Photonic Aspects of MB Degradation on Fe-carbon/TiO₂ Composites under UV Light Irradiation

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ABSTRACT

Fe-carbon/TiO₂ composites were prepared by a sol-gel method using AC, ACF, CNT and C₆₀ as carbon precursors and were characterized by means of BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). The activity of the prepared photocatalysts was investigated by degradation reaction of methylene blue (MB) irradiated with UV lamp. Effects of different carbon sources and irradiation time on photocatalytic activity were also investigated. The results showed that the photocatalytic activity of the Fe-carbon/TiO₂ composites was much higher than that of pristine TiO₂ and Fe/TiO₂ composites. The prominent photocatalytic activity of Fe-carbon/TiO₂ composites could be attributed to both the effects of photo-adsorption and electron transfer by carbon substrate. In addition, the higher photocatalytic activity of Fe-carbon/TiO₂ composites can be compared with that of carbon/TiO₂ and Fe/TiO₂ composites due to cooperative effects between Fe and carbon.

Key words : Fe-carbon/TiO₂ composites, Photocatalytic activity, Photo-Fenton, MB

1. Introduction

In the past three decades, Titanium dioxide (TiO₂) has been extensively employed as a photocatalyst in wastewater treatment by oxidative degradation,¹⁻⁴ because TiO₂ has sufficient energy to excite the electrons from the valence band to the conduction band by irradiation of light, which generates extremely reactive electron/hole (e⁻/h⁺) pairs that migrate to the surface of the TiO₂ where they can react with adsorbed species. Positively charged holes react with adsorbed water molecules or hydroxyl anions, leading to the formation of the hydroxyl radical,⁵ $h_{\nu}^{+} + H_2O/OH^{-} \rightarrow \cdot OH$. The surface electrons are transferred to the adsorbed oxygen originating from the superoxide radical anion,⁵ $e^{-} + O_2 \rightarrow O_2^{\cdot -}$. Some other adsorbed compounds can react with the surface holes and/or electrons resulting in oxidation and/or reduction products. Although radical species such as $\cdot OH$ and $O_2^{\cdot -}$ are able to oxidize most of the organic compounds, the hydroxyl radical is regarded as the major responsible species for the complete oxidation of organic pollutants.^{6,7} Therefore, to enhance the photocatalytic efficiency of TiO₂, study has focused on the increased amount of hydroxyl radical. The relevant mechanism can be classified as:

(1) Facilitated electron-hole separation and promoted interfacial electron transfer. For example, Fe,⁸⁻¹⁰ Pt,^{11,12}

Au,¹² treated with TiO₂, act as electron traps, and as a result the amount of holes is enhanced, favoring the increase of dye substrates.

(2) Decreased TiO₂ band gap, which benefits the electron transfer from valence band to conduction band,¹³ which in turn facilitates the formation of hydroxyl radicals.

(3) Modified surface properties of TiO₂ photocatalyst, as with any kind of carbon¹⁴⁻¹⁹ that attracts more water molecules and/or cationic dye on the TiO₂ surface due to highly adsorptive capability.

In this work, AC, ACF, CNT and C₆₀ were used as carbon precursor and Fe was selected to modify TiO₂ in order to enhance the photocatalytic activity of TiO₂. The Fe-carbon/TiO₂ composites were prepared by sol-gel method. The Fe-carbon/TiO₂ composites were characterized by BET, SEM, TEM, XRD and EDX. The photoactivity of the Fe-carbon/TiO₂ composites was assessed by the photocatalytic degradation of MB dye in aqueous solution under UV irradiation at 365 nm wavelength.

