

# Comparison of the Photonic Effects of Mn-CNT/TiO<sub>2</sub> Composites Modified by Different Oxidants<sup>1</sup>

Zhang Feng Jun<sup>a, b</sup> and Won Chun Oh<sup>b</sup>

<sup>a</sup> Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Anhui Hefei, P.R. China

<sup>b</sup> Department of Advanced Materials & Engineering, Hanseo University, Seosan-si, Chungnam-do, Korea

e-mail: wc\_oh@hanseo.ac.kr

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**Abstract**—Manganese–carbon nanotubes (CNTs) on titania (TiO<sub>2</sub>) composites modified by different oxidants (KMnO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and *m*-chloroperbenzoic acid (MCPBA)) were prepared with a sol–gel method. These composites were comprehensively characterized by the Brunauer–Emmett–Teller (BET) method, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy EDX, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. The photoactivity of these materials prepared under visible light irradiation was tested using methylene blue in aqueous solution. The result shown that among the three oxidants, the MCPBA was the best one for the surface functionalization of CNTs and the manganese treated CNT/TiO<sub>2</sub> composite can enhance the photocatalytic activity. The proposed mechanism of the photodegradation of methylene blue on Mn-CNT/TiO<sub>2</sub> composites was present.

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Wastewater effluents in some industries, such as dyestuff, textiles, leather, paper, and plastics, contain several kinds of synthetic dyestuffs. A very small amount of dye in water is highly visible and can be toxic to life and harmful to human beings. Hence, the removal of colour from process or waste effluents becomes of fundamental importance to the environment [1, 2].

In recent years, photocatalytic degradation of various toxic hazardous organic compounds dissolved in water using TiO<sub>2</sub> and modified TiO<sub>2</sub> photocatalysts under visible light irradiation has been widely studied [3–6]. However, only the ultraviolet fraction of the solar irradiation (about 5%) is active in the photo excitation processes using pure TiO<sub>2</sub> solids. It is therefore necessary to develop a photocatalytic system that can be applied under visible or solar light irradiation [6–9]. Titania is known to be a large band gap (3.0–3.2 eV) semiconductor and is very stable under illumination in the process of H<sub>2</sub>O photolysis because absorbs only UV part of the solar emission. Doping titania with transition metal ions has been tested as a promising way for improving the photocatalytic activity of semiconductor oxides [10–13]. The incorporation of metal ions into titania crystal lattice can significantly extend the absorptivity of photocatalysts in visible range. The effect of doping consists in change of the equilibrium concentration of electrons or holes [14–16].

Manganese oxide is among the oldest examined metal oxide catalyst and found to possess a potential activity in redox reactions. Manganese oxide surface has been found to expose metal (Mn<sup>n+</sup>), oxide (O<sup>2-</sup>) and defect sites of various oxidation states, and exhibits acid and base properties. Furthermore, the *d*–*d* electron exchange interactions between intimately coupled manganese ions in different oxidation states [Mn<sup>n+</sup>–O–Mn<sup>(n+1)+</sup>] furnish the electron-mobile environment necessary for the surface redox activity. Arroyo et al. [17] reported that manganese (Mn<sup>2+</sup>) doped titania, promotes the stabilization of the anatase phase of titania at low doping levels, but stabilizes the rutile phase at higher concentrations of the doping compounds due to segregation of the dopant on the surface. Matsui et al. have reported the visible light-responsive oxidation-reduction function of the composite consisted of TiO<sub>2</sub>, manganese oxide and carbon clusters [18]. MnO<sub>x</sub>/TiO<sub>2</sub> mixed oxides have shown better photocatalytic activity than pure TiO<sub>2</sub> for oxidation of different organic compounds [19].

Moreover, carbon nanotubes (CNTs), as a new class of nanomaterials, have been drawn considerable attention for their applications as catalyst supports [20–25] owing to their unique electrical properties, high chemical stability and high surface-to-volume ratio. CNTs have a large electron-storage capacity (one electron for every 32 carbon atoms) [26], and can promote the electron-transfer reactions at carbon nanotubes modified electrodes. However, weak cou-

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Some characteristics of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites

