

Preparation and photocatalytic activity of ACF/TiO₂ composites by using titanium *n*-butoxide and acid modified activated carbon fiber

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Abstract Photocatalytic degradation of methylene blue (MB) in aqueous solution was investigated using TiO₂ coated on various acid modified activated carbon fiber (ACF). The ACFs/TiO₂ composites were prepared from titanium *n*-butoxide (TNB) as titanium precursor and various acid modified ACFs. The prepared samples are heat treated at 973 K. Then the ACF/TiO₂ composites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX). Moreover, photocatalytic degradation of MB by the ACF/TiO₂ composites was determined under UV irradiation. The results shows that the photocatalytic activity of ACF/TiO₂ composites (AT1-AT4) prepared with TNB and various acid modified ACF was much better than that of ACF/TiO₂ composite (AT) prepared with TNB and non-acid modified ACF, and the effects improved with order of sample AT3 > AT4 > AT1 > AT2.

Key words Titanium *n*-butoxide, ACF, UV, Photocatalytic degradation

1. Introduction

Recently, industrialization and agricultural development, together with population growth, has drastically reduced clean water resources with various kinds of contaminants entering water. Developments in the field of chemical water purification have led to an improvement in oxidative degradation processes applying catalytic and photochemical methods [1, 2]. In last decade, environmental purification using TiO₂ as a photocatalyst has attracted a great deal of attention because of its chemical stability, robustness against photo corrosion, low toxicity, low pollution load, and availability at low cost [3, 4]. However, the fine TiO₂ represents high photoactivity and a significant quantum effect is commonly in nanometer size, the problem of separation and recovery of photocatalyst from the reaction medium exists.

Activated carbon (AC) is has widely been used as a support in gas and water remediation because of its good adsorption, and supported TiO₂ exhibits a synergism that has marked effects on the kinetics of disappearance of pollutants, each pollutant being more rapidly photodegraded [5-8]. However, AC is commonly used in the forms of granules and powder, and there remain some difficulties in filtering and recovery from water. The ACF has received

increasing attention in recent years as an adsorbent. Comparing to AC, ACFs are produced in the form of felt or cloth, with high BET surface area and micropore volume [9]. However, common ACF have inadequate adsorption capacity for toxic gases (especially for basic gases), because they usually possess a nonpolar surface due to the high temperature conditions of their manufacture (their polar components feature a basic nature). It is a well-known fact that surface oxygen complexes including carboxyl and phenolic hydroxyl groups have an acidic nature, and acidic adsorbents strongly interact with basic adsorbates due to the Lewis acid-base interaction [10-13].

Therefore, in this work, acid treatment was applied to ACF surfaces in order to introduce surface oxygen complexes, and ACF was selected as an adsorptive support for TiO₂ loading. The composites were prepared using TNB and various acid modified ACF, following by heat treatment at suitable temperature. The ACF/TiO₂ composites were characterized by SEM, XRD and EDX. To determine the photocatalytic decomposition of the composites, methylene blue (MB) was chosen as the model pollutant under UV irradiation.

2. Experimental

2.1. Materials

TNB (99.9 %) was purchased from Acros organics

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Table 1
The properties of ACF

Physical properties	Units
Density	1.23~1.91 g/ml
Electrical resistivity	$5.2 \times 10^{-3} \sim 6.8 \times 10^{-3} \Omega \cdot \text{cm}$
Diameter	12~15 μ
Tensile strength	$4 \sim 6 \times 10^8 \text{ Pa}$
Tensile modulus	$3 \times 10^{10} \sim 4 \times 10^{10} \text{ Pa}$
Elemental carbon	$\geq 95 \text{ wt\%}$

Co., Ltd, USA, as the titanium source. ACF were purchased from EAST ASIS Carbon Fibres Co., Ltd, Anshan, China. The properties of ACF were shown at Table 1. The acids HCl, HNO₃, H₂SO₄ and H₃PO₄ which used to modify the ACF, were obtained from Duksan Pure Chemical Co., Ltd, Korea. Benzene (99.5 %) was used as organic solvents which were purchased from Samchun Pure Chemical Co., Ltd, Korea. The methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) was used as analytical grade which was also obtained from Duksan Pure Chemical Co., Ltd, Korea.