2. Experimental

2.1. Materials

The porous and granular AC used in this study was prepared from coconuts. The coconut shell was pre-carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylindrical quartz tube at 1023 K for 30 min. This AC was washed with deionized water and dried overnight in a vacuum drier at over 683 K. Activated Carbon Fiber (ACF) was purchased from EAST ASIA Carbon Fibers Co., Ltd, (Anshan, China). CNT (Carbon

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Table 1. BET Surface Area and EDX Elemental Microanalysis (wt%)

Samples	S_{BET} (m^2/g)	Elements (wt%)				
		C	O	Ti	Fe	Other
Pure TiO_2	8.3	0	19.57	80.43	0	0
pristine AC	1083	83.2	9.53	0	0	7.27
pristine ACF	1842	88.2	5.67	0	0	6.13
pristine CNT	299	87.9	5.75	0	0	6.35
pristine C_{60}	1.9	85.5	8.80	0	0	5.7
Fe-AC/ TiO_2	533	43.16	22.23	26.59	4.72	4
Fe-ACF/ TiO_2	782	52.45	19.21	19.63	5.15	3.56
Fe-CNT/ TiO_2	156	48.73	28.36	20.35	2.56	0
Fe- C_{60} / TiO_2	31.2	20.12	41.00	37.80	1.08	0

Nano-material Technology Co., Korea) and C_{60} (Tokyo Kasei Kogyo Co. Ltd., Japan) were purchased, and used without further purification. *m*-chloroperbenzoic acid (MCPBA) was used as an oxidized reagent; it was purchased from Acros Organics (New Jersey, USA). Benzene (99.5%) was used as an organic solvent; it was purchased from Samchun Pure Chemical Co., Ltd. (Korea). Titanium (IV) oxysulfate hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$ (TOS), Sigma-Aldrich, Germany) as a titanium source for the preparation of Fe-carbon/ TiO_2 composites was purchased from Acros Organics Co., Ltd, USA. And $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the ferric source was purchased from Duksan Pure Chemical Co., Ltd. (Korea). The MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S} \cdot \text{Cl} \cdot 3\text{H}_2\text{O}$) was used at analytical grade; it was obtained from Duksan Pure Chemical Co., Ltd, Korea.

2.2. Preparation of samples

The CNT or C_{60} powder was oxidized using MCPBA dissolved in benzene solution. 0.2 g of AC, ACF, and oxidized CNT or C_{60} was added to separate 5 mL 0.1 M $\text{Fe}(\text{NO}_3)_3$ solutions. Then, the mixture was stirred for 1 h, clarified and poured out of the super water. The sediments of Fe/carbon were dried naturally at 373 K. 2 g TOS was dissolved in 200 mL of 5% concentration H_2O_2 to prepare the TOS solution. The Fe/carbon prepared above was put into the prepared TOS solution and stirred for 5 h at 343 K. Then the solvent was dried at 373 K. Finally, the solid precipitates obtained above were heated at 973 K for 1 h. The nomenclatures of the samples prepared are listed in Table 1.

2.3. Characterization of Fe-carbon/ TiO_2 composites

For the measurement of structural variations, XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio. XRD patterns were obtained at room temperature with a diffractometer [Shimata XD-D1 (Japan)] using $\text{Cu K}\alpha$ radiation. The morphology of the Fe-AC/ TiO_2 and Fe-ACF/ TiO_2 composites was examined via an SEM (JSM-5200, 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 C_{60} surfaces of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid. EDX was used to measure the elemental analysis of the Fe-carbon/ TiO_2 composites. For the measurement of photo-degradation effects, UV-VIS spectra of Fe-carbon/ TiO_2 composites were recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.4. Analysis of photocatalytic effect

For MB, initial concentration was set at about 1.0×10^{-5} mol/L. Then, each of the 0.05 g composite photocatalysts (as listed in Table 1) was used to degrade the MB solution. For UV irradiation, a UV lamp (20 W, 365 nm) was used at a distance of 100 mm from the solution in darkness box. After irradiation at 30 min, 60 min, 90 min, and 120 min, the samples were examined to test the change of MB concentration to compare the different photocatalytic effects among the Fe-carbon/ TiO_2 composites prepared. The blue color of the solution faded gradually with time due to the adsorption and degradation of MB. Specifically, by sampling 3 mL of solution using a centrifuge after removal of the dispersed powders, the concentration of MB in the solution was determined to be a function of Fe, carbon and TiO_2 from the absorbance change.

