Photodecomposition of Different Organic Dyes Using Fe-CNT/TiO$_2$
Composites under UV and Visible Light

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(Received October 28, 2009; Revised December 25, 2009; Accepted January 21, 2010)

ABSTRACT
The Fe-treated CNT/TiO$_2$ photocatalysts mixed with anatase and rutile phase have been developed for the decomposition of non-biodegradable different organic dyes like methylene blue (MB), rhodamine B (Rh.B), and methyl orange (MO) in two conditions as ultraviolet and visible light respectively. The results indicate that all the Fe-CNT/TiO$_2$ composites proved to be more efficient photocatalysts since degradation of MB at higher reaction rates, the decomposition rate of different dyes increases with an increase of Fe$^{3+}$ concentration in composites; the highest rate of decomposition of different dyes was noted under UV irradiation. These results can indicate that the large CNT network is facilitate the electron transfer and strongly adsorb dye molecules on the texted photocatalysts, iron is reactive in the photo-Fenton process resulting in high production of OH radicals and also high activity of the photocatalyst. And Fe particles can generate more photoinduced electrons to conduction band of TiO$_2$ under visible light irradiation. The composites of Fe-CNT/TiO$_2$ photocatalysts synthesized by a sol-gel method were characterized by BET, TEM, SEM, XRD and EDX.

Key words: Photocatalytic activity, Fe-CNT/TiO$_2$ composites, Ultraviolet, Visible light

1. Introduction
Over the past few decades, semiconductor photocatalysis has become more and more attractive due to its great potential to solve environmental problems. Among the various semiconductors employed, titania (TiO$_2$) is known to be a good photocatalyst for the decomposition of a wide variety of organic and inorganic substances due to its high photocatalytic activity, non-toxic, stable performance, and anti-chemical and anti-optical corrosion. When illuminated with an appropriate light source, the TiO$_2$ photocatalyst generates electron/hole pairs to initiate a series of chemical reactions that eventually mineralize the organic pollutants. However, the photocatalytic efficiency of TiO$_2$ decreases substantially due to the high recombination ratio of electrons (e$^-$) and holes (h$^+$) produced, and TiO$_2$ has a high band gap (E$_g$=3.2 eV), so it is excited only under UV light. Therefore, in the last decade, much research has been undertaken to enhance the photocatalytic activity of TiO$_2$ and to extend the light absorption of TiO$_2$ photocatalysts to the visible region. These studies include increasing its interface area, treatment with noble metal(s), or nonmetals, and impregnation of metal ions.

In particular, metal ions-modified TiO$_2$ has become of current importance for factual application and maximizing the efficiency of photocatalytic reactions. In particular, iron ions used as dopants show a high combination capacity with many organic molecules. The Fe combination ability with olephinic and carbonylic groups is well known. In the case of TiO$_2$, when Fe$^{3+}$ is deposited on its surface, many of its surfacial combination properties may be modified. It was considered that the iron ions can play an important role in the degradation of organic compounds through photo-Fenton reaction and electron traps under UV irradiation. In addition, more and more studies have reported on visible-light-induced photocatalytic reactions using Fe$^{3+}$-modified TiO$_2$.

It is expected that Fe$^{3+}$ treated with TiO$_2$ may show different effects on the photocatalytic activity depending on the wavelength of light illuminating photocatalyst systems. Because the photocatalytic mechanism under UV irradiation is generally different from that under visible light irradiation because the dye can act as a photoinitiator as well as a degraded substrate under visible light irradiation. Therefore, the charge separation within TiO$_2$ particles and subsequent electron transfer may be enhanced by Fe$^{3+}$ deposition on TiO$_2$ particles. Moreover, the transition metal ions of modified TiO$_2$ particles can narrow the band gap or introduce intra-band gap energy states.

However, since Fe$^{3+}$ deposited on TiO$_2$ particles presents some drawbacks, such as the powders not being easily precipitated and recovered from water, which are harmful to their regeneration and reuse. In a recent review, attention was called to the fact that carbon nanotubes (CNTs) are attractive and competitive catalyst supports
when compared to activated carbon due to the combination of their electronical, adsorption, mechanical, and thermal properties. This concept can then be extended to cooperative or synergetic effects between TiO$_2$ and CNT phases under visible light.

