

Preparation of AC/TiO₂ Composites from Activated Carbon Modified by HNO₃ and Their Photocatalytic Activity

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Abstract

In this work, activated carbon (AC) after HNO₃ modification was used as the support during the production of supported TiO₂ to increase the high deposition efficiency and the photocatalytic activity. The results of N₂ adsorption showed that the BET surface area of samples decreased with an increasing of the concentration of HNO₃ due to the penetration of TiO₂. From XRD data, a single crystal structure of anatase peak was observed in diffraction patterns for the AC coated with titanium complexes. From the SEM results, almost all particles were aggregated with each other at the carbon surface and AC was covered with TiO₂ particles in all of the samples. The EDX spectra show the presence of C, O, Ti and other elements. It was also observed a decreasing of amount of C content with increasing Ti and O content from the EDX. The results of FT-IR revealed that the modified AC contained more surface oxygen bearing groups than that of the original AC. The effect of surface acidity and basity calculated from Boehm titration method was also evaluated from correlations as a function of NaOH, NaHCO₃, and Na₂CO₃ uptake. The surface modification of AC by HNO₃ leads to an increase in the catalytic efficiency of AC/TiO₂ catalysts, and the catalytic efficiency increases with increasing of HNO₃ concentration.

Keywords : Activated carbon, TiO₂, SEM, XRD, EDX, FT-IR, Boehm titration, Photocatalytic activity

1. Introduction

Environmental pollution by pollutants in air and in water has caused various serious problems for human health. The decomposition of these pollutants using TiO₂ photocatalysts has been one of the most promising methods for dealing with the problem [1-3]. For some practical applications, the particles of photocatalyst TiO₂ were either mounted on adsorbents, or fixed on a substrate by using a binder [4-6].

Early work mainly focused on coating TiO₂ on fixed supports, such as glass fibers, glass, quartz, and stainless steel, etc [7, 8]. The efficiency of pollutant degradation on TiO₂ particles so immobilized is usually decreased because of the mass transfer limitation. To enhance mass transfer, a system of particles suspension is preferred for a better mixing of catalysts with both light beams and pollutants in water. Therefore, much attention was paid to supporting TiO₂ on particle supports, such as alumina, zeolite, activated carbon, silica gel and glass beads. The particles are selected so that they can be easily suspended by either air bubbling or mechanical stirring [9, 10]. Among these particle supports, activated carbon is very promising for three reasons. First, activated carbon is able to adsorb the pollutants and then release them onto the surface of TiO₂. Consequently, a higher concentration of pollutants around TiO₂ than that in the bulk solution is created leading to an increase in the

degradation rate of the pollutants [11-14]. Second, the charge transference between TiO₂ and AC can cause an acidification of surface hydroxylic groups in the TiO₂. This will enhance the interaction between some pollutants and TiO₂ to further promote the degradation. Moreover, the ability to absorb visible light of the supported TiO₂ is also enhanced [15, 16]. Third, the intermediates produced during degradation can be also adsorbed by activated carbon and then further oxidized. Thus, secondary pollution of the intermediates can be reduced [17].

A proficient way to enhance the mesopores surface area and the amount of oxygen bearing groups of activated carbon simultaneously is modified by acid treatment such as HNO₃ oxidization [18]. Therefore, the surface modification of activated carbon post-treated with HNO₃ may lead to a significant increase in the deposition rate of TiO₂. Moreover, it is also reported that an increase in the concentration of oxygen bearing groups providing more nucleation sites and an activated carbon with acidic functional groups can result in smaller-sized titanium complex particles well dispersed leading to high catalytic activity [19, 20].

In this present work, we have prepared AC/TiO₂ composite after surface modification of activated carbon by acid treatment. The transformation of titanium n-butoxide (TNB) to TiO₂ on the carbon surface during heat treatment must be improved. For the preparation of AC/TiO₂ composite, the

main aim of this paper are: (i) to investigate the changes in textural and surface chemical properties of AC/TiO₂ by surface modification by post treatment of HNO₃ with various concentrations and (ii) to study the effects of photocatalytic activity of AC/TiO₂ composite prepared with TBN. The prepared catalysts were characterized by N₂ adsorption, X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersion X-ray analysis (EDX), FT-IR and Boehm titration. The catalytic efficiency of the developed catalysts was evaluated by the photodegradation of an azo compound, methylene blue.

2. Experimental

2.1. Materials

The powdered typed activated carbon (ca. 80 μm) was purchased from Dong Yang Carbon Co., Ltd. Titanium n-butoxide (TNB, 99%) was obtained from ACROS, ORGANICS, USA. The HNO₃ (66%) for the surface modification of activated carbon was obtained from Duksan Pure Chemical Co., Ltd. The Methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) was analytical grade which was also purchased from Duksan Pure Chemical Co., Ltd.

