

A Novel Synthesis and Photonic Effect of Fe-CNT/TiO₂ Composites by Controlling of Carbon Nanotube Amounts

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Abstract Titanium dioxide (TiO₂) particles deposited on different quantitative Fe-treated carbon nanotube (CNT) composites with high photocatalytic activity of visible light were prepared by a modified sol-gel method using TNB as a titanium source. The composites were characterized by BET, XRD, SEM, TEM and EDX, which showed that the BET surface area was related to the adsorption capacity for each composite. From TEM images, surface and structural characterization of for the CNT surface had been carried out. The XRD results showed that the Fe-ACF/TiO₂ composite mostly contained an anatase structure with a Fe-mediated compound. EDX results showed the presence of C, O, and Ti with Fe peaks in the Fe-CNT/TiO₂ composites. The photocatalytic activity of the composites was examined by degradation of methylene blue (MB) in aqueous solution under visible light, which was found to depend on the amount of CNT. The highest photocatalytic activity among the different composites was related to the optimal content of CNT in the Fe-CNT/TiO₂ composites. In particular, the photocatalytic activity of the Fe-CNT/TiO₂ composites under visible light was better than that of the CNT/TiO₂ composites due to the introduction of Fe particles.

Key words Fe-CNT/TiO₂ composites, photocatalytic activity, visible light, MB.

1. Introduction

Composites, formed by two or more distinct materials, have desirable combinations of properties that are not found in the individual component.¹⁾ Carbon nanotube (CNT)-based composites have attracted much attention due to their unique properties and promising applications. Since the discovery of CNT efforts have been made to explore their applications using various approaches as fact one of the most remarkable emergent materials.²⁾ In a recent review, attention has been drawn to the fact that CNT can compete with activated carbon as catalyst, which supported TiO₂,³⁻⁶⁾ ZnO⁷⁾ and WO₃⁸⁾ due to the combination of their fascinating electronic, special structure, extraordinary mechanical and thermal properties.⁹⁾ These studies have reported that CNT-supported semiconductor catalyst enhanced the photocatalytic activity of semiconductor.

Since water pollution has become a global concern threatening the survival of human beings. Photocatalysis was considered that is a novel method for the treatment of air and water pollutants.¹⁰⁾ Thus, semiconducting photocatalysts are widely used in the destruction of organic pollutants due to their high photocatalytic activity. Now TiO₂ is the focus.

Composite materials containing CNT and TiO₂ are

believed to provide many applications and exhibit cooperative and synergetic effects between the metal oxides and carbon phases. However, some recent works showed that the only reported study on this matter with low CNT content (1.5 wt.%) failed to confirm this prediction in phenol degradation under UV light.¹¹⁾ Subsequently, it was reported that a considerable synergetic effect of CNT and TiO₂ composite catalysts with higher CNT content on phenol degradation under UV light.¹²⁾ In addition, it was also reported that the photocatalysis activity of CNT/TiO₂ composites can be affected in different CNT content due to multiple roles of CNT as adsorbent, dispersing agent and photosensitizer, respectively.¹³⁾

Otherwise, because of their great hardness and toughness, CNT keep their morphology and structure even at high nanoparticle loadings. Many types of metal such as Au,¹⁴⁾ Ag,¹⁵⁾ Fe¹⁶⁾ and Pt¹⁷⁾ have been coated on CNT using different methods. The metal modified CNT is also promising applications in heterogeneous catalysis.¹⁸⁾

In this paper, TiO₂ was modified by Fe treated CNTs as additives of five kinds of different amounts. The effects of Fe-CNT/TiO₂ on photocatalytic activities were studied by destructing the MB dye under visible light.

