

Electro-chemical preparation of TiO₂/ACF composites with TNB electrolyte and their photocatalytic effect

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In this study, we have investigated a method for the electro-chemical preparation of TiO₂/ACF composites involving the electro-plating of Ti in titanium n-butoxide (TNB) electrolyte into an activated carbon fiber matrix. The surface textural properties showed that the BET surface area and the total pore volume decrease as the distribution of TiO₂ on the activated carbon fiber surfaces with electro-chemical operating time. The changes in XRD patterns showed typical anatase type on the TiO₂/ACF composite prepared with activated carbon fiber matrix by the electro-plating method in the TNB solution. In SEM micrographs, the titanium complex particles are uniformly distributed on and the around the fibers. And some large clusters were found when the electro-chemical operating time increases. The results of chemical elemental analysis for the TiO₂/ACF composites showed that most of the spectra for these samples gave stronger peaks for carbon and Ti metal than that of any other elements. From the results of thermal analysis, it could be considered that the amounts of the TiO₂ components in the composite increase with an increase of the electro-chemical operating time. Finally, the prominent photocatalytic activity of the TiO₂/ACF composites between c/c_0 and time could be attributed to both the effects of catalytic decomposition and adsorptivity between the supported TiO₂ and the porous fiber matrixes.

Key words: Activated carbon fiber, TNB, BET, XRD, SEM, EDX, TG, Photocatalytic activity.

Introduction

Environmental pollution by NO_x and SO_x in the atmosphere and various organic compounds in water has caused various serious problems for human health. The degradation of these pollutants using titanium-carbon system photocatalysts has been one of the most promising methods for the treatment of these problems [1,2]. These systematic photocatalysts have started to be utilized as ventilation filters, built into purification systems for air and water, and also as additive materials in paints and coatings, tiles, window glass, building blocks and textiles for tents and cloths [3-6]. For practical applications, the particles of the photocatalyst TiO₂, were either mounted on porous and non-porous materials, such as activated carbon, activated carbon fiber (ACF), zeolites and glasses or fixed on a substrate by dispersion with a binder. In the porous materials, the pollutant molecules could be adsorbed onto porous adsorbents. In the past few years, research to study the preparation of metal-carbon composites from aqueous solutions using carbon electrodes has been carried out [7-11]. The proposal was to capture any special ions and compounds onto the carbon electrodes by transport of the ions or interaction of dipole moments using the electrostatic force. The technique of electro-plating is

an added electrical driving force to the traditional adsorption. The use of a metal-ACF composite for an efficient separation of trace components from a liquid system is of highly homogeneous distribution of metal elements in an electro-catalytically designed device. The purpose of this study is to propose a preparation of a homogenous titanium treatment by an electro-chemical method to effectively prepare a TiO₂-carbon composite by heat treatments using highly porous carbon material homogenous distributed with metal and to develop a new method to regenerate TiO₂/ACF composites. The electrical driving force may play role in the sorption and deposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and prevent molecules from occupying the most energetically favorable positions on the carbon surface [9,10]. Because of the increase of polar surface functional groups on the carbon surfaces by an electro-chemical technique, the conversion of TNB to TiO₂ in pores or on surfaces in activated carbon fibers should be complicated.

In this study, we have focused on the characterization of the TiO₂/ACF composite obtained in the porous carbon increased polar surface by the electrical driving force. The conversion of TNB to TiO₂ during heat treatment will be important for the preparation of TiO₂/ACF composites. Moreover, the morphological studies of the converted TiO₂ should be strongly affected by the porous structure of the activated carbon fiber, if the TiO₂ on the fiber surface was properly formed in the restricted space in the activated carbon fiber. We have

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studied the chemical and morphological structure of TiO₂/ACF composites by means of BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, TG analysis and UV/VIS spectrophotometer.