2.2. Preparation of AC/TiO₂ composites

For the preparation 5.0 g of powdered activated carbon was boiled in None, 0.05, 0.1 and 0.5 mol/L HNO₃ solution at 373 K for 60 min to obtain sufficient oxygen-containing groups. The oxidized activated carbon put into 200 mL TBN solution. The mixing solution was stirred by using a Hot plate & stirrer (DMS Co., DS-201HS, Korea) at 343-353 K for 5 h. The obtained mixture was subjected to heat treatment at 973 K for 1 h. The preparation conditions, concentration of used HNO₃ are listed in Table 1, together with the nomenclatures used in the present paper.

2.3. Characterization

Surface textures were measured using an adsorption apparatus (ASAP 2010, Micrometrics, USA) at 77 K. Before the experiment the samples were heated at 473 K and then out gassed at this temperature under a vacuum of 1.33×10^{-3} Pa to a constant pressure. The isotherms were used to calculate the specific surface area and pore volume. Scanning electron microscopy (SEM, JSM-5200 JEOL, Japan) was used to observe the surface state and pore structure of AC/TiO₂ composites. The crystal structure of TiO₂ was identified by X-ray diffraction (XRD, Shimatz XD-D1, Japan). For the elemental analysis of AC/TiO₂ samples, EDX was also used. The AC/TiO₂ composites prepared by surface modification of activated carbon post-treated with nitric acid were ex-

Table 1. Nomenclatures of AC/TiO₂ Composites Prepared with Different Concentrations of Nitric Acid to Activated Carbon

Preparation method	Nomenclatures
Activated Carbon + Non (HNO ₃) + Titanium n-butoxide (99.99%)	AT
Activated Carbon + 0.05M HNO ₃ + Titanium n-butoxide (99.99%)	AT1
Activated Carbon + 0.10M HNO ₃ + Titanium n-butoxide (99.99%)	AT2
Activated Carbon + 0.50M HNO ₃ + Titanium n-butoxide (99.99%)	AT3

amined by a KBr method using Fourier transform infrared (FT-IR) spectroscopy. Discs for the method were prepared by first mixing 1 mg of powdered oxidized AC with 600 mg of KBr (for FT-IR spectroscopy) in an agitate mortar, and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 minutes. The spectra of the samples were measured between 4000 and 500 cm⁻¹ using a FTS 3000MX (Biored Co. USA) spectrophotometer.

2.4. Boehm titration

Surface acidic oxygen functional groups and basic groups/sites were determined using Boehm titration [21-23]. On the Boehm titration different batch of 1 g of AC/TiO₂ composite were in contact with 50 mL of solutions of NaHCO₃ (0.05 M), NaCO₃ (0.05 M) and NaOH (0.05 M) for acidic groups, and HCl (0.05 M) for basic groups/sites, respectively, at room temperature for more than 2 days. Subsequently, the aqueous solutions were back titrated with HCl (0.05 M) for acidic and NaOH (0.05 M) for basic groups. According to the method, NaHCO₃ neutralizes only carboxylic groups, lactones are determined by the difference between the groups neutralized by Na₂CO₃ and NaHCO₃, and the difference between the groups neutralized by NaOH and Na₂CO₃ is phenols [24], and HCl does basic groups. Neutralization points were known using pH indicators of phenolphthalein solution for titration. In order to neutralize basic groups/sites, remaining HCl in the solution is back titrated with NaOH (0.05 M).

2.5. Photocatalytic degradation of Methylene blue (MB)

Methylene blue (MB) was dissolved in purified water to a concentration of 5.0×10^{-5} mol/L. Powder samples of 0.05 g were dispersed into 70 mL MB solution thus prepared in a glass bottle. The bottle was irradiated under UV Lamp (356 nm, 1.2 mW/cm²) for 10 min, 30 min, 40 min, and 50 min in the dark. The blue color of the solution faded gradually with time due to the adsorption and decomposition of MB. The concentration of MB after photo-degradation by AC/TiO₂ composite was determined by using a UV/VIS spectrophoto-

meter (660 nm, Genspec III (Hitachi), Japan) [25]. From the experiments in the dark, the adsorption of MB into the samples could be followed. In the experiments under UV irradiation, the color fading was due to both adsorption and decomposition of MB by the sample powders.