Consequently, combination of CNT and TiO$_2$ with Fe$^{3+}$ (Fe-CNT/TiO$_2$ composite) is expected to show various effects on the photocatalytic activity of TiO$_2$ by the different mechanisms that follow, and it may act separately or simultaneously depending on the photoreaction conditions: (1) enhance the electron-hole pairs separation by acting as electron traps, (2) extend the light absorption into the visible range and enhance surface electron excitation by electron traps, (3) narrow band gap by Fe$^{3+}$ visible range and enhance surface electron excitation by electron traps, (4) extend the light absorption into the visible range and enhance surface electron excitation by electron traps, and (5) narrow band gap by Fe$^{3+}$.

In this paper, we report an efficient strategy to selectively solve low photocatalysis activity and difficult precipitation of TiO$_2$ via the simple treatment of Fe(NO$_3$)$_3$ impregnated around CNT and subsequent TiO$_2$ attached. We examined the photocatalytic degradation of the organic dye in the aqueous suspensions of CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites under visible and UV light irradiation in order to evaluate and distinguish the various effects of Fe modified TiO$_2$ photocatalytic activity. The activities of the synthesized Fe-CNT/TiO$_2$ composites were further compared to those of the mechanical mixture of Fe, CNTs and TiO$_2$ in the same photocatalytic condition. The effect of synthesized Fe-CNT/ TiO$_2$ composites on degradation of different dyes (MB, RR, and MO) was also investigated. The experimental results are discussed by the different roles of Fe in the dye photodegradation on Fe-CNT/TiO$_2$ photocatalyst through different mechanisms under visible and UV light irradiation.

2. Experimental Procedure

2.1. Materials

Carbon nanotubes (CNTs) (diameter: ~20 nm, length: ~5 nm) as the support material for preparation of Fe-CNT/TiO$_2$ were purchased from Carbon Nano-material Technology Co., Ltd, Korea. m-chloroperbenzoic acid (MCPBA) was used as an oxidizing agent and was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%), which was used as an organic solvent, was purchased from Samchun Pure Chemical Co., Ltd, Korea. TiOSO$_4$·9H$_2$O (TOS), Sigma-Aldrich, Germany) was selected as a titanium source for the preparation of CNT/TiO$_2$ composites, and Fe(NO$_3$)$_3$·9H$_2$O as the ferric and magnetic source was purchased from Duksan Pure Chemical Co., Ltd, (Korea). The Fe(NO$_3$)$_3$·9H$_2$O solution: 0.1, 0.2 and 0.3 M, 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-CNT. The Fe-CNT was put into the prior mixture of TOS and H$_2$O$_2$ (5%). 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 923 K for 1 h. Then, the Fe-CNT/TiO$_2$ composites were obtained. The procedure and nomenclatures of prepared samples are listed in Table 1 and Fig. 1. respectively.

2.2. Preparation of samples

First, 2 g MCPBA was dissolved in 80 mL benzene. Then, 1 g CNT power was put into the oxidizing agent solution, refluxed at 353 K for 6 h. Solid precipitates formed and were dried at 363 K. The oxidized CNT was added to 10 mL different concentrations of Fe(NO$_3$)$_3$·9H$_2$O solution: 0.1, 0.2 and 0.3 M, 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-CNT. The Fe-CNT was put into the prior mixture of TOS and H$_2$O$_2$ (5%). 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 923 K for 1 h. Then, the Fe-CNT/TiO$_2$ composites were obtained. The procedure and nomenclatures of prepared samples are listed in Fig. 1. and Table 1. respectively.

2.3. Characteristics and investigations of the samples

The BET surface area by N$_2$ adsorption method was measured at 77 K using a BET analyzer (Monosorb, USA). XRD (Shimadzu XD-D1, Japan). The result was used to identify the crystallinity with Cu Kα radiation. SEM was used to observe the surface state and structure of Fe-CNT/TiO$_2$ composites using an electron microscope (JSM-5200).
TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200kV was used to investigate the size and distribution of the yttrium 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 CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites. UV-vis absorption parameters for the Rh.B solution decomposed by CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites under UV and visible light irradiation were recorded using a Spectronic (USA) spectrometer.