Preparation of sample	Sample name	$S_{\text{BET}}$ , m <sup>2</sup> /g	$k_{\text{app}} \times 10^{-3}$ , min <sup>-1</sup>	Content, wt %			
				C	O	Ti	Mn
1.6 g KMnO <sub>4</sub> + 0.6 g CNT + 1.3 g MnO <sub>2</sub> + 4 ml TNB	MCT1	75	3.07	20.7	48.8	23.2	7.3
2.3 g (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + 0.6 g CNT + 1.3 g MnO <sub>2</sub> + 4 ml TNB	MCT2	96	3.22	21.5	45.1	21.2	12.2
2.0 g MCPBA + 0.6 g CNT + 1.3 g MnO <sub>2</sub> + 4 ml TNB	MCT3	106	3.29	27.1	40.6	26.4	5.9
2.0 g MCPBA + 0.6 g CNT + 4 ml TNB	CT	198	1.32	53.3	23.0	21.7	0

pling between CNTs and metal oxides is due to van der Waals interactions. Nowadays, techniques improving functionalities of CNT surfaces include chemical treatments using high concentration acids or some other oxide agents. The chemical covalent bond mechanism is considered most useful to maintain the stable and strong bonds, and significant efforts have been directed towards the establishment of chemical functionalities on the CNT surface.

In the present study, we selected TiO<sub>2</sub> and MnO in combination with CNTs to study their photocatalytic activity. The combination of these metal oxides and CNTs is expected to give rise to the photocatalytic activity [27]. We have studied the preparation of MnO and TiO<sub>2</sub> supported on CNTs modified by different oxidants. The composite photocatalysts were characterized by Brunauer–Emmett–Teller (BET), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and UV–vis absorption spectra. Finally, the photooxidation of methylene blue (MB) under visible light illumination was investigated for all the samples prepared.

## EXPERIMENTAL

CNTs selected as the support material (Multiwall nanotubes, diameter ~20 nm, length ~5 μm) were supplied from Carbon Nano-Material Technology Co., Ltd. (Korea) and used without further purification. Titanium *n*-butoxide Ti(OC<sub>4</sub>H<sub>7</sub>)<sub>4</sub> (TiNB) (99%) as titanium alkoxide precursor for TiO<sub>2</sub> was purchased from Acros Organics (New Jersey, USA). MnO<sub>2</sub> was received from Samchun Pure Chemical Co., Ltd. (Korea). KMnO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> used for oxidation were purchased from the same company. *m*-Chlorperbenzoic acid (MCPBA) (Acros Organics), New Jersey USA were chosen as the oxidizing agents. Benzene (99.5%, Samchun Pure Chemical Co. Ltd, Korea) was used as the organic solvent. MB (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl · 3H<sub>2</sub>O) of analytical purity was purchased from Dukan Pure Chemical Co., Ltd (Korea).

Chemical oxidation was carried out using three kinds of oxidizing reagents which were KMnO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and MCPBA. For the oxidative treatment, ca 0.6 g CNTs was mixed with 60 ml of oxidizing reagent solutions. The mixture was stirred on a hot plate with a magnet stirrer for 6 h at 343 K in a closed container. Then the CNTs were dried at 373 K in air.

To prepare the Mn-CNT/TiO<sub>2</sub> composites, the surface functionalized CNTs were treated at first by the solution of MnO<sub>2</sub> in 0.5 M HNO<sub>3</sub>. Surface functionalized CNTs (0.6 g) was put into 50 ml of this MnO<sub>2</sub> solution and heated under stirring on hot plate for 6 h at 343 K followed by drying at 373 K and heat treatment at 773 K for 1 h. Titanium alkoxide precursors were dissolved separately in benzene at 1 : 1 ratio. The solution was stirred magnetically for 30 min to obtain TiNB-benzene solution. Then the Mn/CNTs mixture was introduced into TiNB-benzene solution. The mixtures were kept stirring magnetically at 343 K for 5 h, until a homogenous CNTs-contained gel formed. The gel was heated at 973 K for 1 h in air to

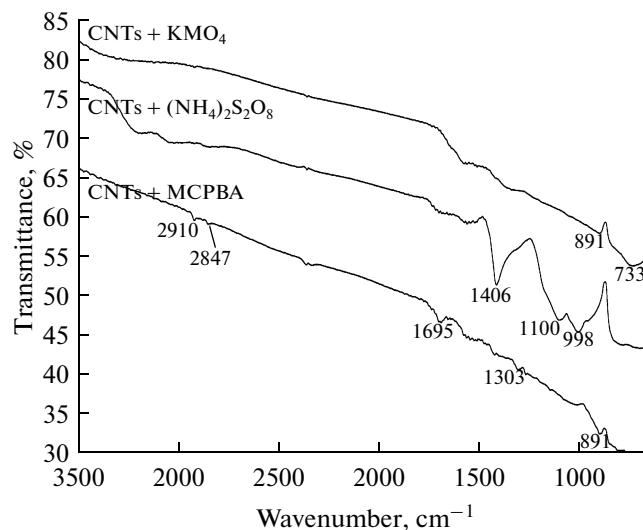


Fig. 1. FT-IR spectra of CNTs oxidized by different agents.