3. Results and Discussion

3.1. Physical properties of AC/TiO₂ composites

The nitrogen adsorption isotherms obtained at 77 K for the AC/TiO₂ composites prepared by surface modification of activated carbon post-treated with HNO₃ were presented in Fig. 1. For comparison, the isotherms in the Fig. 1 show that the total sorption uptake decreases with an increasing concentration of acid treatment. Differences in the shape of these isotherms are not very significant, evidencing general similarities in the pore structure of the AC/TiO₂ composites. It can be also seen that the N₂ adsorption capacity of AT is much larger than that of AT1, AT2 and AT3, suggesting the pore structure of AT is much more than that of AT1, AT2

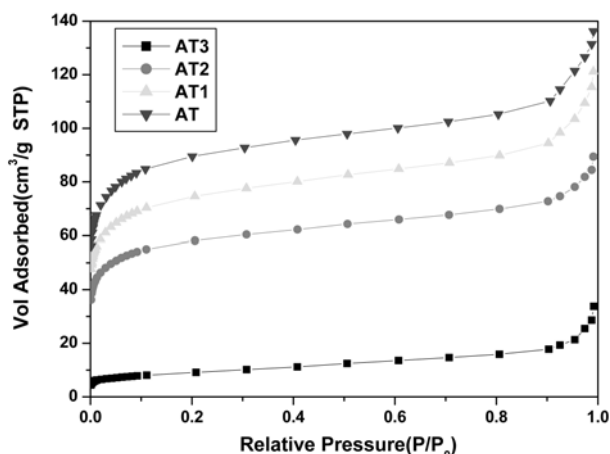


Fig. 1. Adsorption isotherm of N₂ at 77 K on the AC/TiO₂ composites prepared with activated carbon modified by HNO₃.

Table 2. Textural Properties of Pristine Materials and AC/TiO₂ Composites

Sample	Parameter		
	S _{BET} (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
As-received TiO ₂	132	–	–
As-received AC	1650	0.1201	7.37
AT	933	0.0823	6.68
AT1	924	0.0835	5.54
AT2	838	0.0765	5.42
AT3	787	0.0711	5.39

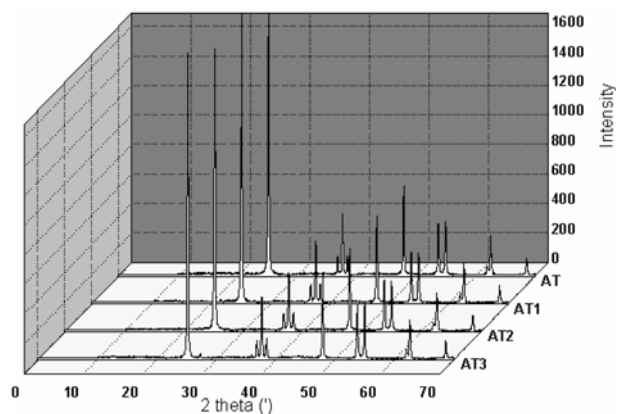


Fig. 2. XRD patterns for the AC/TiO₂ composites prepared with activated carbon modified by HNO₃.

and AT3. The porosities of these samples are listed in Table 2. A slight decrease in the BET surface area of activated carbon after the HNO₃ modification has also been reported [26]. In this work, the BET surface area, pore volume and average pore diameter decreased due to the penetration of TiO₂, and recovered somewhat on heat treatment for crystallization.

It is well known that the crystal structure of the deposited material is mainly determined by the deposition temperature. Fig. 2 depicts XRD pattern of AT, AT1, AT2 and AT3 prepared under a deposition temperature of 973 K. The peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the prepared TiO₂ existed in anatase state. Therefore, it can be concluded that the developed TiO₂ has a single crystal structure, i.e., anatase. So it is suggesting the modification of activated carbon by HNO₃ has no effect on the crystal structure of TiO₂. It has been reported that the diffraction peak of TiO₂ on the modified activated carbon is broader than that on the original activated carbon, indicating the modification of activated carbon by HNO₃ can result in much smaller TiO₂ particles [26].

These observations are understandable because the modification of activated carbon by HNO₃ enhances the concentration of oxygen bearing groups, which provides more nucleation sites of TiO₂ leading to the formation of smaller-sized titanium complex particles well dispersed. On the other hand, an AC with acidic functional groups and a well developed porosity commonly result in the particles well dispersed [19, 20]. Quantum yields of the photocatalytic reaction commonly increases as the particle size of TiO₂ decreases. So the increase in the photocatalytic activity of TiO₂ resulting from the modification of smaller TiO₂ particles well dispersed.