### 2.4. Photocatalytic activity of samples

The photocatalytic decomposition was tested by different Fe-CNT/TiO$_2$ composites powder and an aqueous solution of organic dyes (MB, Rh.B and MO) in a 100 mL glass container and then irradiation system with UV light at 365 nm and visible light (8 W), respectively, which was used at the distance of 100 mm from the solution in dark box. The same amount of Fe-CNT/TiO$_2$ composites (0.05 g) was suspended in 50 mL of organic dyes (MB, Rh.B and MO) solution with a concentration of $1.0 \times 10^{-5}$ M. Then, the mixed solution was placed 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. Experiments were then carried out under UV or under visible light. Solution was 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 extent of dye decomposition was estimated spectrophotometrically at the absorption maximum ($\lambda_{\text{max}}$) of the concerned dye. Molecular structure of the dyes is shown in Table 2.

### 3. Results and Discussion

#### 3.1. Structure and morphology

The value of BET surface area of pristine CNT, CNT/TiO$_2$ and different Fe-CNT/TiO$_2$ samples are presented in Table 1 and were ordinal denoted as CT, FCT1, FCT2, and FCT3, respectively. As the results of Table 1 show, the BET surface area of the as-received CNT was 299 m$^2$/g, while the BET surface area of CNT/TiO$_2$ decreased to 185.32 m$^2$/g and decreased to average 147 m$^2$/g when Fe compounds were introduced in Fe-CNT/TiO$_2$ composites. It can be evidently seen that there was a large change of the micropore size distribution for CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites compared to that of corresponding CNT. It had been considered that the invading TiO$_2$ and/or Fe particles can be blocked to micropores in CNT.

In Fig. 2, we present the morphological characterization of the CNT/TiO$_2$ (Fig. 2(a) and Fe-CNT/TiO$_2$ composites prepared (Figs. 2(b), (c), (d)). These micrographs show the general morphology of CNT, which is similar. The particles of TiO$_2$ were uniformly distributed on the whole CNTs surface. It is considered that better dispersion enables larger number of active catalytic centers available for the photocatalytic reaction. However, some TiO$_2$ particles aggregated to bundles in Fig. 2(d). Possibly, disintegration of these bundles may diffuse as they were not well homogenized during the vigorous stirring.

Fig. 3 shows the TEM image of the Fe-CNT and Fe-CNT/TiO$_2$ composites. The CNT with a diameter of about 15-20nm is very clean, as shown Fig. 3. Fig. 3(a) shows that all of the Fe particles are agglomerated on the surface of CNT and Numerous CNT are removed. Fig. 3(b) shows all of the Fe and TiO$_2$ particles are dispersed on the surface of CNT and surface area of Fe-CNT/TiO$_2$ composites should have a strong interphase structural effect between the carbon and

### Table 2. Structural Representation of Some Selected Organic Dyes

<table>
<thead>
<tr>
<th>Name of dyes</th>
<th>Molecular structure of dyes</th>
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<tbody>
<tr>
<td>MB $\lambda_{\text{max}} = 660$ nm</td>
<td></td>
</tr>
<tr>
<td>Rh.B $\lambda_{\text{max}} = 550$ nm</td>
<td></td>
</tr>
<tr>
<td>MO $\lambda_{\text{max}} = 476$ nm</td>
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**Fig. 2.** SEM micrographs of CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites: (a) CT, (b) FCT1, (c) FCT2, and (d) FCT3.
metal oxide phases. Moreover, a few black dots can be observed; they correspond to the deposition of Fe particles. In comparison of Fe-CNT and Fe-CNT/TiO$_2$, the size of the Fe particles was clearly decreased, and most particles were quasi-spherical in shape. It is concluded that the treatment with TiO$_2$ suppresses the agglomeration of Fe nanoparticles. However, larger-sized particles can be observed in Fig. 3(b). It is considered that there is evidence of the formation of Fe doped TiO$_2$ outside the pores in some segments. This was possibly associated with the formed crystalline of Fe and TiO$_2$, which also agreed with their XRD results.

The XRD patterns of CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites are shown in Fig. 4. The XRD results illuminated that the CNT is coated with a mixing type of anatase and rutile TiO$_2$ particles. The major peaks were diffractions from (101), (004), (200), and (204) planes of anatase, and (110), (101), (111), and (211) of rutile. The results indicate that the phase
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transition from TOS to the anatase and rutile phases took place at 923 K with formation of crystalline titania. For the CNT/TiO₂ composite, the TiO₂ results only exhibit a typical single and clear anatase phase. In addition, it is noteworthy that the FeO+TiO₂ peaks in Fe-CNT/TiO₂ composites.