2. Experimental Procedure

2.1 Materials

Carbon nanotube (CNT) as the support material for

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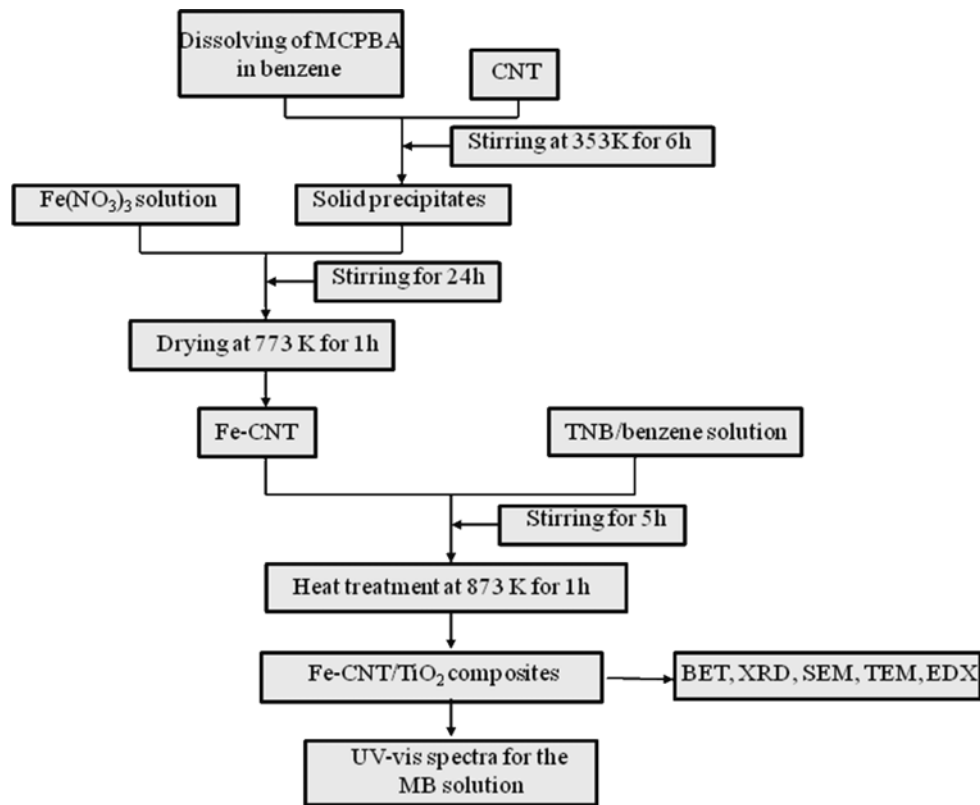


Fig. 1. The preparation procedure of Fe-CNT/TiO₂ composites.

Table 1. Nomenclatures, BET surface area and EDX elemental microanalysis (wt.%) of Fe-CNT/TiO₂ composites.

Samples	Nomenclatures	S_{BET} (m ² /g)	Elements (wt.%)			
			C	O	Ti	Fe
CNT (0.2) + Fe(NO ₃) ₃ + TNB	FC2T	24.8	6.46	44.58	47.95	1.01
CNT (0.4) + Fe(NO ₃) ₃ + TNB	FC4T	57.4	18.03	36.30	44.41	1.26
CNT (0.6) + Fe(NO ₃) ₃ + TNB	FC6T	89.3	23.50	32.80	42.59	1.10
CNT (0.8) + Fe(NO ₃) ₃ + TNB	FC8T	117.6	31.38	29.01	37.84	1.78
CNT (1.0) + Fe(NO ₃) ₃ + TNB	FC10T	147.5	48.73	28.36	20.35	2.56

preparation of Fe-CNT/TiO₂ composite was purchased from carbon nano-material technology Co., Korea (diameter: ~20 nm, length: ~5 nm). *m*-chloroperbenzoic acid (MCPBA) was used as an oxidized reagent which was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as an organic solvent which was purchased from Samchun Pure Chemical Co., Ltd, Korea. The TNB (Ti (OC₄H₇)₄) as a titanium source for the preparation of composites was purchased from Acros Organics, New Jersey, USA. And Fe (NO₃)₃ · 9H₂O as the ferric source was purchased from Duksan Pure Chemical Co., Ltd, (Korea). The MB (99.99+ %) was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, (Korea).

2.2 Preparation of samples

First, 5 g MCPBA was dissolved in 100 mL benzene.

And then, 3 g CNT powder was put into the oxidizing agent solution, refluxed at 353 K for 6 h then the solid precipitates was formed and dried at 363 K. The requisite amounts of oxidized CNT (0.2, 0.4, 0.6, 0.8 and 1 g) was added into to 5 mL 0.1M Fe (NO₃)₃ · 9H₂O solution respectively, and the mixtures were stirred for 24 h using a non-magnetic stirrer at room temperature. After the heat treatment at 773 K, we obtained the Fe-treated CNT. The Fe-treated CNT was put into the mixing solution of TNB and benzene with a volume ratio of 10:30 mL. And then the mixed solution was stirred for 5 h in an air atmosphere. After stirring the solution transformed to gel state, and these gels were heat treated at 873 K for 1h. And then the Fe-CNT/TiO₂ composites were obtained. The procedure and nomenclatures of prepared samples are shown in Fig. 1 and listed in Table 1, respectively.