The surface morphology and crystal grown state of TiO₂ on the activated carbon surfaces were observed by scanning electron microscopy. The samples obtained after heating at

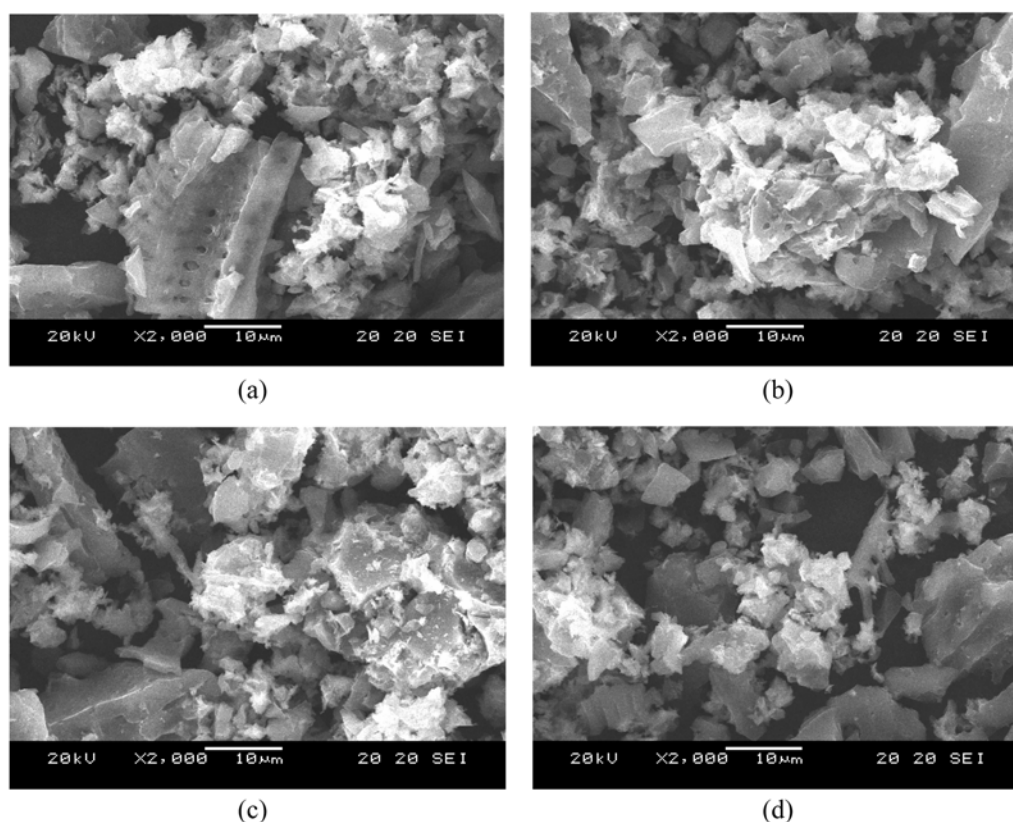


Fig. 3. SEM micrographs of the AC/TiO₂ composites prepared with activated carbon modified by HNO₃; (a) AT ($\times 2000$), (b) AT1 ($\times 2000$), (c) AT2 ($\times 2000$) and (d) AT3 ($\times 2000$).

973 K looked black, so the particles of TiO₂ were covered with carbon which produced by the carbonization. The TiO₂ coating of solid particles has been reported on various ceramics, including graphite and metals [27-31]. SEM micrographs of samples, AT, AT1, AT2 and AT3, are shown in Fig. 3. After 973 K heating, almost all particles were aggregated with each other in all of the samples. It was also observed that activated carbon was covered with TiO₂ particles (ascertained in the EDX microanalysis). The TiO₂ particles were regularly dispersed on activated carbon surface and a homogeneous distribution of activated carbon with providing the large surface area can be promoting the photocatalytic efficiency for the removal of MB in aqueous solution.

For elemental analysis of AC/TiO₂ composites after heat treatment, samples were analyzed by the EDX. The EDX spectra of AC/TiO₂ composites are shown in Fig. 4. The rustles of typical EDX elemental microanalysis of AC/TiO₂ composites after heat treatment are shown in Table 3. The results show the presence of C, O, Ti and other elements, i.e., Cu, K, Si and so on. Because the AC contain the impurities other elements, i.e., Cu, K, Si and so on were also shown in Table 3. In case of most of samples, carbon and titanium are present as major elements in the AC/TiO₂

composites. It can be also seen that a decreasing of amount of C content with increasing Ti and O content in Table 3, as the carbon surface is much more oxidized due to the increasing concentration of HNO₃, and the functional groups of activated carbon surfaces by acid treatment are affects due to the dispersion of the Ti.