Experimental

Materials

Self-made ACFs used as a raw material were prepared from commercial PAN fibers (T-300 Amoco, USA). The carbonized PAN fiber was heated first at 823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylindrical quartz glass tube at a temperature of 1073 K for 30 minutes. These activated carbon fibers were washed with deionized water and dried for 24 h at ambient temperature. 0.01 M dilute sulfuric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without damaging the ACF surfaces. The oxidation was carried out at the boiling temperature for 1 h. The oxidized ACFs were washed and dried at 323 K for 24 h. We used an electrolyte solution with pristine concentrations of 50 ml of titanium n-butoxide (TNB, C₁₆H₃₆O₄Ti, Acros Organics, USA) for the preparation of TiO₂/ACF composites.

Electro-chemical characteristics

The ACFs of test electrodes consisted of a size of 40 × 15 × 3 mm felt typed ACFs. The counter electrode of the same size was artificial graphite (TCK, Korea). A pristine concentration of 50 ml of titanium n-butoxide was used as an electrolyte. The conditions of the electro-chemical reaction for the measurements and the preparation of TiO₂/ACF composites was 0.5 mAcm⁻² at room temperature. The applied voltage was set to 4.5 V. Then, felt typed ACFs treated with TNB were heated at 973 K for 1 h. Before heat treatment, the solvent in the felts was vaporized at 343 K for 1 hour. The nomenclatures of prepared samples are listed in Table 1. The prepared samples were agitated as 80 mesh size for measurements. The preparation conditions and procedure of TiO₂/ACF composites are shown Fig.1.

Measurements

For the surface chemical parameter measurement, the BET specific surface areas were measured using a

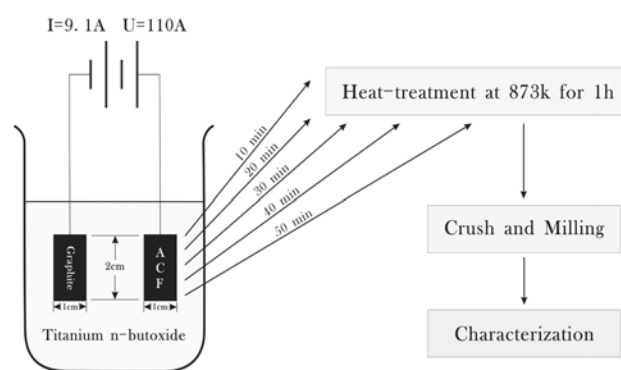


Fig. 1. Preparation conditions and procedure for TiO₂/ACF composites.

Quantachrome Autosorb Automated Gas System (Quantachrome Corporation, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JEOL, Japan) was used to observe the surface states and structures of TiO₂/ACF composites. For the elemental analysis in TiO₂/ACF composites, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimadzu XD-D1, Japan) with Cu K α radiation. As an analysis of photocatalytic activity, a UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of catalytic efficiency of TiO₂/ACF photocatalysts. Characterization of methylene blue (C₁₆H₁₈N₃S, MB) in water was determined by the following procedure. A TiO₂/ACF composite powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10^{-4} mol/l in a dark room at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance in the range of 550-750 nm wavelength of MB measured by a UV/VIS spectrophotometer.

Photocatalytic effect

In order to study the photocatalytic effect of the prepared samples, the decomposition reaction of MB in water was followed. Powdered samples of 0.05 g were dispersed by ultra sonicate for 3 minutes. For the UV irradiation a UV lamp (20 W, 365 nm) was used at a distance of 100 mm from the solution in a dark box. By sampling 3ml of solution after removal of dispersed powders through centrifuging, 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.