2.2. Preparation of ACF/TiO₂ composites

For the preparation of ACF/TiO₂ composites, 5.0 g ACFs were milled to powders. And then the ACFs powders were boiled in 100 ml 0.1 M HCl, HNO₃, H₂SO₄ and H₃PO₄ at 333 K for 3 h, respectively. Acid modified ACF powders were dried at 378 K to remove the acid which remained in the ACF powders. The dried ACF powders were mixed in a mixing solution of TNB and benzene with a regular ratio of 50 : 50, stirring at 343 K for 5 h in an airtight container. After the stirring the solutions were transformed to the ACF and TiO₂ mixed gels, and these gels were heat treated at 973 K for 1 h with a heating rate of 279 K/min. The preparation condition and code of samples were listed in Table 2.

Synthesized powders were characterized by various techniques. SEM was used to observe the surface state and structure of the ACF/TiO₂ composites. The analyses were carried out by using a JSM-5200 JOEL elec-

tron microscope (Japan). XRD was used for crystal phase identification. XRD patterns were obtained at room temperature with a Shimata XD-D1 (Japan) using CuK α radiation. EDX was used to measure the elemental analysis of the ACF/TiO₂ composites. UV-vis spectra for the MB solution degraded by ACF/TiO₂ composites under UV lamp irradiation were recorded using a Genspec (Hitachi, Japan) spectrometer.

2.3. Photocatalytic decomposition for MB solution

The photocatalytic effects of ACF/TiO₂ composites were determined using MB decomposition in aqueous solution under an UV lamp (356 nm, 1.2 mW/cm²). According to former works [14, 15], the initial MB concentration was chosen $1.0 \times 10^{-5} \text{ mol/l}$, and the amount of suspended composites was kept at 1 g/l in 50 ml MB solution. Before turning on UV lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 30 min, 90 min, 150 min and 300 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by a UV-vis spectrophotometer [16, 17]. The spectra (550~750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

3. Results and Discussion

3.1. Morphology and structure of ACF/TiO₂ composites

The surface morphology and crystal grown state of

Table 2
Nomenclatures of ACF/TiO₂ composites prepared with TNB and various acids modified ACF

Samples	Nomenclatures
ACF + titanium <i>n</i> -butoxide (50 ml)	AT
HCl treated ACF + titanium <i>n</i> -butoxide (50 ml) + benzene (50 ml)	AT1
HNO ₃ treated ACF + titanium <i>n</i> -butoxide (50 ml) + benzene (50 ml)	AT2
H ₂ SO ₄ treated ACF + titanium <i>n</i> -butoxide (50 ml) + benzene (50 ml)	AT3
H ₃ PO ₄ treated ACF + titanium <i>n</i> -butoxide (50 ml) + benzene (50 ml)	AT4