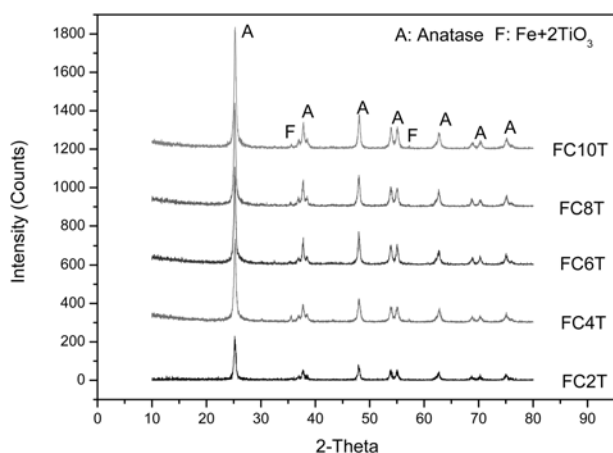


Fig. 2. XRD patterns of powdered Fe-CNT/TiO₂ composites.

2.3 Characteristics and investigations of the samples

The BET surface area by N₂ adsorption method was measured at 77 K using a BET analyzer (Monosorb, USA). XRD (Shimadzu XD-D1, Japan) result was used to identify the crystallinity with Cu K α radiation. SEM was used to observe the surface state and structure of Fe-treated CNT/TiO₂ composites using an electron microscope (JSM-5200 JOEL, Japan). TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200kV was used to investigate the size and distribution of the ferric and titanium deposits on the CNT surface of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid. EDX spectra were also obtained for determining the elemental information of Fe-CNT/TiO₂ composites. UV-vis absorption parameters for the MB solution decomposed by Fe-CNT/TiO₂ composites under visible light irradiation were recorded by a UV-vis (Optizen Pop Mecasys Co., Ltd., Korean) spectrophotometer.

2.4 Photocatalytic activity of samples

The photocatalytic decomposition was tested by Fe-CNT/TiO₂ composites powder and an aqueous solution of MB in a 100 mL glass container and then irradiation system with visible light (8W), which was used at the distance of 100 mm from the solution in dark box. The same amount of different CNT content of Fe-CNT/TiO₂ composites (0.05 g) was suspended in 50 mL of MB solution with a concentration of 1.0×10^{-5} M respectively. Then, the mixed solution was emplaced in the dark for at least 2 h, in order to establish an adsorption-desorption equilibrium, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Then, experiments were carried out under visible light. Solution was then withdrawn regularly from the reactor by an order of 30 min, 60 min, 90 min, and 120 min; afterwards, 10 mL of solution was taken out and immediately centrifuged to separate any suspended solid. The clean transparent

solution was analyzed by using a UV-vis spectrophotometer. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. And then the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

3. Results and Discussion

3.1 Structure and morphology

The values of the BET surface areas of TiO₂ and Fe-CNT/TiO₂ composites are shown in Table 1. The Fe-CNT/TiO₂ composite catalysts prepared with different amounts of CNTs component were denoted as FC2T, FC4T, FC6T, FC8T and FC10T, respectively. From the results of Table 1, the BET surface areas of initial Fe-CNT/TiO₂ (0.2 g) and pristine CNT were 24.8 and 299.2 m²/g, respectively. The result demonstrated that there are remarkable increases of the BET surface area of Fe-CNT/TiO₂ composites with an increase of the amounts of CNTs. However, the BET surface area of all composites was small, and all surface areas showed considerably decrease compared to that of pristine CNT. The same phenomena had also been observed in previous study.¹⁹⁾

The XRD patterns of the sample prepared with the different amounts of CNTs are displayed in Fig. 2, which demonstrates the highly crystalline nature of the composites. The main diffraction peaks in the range of $10^\circ < 2\theta < 80^\circ$ correspond to the 101, 004, 100, 200, 105, 211, 204, 116, 220 and 215 reflections of anatase,²⁰⁾ respectively. It suggested that the nanoparticles of TiO₂ decorated on the CNTs surface are anatase. The results indicated that phase transition from TNB to the anatase phases took place at 873K with the formation of crystalline titania. According to the former study,²¹⁾ pure anatase nanocrystallites are very efficient photocatalysts, causes their superior photocatalytic properties. In addition, it is noteworthy that the 'FeO + TiO₂' peaks were present in all of Fe-CNT/TiO₂ composites.