3. Results and Discussion

3.1. Structural analysis

The values of BET surface area of pristine carbon and Fe-carbon/ TiO_2 composites are presented in Table 1. As can be seen in the results in Table 1, The BET surface areas of pristine AC, ACF, CNT and C_{60} were 1083, 1842, 299 and $1.9 \text{ m}^2/\text{g}$, respectively. While the BET surface areas of Fe-carbon/ TiO_2 increased to 533, 782, 156 and $31.2 \text{ m}^2/\text{g}$, it is clear that almost all BET surface areas for the Fe-AC/ TiO_2 , Fe-ACF/ TiO_2 and Fe-CNT/ TiO_2 composites have decreased considerably compared with those of corresponding pristine AC, ACF and CNT. This result indicates that the surface area decreased after formation of TiO_2 particles by Ti precursor treatment. It was considered that the invaded TiO_2 particles can be blocked from pores in AC, ACF and CNT. a similar phenomenon was also observed in work cited in the references.^{20,21)} On the contrary, the surface area of Fe- C_{60} / TiO_2 composites increased compared with the addition of pristine C_{60} . However, compared with pure TiO_2 , the surface area of Fe- C_{60} / TiO_2 composites was also increased. This suggests that the C_{60} can be distributed on the TiO_2 matrix.

Fig. 1 shows SEM images of the Fe-AC/ TiO_2 and Fe-ACF/ TiO_2 . From the results, it can be observed that TiO_2 particles were immobilized on the surface of AC or ACF; the fixed TiO_2 particles did not form compact configuration on the AC or ACF surface, as shown in Fig. 1. The morphological evidence is of TiO_2 units fixing onto the Fe-AC structure; these units seem to cover the polymer surface. As shown in Figs. 1 (a) and (b), TiO_2 units are evenly distributed on the Fe-AC structure and continuous TiO_2 units are immobilized

Fig. 1. SEM images of Fe-AC/TiO₂ and Fe-ACF/TiO₂ composites: Fe-AC/TiO₂: (a)×1000, (b)×10000; Fe-ACF/TiO₂: (c)×1000, (d)×10000.

on almost every grain of AC. However, rather small clusters of TiO₂ crystals spread over the ACF surface with irregular shapes, and the interstices among crystalline particles provide an ideal path for the transport and adsorption of organic molecules. As can be seen in Figs. 1(c) and (d), the TiO₂ particles were finely distributed on the surface of ACF with a few of them agglomerating. Although we could not clearly find Fe particles in the SEM images of Fe-AC/TiO₂ and Fe-ACF/TiO₂ composites, and it may be that the size of the Fe particles was estimated to be very small, but the presence of Fe particles was confirmed in XRD and EDX results.

It is not exactly clear which nanocarbon, CNT or C₆₀, was present within SEMs, so the TEM images are further complicated by the fact that the higher nanocarbons exhibit multiple isomeric forms with shapes ranging from approximately ellipsoidal to spheroidal for C₆₀ and a wall tube for CNT, as can be seen in Fig. 2. The Fe-CNT/TiO₂ and Fe-C₆₀/TiO₂ composites were investigated by TEM to obtain detailed information about the interfacial region of the CNT and C₆₀ crystals and surface. Fig. 2 shows that the surface of the Fe-CNT/TiO₂ composites should have a strong interphase structural effect between the carbon and metal oxide phases. Fig. 2 (a) reveals that the TiO₂ particles were strongly adhered on the sidewalls of the CNT. In addition, it reveals a generally precipitate-free and smooth interface between the Fe and TiO₂ matrix and the C₆₀ crystals, as shown in Fig. 2 (b). According to our previous study,²²⁾ the homogeneous distribution of TiO₂ on the nanocarbon external surface could be formed by the MCPBA oxidation method. The black dots distributed in Fig. 2 correspond to the Fe particles. This can possibly be associated with the formed crystalline of Fe and TiO₂, which also agrees with the XRD results.

(a)

(b)

Fig. 2. TEM micrograph of the Fe-CNT/TiO₂ and Fe-C₆₀/TiO₂ composites: (a) Fe-CNT/TiO₂ and (b) Fe-C₆₀/TiO₂.