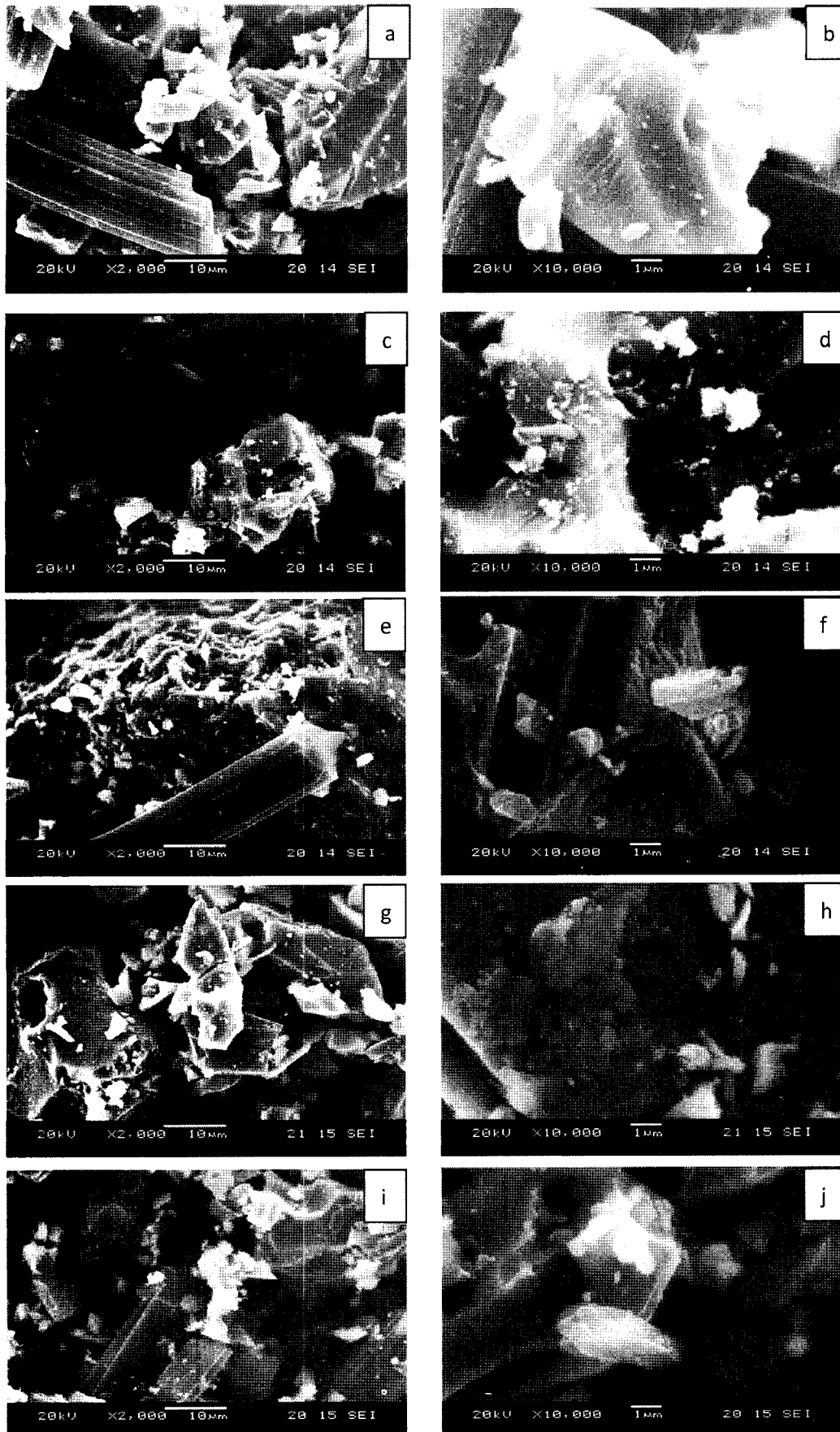


Fig. 1. Scanning electron micrographs of ACF/TiO₂ composites prepared with TNB and various acids modified ACF. AT: (a) and (b); AT1: (c) and (d); AT2: (e) and (f); AT3: (g) and (h) and AT4: (i) and (j).

TiO₂ on the surface of various acid modified ACF were observed by SEM. The samples obtained after heat-treating at 973 K turned to black color, so the particles of TiO₂ were covered on the ACF surface which produced by the carbonization. The SEM morphology of ACF/TiO₂ composites prepared with TNB and various acid modified ACF was shown in Fig. 1. After heat treatment of 973 K, the TiO₂ particles were coherent each other, which formed the TiO₂ clusters on the surface of ACF. And the titanium complex particles regularly distribute on and around the ACF surfaces because the surface of ACF was full of grooves. These results were agreed to former studies [18, 19], it could be considered that ACF/TiO₂ composites have much more photocatalytic activity.

It is well known that the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature. Fig. 2 depicts XRD patterns of original ACF and ACF/TiO₂ composites prepared with TNB and various acid modified ACFs heat-treated at 973 K for 1 h. It was also well known that the anatase phase formed below 773 K begin to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973~1173 K, and the TiO₂ composited by carbon could confirm to suppress the phase transformation from anatase to rutile [20-22]. 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 developed composites existed in anatase state. There are no peaks found at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. Therefore, it can be suggested that the sam-