Fig. 5 shows the results of elemental analysis by EDX spectra of CNT/TiO₂ and Fe-CNT/TiO₂ composites. These spectra show the presence of peaks from the C, O, and Ti elements. For the Fe-CNT/TiO₂ composites, we observed the peaks of the Fe element. The results of elemental composition analysis of the composite series are also listed in Table 1. From the table, it is shown that carbon and Ti are present as major elements in the composite series. As expected, it was observed that the Fe contents of Fe-CNT/TiO₂ composites show an increase with an increase of Fe(NO₃)₃ concentration.

3.3. Degradation of organic dyes

3.3.1. Organic dyes photodegradation under UV irradiation

Removal of various organic dyes in the aqueous solution on UV irradiation time for pristine CNTs, the pure TiO₂, CNT/TiO₂, and Fe-CNT/TiO₂ composites via adsorption, and photodegradation are shown in Figs. 6 (a), (b), and (c), respectively. According to Figs. 6 (a), (b), and (c), it can be seen that adsorptive effect of three kinds of dye molecules could be arrived at within 120 min by CNT sorbent, which implied that MB and MO was adsorbed more easily by CNT sorbent. The difference in the adsorption abilities can be explained two ways: physical interactions and chemical interactions. Generally, absorption capacity of CNT depends on pore diameter of sorbent and size of the molecules of the adsorbed substance. Table 2 shows the molecule size of MB, MO, and Rh.B. There were three tropisms when a molecule was adsorbed on a sorbent; for example, for MB molecules, which have obverse tropism (1.43 nm × 0.61 nm), end tropism (1.43 nm × 0.4 nm), and side tropism (0.61 nm × 0.4 nm), respectively. Because the width and height of Rh.B molecule (1.09 nm and 0.64 nm) were larger than MB and MO, these pores could absorb more MB and MO molecules than that of Rh.B from obverse tropism, side tropism, and end tropism. Nevertheless, absorptive capacity of pristine CNT was lower than TiO₂ and Fe treated with CNT composites; this indicates that adsorption likely also depend upon the surface chemistry of CNT.

To evaluate the actual photocatalytic activity of Fe-CNT/TiO₂ photocatalysts compared with the decomposition processes of three organic dyes, namely photolysis and photo-Fenton reaction, the results were arrived at within 120 min under UV irradiation. It can be found that MB can be decomposed at a higher degree than that of MO and Rh.B, as shown with the curves of photolysis. According to previous studies, 28,29) -CH₃ elimination and C-N scission can positively occur on MB molecules via formation of hydroxyl radical (OH). For degradation of MB, Rh.B, and MO using pristine TiO₂, CNT/TiO₂ and Fe-CNT/TiO₂ composites, Fe-CNT/TiO₂ composites have been found to be more photoactive towards three dye solutions than pristine TiO₂ and CNT/TiO₂. It is
noteworthy that the Fe treated CNT/TiO$_2$ enhances the photocatalytic activity greatly, which may be enhanced through the following mechanisms: first, Fe particles deposited on CNT/TiO$_2$ act as electron traps, enhancing the electron-hole separation and the subsequent transfer of the trapped electron to the adsorbed O$_2$ acting as an electron acceptor; second, Fe (III) could work as photocatalyst for decomposition of organic dye via the photo-Fenton process under UV light.

The photocatalytic behaviors of the simple mechanical mixture of CNT, TiO$_2$ and Fe, and Fe-CNT/TiO$_2$ composites were examined as shown in Fig. 7. In the comparison of Fe-CNT/TiO$_2$ composites and the simple mixture of Fe-CNT/ TiO$_2$ composites, the decomposition efficiency of Fe-CNT/ TiO$_2$ composites is comparatively higher. One possible reason may be that another mechanism of electronic transfer is supposed to occur among TiO$_2$, Fe and CNTs. An electron transfer in composite may take place in the process of TiO$_2$ $\rightarrow$ CNT or TiO$_2$ $\rightarrow$ Fe$^{3+}$ $\rightarrow$ Fe$^{2+}$ to effectively decrease the recombination of electron/hole pairs. As mentioned above, the possible reaction mechanism of Fe-CNT/TiO$_2$ under UV light is shown in Fig. 8.

