Relative Photonic Properties of Fe/TiO₂-Nanocarbon Catalysts for Degradation of MB Solution under Visible Light

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Nanocarbon supported Fe/TiO₂ composite catalysts were prepared using CNTs (carbon nanotubes) and C₆₀ (fullerene) as nanocarbon sources by a modified sol-gel method. The Fe/TiO₂-nanocarbon composites were characterized by the BET surface area, scanning electron microscope (SEM), Transmission Electron Microscope (TEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) and UV-vis spectra. In comparison with non-nanocarbon doped Fe/TiO₂ composites, the nanocarbon supported Fe/TiO₂ composites had higher absorption ability with a larger specific surface area, and showed higher photocatalytic activity during the degradation of methylene blue (MB) under visible light. The reasons for the obvious increase of photocatalytic activity indicated that the photoactivity not only benefits from nanocarbon introduced, but also relates to the cooperative effect of the Fe as a dopant.

Key Words: Fe/TiO₂-nanocarbon composites, Photocatalytic activity, Visible light, MB

Introduction

Metal ions dopants with TiO₂ photocatalyst have been widely applied to extend the shift of photoreponse towards visible range of TiO₂. It was reported that Fe³⁺ dopant proved to be better than Cr³⁺, Ni²⁺ and Zn²⁺ by contrastive effects among of different metals on the photoreactivity of TiO₂.¹ Otherwise, Fe³⁺ ion with the band gap of 2.6 eV seems to be an interesting dopant, which can extend the adsorption threshold towards visible range.^{2,3} It had been proved that doping of low concentrations of Fe³⁺ cations can change the dynamics of the photocatalytic processes and substantially reduce the recombination process between dopant cation and titania matrixes.⁴ Although Fe³⁺ modified TiO₂ photocatalysts are active under visible light irradiation, the efficiency is still low for practical use.⁵ At the same time, the photocatalytic processes, mechanisms and kinetics on the doped TiO₂ are complex physical process and often make it difficult to draw the uniform conclusions, which lead to the controversies.

Recently, doping nonmetal atoms, such as C,⁶ N⁷ and S⁸ have received much attention. Theoretical calculations showed that the p-orbitals of these dopants significantly overlapped with the valence band O 2p-orbitals, which facilitated the transport of photo-generated charge carriers to the surface of the catalyst. Especially, some authors reported the shift of photo response of TiO₂ from UV to the infrared region by a carbon dopant.⁹ However, the enhancement of activity on TiO₂ is still slight.

Thus, it is of great interest to investigate the synergetic effect of multiple dopants. C and Fe co-doped TiO₂ showed higher activity than pristine TiO₂ in multiple uses.¹⁰ Another previous research also showed two dopants had more beneficial effect than a single one for improving adsorption ability and photocatalytic activity under the visible light irradiation.¹¹ Generally, many parameters for photocatalytic activity such as the optical shift, photonic activity, surface area are important. Thus, in the field of carbon modified TiO₂, the use of nano-size carbon as

CNTs and C₆₀ have gained in popularity in recent years due to their unique properties.^{12,13} The characteristic electronic properties of CNTs are that they can be either metallic or semiconducting, depending on their geometry.¹⁴ C₆₀ have energy-sensitizing capabilities for improving quantum efficiency and the increase in charge transfer between the fullerene and TiO₂.¹⁵ In this work, the nanocarbon deposited with Fe/TiO₂ were synthesized by a two-step sol-gel process, and the application of these photocatalysts are here extended for the first time to visible light photodegradation of MB solution.

Experimental

Materials. CNT (Carbon nano-material Technology Co., Korea) and C₆₀ (Tokyo Kasei Kogyo Co. Ltd., Japan) as the support material for preparation of Fe/TiO₂-nanocarbon were purchased, and used without further purification. *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). TNB (C₁₆H₃₆O₄Ti) as a titanium dioxide source for the preparation of the Fe/TiO₂-nanocarbon composites was purchased from Aldrich Chemical Co., Ltd. (USA), and Fe(NO₃)₃·9H₂O as the ferric source was purchased from Duksan Pure Chemical Co., Ltd. (Korea). Analytical grade MB (99.99+%) was used and was purchased from Duksan Pure Chemical Co., Ltd. (Korea).

