respectively; however, the BET surface area of the CTNBB3 sample is much lower than either of the CTNBB1 and CTNBB2 samples, which was only 6.662 m<sup>2</sup>/g. Thus, the MB degradation effect via adsorption of MWCNT was very small. We can consider the possibility that the connection between MWCNTs and TiO<sub>2</sub> particles may play a key role in electron transfer. On the other hand, as indicated earlier, the TiO<sub>2</sub> particles with anatase structure have a better photocatalytic activity.<sup>16,17</sup> However, the present results indicate that the CNT/TiO<sub>2</sub> composites contained both anatase and rutile structures. This observation matched the work of Ohno *et al.*<sup>18</sup> who showed that the co-existence of anatase and rutile structures leads to a synergistic effect.

Finally, it can be considered that the MWCNT could act as a photosensitizer. MWCNT, having absorbed the (electromagnetic) radiation and injected photo-induced electrons

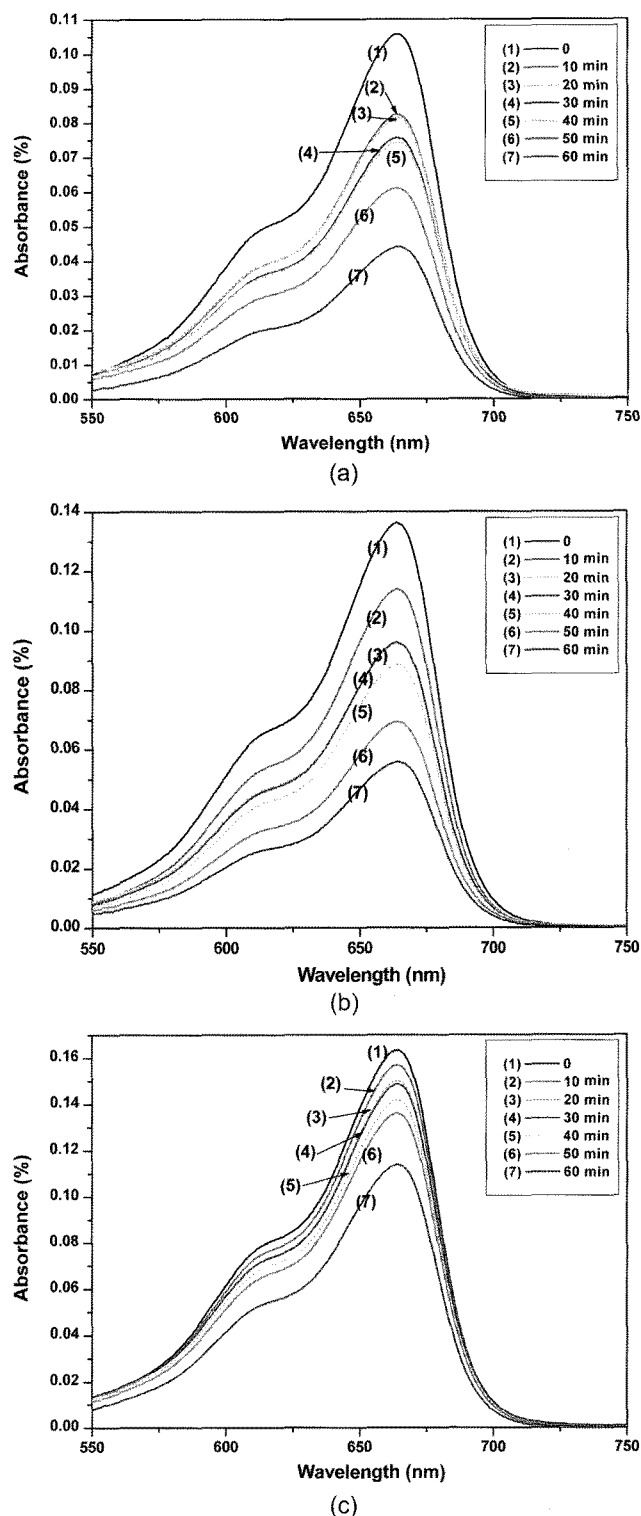


Fig. 6. Dependence of relative concentration of MB in the aqueous solution  $C/C_0$  on time of UV irradiation for the CNT/TiO<sub>2</sub> composites; MB :  $1.0 \times 10^{-5}$  mol/L.

into the TiO<sub>2</sub> conduction band, can trigger the formation of very reactive radicals: superoxide ionic O<sub>2</sub><sup>-</sup> and hydroxyl HO. Both of those are responsible for the degradation of the organic compound. The suggested electron transfer mecha-

nism between carbon and TiO<sub>2</sub> was experimentally supported by our early investigation.<sup>19)</sup>

#### 4. Conclusions

The CNT/TiO<sub>2</sub> composites were prepared with surface modified MWCNT using different ratios of titanium (VI) n-butoxide with benzene. The BET surface area of the CNT/TiO<sub>2</sub> composites decreased with increasing ratio of TNB with benzene. The SEM analyses indicate that the synthesized powder consisted of an irregular aggregate of particles containing a large amount of TiO<sub>2</sub> particles and a small amount of CNT particles. XRD analyses indicate that a mixed structure of anatase and rutile existed in all of the composites which heat-treated at 973 K. The EDX analyses indicate the presence of the main elements C, O, and Ti. The analyses also indicate that other impure elements, derived from TNB, were also present. The FT-IR spectra are shown same function groups in the CNT/TiO<sub>2</sub> composites, indicating complete oxide of MWCNT. The CTNBB1 sample has many more function groups than the other CTNBB2 and CTNBB3 samples. Finally, according to the results of the MB removal experiment, we could see that CTNBB1 and CTNBB2 have better MB removal effect than that of CTNBB3. We can consider that the MB removal effect of the CNT/TiO<sub>2</sub> composites is adsorption of MWCNT, photocatalytic degradation of TiO<sub>2</sub>, and electron transfer between MWCNT and TiO<sub>2</sub>.

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