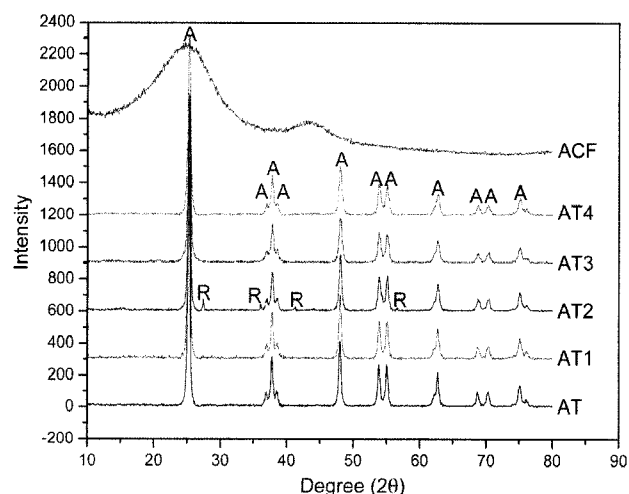


Fig. 2. XRD patterns of original ACF and ACF/TiO₂ composites prepared with TNB and various acids modified ACF with heat treatment at 973 K for 1 h.

ples AT, AT1, AT3 and AT4 among the developed ACF/TiO₂ composites have a single and clear crystal structure, with type of anatase. But only the sample AT2 has a mixture structure of anatase and rutile.

The EDX spectra of ACF/TiO₂ composites prepared with TNB and various acid modified ACF are shown in Fig. 3. From the spectra, all of the ACF/TiO₂ composites show the main peaks of C, O and Ti, though a few of impure elements of P was existed (which may be introduced from experimental procedure). So it is considered that the ACF/TiO₂ composites contained these three main elements. The EDX elemental microanalysis (wt%) for ACF/TiO₂ composites are listed in Table 3. From the data, we can see that all of the samples are rich in C, O and Ti elements with a very poor in impure elements. On the other hand, it is noticed that the amount of C element of sample AT3 is much less than that of other samples and the amount of Ti and O elements of sample AT3 is much more than that of other samples. So it considered that sample AT3 have much more photocatalytic activity than other samples.

3.2. Photocatalytic activity of ACF/TiO₂ composites

Fig. 4 showed the UV-vis spectra of ACF/TiO₂ composites prepared with TNB and various acid modified ACF which calcined at 973 K. The absorption edge of ACF/TiO₂ composites occurred at 550 to 750 nm, and all of the samples showed strongest absorption in the 660 nm. From the spectra of Fig. 4, we can observe that the absorbance maxima for all samples at 660 nm were decreased with an increase of UV irradiation time. This result suggests that the color of MB solution is changed increasingly with an increase of UV irradiation time, so the concentration of MB solution is also decreased increasingly with an increase of UV irradiation time (it can be ascertained in the further results). Fig. 5 showed the results of photocatalytic decomposition of MB over ACF/TiO₂ composites prepared with TNB and various acid modified ACF. According to former studies [23, 24], the acid oxidized activated carbon contains much more surface oxygen bearing groups than the original activated carbon, and the acid modified activated carbon enhances the loading of TiO₂ as resulting the increase of active sites. So we can find that the photocatalytic activity of ACF/TiO₂ composites prepared with TNB and various acids modified ACF was much better than that of ACF/TiO₂ composite prepared with TNB and non-acid modified ACF, due to the modified ACF had much more surface oxygen bearing groups to