3.2. FT-IR Chemical functional group study

FT-IR spectra of AC/TiO₂ composite prepared by surface modification of activated carbon post-treated with HNO₃ were depicted in Fig. 5. After modification, the band at 1380 cm⁻¹ ascribed to alcoholic C-O stretching vibration shows a defined peak and at 1719 cm⁻¹ ascribed to N-O stretching vibration. From the results, it observed that characteristic bands in the region of 1400-1300 cm⁻¹ corresponding to C-H bonds or to aromatic C=C bonds and various substitution modes of the aromatic ring appear. It was observed that intensity of these new bands increase with increasing of acid concentration. It can be consider that increase of a number of functional groups is concerned with formation of titanium complexes on carbon surfaces by transformation of TNB. A new band at 1595 cm⁻¹ corresponding to Ti-O is found: A new band at 1660 cm⁻¹ corresponding to quinone or conju-

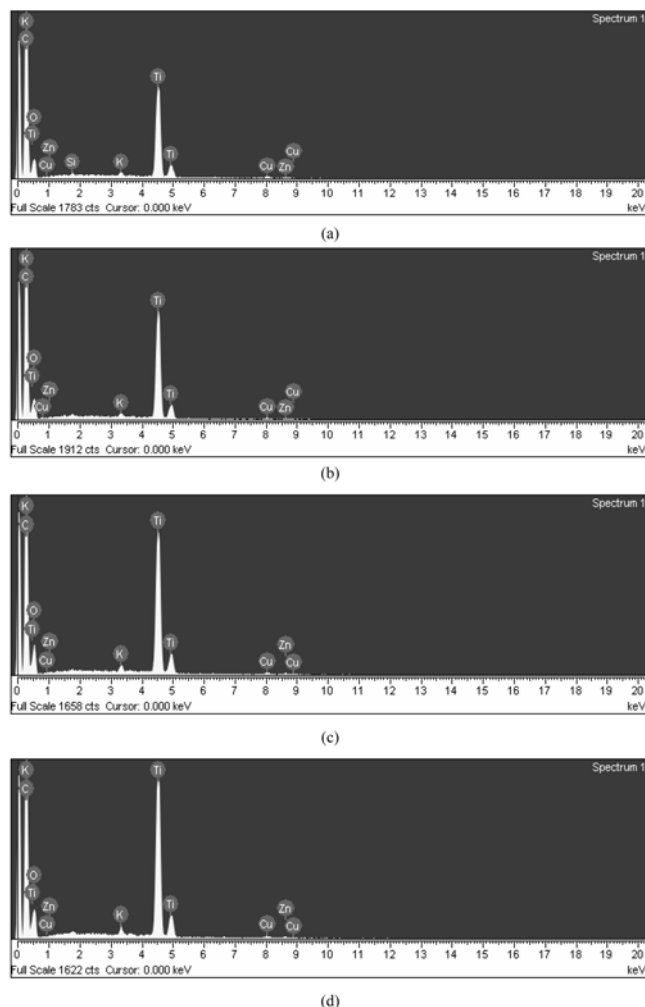


Fig. 4. EDX elemental microanalysis of the AC/TiO₂ composites prepared with activated carbon modified by HNO₃; (a) AT, (b) AT1, (c) AT2 and (d) AT3.

Table 3. EDX Elemental Microanalysis of AC/TiO₂ Composites Prepared with Different Concentrations of Nitric Acid to Activated Carbon

Sample (wt.%)	Ti	C	O	Cu	Others
AT	18.5	57.8	21.1	1.17	1.37
AT1	20.3	56.6	21.2	0.83	1.19
AT2	23.3	51.5	23.2	0.77	1.24
AT3	24.5	49.5	23.6	1.03	1.37

gated ketone is also found: Bands in the region of 1650-1860 cm⁻¹ which are assigned to the C=O stretching vibration corresponding to carbonyl and carboxyl groups, are more pronounced than the original activated carbon [32]. Bands in the region of 3100-3500 cm⁻¹ attributed to O-H deformation vibration in carboxyl groups were found. These results directly reveal that the oxidized activated carbon contains

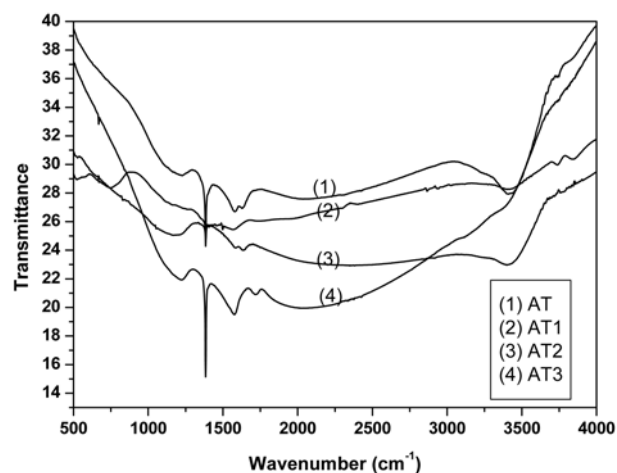


Fig. 5. FT-IR spectra for the AC/TiO₂ composites prepared with activated carbon modified by HNO₃.