Preparation of samples. Fe/TiO₂ composites were performed by TNB as TiO₂ source with aqueous solutions of Fe(NO₃)₃ by a sol-gel method. The 3 mL TNB was dissolved in 20 mL of benzene to prepare the TNB solution. The 5 mL 0.1 M Fe(NO₃)₃ solutions were slowly dropped into the TNB solution prepared and vigorously stirred at 353 K for 5 h. The solution transformed to Fe/TiO₂ sol state, and was then dried at 363 K. Finally, the mixture was heat treated at 873 K. For preparation of Fe/TiO₂-nanocarbon composites, first, 2 g MCPBA was dissolved in

80 mL benzene. And then, 20 mg CNT or C₆₀ powder was put into the oxidizing agent solution, refluxed at 353 K for 6 h then the solid precipitates were formed and dried at 363 K. The oxidized CNT or C₆₀ was added into to the same amount of Fe(NO₃)₃ solutions as Fe/TiO₂ composites prepared, and the mixtures were stirred for 24 h using a non-magnetic stirrer at room temperature. After the heat treatment at 773 K, the Fe-nanocarbon was obtained. The Fe-nanocarbon was put into the TNB solution prepared as above 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 reacted at 873 K for 1 h. The Fe/TiO₂-nanocarbon composites were then obtained. The procedure of prepared samples is showed in Fig 1.

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/TiO₂-nanocarbon composites using an electron microscope (JSM-5200 JOEL, Japan). TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the ferric and titanium deposits on the CNT or C₆₀ 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/TiO₂-nanocarbon composites. UV-vis absorption parameters for the MB solution decomposed by Fe/TiO₂ and Fe/TiO₂-nanocarbon composites were recorded by a UV-vis (Optizen Pop Mecasys Co., Ltd., Korean) spectrophotometer.

Photocatalytic activity of samples. The photocatalytic decomposition was tested by Fe/TiO₂ and Fe/TiO₂-nanocarbon composite 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 a distance of 100 mm from the solution in dark box. The Fe/TiO₂ or Fe/TiO₂-nanocarbon composites (0.05 g) were suspended in 50 mL of MB solution with a concentration of 1.0×10^{-5} M. Then, the mixed solution was em-

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. The 10 mL of solution was taken out and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by a UV-vis spectrophotometer. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. 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.

Results and Discussion

BET surface area analysis. The values of the BET surface area of pristine TiO₂, Fe/TiO₂ and Fe/TiO₂-nanocarbon samples are presented in Table 1. As the results of Table 1, The BET surface areas of pristine TiO₂ and Fe-TiO₂ were 8.3 and 11.9 m²/g, respectively. The BET surface areas of Fe/TiO₂-CNT and Fe/TiO₂-C₆₀ increased to 58.7 and 31.2 m²/g, respectively. When CNT and C₆₀ compounds were introduced in Fe/TiO₂ composites, it can be evidently seen that there was large change of the micro-pore size distribution for Fe/TiO₂-CNT and Fe/TiO₂-C₆₀ composites compared to that of corresponding Fe/TiO₂. This indicated that the supported CNT and C₆₀ were directly related to adsorption ability of TiO₂.

SEM and TEM analysis. The SEM images of the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites are shown in Fig. 2. SEM images of Fe/TiO₂ composites are shown in Fig 2 (a) and (b). The global and unequal size particles are coherent together. It is clear that the surface of the Fe/TiO₂ composites has densely packed flat pieces composed of the aggregation of nanoparticle TiO₂. The ultra structure was acquired on the outer Fe/TiO₂-C₆₀ surface, as shown in Fig. 2 (c) and (d). The TiO₂ grain structure

Figure 1. The preparation procedure of Fe/TiO₂ and Fe/TiO₂-nanocarbon composites.