Table 1. Nomenclatures of TiO₂/ACF Composites Prepared with Different Electro-chemical Operation Time to Activated Carbon Fiber

Preparation method		Electrochemical Operation Time (minute)	Nomenclatures
Carbon matrix	Electrolyte		
Activated Carbon Fiber	Titanium n-butoxide (TNB, 99.9%)	10	AFT1
		20	AFT2
		30	AFT3
		40	AFT4
		50	AFT5

Results and discussion

The BET analysis result measured by a nitrogen adsorption method revealed that the porous catalyst had a surface of 969~1175 m²/g, which is 7~9 times higher than commercial TiO₂ power (132 m²/g). The large surface areas of the photocatalyst provided more space for the adsorption of molecules, enriching them on the fiber surfaces. Therefore, the MB degradation rate on the TiO₂/ACF catalyst surface will be raised on adsorption equilibrium. The textural properties of pristine materials and TiO₂/ACF composites prepared with different electro-chemical operation times to activated carbon fiber are shown Table 2. It can be seen that both the BET surface area and the total pore volume decrease as the distribution of TiO₂ on the activated carbon fiber surfaces with increasing electro-chemical operation time. According to former studies [8-10], the BET surface area is considerably decreased due to the blocking of the pores by surface complexes introduced by the electro-chemical treatment. Almost all surface textural parameters for the composites are considerably decreased compared to that of the pristine activated carbon fiber. This can be attributed to the blocking of micropores with the formation of titanium complexes by surface modification on the fibers with the electro-chemical operation. It is expected that the formation of titanium complexes with an increase of the surface charges can be blocked to pores on the fiber surfaces, but the porosity of ACF is reproduced by the heat treatment. The pore volume of micropores decreases with increasing operation time, which is a result of chemical and physical changes of the external surfaces in the TiO₂/ACF composites.

The XRD analysis results for the catalyst samples are shown in Fig. 2. The structure for the TiO₂/ACF composites shows a typical anatase type. After the heat treatment at 973 K for 1 h, the main crystalline phase is not transformed to the rutile structure. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are diffractions from the (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the prepared TiO₂ existed in the anatase crystal phase. XRD patterns of all composites did not give any diffraction peaks cor-

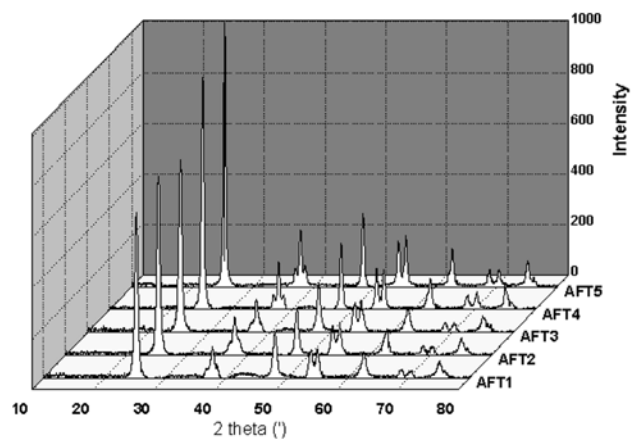


Fig. 2. XRD patterns of the TiO₂/ACF composites prepared with different electro-chemical operating times to activated carbon fiber.

ponding to other inorganic phases. Anatase is a metastable polymorphic form of titania at all temperatures and transforms to rutile upon heating [12]. The XRD patterns of TiO₂/ACF composites showed narrow diffraction peaks reflecting that, during burn-off of the carbon phase of ACF, the TiO₂ particles were formed on the fiber surfaces.

Fig. 3 shows the SEM surface morphology of the TiO₂/ACF composites. It shows that layer of nano-size TiO₂ balls uniformly coated the surface of ACF, which was beneficial for the photocatalytic reaction because the photocatalytic reaction is carried out on the external surfaces of the TiO₂/ACF composites catalysts by existing reactants using UV light and the nano-size structured catalyst could provide a more effective surface for MB adsorption and UV light absorption. It was observed that titanium complexes covered the fiber surfaces. The titanium complex particles regularly distributed on and the around the activated carbon fiber surfaces. And some large clusters were found when the time of the electro-plating operation was increased. It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. The titanium complexes particles on the fiber surfaces became pronounced and the size of the particles became large with an increase of the