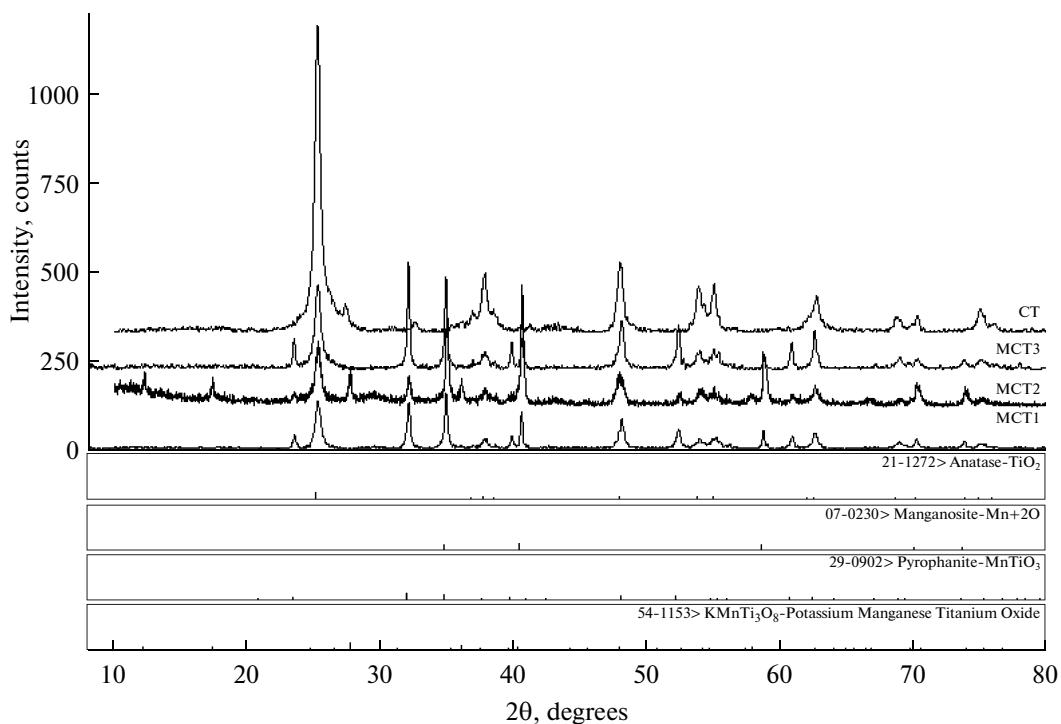


Fig. 2. XRD patterns of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites.

obtain Mn-CNT/TiO<sub>2</sub> composite catalysts. By changing the oxidants, different samples were obtained. The preparation condition and code of the samples are listed in the table.

Synthesized powders were characterized by various techniques. The functional groups formed on the surface were investigated by a KBr matrix method using FT-IR spectroscopy. Discs for analysis were prepared by mixing 1 mg of powdered oxidized CNTs with 600 mg of KBr in an agate mortar, and then pressed under a pressure of 450 Pa for 3 min. The spectra of the samples were obtained at wavenumbers between 4000 and 500 cm<sup>-1</sup> using a spectrophotometer FTS 3000MX (Biored Co., USA). BET surface area was measured using a Surface Area analyzer (MONOSORB, Quantachrome Instruments Ltd., USA). XRD (Shimata XD-D1, Japan) was used for crystal phase identification and estimation of the anatase-to-rutile ratio at room temperature. The surface state and structure of the Mn-CNT/TiO<sub>2</sub> composites was studied by SEM (JSM-5200 JOEL, Japan). Finally, UV-vis spectra of the MB aqueous solution degraded on Mn-CNT/TiO<sub>2</sub> composites under visible light irradiation were recorded using an Optizen Pop spectrometer (Mecasys Co., Ltd., Korea).