Fig. 3. XRD patterns of Fe-carbon/TiO₂ composites.

Fig. 3 shows the XRD results of the Fe-carbon/TiO₂. The

Fig. 4. EDX elemental microanalysis of Fe-carbon/TiO₂ samples: (a) Fe-AC/TiO₂, (b) Fe-ACF/TiO₂, (c) Fe-CNT/TiO₂, and (d) Fe-C₆₀/TiO₂.

presented XRD patterns of the Fe-AC/TiO₂, Fe-ACF/TiO₂ and Fe-CNT/TiO₂ composites consist of mixed phases such as anatase and rutile phases. The main diffraction peaks are diffractions of (101), (004), (200), (105), (200) and (204) planes of anatase and (110), (101), (111) and (211) plans of rutile. The phase transition can be attributed to the formation of pure oxides due to the high temperatures of 973~1173 K.²³⁾ But the phase transition temperature has been shown to depend on impurity contents, particle size and surface area.²⁴⁾ However, XRD patterns of the Fe-C₆₀/TiO₂ composites show typical single anatase crystallites; no significant diffraction peaks of rutile-phase TiO₂ were detected. This reflected the fact that C₆₀ can effectively suppress phase transformation from anatase to rutile during heat treatment at high temperatures. Moreover, the Fe-carbon/TiO₂ composites show that the intense peaks of carbon correspond to the (002) reflection and to the (10) band. It should be noted that the (101) anatase reflection can overlap with the (002) reflection of nanocarbon. In addition, it is noteworthy that uniform peaks of 'FeO+2TiO₃' and pure maghemite (γ -Fe₂O₃) were detected in all of the Fe-

Fig. 5. Apparent first order kinetics of MB degradation for Fe/TiO₂ and Fe-carbon/TiO₂ composites under UV irradiation.

Table 2. Photodegradation Rate Constant of Fe/TiO₂ and Fe-carbon/TiO₂ Composites

Samples	K_{app} (min ⁻¹)
Fe/TiO ₂	3.74×10^{-3}
Fe-AC/TiO ₂	5.41×10^{-3}
Fe-ACF/TiO ₂	6.77×10^{-3}
Fe-CNT/TiO ₂	8.63×10^{-3}
Fe-C ₆₀ /TiO ₂	7.14×10^{-3}

carbon/TiO₂ composites.

Fig. 4 shows the results of the EDX for Fe-carbon/TiO₂ composites. These spectra show the presence of peaks from the C, O, Ti and Fe elements. The numerical contents for the various elements are listed in Table 1. These data show that the quantities of carbon and Fe in the Fe-carbon/TiO₂ composites were small, with a major element of Ti.

3.2. Degradation of MB Photocatalytic activity

The photocatalytic degradation of MB over Fe/TiO₂ and Fe-carbon/TiO₂ composites with different carbon precursors was used to evaluate the influence of carbon; the results are shown in Fig. 5. To infer the reaction kinetics of the photodegradation of MB, the data of $-\ln(C/C_0)$ for the first-order reaction as a function of irradiation time (t) were calculated by an apparent first-order equation:

$$-\ln(C/C_0) = K_{app} t$$

Where C and C₀ are the initial concentration of MB, K_{app} is the degradation rate of the reactant (min⁻¹), c is the concentration of the reactant (mol), and t is the irradiation time. In fact, the K_{app} calculated for each sample is shown in Table 2; the results indicate that the photocatalytic reactivity of Fe-carbon/TiO₂ composites was higher than that of Fe/TiO₂ (3.74×10^{-3}); this result is consistent with the adsorption capacity of Fe-carbon/TiO₂ composites, which is higher than

Fig. 6. Apparent first order kinetics of MB degradation for pure TiO₂, ACF/TiO₂ and CNT/TiO₂ composites under UV irradiation.