The SEM images of Fe-CNT/TiO₂ composites are shown in Fig. 3. These micrographs showed the surface morphology of Fe-CNT/TiO₂ composites. According to Fig. 3, it can be clearly seen that the detail of all of Fe-CNT/TiO₂ composites are significant difference. In comparison of different samples, TiO₂ particles were agglomerated on surface of CNT as shown in Fig. 3 (a)-(d) when the amounts of CNT is low. Therefore, high amounts of CNT have been bared, which is not necessarily. However, quite even surface shape was found in Fig. 3(e) and (f). This result reveals that homogeneous TiO₂ particles are uniformly distributed on the whole CNT surface without apparent agglomeration of TiO₂ particles. Generally, it was considered that good dispersion enables

a larger number of active catalytic centers for the photocatalytic reaction.¹³ In addition, general morphology of CNT can be clearly observed in Fig. 3(g)-(i). A few TiO_2 particles were aggregated to be clusters, which can be resulted in the presence of a dense CNT.

TEM images of the Fe-CNT/ TiO_2 composites are shown in Fig. 4. The CNT with a diameter of about 15-20 nm was very clean. Fig. 3(a)-(c) showed that microstructure of Fe-CNT/ TiO_2 composites are similar to SEM images, and the TEM images are further shown by the fact on the different shape on CNT surface as bare CNT in Fig. 4(a), uniform dispersions in Fig. 4(b) and a few conglomeration in Fig. 4(c). The black dots distributed in Fig. 4 corresponded to the Fe particles, there was

evidence of the formation of doped TiO_2 outside the pores in some segments, this is possibly associated with the formed crystalline of Fe and TiO_2 , which was finely agreed with the XRD results.

The EDX spectra of the Fe-CNT/ TiO_2 composites are shown in Fig. 5. The quantitative microanalysis of C, Ti and Fe as major elements for the Fe-CNT/ TiO_2 composites was performed by EDX. The numerical contents for the various elements were listed in Table 1. According to Table 1, it is obvious that an increase content of C element occur with a decrease content of Ti from FC2T to FC10T, which was considered the change of C and Ti content was relative. However, the relative amounts of Fe for all of Fe-CNT/ TiO_2 composite were stable.