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

Samples	S _{BET} (m ² /g)	Elements (wt %)			
		C	O	Ti	Fe
Fe(NO ₃) ₃ + TNB	11.9	0.00	55.5	43.4	1.11
C ₆₀ + Fe(NO ₃) ₃ + TNB	31.2	20.1	41.0	37.8	1.08
CNT + Fe(NO ₃) ₃ + TNB	58.7	22.5	36.8	39.6	1.10
Pure TiO ₂	8.3	0.00	19.6	80.4	0.00

Table 2. Photodegradation rate constant of pure TiO₂, Fe/TiO₂ and Fe/TiO₂-nanocarbon composites

Samples	K _{app} (min ⁻¹)
Pure TiO ₂	3.14×10^{-4}
Fe/TiO ₂	2.46×10^{-3}
Fe/TiO ₂ -C ₆₀	3.73×10^{-3}
Fe/TiO ₂ -CNT	4.38×10^{-3}

Figure 2. SEM micrographs of Fe/TiO₂ and Fe/TiO₂-nanocarbon composites: Fe/TiO₂: (a) $\times 5000$, (b) $\times 10000$, Fe/TiO₂-C₆₀: (c) $\times 5000$, (d) $\times 10000$ and Fe/TiO₂-CNT: (e) $\times 5000$, (f) $\times 10000$.

is clearly visible with a great distribution on C₆₀ surface due to considerable portion of TiO₂ attached in the 3-D matrix. However, these TiO₂ particles have a large size in clusters and agglomerate shape. But the rough grain structure can be considered to provide an ideal entrance pathway for diffusion of oxygen and organic molecules between the grains and C₆₀. The morphological characterization of the Fe/TiO₂-CNT composites was present in Fig 2 (e) and (f). These micrographs showed the general morphology of CNT, and which was decorated with well-dispersed TiO₂ particles. However, small amounts of TiO₂ particles were also aggregated to be bundles, which possibly are not well homogenized during vigorous stirring. It was considered that better dispersion enables larger number of active catalytic centers for the photocatalytic reaction.¹⁶

It was not exactly clear which nanocarbon was present within SEM images, so the TEM images were further complicated by the fact that the higher nanocarbons exhibited multiple isomeric forms with shapes ranging from approximately ellipsoidal to spheroidal for C₆₀ and a wall tube for CNT as shown in Figs. 3 (c)-(f). The TEM images of Fe/TiO₂ are shown in Fig. 3 (a) and (b), which showed that the size of TiO₂ particle observed was about 10 ~ 20 nm. Moreover, a few black dots were observed from the image, they correspond to the deposition of Fe particles. The Fe/TiO₂-nanocarbon composites were investigated by TEM to obtain additional information about the interfacial region of the C₆₀ and CNT crystals and surface areas. It revealed a generally precipitate-free and smooth interface between the Fe and TiO₂ matrix and the C₆₀ crystals, as shown in Figs. 3 (c) and (d). Occasionally a 0.1 - 0.5 nm thin layer was observed at the periphery of the C₆₀ crystals. The Figs. 3 (e) and (f) show that the surface areas of Fe/TiO₂-CNT composites should be a strong

Figure 3. TEM micrograph of the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites: (a) and (b): Fe/TiO₂, (c) and (d): Fe/TiO₂-C₆₀, (e) and (f): Fe/TiO₂-CNT.

interphase structural effect between the carbon and metal oxide phases. A homogeneous dispersion of CNT in TiO₂ matrix implied a possible disappearance of CNT characteristic peaks in their XRD patterns. According to the previous study,¹⁷ the homogeneous distribution of TiO₂ on the nanocarbon external surface could be formed by the MCPBA oxidation method. The black dots distributed in Fig. 3 (c)-(f) also corresponded to the Fe particles. It was considered that there is evidence of the formation of Fe doped TiO₂ outside the pores in some segments. This was possibly associated with the formed crystalline of Fe and TiO₂, which was also agreed with their XRD results.

XRD analysis. The XRD patterns are given in Fig. 4. The Fe-nanocarbon presented that the intense peaks of CNT and C₆₀ correspond to the (002) reflection and to the (10) band. In the case of the Fe/TiO₂-nanocarbon composites, the additional peaks presented in all the diffractograms correspond to the single anatase form of TiO₂. It was noticed that the (101) anatase reflection overlaps the (002) reflection of nanocarbon. The XRD results illuminated that the nanocarbon in Fe/TiO₂-nanocarbon composites is coated with a typical single anatase crystallites. In XRD patterns of the Fe/TiO₂, significant diffraction peaks of rutile-phase TiO₂ were detected. It reflected that the nanocarbon suppressed phase transformation from anatase to rutile during heat treatment at high temperature. According to the former study,¹⁸ pure anatase nanocrystallites are very efficient photocatalysts and have superior photocatalytic properties. Especially, pure maghemite (γ -Fe₂O₃) (JCPDS card no. 19-0629) could be obtained from only Fe-nanocarbon composites.¹⁹ In comparison of Fe/TiO₂ and Fe/TiO₂-nanocarbon composites, there was significantly difference. It is noteworthy that uniform peaks of 'FeO+2TiO₃' were detected in both Fe/TiO₂ and Fe/

Figure 4. XRD patterns of Fe-nanocarbon, Fe/TiO₂ and Fe/TiO₂-nanocarbon composites.