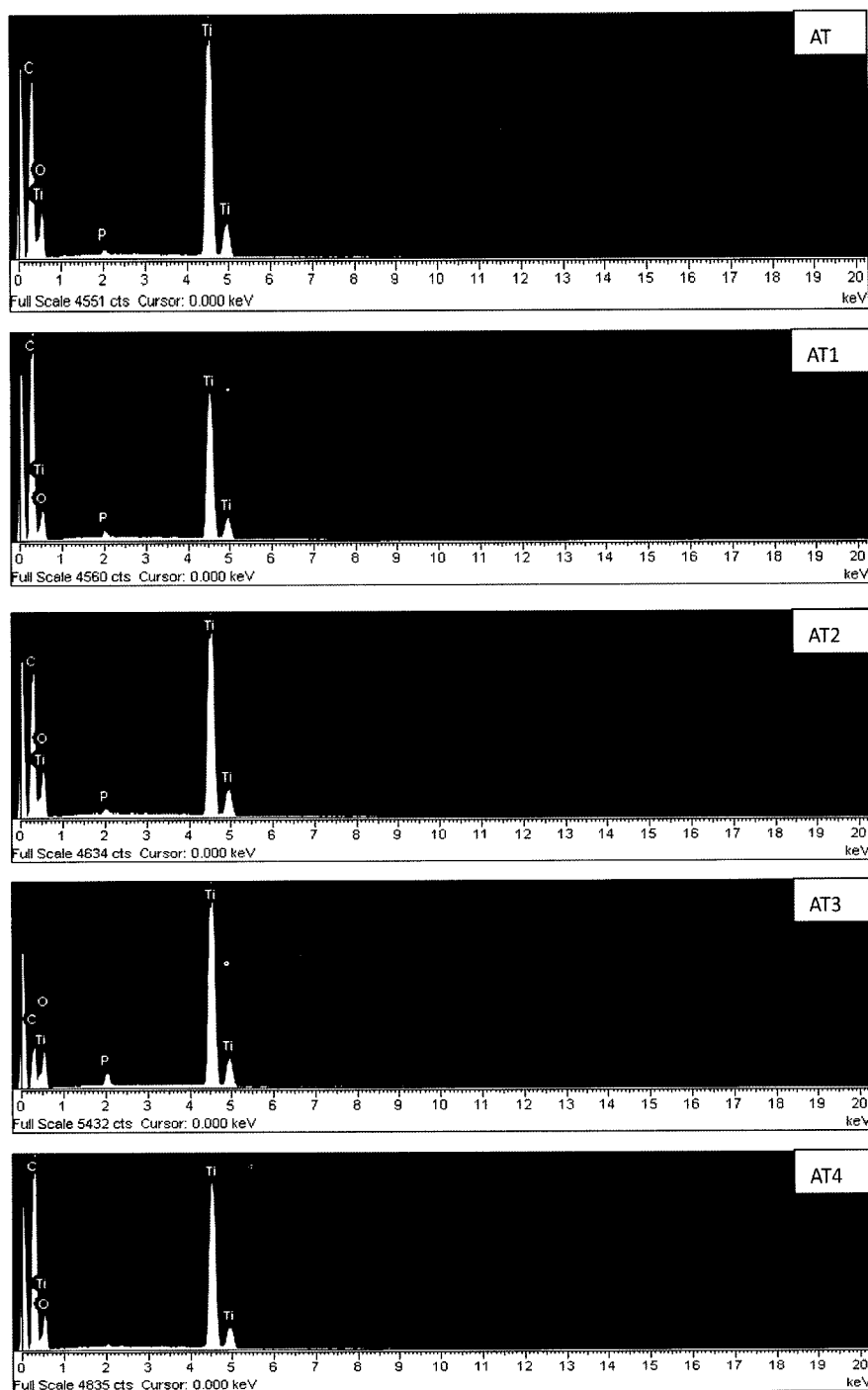


Fig. 3. EDX elemental microanalysis of ACFs/TiO₂ composites prepared with TNB and various acids modified ACF.

Table 3
EDX elemental microanalysis (wt%) of ACF/TiO₂ composites prepared with TNB and various acids modified ACF

Samples	Elements			
	C	O	Ti	Others
AT	40.70	27.42	31.56	0.32
AT1	53.84	21.79	23.90	0.46
AT2	38.92	30.51	30.24	0.32
AT3	19.47	36.81	42.36	1.37
AT4	49.25	24.50	26.25	-

enhance the loading of TiO₂ as resulting the increase of active sites. And the photocatalytic activity of ACF/TiO₂ composites decreased with an order of sample AT3 > AT4 > AT1 > AT2, which represented ACF was treated by H₂SO₄, H₃PO₄, HCl and HNO₃. As described in the EDX results, the sample AT3 treated with H₂SO₄ have a much amounts of TiO₂ particles, so it shows the best photocatalytic activity.