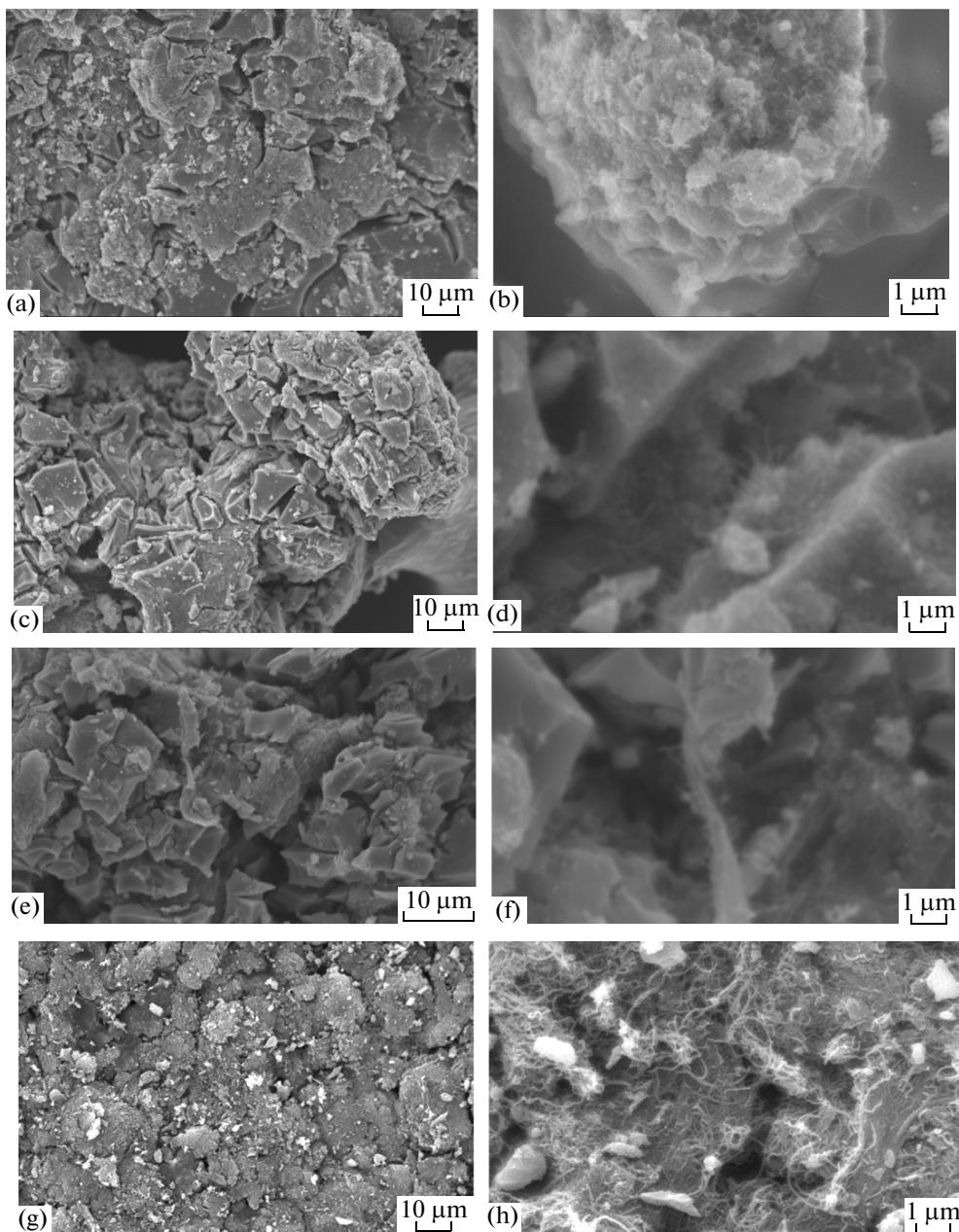
The photocatalytic effect of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites was determined using MB decomposition in aqueous solution under visible light (8 W, KLD-08L/P/N, Fawoo Technology). The initial

MB concentration ( $C_0$ ) was  $1.0 \times 10^{-5}$  mol/l. The suspended composites (1 g/l) were kept in 50 ml MB solution. The weight ratio of composite to dye was 1 : 32. Before irradiation under visible 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 visible 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 MB concentration in solution, which was hereafter considered as the initial concentration after dark adsorption. Samples were then withdrawn regularly from the reactor at 30, 60, 90, and 120 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed using the UV-vis spectrophotometer. The absorbance at a characteristic wavelength 660 nm was measured for each MB solution degraded.