Table 2. Textural Properties of Pristine Materials and TiO₂/ACF Composites Prepared with Different Electro-chemical Operation Times to Activated Carbon Fiber

Sample	Parameter		
	S _{BET} (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
As-received TiO ₂	132	-	-
As-received ACF	1735	0.2374	5.83
AFT1	1175	0.1382	5.24
AFT2	1067	0.1315	5.03
AFT3	992	0.1236	4.73
AFT4	980	0.1156	4.73
AFT5	969	0.1132	4.72

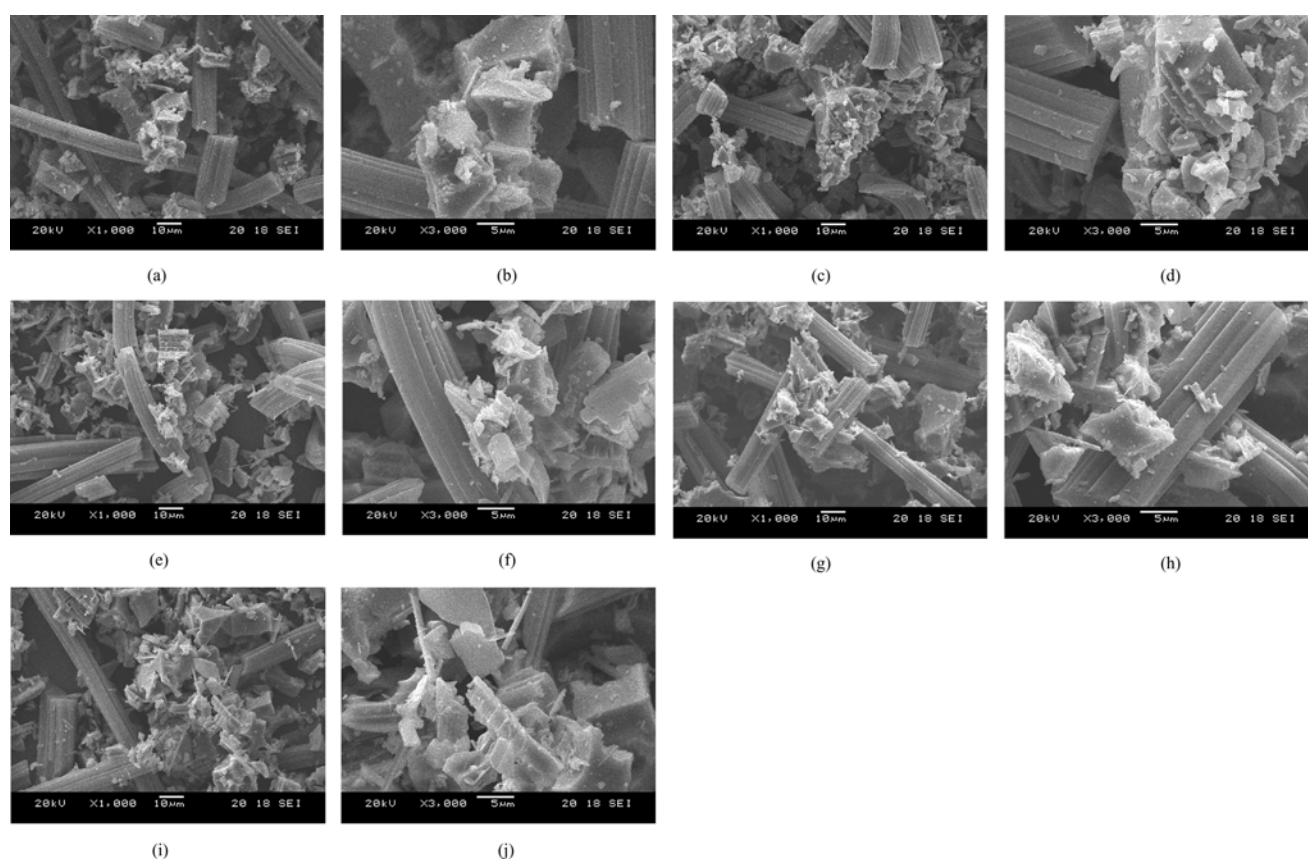


Fig. 3. SEM micrographs of the TiO₂/ACF composites electrochemically prepared from TNB; (a) AFT1 (overall), (b) AFT1 (close-up), (c) AFT2 (overall), (d) AFT2 (close-up), (e) AFT3 (overall), (f) AFT3 (close-up), (g) AFT4 (overall), (h) AFT4 (close-up), (i) AFT5 (overall), (j) AFT5 (close-up).

operation time. Accordingly, a high photocatalytic yield was expected for a homogenous TiO₂ particle distribution. Therefore, the higher photocatalytic activity of the TiO₂/ACF composite prepared might be attributed to chemical degradation by the homogenous distribution of titanium complexes including titanium dioxide and physical adsorption by the activated carbon fiber.

For the elemental composition analysis of the TiO₂/ACF composites as a function of the electrochemical operating time, these catalysts were analyzed by EDX. Fig. 4 shows the results of elemental analysis by EDX spectra of TiO₂/ACF composites. These