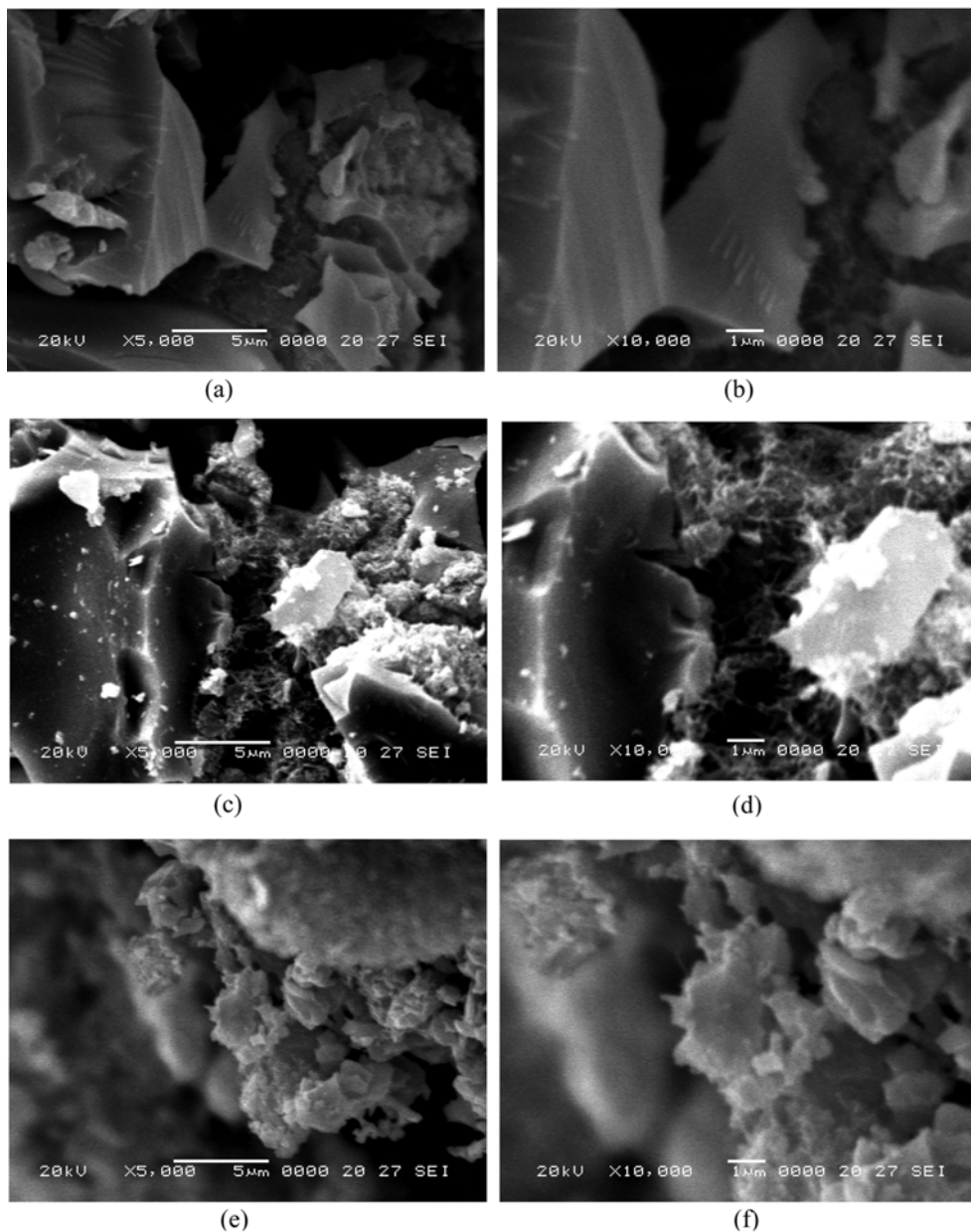


Fig. 3. SEM micrographs of Fe-CNT/ TiO_2 composites: FC2T: (a) $\times 5000$, (b) $\times 10000$, FC4T: (c) $\times 5000$, (d) $\times 1000$ and FC6T: (e) $\times 5000$, (f) $\times 1000$.

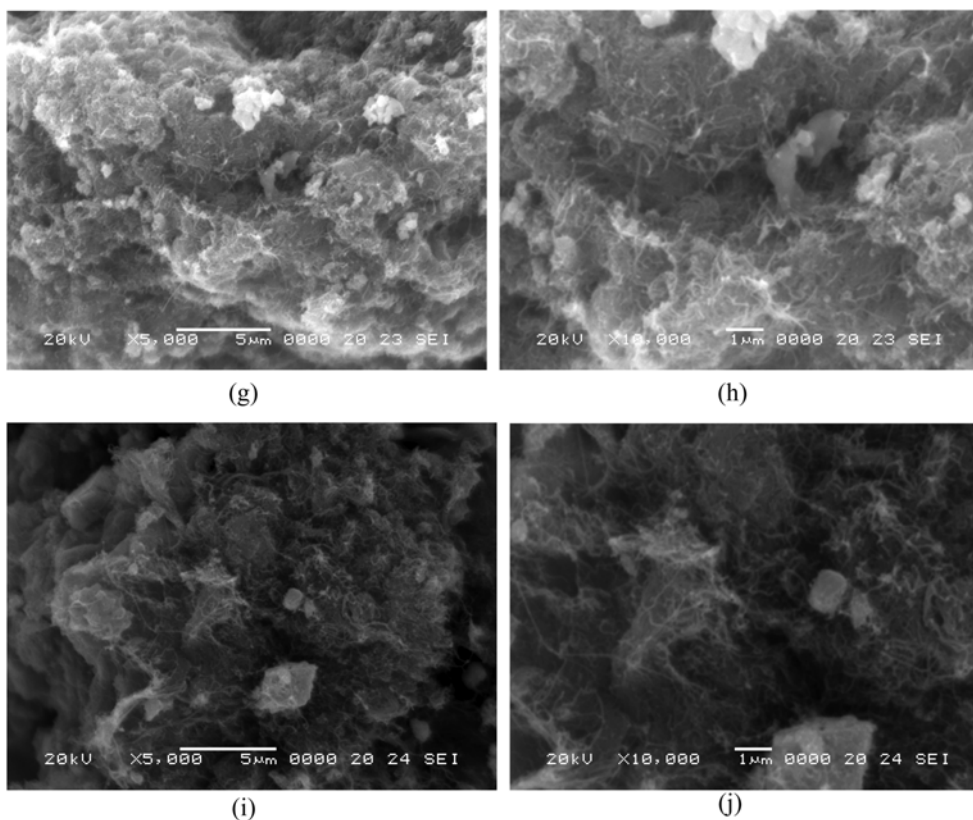


Fig. 3. (continued) SEM micrographs of Fe-CNT/TiO₂ composites: FC8T: (g) × 5000, (h) × 1000 and FC10T: (i) × 5000, (j) × 1000.