The efficiency of the photodegradation by TiO₂ depends

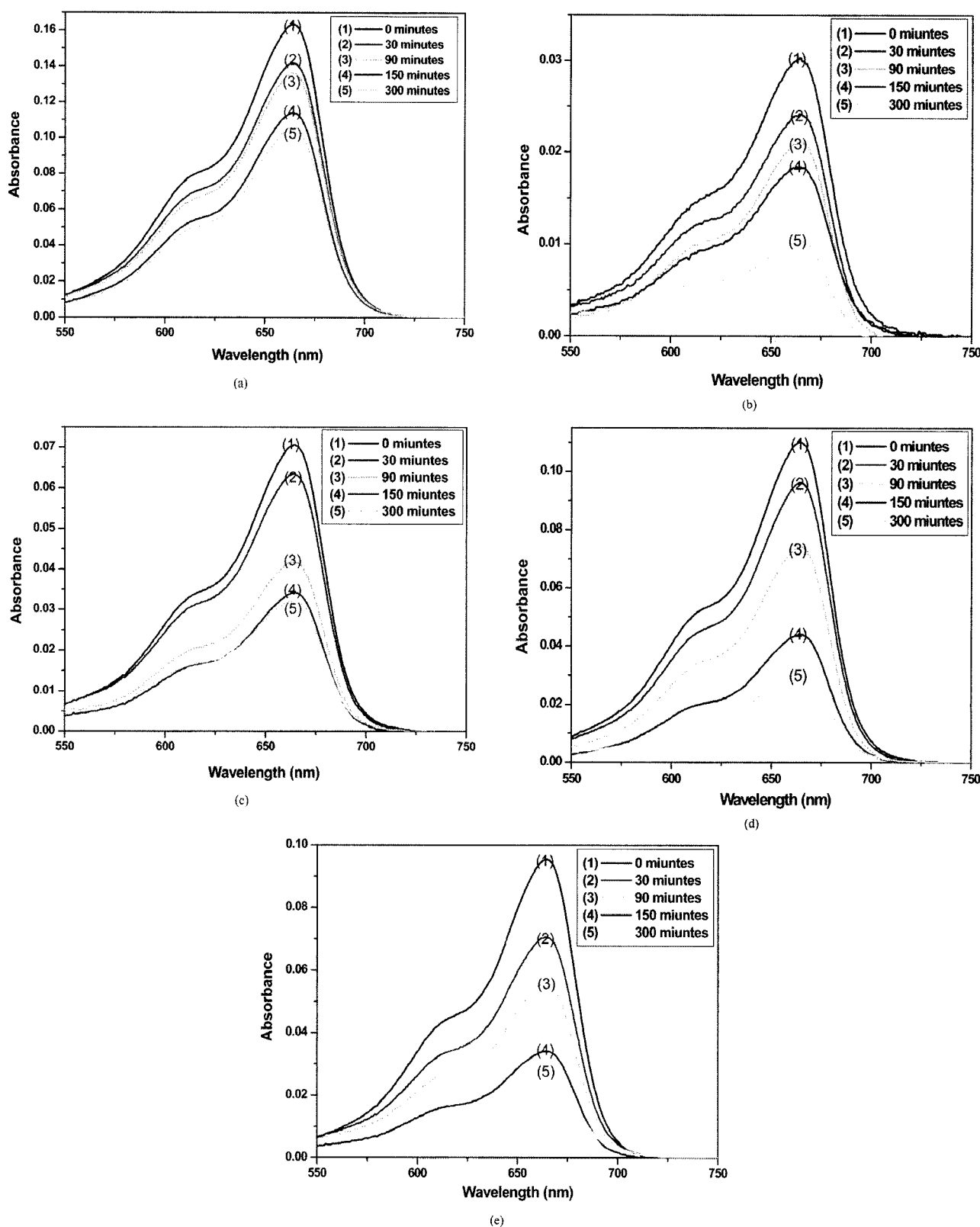


Fig. 4. UV-vis spectra of MB concentration against the ACF/TiO₂ composites prepared with TNB and various acids modified ACF; (a) AT, (b) AT1, (c) AT2, (d) AT3 and (e) AT4.

on the catalyst surface area in contact with the solution and on the amount of electron transfer to the catalyst surface [25]. For the ACF/TiO₂ composites, removal of

MB molecules was possible by the following process. Because of the strong adsorption ability of ACF, MB molecules concentrated around ACF/TiO₂, increasing the