Figure 5. EDX elemental microanalysis of Fe/TiO₂ and Fe/TiO₂-nanocarbon composites: (a) Fe/TiO₂, (b) Fe/TiO₂-C₆₀, and (c) Fe/TiO₂-CNT.

TiO₂-nanocarbon composites, which indicated that the Fe/TiO₂ was successfully deposited on nanocarbon surface by our experimental method. It was considered that the addition of TNB results in phase transformation from γ -Fe₂O₃ to FeO+2TiO₃

Figure 6. Absorption spectral changes of MB in the Fe/TiO₂ and Fe-nanocarbon composites as a function of irradiation time (visible light). (a): Fe/TiO₂, (b): Fe/TiO₂-C₆₀ and (c): Fe/TiO₂-CNT.

during reaction at high temperature.

EDX analysis. Fig 5 shows the results of the EDX for Fe/TiO₂-nanocarbon and Fe/TiO₂ composites. These spectra showed the presence of peaks from the C, O, Ti and Fe elements, and the numerical contents for the various elements are listed in Table 3. The quantities of carbon and Fe in the Fe/TiO₂-nanocarbon composites were small with a major element of Ti. According to former studies,^{4,20} the higher concentration of

Figure 7. Adsorption capability of pure TiO₂, Fe/TiO₂, and Fe/TiO₂-nanocarbon for MB dyes under dark condition. η

Figure 8. Apparent first order kinetics of MB degradation for pure TiO₂, Fe/TiO₂, and Fe/TiO₂-nanocarbon composites.

dopant in TiO₂ matrix can be detrimental in formation of hole/electron recombination centers and an increase of negative charge capabilities.

Photocatalytic activity of the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites. The photocatalytic activity of the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites was assessed from the kinetics of the photodegradation of MB solution under visible light. An initial concentration of 1×10^{-5} mol/L for MB solution and a maximum reaction time of 2 h were experimentally determined. The spectral changes of MB in the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites are shown in Fig. 6. The UV-vis absorption spectra in Fig. 6 gave absorption maximum values at a wavelength of 660 nm simultaneously with a large decrease in the absorbance as a function of irradiation time.

The adsorption abilities of pure TiO₂, Fe/TiO₂ and Fe/TiO₂-nanocarbon composites were evaluated within 120 min before the visible light excitation. It was quite easy to draw a causal relationship between surface areas in Table 1 and adsorption efficiency in Fig. 7. From the Fig 7, it was clear that degradation of MB on Fe/TiO₂ composites is faster than that of pure TiO₂

Figure 9. Schematic diagram of Fe/TiO₂, Fe/TiO₂-nanocarbon and initial electrons excited process after activation by visible light. (a): Fe/TiO₂, (b): Fe/TiO₂-C₆₀ and (c): Fe/TiO₂-CNT.

powder. This can be attributed to the high porosity of Fe/TiO₂ surface due to introduction of Fe component, which correlated with an increase of adsorption ability. For higher absorption capability of Fe/TiO₂-nanocarbon composites, a direct cause in nanocarbon themselves had a high pore value.

The photocatalytic activities of the pure TiO₂, Fe/TiO₂ and Fe/TiO₂-nanocarbon composites were tested on the photocatalytic degradation of MB solution under visible light irradiation as a test reaction. Fig. 8 shows that the Fe/TiO₂ exhibited a much higher activity than undoped TiO₂, and the Fe/TiO₂-nanocarbon composites exhibited a higher activity than Fe/TiO₂ composites. To quantitatively evaluate the photocatalytic activities of samples, the kinetics of photodegradation of MB over the above samples were studied. The photocatalytic degradation reaction with suspended samples approximately obeys the first-order kinetics. The representation for the rates of degradation of MB is given by:

$$\ln(C/C_0) = kt_0$$

Where C and C_0 are the initial concentration of MB, t_0 is the irradiation time, and k denotes the overall degradation rate constant. By plotting $\ln(C/C_0)$ as a function of time through regression, the k (min^{-1}) constant for each samples was obtained from the slopes of the simulated straight lines, as listed in Table 2. According to results in Table 2, the Fe/TiO₂ composites showed a higher enhancement in the MB photodegradation than that of pure TiO₂, which illuminated that Fe dopant is one of the vital factors in determining the photocatalytic activity of the catalysts under visible light. We also can see that the nanocarbon can be definite benefiter for photocatalytic activity. The photocatalytic activities of Fe/TiO₂-nanocarbon composites were significant higher than that of Fe/TiO₂ composites.