spectra show the presence of peaks from the C, O, P and Ti elements. It was observed that for most of these spectra from these samples stronger peaks from carbon and Ti metal are seen than for any other elements. The results of

elemental composition analysis of the TiO₂/ACF composite series are listed in Table 3. From the table, it is shown that carbon and Ti are present as major elements in the TiO₂/ACF composite series. And, it was observed that the contents of each sample show an increase in O and Ti elements with a decrease in C element by an increase of the electro-chemical operating time. It was noted that a decrease of the C content with an increase of the Ti content is observed for the overall TiO₂/ACF composite series.

Fig. 5 shows TG curves of the TiO₂/ACT composites prepared with different electrochemical operating times to activated carbon fiber. It was observed that major differences were found between temperature and the gravimetric decrease scale. The beginning of a decrease in weight at around 450°C is due to oxidation of the

Table 3. Elemental Composition Analysis of TiO₂/ACF Composites Prepared with Different Electro-chemical Operation Times to Activated Carbon Fiber

Sample	Elements (wt%)			
	C	Ti	O	P
AFT1	65.5	18.9	15.4	0.22
AFT2	50.5	23.2	17.1	0.29
AFT3	56.9	24.3	28.4	0.36
AFT4	42.1	30.1	27.6	0.19
AFT5	45.6	32.7	21.5	0.23