Table 4. Number of Surface Species (meg/g) Obtained from Boehm Titration

Sample	Functional Group (meg/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
AT	0.125	0.510	0.413	1.048	0.033
AT1	0.135	0.530	0.431	1.096	0.038
AT2	0.141	0.538	0.432	1.111	0.037
AT3	0.149	0.544	0.445	1.138	0.043

more surface oxygen bearing groups than the original activated carbon.

3.3. Boehm titration oxygen group study

The type and quality of oxygen groups are determined by the Boehm titration method. The results obtained from the method proposed by Boehm are collected in Table 4. It can be observed that the total acidity and the distributions of groups of various strengths have very different values. The effect of surface acidity and basicity was also evaluated from correlations as a function of NaOH, NaHCO₃ and Na₂CO₃ uptake. It is noteworthy that carboxylic groups and basic groups were increased by nitric acid oxidation. This may contribute to the increasing local pH of this carbon surface due to acid treatment. A positive influence of the acidic groups on the carbon surface by acid treatment is also demonstrated from Boehm titration. It is considered that the affinity of activated carbon depends on the amount of surface functional groups. When a distribution of acidic groups is properly introduced, active sites on the carbon surface should play an important role. As expected, acid oxidation introduces a significant number of oxygen-containing groups in almost each category classified by Boehm. It could be considered that the increases of functional groups

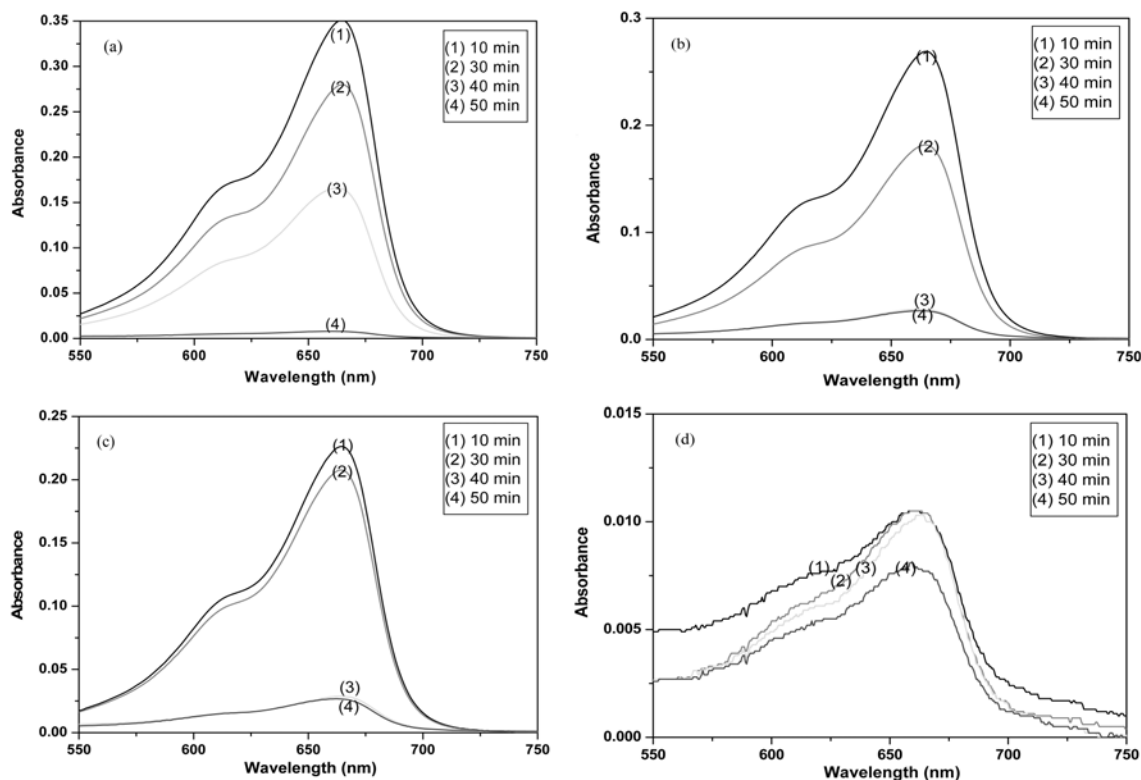


Fig. 6. UV-VIS spectra of MB concentration by AC/TiO₂ composites with various time conditions; (a) AT, (b) AT1, (c) AT2, (d) AT3.

on the carbon surface increase the formation of titanium complexes with original functional groups.