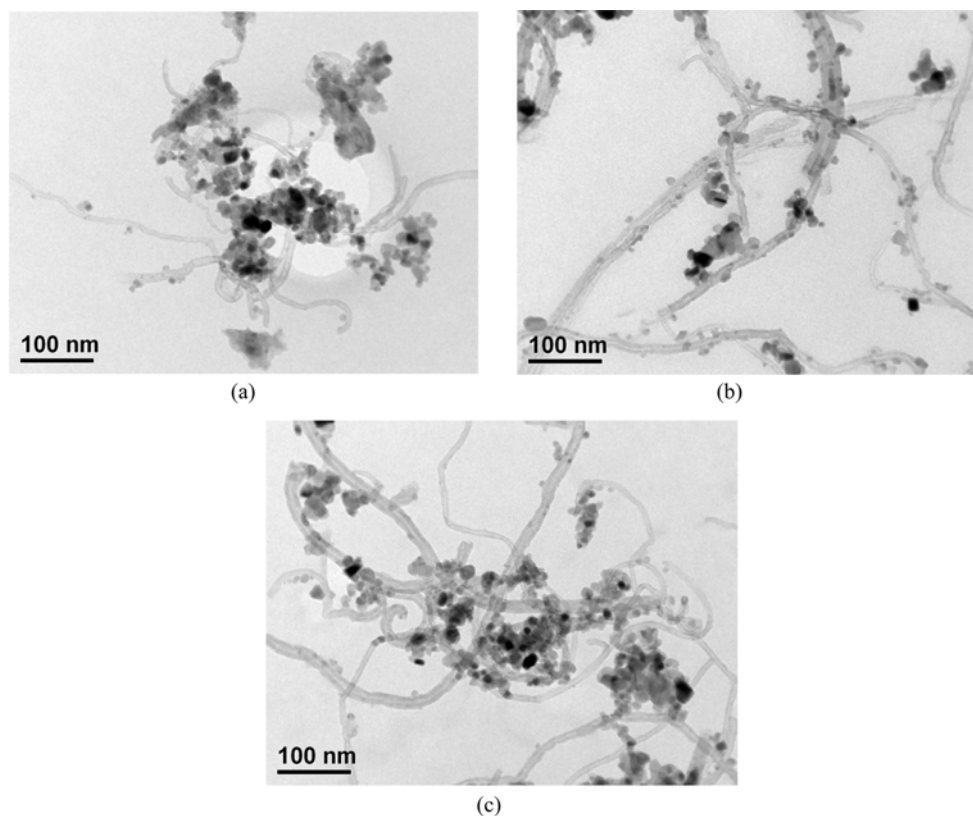


Fig. 4. TEM micrograph of the Fe-CNT/TiO₂ composites (a) FC2T, (b) FC6T and (c) FC10.