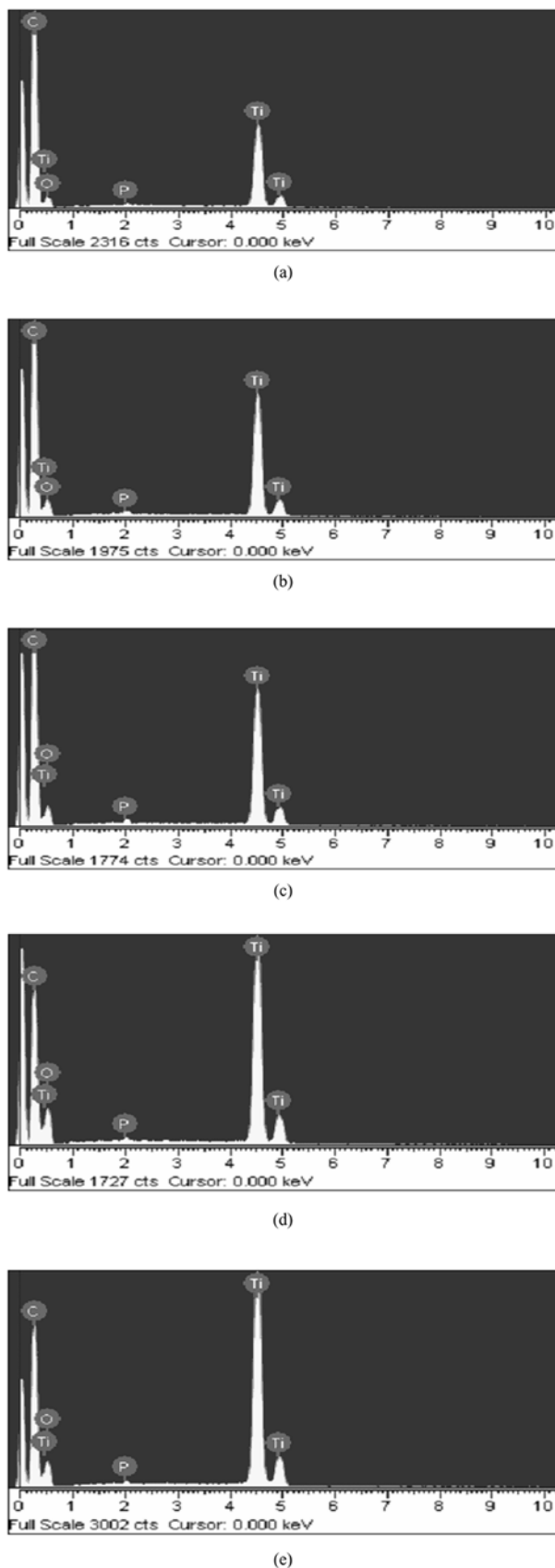


Fig. 4. EDX elemental microanalysis of the TiO_2/ACF composites prepared with different electro-chemical operating times to activated carbon fiber; (a) AFT1, (b) AFT2, (c) AFT3, (d) AFT4 and (e) AFT5.

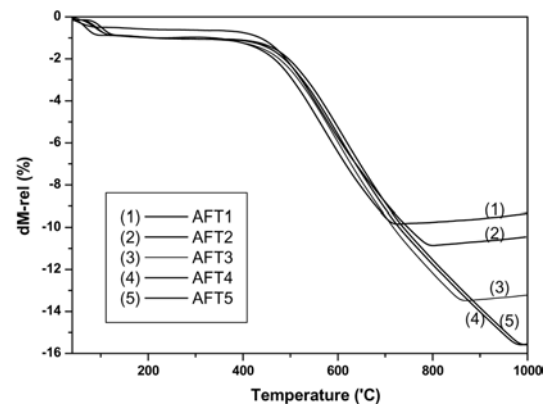


Fig. 5. TG curves of the TiO_2/ACT composites prepared with different electro-chemical operating times to activated carbon fiber.

carbon component in the TiO_2/ACT composites. Since TiO_2 components in the TiO_2/ACT composite are thermally more stable than carbon components, the thermal diagrams show a second horizontal region above 700°C . From these results, it could be suggested that the amounts of the TiO_2 component in AFT4 and AFT5 are much more than that in AFT1, AFT2 and AFT3. It was thus shown that the amounts of Ti component in the composite increase with an increase in the electrochemical operating time.

The UV/VIS absorbance spectra of MB concentration at 1.0×10^{-4} mol/l against the TiO_2/ACF composite series prepared by different electro-chemical operating times in the TNB electrolyte are shown in Fig. 6. In Fig. 6, the color variation of the MB solution in the dark box, which is due to adsorption of MB into the sample particles, is shown on the samples with different electro-chemical operating times. The absorbance values decreased with an increase in UV irradiation time. It is shown that the absorbance of AFT4 and AFT5 is lower than that of AFT1, AFT2 and AFT3. However, all the samples showed marked and fast adsorption of MB. The effect of the high crystallinity of anatase phase on photocatalytic degradation of MB has been shown [13]. Potential transformation of the structural phase to rutile was shown to reduce the photocatalytic activity of carbon/ TiO_2 catalysis [14]. These results indicate that photocatalytic degradation of MB certainly occurs on TiO_2 particles, even on these electro-plated on to the carbon matrix, and that MB adsorption and degradation were performed on TiO_2/ACF particles. Fig. 7 shows changes in relative concentration (c/c_0) of MB under UV light irradiation in the solution. MB removal with TiO_2/ACF composite photocatalysts is carried out to observe the UV photolysis effect for the MB solution. From the result between c/c_0 and time, it was observed that the removal efficiency of MB for the composites is ever better than that of pristine TiO_2 . For all samples, a decaying speed of relative concentration is rather slow in the beginning, probably because the degradation of adsorbed MB is the main photocatalytic reaction. The