3.4. Photocatalytic activity of AC/TiO₂ composites

Fig. 6 shows the absorbance of AC/TiO₂ composites in MB solution concentration of 5×10^{-5} mol/L under UV irradiation after 10 min, 30 min, 40 min, and 50 min. It can be demonstrated that the absorbencies of AT, AT1, AT2 and AT3 were decreased by following the order of UV irradiation time with 10 min, 30 min, 40 min and 50 min. This implies that the transparent of the MB concentration highly increase by photocatalytic degradation effect of AC/TiO₂ catalysts. Fig. 7 depicts the changes in MB concentration under UV irradiation in the solution. MB removal with AC/TiO₂ photocatalysts is carried out to observe the UV photolysis effect for the MB solution. The changes are plotted on the relative concentration (c/c_0) of MB in the aqueous solution with UV irradiation time for sample series. It is observed that MB solution is quite unstable with variation of concentration when it is irradiated under UV with AC/TiO₂ catalysts, suggesting that the disappearance of MB caused by UV irradiation is presented. The relationship was shown approximately linearity properties depending on irradiation time, as reported on similar modified TiO₂ samples [33, 34]. Because the present of the activated carbon in AC/TiO₂

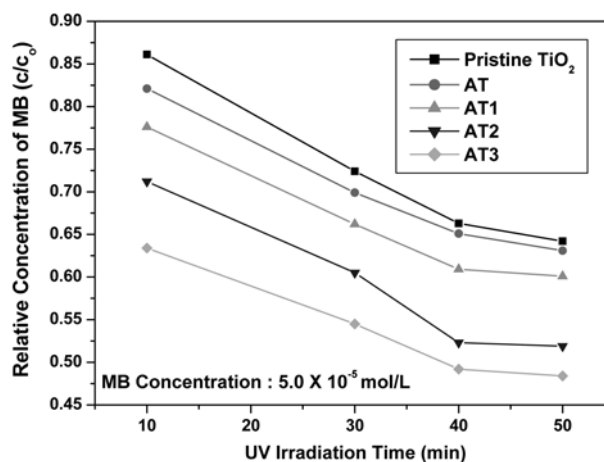


Fig. 7. Dependence of relative concentration of MB in the aqueous solution on time of UV irradiation for the AC/TiO₂ composites prepared with activated carbon modified by HNO₃.

composites had a large adsorptivity, as above mentioned, it is believed that the decrease of MB concentration in the aqueous solution can be occurred in two physical phenomena such as adsorption by activated carbon and photocatalytic decomposition by TiO₂. It is also observed that the surface modification of activated carbon by HNO₃ leads to an increase in the catalytic efficiency of AC/TiO₂ catalysts, and

the catalytic efficiency increases with an increasing of HNO₃ concentration. The reason of this observation is that the surface modification of activated carbon by HNO₃ enhances the loading of TiO₂ resulting in the increase in active material.

4. Conclusions

AC/TiO₂ composite prepared after surface modification of activated carbon by acid treatment provided high deposition efficiency and photocatalytic activity. The results of N₂ adsorption showed that the BET surface area of samples decreased with the concentration of HNO₃ increasing due to the penetration of TiO₂. From XRD data, a single crystal structure anatase peak was observed in diffraction patterns for the AC/TiO₂ composites. From the SEM results, almost all particles were aggregated with each other and activated carbon was covered with TiO₂ particles in all of the samples. The EDX spectra show the presence of C, O, Ti and other elements. It was also observed a decreasing of amount of C content with increasing Ti and O content from the EDX. The results of FT-IR revealed that the modified AC contained more surface oxygen bearing groups than that of the original activated carbon. The effect of surface acidity and basity calculated from Boehm titration method was also evaluated from correlations as a function of NaOH, NaHCO₃, and Na₂CO₃ uptake. The surface modification of activated carbon by HNO₃ leads to an increase in the catalytic efficiency of AC/TiO₂ catalysts, and the catalytic efficiency increases with increasing of HNO₃ concentration.