Table 3. Photodegradation Rate Constant of Pure TiO₂, ACF/TiO₂ and CNT/TiO₂ Composites

Samples	$K_{app} (min^{-1})$
Pure TiO ₂	2.31×10^{-3}
ACF/TiO ₂	3.3×10^{-3}
CNT/TiO ₂	3.81×10^{-3}

that of Fe/TiO₂. However, it was noticeable that the highest adsorption capacity on the Fe-ACF/TiO₂ composites did not lead to the highest photocatalytic activity, as shown in Fig. 5. The order of photocatalytic activity of different Fe-carbon/TiO₂ composites was as follows: Fe-CNT/TiO₂ (8.63×10^{-3}) > Fe-C₆₀/TiO₂ (7.14×10^{-3}) > Fe-ACF/TiO₂ (6.77×10^{-3}) > Fe-AC/TiO₂ (5.41×10^{-3}), which might be limited by the different aperture structures of carbon. As is known, because large surface areas of carbon can adsorb oxygen and dye on the inside or outside of the surface, carbon has definite electron acceptability. Thus, the photocatalytic activity of Fe-carbon/TiO₂ composites was higher than that of Fe/TiO₂. However, due to nanocrystalline CNT and C₆₀, UV light could enter the inner CNT or C₆₀ easily because of their open ends.²⁵⁾ In addition, CNT and C₆₀ are eminent electronic conductors, which can rapidly transfer electrons by CNT network or C₆₀ surface.

The photocatalytic degradation of MB over selective pure TiO₂, ACF/TiO₂ and CNT/TiO₂ composites was used to evaluate the influence of Fe; the results are shown in Fig. 6. The results with reaction time as first order confirmed by the linear transforms, as in the above equation, are listed in Table 3. Compared with results shown in Table 2, the Fe/TiO₂, Fe-ACF/TiO₂ and Fe-CNT/TiO₂ composites prepared showed much higher activity than the pure TiO₂ (2.31×10^{-3}), ACF/TiO₂ (3.3×10^{-3}) and CNT/TiO₂ (3.81×10^{-3}) respectively. This suggests that the combining of Fe or Fe-carbon and TiO₂ should be taken into account to explain the

photocatalytic activity for degradation of MB. According to our previous works,^{26,27)} it has been considered that the introduction of Fe particles can work in a photo-Fenton reaction under UV irradiation. The photo-Fenton reaction can give rise to the formation of OH radicals, which have been known to be strong and not selective oxidizers of organic matter in water. On the other hand, the Fe ions can create complexing ligands with the OH⁻ to enhance change of combining with h⁺ through the formation of complex [Fe²⁺(OH⁻)₂] and/or [Fe³⁺(OH⁻)₃].

As can be seen in Table 2 and Table 3, the degradation rate of Fe-carbon/TiO₂ generally occurs faster than that of respective Fe/TiO₂ and carbon/TiO₂ composites. Meaningfully, there appears to be a synergistic effect among Fe, carbon and TiO₂ since rate constants of the combined process are greater than the sum of the rate constants of Fe/TiO₂ and carbon/TiO₂ composites, which is particularly clear for Fe-CNT/TiO₂ composites. The synergistic effect may be attributed to two reasons, namely: (1) Another kind of electronic transfer is occurred among TiO₂, Fe and carbon. An electron transfer in the composite may take place in the process of TiO₂ → carbon or TiO₂ → Fe³⁺ → Fe²⁺ to effectively decrease the recombination of electron/hole pairs. (2) We would like to postulate that the band gap energies of TiO₂ may be narrowed due to a multi-electron transfer from carbon to iron oxides.

4. Conclusion

Fe-carbon/TiO₂ composites were successfully synthesized by a sol-gel method using different carbon precursors. The composites exhibit enhanced photocatalytic degradation property of the MB solution, which is probably caused by the photo-Fenton effect or/and electron transfer processes from the Fe and TiO₂ attached to carbon. In comparison to different Fe-carbon/TiO₂ composites, use of nanocarbon as CNT and C₆₀ can more effectively enhance the photocatalytic activity of TiO₂, which enhancement can be attributed to the excellent electron transfer ability. The higher photocatalytic activity of the Fe-carbon/TiO₂ composites can also be related to the cooperative effects between Fe and carbon.

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