## RESULTS AND DISCUSSION

### *Characterization of the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> Composites*

The BET surface areas of the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites are listed in the table. The surface area of MCT3 is much lower than that of CT with the same oxidizing agent (MCPBA). The surface areas of the Mn-CNT/TiO<sub>2</sub> composites with different oxi-

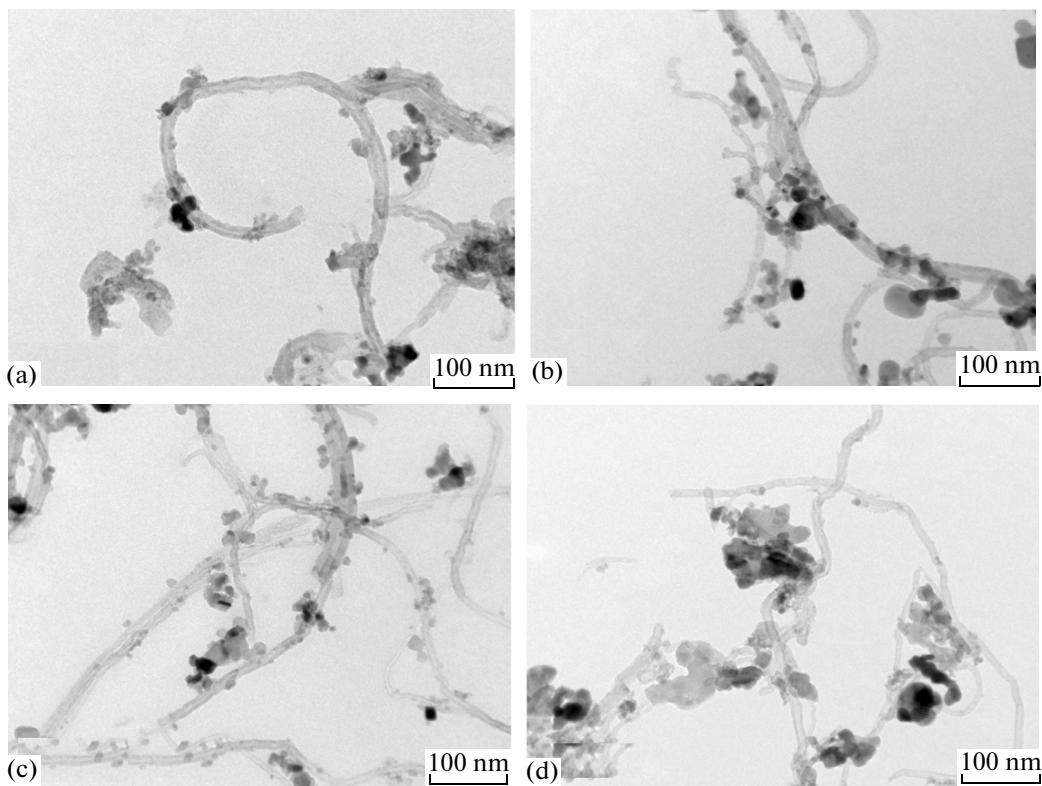


**Fig. 3.** SEM images of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites modified by different oxidizing agents: a, b—MCT1; c, d—MCT2; e, f—MCT3; g, h—CT.

dizing agents were different. It can be suggested that the manganese oxide particles, titania particles on the surface of CNTs and titania particles agglomerated together with the metal oxide particles decreased the surface area of composites.

The FT-IR spectra of surface functionalized CNTs are shown in Fig. 1. After oxidation by three kinds of strong oxidants (KMnO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and MCPBA), the CNTs have various functional groups. After oxidation by a KMnO<sub>4</sub> solution, the IR spectrum of the oxidized CNTs shows important absorption bands at 891

and 733 cm<sup>-1</sup> (assigned to C—H stretching). After oxidation by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> the IR spectrum shows bands at 1406 (N—H stretching of NH<sup>+</sup>), 1100 (C—O stretching) and 998 cm<sup>-1</sup> (C—N stretching) in agreement with the literature data [28]. The bands at 2910 and 2847 cm<sup>-1</sup> which appeared after oxidation by MCPBA can be attributed to C—H stretching vibration and the bands at 1695, 1303 and 891 cm<sup>-1</sup> can be assigned to C=O, S=O and C—H stretching vibration, respectively. The above observations suggest that oxidation was promoted by all treatments, and functional groups



**Fig. 4.** TEM micrographs obtained from powdered CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites: a—MCT1, b—MCT2, c—MCT3, d—CT.

formed can increase the quantity of active sites on the surface of CNTs.