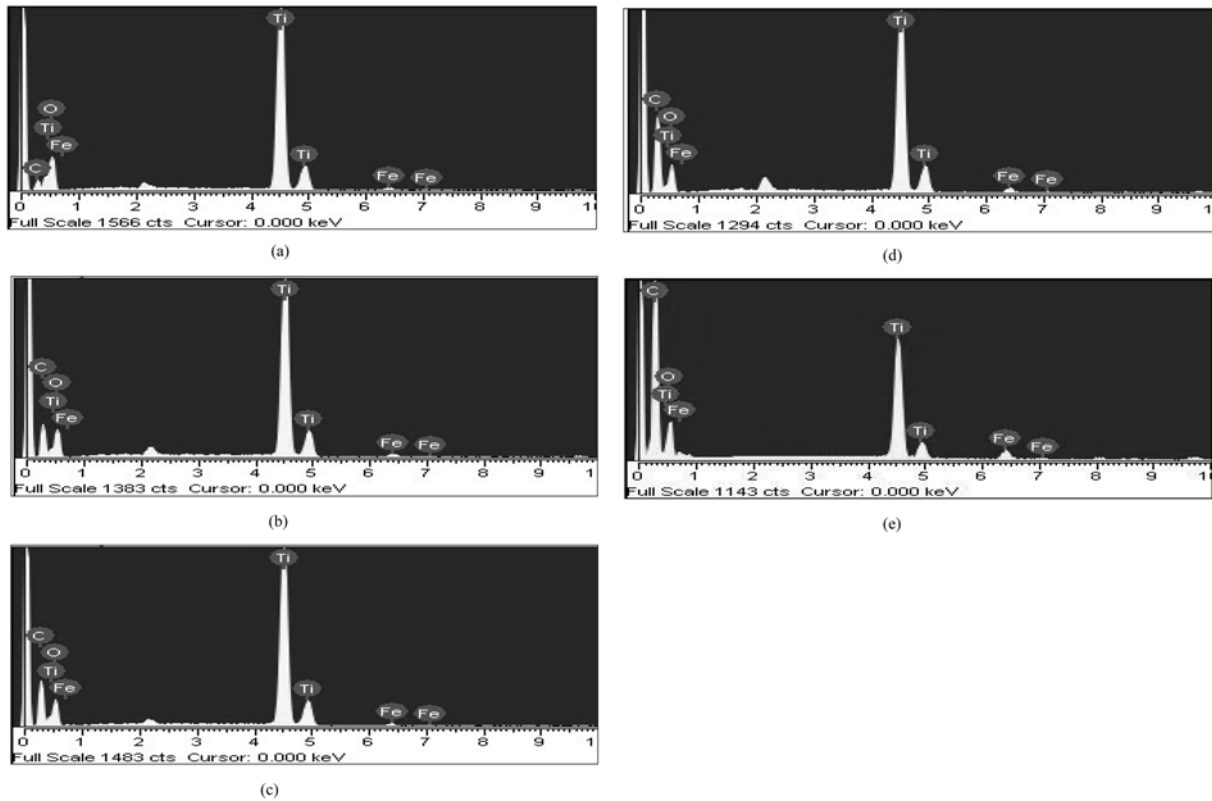


Fig. 5. EDX elemental microanalysis of Fe-CNT/TiO₂ composites: (a) FC2T, (b) FC4T, (c) FC6T, (d) FC8T and (e) FC10T.

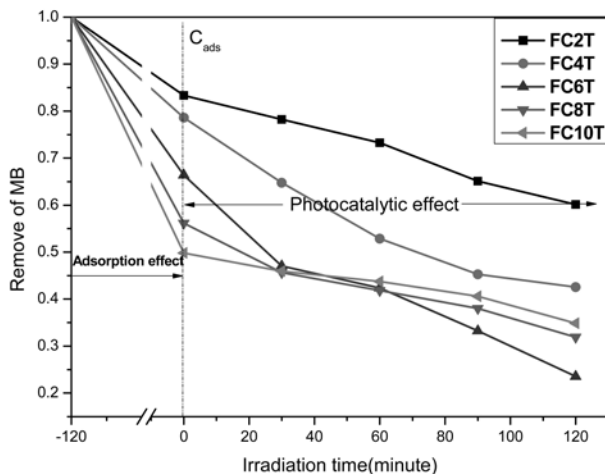


Fig. 6. Remove of the MB solution by Fe-CNT/TiO₂ composites under visible light.

3.2 Photocatalytic degradation of MB on Fe-CNT/TiO₂ composites

The photocatalytic conversions of MB over different Fe-CNT/TiO₂ composites under the visible light irradiation are shown in Fig. 6. According to adsorption effect within 120 min before the visible light excitation, this clearly indicated that CNT display the high sorption capacity for MB molecules. The adsorption capacity is expected based on the large number of vacant surface

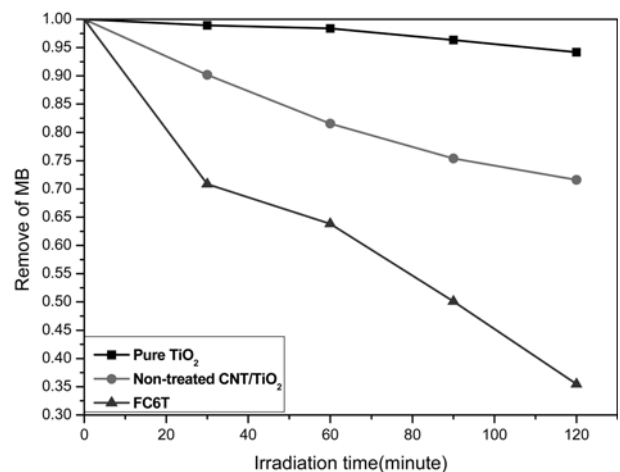


Fig. 7. Dependence of relative concentration of MB in the aqueous solution $\ln \text{Abs}(\text{max})_t / \text{Abs}(\text{max})_{t=0}$ on visible light irradiation time for the pure TiO₂, CNT/TiO₂ and Fe-CNT/TiO₂ composites.