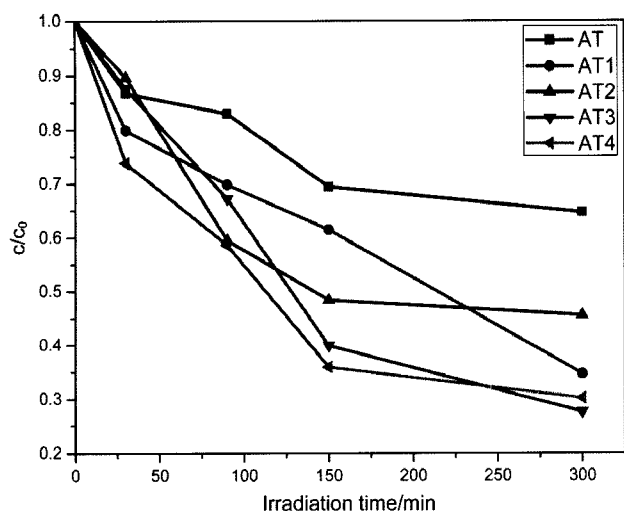


Fig. 5. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the ACF/TiO₂ composites prepared with TNB and various acids modified ACF; MB : 1.0×10^{-5} mol/l.

probability of localized free MB molecule diffusion and immigration to the surface of TiO₂ under the concentration gradient. Thus, the initial reaction rate for ACF/TiO₂ is faster than that for TiO₂ suspension. The molecular size of MB is $1.36 \times 0.47 \times 0.24$ nm [26], and it can access pores with diameters larger than 1.5 nm [27]. However, the pore diameter of ACF is less than 2 nm, and most pores of ACF have diameters around 0.63 nm [28]. So it is difficult for MB molecules to be adsorbed into micropores, and most of them were adsorbed on the edges of the micropores of ACF where they could easily migrate to the TiO₂ surface and be captured by photogenerated oxidizing species and degraded immediately, resulting in a decline of MB concentration in solution.

4. Conclusions

The ACF/TiO₂ composites were prepared from TNB and various acid modified ACF by a sol-gel method. From the SEM images, it is clear that the particles of TiO₂ aggregated into clusters were attached on the surface of ACF. From the XRD patterns, it concluded that the developed ACF/TiO₂ composites have a single and clear crystal structure, just is anatase, except sample AT2 which has a mixture structure of anatase and rutile. The EDX results show the developed ACF/TiO₂ composites have three kinds of main elements of C, O and Ti. Finally, the photocatalytic activity for ACF/TiO₂ composites was evaluated using the MB solution. The results shows that the photocatalytic activity of ACF/

TiO₂ composites (AT1~AT4) prepared with TNB and various acid modified ACF was much better than that of ACF/TiO₂ composite (AT) prepared with TNB and non-acid modified ACF, and the effects increased with order of sample AT3 > AT4 > AT1 > AT2.

References

- [1] V. Vamathevan, R. Amal, D. Beydoun and G. Low, "Photocatalytic oxidation of organics in water using pure and silver-modified titanium dioxide particles", *J. Photochem. Photobiol. A: Chem.* 148 (2002) 237.
- [2] P.J. Senogles, J.A. Scott, G. Shaw and H. Stratton, "Photocatalytic degradation of the cyanotoxin cylindrospermopsin, using titanium dioxide and UV irradiation", *Water Res.* 35 (2001) 1245.
- [3] J. Yu and X. Zhao, "Effect of surface treatment on the photocatalytic activity and hydrophilic property of the sol-gel derived TiO₂ thin films", *Mater. Res. Bull.* 36 (2001) 97.
- [4] C. Trapalis, A.D. Modestov and O. Lev, "Sol-gel processing of titanium-containing thin coatings", *J. Mater. Sci.* 28 (1993) 276.
- [5] J.M. Herrmann, J. Matos, J. Disdier, C. Guillard, J. Laine, S. Malato and J. Blanco, "Solar photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon in aqueous suspension", *Catal. Today* 54 (1999) 255.
- [6] J. Matos, J. Laine and J.M. Herrmann, "Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania", *J. Catal.* 200 (2001) 10.
- [7] T. Torimoto, S. Ito, S. Kuwabata and H. Yoneyama, "Effects of adsorbents used as supports for titanium dioxide loading on photocatalytic degradation of propylamide", *Environ. Sci. Technol.* 30 (1996) 1275.
- [8] T. Tsumura, N. Kojitani, H. Umemura, M. Toyoda and M. Inagaki, "Composites between photoactive anatase-type TiO₂ and adsorptive carbon", *Appl. Surf. Sci.* 196 (2002) 429.
- [9] P. Le Cloirec, C. Brasquet and E. Subrenat, "Adsorption onto fibrous activated carbon: applications to water treatment", *Energy Fuels* 11 (1997) 331.
- [10] Y. El-Sayed, T.J. Bandoz, H. Wullens and P. Lodewyckx, "Adsorption of ethylmethylamine vapor by activated carbon filters", *Ind. Eng. Chem. Res.* 45 (2006) 1441.
- [11] Y. El-Sayed and T.J. Bandoz, "Role of surface oxygen groups in incorporation of nitrogen to activated carbons via ethylmethylamine adsorption", *Langmuir* 21 (2005) 1282.
- [12] A. Turk, S. Mehlman and E. Levine, "Comparative odor control performance of activated carbon and permanganated alumina", *Atmos. Environ.* 7 (1973) 1139.
- [13] S.J. Park and S.Y. Jin, "Effect of ozone treatment on ammonia removal of activated carbons", *J. Colloid Interface Sci.* 286 (2005) 417.
- [14] M.L. Chen, J.S. Bae and W.C. Oh, "Photocatalytic