Effects of Fe and nanocarbon under visible light irradiation.

The photocatalytic activities of Fe/TiO₂ for the degradation of MB were enhanced by the Fe dopant through the following mechanisms as shown in Fig 9 (a). First, Fe particles dopant on TiO₂ acted 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.^{21,22} Second, the surface plasmon resonance of Fe particles is excited by visible light, facilitating the excitation of the surface electron and interfacial electron transfer.²³

The significantly enhanced photodegradation of MB in the Fe/TiO₂-nanocarbon composites under visible light irradiation may be ascribed to the cooperative effect of Fe and nanocarbon dopants, as shown in Figs. 9 (b) and (c). The photodegradation rate kinetic of the C₆₀ and CNT was different due to their different nanostructures.

Kamat *et al.* reported that C₆₀ could accept electron or donate electron to the TiO₂ semiconductor depending on different conditions.^{24,25} Basically, TiO₂ leads to the trapping of holes and electrons which can be suppressed by C₆₀ under UV irradiation.²⁴ Simultaneously, C₆₀ could also donate electron to TiO₂ semiconductor. Moreover, in the previous study,²⁶ the Pt treated C₆₀/TiO₂ composites could powerfully degrade the organic dye by the organo-metallic reaction on the Pt compound and energy transfer effects such as quantum efficiency of the fullerene. It suggested that the metal in C₆₀/TiO₂ matrix can act as electron recipient to cooperate with C₆₀ under UV irradiation. In this case, excitation of visible light injects electrons from Fe-C₆₀ to TiO₂ through a biphotonic electron ejection mechanism. This can be seen in Fig. 9 (b), when the light impinges on Fe/TiO₂-C₆₀ composites, C₆₀ and Fe can be excited to simultaneously generate electron in the visible region. Especially, the excited C₆₀ can inject one electron to the separated hole of TiO₂. This can be represented by the following reaction:

Where the hole generated can combine with electrons injected by C₆₀ into the valence band, hence the electron generated is promoted to conduction band, which results in photocurrent increase. In addition, the Fe particles on the TiO₂ surface can also act as electron traps facilitating the electron transfer.

An *et al.* reported that CNT may absorb the irradiation and transfer the photo-induced electron (e^-) into the conduction band of the TiO₂ particles.^{27,28} Their study showed that the photo

generation of charges involving CNT was the major contribution to the photo action spectrum. As for present experiment, Fe-CNT is energetic enough and read to inject one electron through the coordinating bands to the conduction band of TiO₂ as shown in Fig 9 (c). In addition, with substitution for oxygen atoms by the CNT and Fe in the anatase crystal structure of TiO₂, new levels are introduced between the conduction and valence band of TiO₂, the electrons generated by TiO₂ can be promoted from the valence band to CNT level introduced by Fe dopant, or from the lower to the higher CNT levels, which results in the quantities of electrons increase. Therefore, the Fe/TiO₂-CNT composites had a narrower band gap than Fe/TiO₂ and could increase the absorption in the visible-light region. The departed holes may migrate to the surface of Fe particles.

Conclusion

In this research, composites of Fe/TiO₂ supported on a nanocarbon surface were successfully prepared by a modified sol-gel method. Only the anatase phase was detected by XRD results for Fe/TiO₂-nanocarbon composites. Otherwise, it was clearly seen that the Fe/TiO₂ and Fe/TiO₂-nanocarbon composites had the same crystalline Fe+2TiO₃. According to the results of the photodegradation of MB, the Fe/TiO₂-nanocarbon composites showed that they could absorb more photoenergy in the visible light region and had a greater surface area than Fe/TiO₂. The high activity was attributed to several different beneficial effects associated with the introduction of C₆₀ and CNT.

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