sites available, which directly related to their BET surface area of Fe-CNT/TiO₂ composites as shown in Table 1. It was considered that higher content of CNT in Fe-CNT/TiO₂ composites could be beneficial for degradation of MB depending of adsorption capability.

The photodegradation efficiencies of MB dye over the Fe-CNT/TiO₂ composites are also illustrated in Fig. 6. It was observed that the degradation ratio of the FC6T

is greater than that of the other samples for degradation of MB. This means that there are the TiO₂ particles deposited on optimal content of carbon nanotubes surface in FC6T. In comparison of FC2T, FC4T and FC6T by SEM and TEM images, it was seen that TiO₂ particles agglomerate are further reduced on CNT surface with high uniform distribution due to an increase of CNT amounts. The role of CNT is an additive, which is likely to be another factor. MB can be degraded simultaneously over both the TiO₂ and main discussed CNT in an undivided cell. The HO[•] radicals produced through the reaction of holes and hydroxide ions or water molecules adsorbed onto the Fe-CNT/TiO₂ surface under illumination with visible light were responsible for the degradation of MB over valence band; O^{2•-} radicals, produced through the reaction of electrons and dissolved oxygen, mediated the degradation over the conduction band. The increase of the amounts of CNTs up to FC6T increased the number of electrons on the conduction band. According to our previous study,²²⁾ CNT are eminent electronic conductors in the solution act as electron recipient, which captured electrons from the valence band of TiO₂ leading to the formation of holes. Consequently, the degradation efficiency was enhanced. In comparison of FC6T, FC8T and FC10T, it was observed that the degradation effect of MB was relatively decreased with a continued increase of the amounts of CNT. It was considered that an excess of CNT can interfere with the absorption of incident light by the Fe-CNT/TiO₂ composites. Thereby degradation efficiency was decreased. Otherwise, it was reported that the light conversion efficiencies decrease at excess amounts of CNT, which should be explained by the light energy loss from the optical absorption of the CNT materials. The results can lead to a lower amount of photo-induced electrons by the dye molecules, hence decreasing the degradation efficiency.²³⁾

3.3 Photocatalytic activity of Fe-CNT/TiO₂ composites

The dependences of relative concentration of MB in the aqueous solution $\ln \text{Abs}(\text{max})_t / \text{Abs}(\text{max})_{t_0}$ on visible light irradiation time for neat TiO₂, CNT/TiO₂ and Fe-CNT/TiO₂ composites are shown in Fig. 7. The original sample of CNT/TiO₂ was quoted from former experiment.¹⁹⁾ It is obvious that neat TiO₂ powders showed little photocatalytic activity, and the non-treated CNT/TiO₂ composites exhibited some activity compared to that of the TiO₂ powder. However, the Fe-CNT/TiO₂ composites prepared in this work showed much higher activity than the CNT/TiO₂. This suggests that the combining way between Fe-CNT and TiO₂ should be taken into account to explain the photocatalytic activity for degradation of MB. It was considered that Fe particles

deposited on CNT/TiO₂ act as electron traps, enhancing the electron-hole separation and the subsequent transfer of the trapped electron to the adsorbed O₂ acting as an electron acceptor.²⁴⁻²⁵⁾ And Fe can generate more photo-induced electrons to the conduction band of TiO₂ under visible light.²⁶⁾ Therefore, Fe is one of the vital factors in determining the photocatalytic activity of the Fe-CNT/TiO₂ composites under visible light.

4. Conclusion

Fe-CNT/TiO₂ composites were successfully prepared by a modified sol-gel method. The composites exhibited higher photocatalytic activity in an optimal content of CNT, which was probably caused by the optical absorption effect and electron transfer processes from the attached TiO₂ to CNT under visible light. In addition, the Fe particles showed excited ability and a vital cooperative effect for CNT and TiO₂ component.

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