- effect for the pitch-coated TiO₂”, Analytical Science & Technology 19 (2006) 301.
- [15] M.L. Chen, J.S. Bae and W.C. Oh, “Characterization of AC/TiO₂ composite prepared with pitch binder and their photocatalytic activity”, Bull. Korean Chem. Soc. 27 (2006) 1423.
- [16] M.L. Chen, C.S. Lim and W.C. Oh, “Preparation with different mixing ratios of anatase to activated carbon and their photocatalytic performance”, J. Ceramic Processing Research 8 (2007) 119.
- [17] M.L. Chen, Y.S. Ko and W.C. Oh, “Carbon/TiO₂ prepared from anatase to pitch and their photocatalytic performance”, Carbon Science 8 (2007) 6.
- [18] M.L. Chen, C.S. Lim and W.C. Oh, “Photocatalytic effect for TiO₂/ACF composite electrochemically prepared with TNB electrolyte”, Carbon Letters 8 (2007) 177.
- [19] W.C. Oh and M.L. Chen, “Electro-chemical preparation of TiO₂/ACF composites with TNB electrolyte and their photocatalytic effect”, J. Ceramic Processing Research 9 (2008) 316.
- [20] M. Inagaki, Y. Hirose, T. Matsunage, T. Tsumura and M. Toyoda, “Carbon coating of anatase-type TiO₂ through their precipitation in PVA aqueous solution”, Carbon 41(2003) 2619.
- [21] M.L. Chen, J.S. Bae and W.C. Oh, “Photocatalytic effect for the carbon-coated TiO₂ prepared from different heat treatment temperature”, Analytical Science & Technology 19 (2006) 460.
- [22] M.L. Chen, J.S. Bae and W.C. Oh, “Preparation of carbon-coated TiO₂ at different heat treatment temperatures and their photoactivity”, Carbon Science 7 (2006) 259.
- [23] M.L. Chen and W.C. Oh, “Preparation AC/TiO₂ composites from activated carbon modified by HNO₃ and their photocatalytic activity”, Carbon Science 8 (2007) 108.
- [24] W.C. Oh and M.L. Chen, “Formation of TiO₂ composites on activated carbon modified by nitric acid and their photocatalytic activity”, J. Ceramic Processing Research 8 (2007) 316.
- [25] S. Fukahori, H. Ichiura, T. Kitaoka and H. Tanaka, “Photocatalytic decomposition of bisphenol A in water using composite-zeolite sheets prepared by a papermaking technique”, Environ. Sci. Technol. 37 (2003) 1048.
- [26] H. Tamai, T. Kakii, Y. Hirota, T. Kumamoto and H. Yasuda, “Synthesis of extremely large mesoporous activated carbon and its unique adsorption for giant molecules”, Chem. Mater. 8 (1996) 454.
- [27] J. Yamashita, T. Hirano and M. Shioya, “Development of mesopores during activation of poly(vinylidene fluoride)-based carbon”, Carbon 40 (2002) 1541.
- [28] R.S. Yuan, R.B. Guan, W.Z. Shen and J.T. Zheng, “Photocatalytic degradation of methylene blue by a combination of TiO₂ and activated carbon fibers”, J. Coll. Inter. Sci. 282 (2005) 87.