References

- [1] Kato, K.; Torii, Y.; Tada, H.; Kato, T.; Butsugan, Y.; Nihara, K. *J. Mater. Sci. Lett.* **1996**, *15*, 913.
- [2] Herrmann, J. M.; Tahiri, H.; Ait-Icho, Y.; Lassaletta, G.; Gonzalez-Elipe, A. R.; Fernandez, A. *Appl. Catal. B.* **1997**, *13*, 219.
- [3] Grechulska, J.; Hamerski, M.; Morawski, A. W. *Water Res.* **2000**, *34*, 1638.
- [4] Hoffman, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- [5] Ollis, D. F.; Turchi, C. *Environ. Prog.* **1990**, *9*, 229.
- [6] Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.
- [7] Peill, N. J.; Hoffmann, M. R. *Environ. Sci. Technol.* **1996**, *30*, 2806.
- [8] Fernandez, A.; Lassaletta, G.; Jimenez, V. M.; Justo, A.; Gonzalez-Elipe, A. R. *Appl. Catal. B.* **1995**, *7*, 49.
- [9] Lu, M. C.; Chen, J. N.; Chang, T. K. *Chemosphere* **1999**, *38*, 617.
- [10] Lei, L. C.; Chu, H.; Hu, X. J.; Yue, P. L. *Ind. Eng. Chem. Res.* **1999**, *38*, 3381.
- [11] Tryba, B.; Morawski, A. W.; Inagaki, M. *Appl. Catal. B.* **2003**, *41*, 427.
- [12] Matos, J.; Lainem, J.; Herrmann, J. M. *J. Catal.* **2001**, *200*, 10.
- [13] Tsumura, T.; Kojitani, N.; Umemura, H.; Toyoda, M.; Inagaki, M. *Appl. Surf. Sci.* **2002**, *196*, 429.
- [14] Torimoto, T.; Ito, S.; Kuwabata, S.; Yoneyama, H. *Environ. Sci. Technol.* **1996**, *30*, 1275.
- [15] Arana, J.; Dona-rodriguez, J. M.; Tello Rendon, E.; Garrigai Cabo, C.; Gonzalez-Diaz, O.; Herrera-Melian, J. A. *Appl. Catal. B.* **2003**, *44*, 161.
- [16] Arana, J.; Dona-rodriguez, J. M.; Tello Rendon, E.; Garrigai Cabo, C.; Gonzalez-Diaz, O.; Herrera-Melian, J. A. *Appl. Catal. B.* **2003**, *44*, 153.
- [17] Yoneyama, H.; Torimoto, T. *Catal. Today* **2000**, *58*, 133.
- [18] Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Orfao, J. J. M. *Carbon* **1999**, *37*, 1379.
- [19] Aksoylu, A. E.; Madalena, M.; Freitas, M. M. A.; Fernando, M.; Pereira, M. F. R.; Figueiredo, J. L. *Carbon* **2001**, *39*, 175.
- [20] Wang, S. B.; Lu, G. Q. *Carbon* **1998**, *36*, 283.
- [21] Boehm, H. P. *Carbon* **2002**, *40*, 145.
- [22] Boehm, H. P. *Carbon* **1994**, *32*, 759.
- [23] Boehm, H. P. *Adv. Catal.* **1996**, *16*, 179.
- [24] Lopez-Garzon, F. J.; Domingo-Garacia, M.; Perez-Mendoza, M.; Alvarez, P. M.; Gomez-Serrano, V. *Langmuir* **2003**, *19*, 2838.
- [25] Inagaki, M.; Miura, H.; Konno, H. *J. Eur. Ceram. Soc.* **1998**, *18*, 1011.
- [26] Zhang, X. W.; Zhou, M. H.; Lei, L. C. *Carbon* **2005**, *43*, 1700.
- [27] Inagaki, M.; Okada, Y.; Vignal, V.; Konno, H.; Oshida, K. *Carbon* **1998**, *36*, 1706.
- [28] Inagaki, M.; Okada, Y.; Miura, H.; Konno, H. *Carbon* **1999**, *37*, 329.
- [29] Konno, H.; Oyamada, K.; Inagaki, M. *J. Eur. Ceram. Soc.* **2000**, *20*, 1391.
- [30] Inagaki, M.; Fujita, K.; Takeuchi, Y.; Oshida, K.; Iwata, H.; Konno, H. *Carbon* **2001**, *39*, 921.
- [31] Tsumura, T.; Katanosaka, A.; Souma, I.; Ono, T.; Aihara, Y.; Kuratomi, J.; Inagaki, M. *Solid State Ionics* **2000**, *135*, 209.
- [32] Moreno-Castilla, C.; Lopez-Ramon, M. V.; Carrasco-Marin, F. *Carbon* **2000**, *38*, 1995.
- [33] Chen, M. L.; Bae, J. A.; Oh, W. C. *Analytical Science & Technology* **2006**, *19*, 301.
- [34] Chen, M. L.; Bae, J. A.; Oh, W. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1423.