![Fig. 7. Removal of Rh.B in the aqueous solution on UV irradiation time for the simple mechanical mixture of CNT, TiO$_2$ and Fe, and Fe-CNT/TiO$_2$ composites.](image)

![Fig. 8. A reaction mechanism of Fe-CNTs/TiO$_2$ composites under UV irradiation.](image)

![Fig. 9. Removal of the different organic dyes solution by pristine CNT, the pure TiO$_2$, CNT/TiO$_2$ and Fe-CNT/TiO$_2$ composites under visible light. (a): MB, (b): MO, and (c): Rh.B](image)
3.3.2. Organic dyes photodegradation under visible light irradiation

The photocatalytic degradation of various organic dyes under visible light was used for evaluating the photocatalytic activities of the TiO₂, CNT/TiO₂, and Fe-CNT/TiO₂ composites. Figs. 9 (a), (b), and (c) show the concentration change of organic dyes (MB, MO, and Rh.B) as a function of irradiation time for different samples under visible light. It can be seen that all the Fe-CNT/TiO₂ composites display higher photocatalytic activity compared to the CNT/TiO₂ composites, and the photocatalytic activity of Fe-CNT/TiO₂ composites increases with the increment of the Fe amount. This may be ascribed to the cooperative roles of Fe deposits.

According to a former study, it is well known that electrons in conduction band and holes valence band are generated on the surface of TiO₂ when it is irradiated with light whose energy equals or exceeds its band gap energy. Theoretically, we consider that the pure TiO₂ cannot be excited under visible light irradiation because of the lower energy than the band gap. However, the pure TiO₂ in our experiment can be excited for three different organic dyes by visible light, respectively, and similar phenomena have also been displayed by many studies. It was considered that most dye molecules themselves have activated into their excited state; for example, Rh.B at λ > 470 nm, and injecting an electron into the conduction band (and/or surface states) of the TiO₂, whereas dye molecules are converted to the cationic radical (Dye⁺). Then, the injected electron reacts with adsorbed O₂ to degrade Dye⁺ by production of reactive oxygen radicals. Under visible light irradiation, the TiO₂ acts only as an electron-transfer mediator and the oxygen as a unique electron acceptor leading to an efficient separation of the injected electron and Dye⁺. Consequently, the CNT sorbent leads to enhanced absorption in the visible light and assists the electron transfer from the TiO₂ surface to the adsorbed O₂. Therefore, the organic dye adsorption as well as charge separation is essential for enhancing degradation effect of organic dye on CNT/TiO₂ under visible light irradiation.

For the organic dye degradation on Fe-CNT/TiO₂ under visible light irradiation, Fe treated CNT/TiO₂ composites can be activated by visible light and generate more photoinduced electrons to participate in the reaction. Also, the Fe partials can act as electron traps facilitating the e⁻/h⁺ pair separation. The possible reaction mechanism of Fe-CNT/TiO₂ under visible light is shown in Fig. 10.

In the comparison of Figs. 9 (a), (b), and (c), degradation effect of MB is still found to be the best. This is attributed to the fact that more MB molecules are adsorbed on the surface of CNT sorbent than those of MO and Rh.B, enhancing the photoexcited electron transfer from the visible light sensitized MB molecules to the conduction band of TiO₂.

4. Conclusion

Fe-CNT/TiO₂ composite is an effective catalyst for photodegradation of various organic dyes (MB, MO, and Rh.B) under both UV and visible light irradiation. In particular, the rate of degradation of MB has been found to be the best among all dyes. The reason can be ascribed to excellent adsorbed ability on a photocatalyst and its molecular structure. The rate of decomposition could be enhanced due to the presence of Fe. For comparison, the FCT3 sample showed the highest photocatalytic activity. Under UV irradiation, Fe components may exhibit the effect known as photo-Fenton reaction, thus increasing photocatalytic activity. Under visible light irradiation, the significant enhancement of photoactivity in the Fe-CNT/TiO₂ photocatalysis can be ascribed to the simultaneous effects of Fe deposits by both acting as electron traps and generating more photoinduced electrons on the Fe-CNT/TiO₂ surface.

Acknowledgments

This work was supported by the Research Foundation of Hanseo University in 2009. The authors are grateful to staff in the University for Financial Support.

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