The XRD results are shown in Fig. 2. All samples exhibit peaks at  $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ, 53.8^\circ, 54.9^\circ$  and  $62.5^\circ$  which are the diffractions of (101), (004), (200), (105), (211) and (204) atase planes, respectively. This indicates that all samples exist only in anatase state. For the manganese treated composites, the peaks attributed to MnTiO<sub>3</sub> (PDF #29-0902) could also be seen on the XRD curves; moreover, the crystal structure of these as-products is confirmed to be the MnO phase (PDF #07-0230) and the six diffraction peaks are well matched to (111), (200), (220), (311), (222), and (400) crystal faces of pure solid MnO phase. The formation of MnO can increase the photo-induced electron generation under the visible light irradiation due to its lower band gap [29]. On the other hand, the characteristic peaks of CNTs could hardly be identified from the XRD patterns of all samples. It was thought that the absence of CNTs aggregated pores was supported by the disappearance of CNTs characteristic peaks in XRD patterns.

The surface microstructure and morphology of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites were characterized by SEM (Fig. 3) and TEM (Fig. 4). Figure 3 shows that in all samples TiO<sub>2</sub> particles are dispersed on the surface of CNTs, although a partial

agglomeration takes place. Unlike the samples without Mn, in Mn-CNT/TiO<sub>2</sub> composites, TiO<sub>2</sub> and manganese oxide particles are mixed with CNT networks and form large blocks, resulting in the decrease of surface areas of the composites. These results are in accordance with the surface areas of the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites and are further confirmed by a TEM inspection of Mn-CNT/TiO<sub>2</sub>. The micrographs (Fig. 4) demonstrate that TiO<sub>2</sub> particles are distributed uniformly on the outside surface of the CNT in the CNT/TiO<sub>2</sub> composites. In Mn-CNT/TiO<sub>2</sub>, TiO<sub>2</sub> particles are still distributed uniformly on the outside surface of the CNT tube, and Mn particles are completely attached to the surface of the tube, although this causes partial agglomeration. It is known that finely dispersed small particles could provide more reactive sites for the reactants than aggregated particles. The much better dispersion of TiO<sub>2</sub> and Mn particles occurs on the outside surfaces of the CNTs modified with MCPBA compared to the modification with KMnO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. At the same time, the conductivity of a CNT network can facilitate the electron transfer between the adsorbed dye molecules and the catalyst substrate. It is a beneficial factor for the enhancement of the photocatalytic activity of these composites.

EDX analysis was performed on several zones of the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites. The main elements and their contents are shown in Fig. 5 and in the table, respectively. As seen from Figs. 5a, 5b and 5c, four principal elements (C, O, Ti and Mn) are present in the Mn-CNT/TiO<sub>2</sub> composites along with some impurity elements. We suppose that the impurity was derived from the CNT (used without further purification) and its content is very small. Moreover, from the table we can see that the content of Mn in MCT2 is much higher than that in MCT1 and MCT3. One can assume that the concentration of KMnO<sub>4</sub> which was used to oxidize the CNTs is too high and increases the Mn content in the composite.

#### Photocatalytic Activity of the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> Composites

Relative concentration ( $C/C_0$ ) of MB solution as a function of visible light irradiation time of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> is depicted in Fig. 6. After adsorption in the dark for 2 h, all samples reach adsorption–desorption equilibrium. The concentrations of MB solutions in the presence of MCT1, MCT2, MCT3 and CT decrease to 42, 50, 55 and 60%, respectively. At 120 min irradiation using MCPBA as the oxidant, the CNT/TiO<sub>2</sub> composite (CT) shows almost no photocatalytic activity because it can utilize only ultraviolet light. But Mn-CNT/TiO<sub>2</sub> (MCT3) exhibits rather good photocatalytic activity under irradiation by visible light. It is concluded that the addition of manganese oxide enhances the photocatalytic activity of the Mn-CNT/TiO<sub>2</sub> composite. The same phenomenon is observed for MCT1 and MCT2. Data related to different initial concentrations, along with the regression coefficients are listed in the table. The apparent rate constants ( $k_{app}$ ) of MB discoloration calculated by the slope of concentration curves for MCT1, MCT2, MCT3 and CT are  $3.07 \times 10^{-3}$ ,  $3.22 \times 10^{-3}$ ,  $3.29 \times 10^{-3}$  and  $1.32 \times 10^{-3} \text{ min}^{-1}$ , respectively. Taking into consideration the adsorption and decomposition effects, MCT3 is found to exhibit good photocatalytic activity and the photodegradation efficiency reaches 30%. It is shown that MCPBA as the oxidant demonstrates the best surface functionalization effect for the CNTs.

#### Proposed Mechanism of Photocatalytic Degradation

Figure 7 presents the reaction mechanism on the investigated catalysts. It is well known that the electrons from the photoinduced electron–hole ( $e^-/h^+$ ) separation process must also be removed from the TiO<sub>2</sub> phase; this removal can be achieved via an oxidant, e.g. adsorbed oxygen molecules from the solution. In the CNT/TiO<sub>2</sub> composites, electrons are transferred from the TiO<sub>2</sub> phase (low electron conductivity) to the

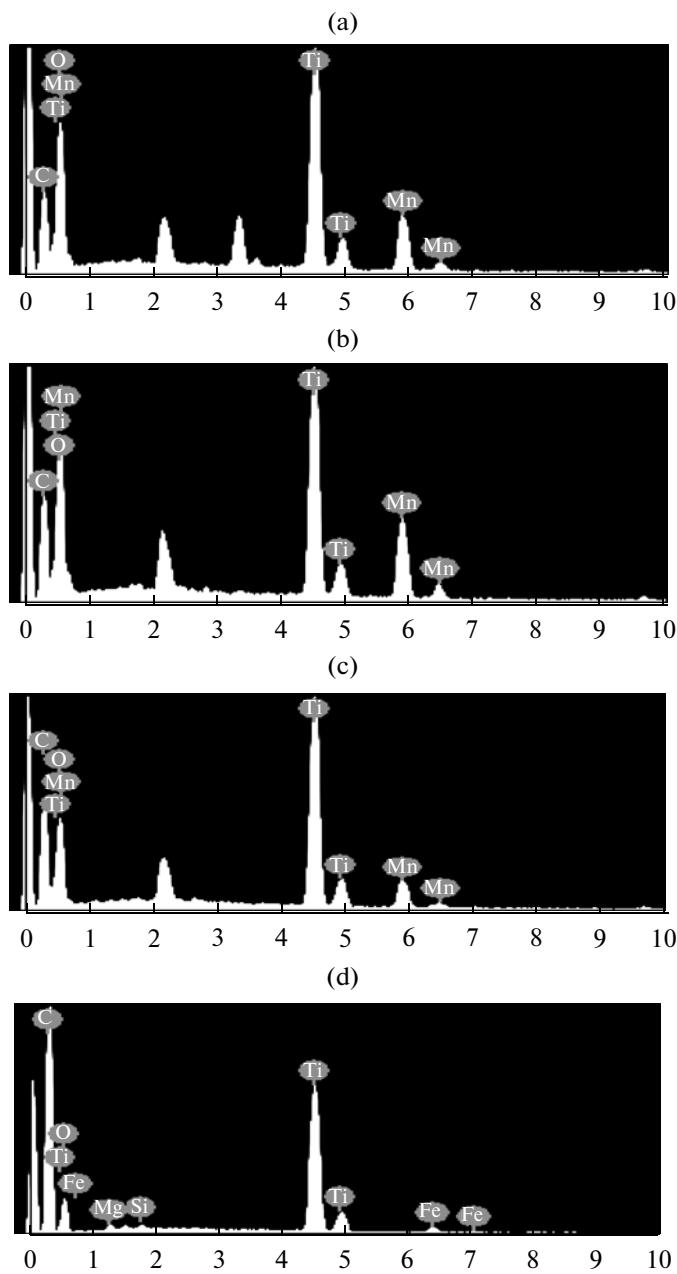
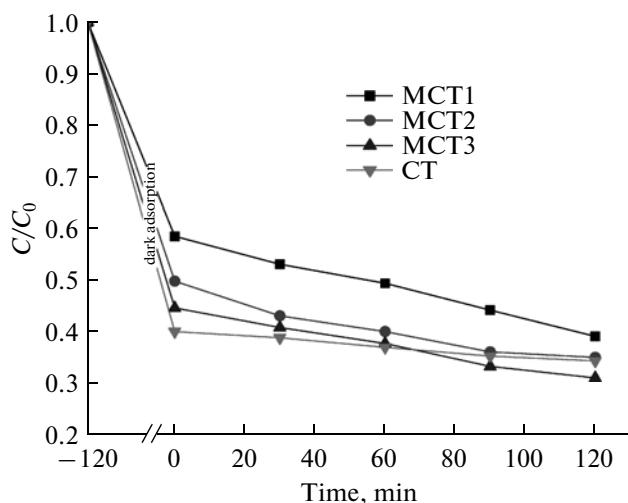


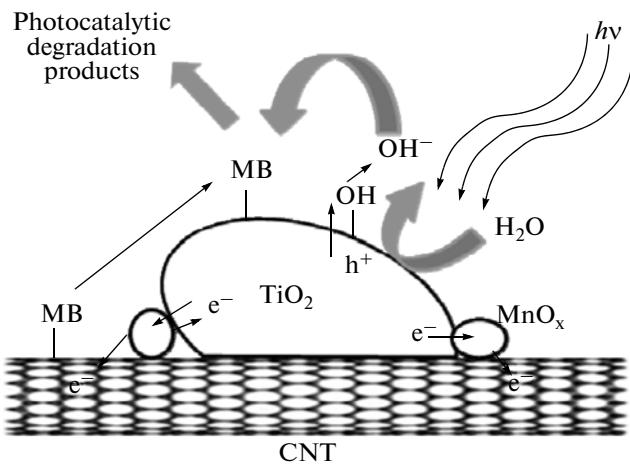
Fig. 5. EDX elemental microanalysis of CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites: a—MCT1, b—MCT2, c—MCT3, d—CT.

carbon phase (high electron conductivity). Furthermore, the TiO<sub>2</sub> particles mixed well with the CNT network create a local potential differences in the TiO<sub>2</sub> phase which spread throughout the sample, resulting in more effective  $e^-/h^+$  separation within the entire sample.

The high rate observed in the photodecomposition of MB on Mn-doped samples could be correlated with the role of exposed Mn species on the surface of the CNT/TiO<sub>2</sub>, which enhance the activity of the photo-



**Fig. 6.** Relative concentration of MB in the aqueous solution as a function of UV irradiation time for the CNT/TiO<sub>2</sub> and Mn-CNT/TiO<sub>2</sub> composites. The concentration of MB solution is  $1.0 \times 10^{-5}$  mol/l.



**Fig. 7.** Proposed mechanism of the MB photodegradation on Mn-CNT/TiO<sub>2</sub> composites.

catalyst by releasing  $e^-/h^+$  pairs under irradiation. The photogenerated  $e^-/h^+$  pairs can easily and quickly diffuse to the surface of catalysts to form active sites at which photocatalytic reactions are produced. More specifically, in Mn-CNT/TiO<sub>2</sub>, the photogenerated electrons transfer from TiO<sub>2</sub> to Mn particles and the holes remain on the TiO<sub>2</sub>, resulting in charge separation of the photoformed  $e^-/h^+$  pairs with good efficiency. Moreover, CNTs act as an electron sensitizer and donator in a composite photocatalysts and may accept  $e^-$  induced by light irradiation. It is considered that photoinduced charge transfer occurs in the electronic interaction between the walls of CNTs and TiO<sub>2</sub> and lead to a higher rate of  $e^-/h^+$  pair recombination and increase the photon efficiency. As a result, the

photogenerated  $e^-/h^+$  are separated efficiently, and the photocatalytic activity is enhanced.

On the other hand, continued adsorption of MB on carbon surfaces has provided the substrate for the photocatalysis by TiO<sub>2</sub>. Obviously, photodecomposition of adsorbed MB increases the rate of MB adsorption by keeping the adsorptive capacity of the support unsaturated. These two mutually enhanced processes are shown in Fig. 7: the combination of adsorption on the CNTs and photocatalysis by deposited TiO<sub>2</sub> create the novel properties of the Mn-treated CNT/TiO<sub>2</sub> photocatalyst.

So, in this study, we describe the synthesis and properties of the Mn-CNT/TiO<sub>2</sub> composites modified by different oxidants. The surface area of Mn-CNT/TiO<sub>2</sub> decreases due to the presence of manganese oxide particles on the surface of CNTs. Using MCPBA as oxidant, it is possible to raise the quantity of functional groups on the surface of CNTs. XRD results show that all samples exist only in anatase state; moreover, the crystal structure of MnO was also confirmed. The results of MB degradation indicate that manganese oxide addition enhances the photocatalytic activity of Mn-CNT/TiO<sub>2</sub>. MCT3 exhibits good photocatalytic activity.

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