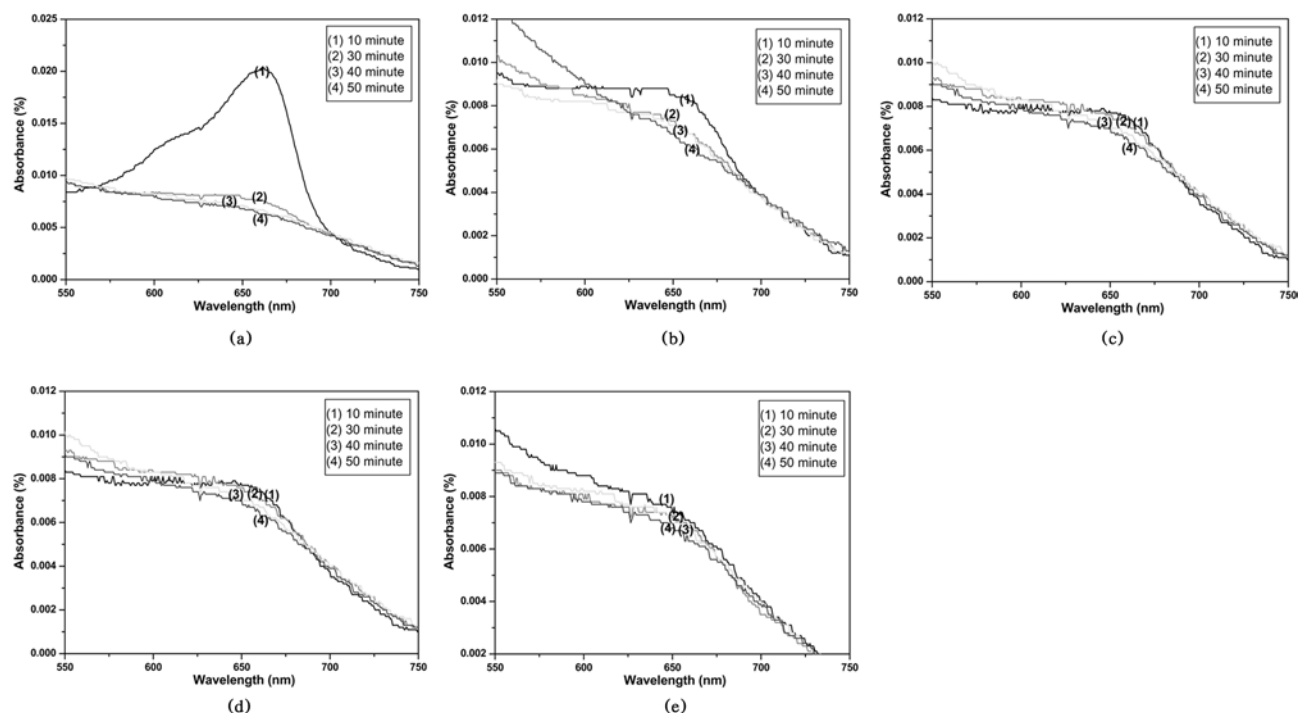


Fig. 6. UV/VIS spectra of MB concentration against the TiO₂/ACF composites prepared with different electro-chemical operating times to activated carbon fiber; (a) AFT1, (b) AFT2, (c) AFT3, (d) AFT4 and (e) AFT5.

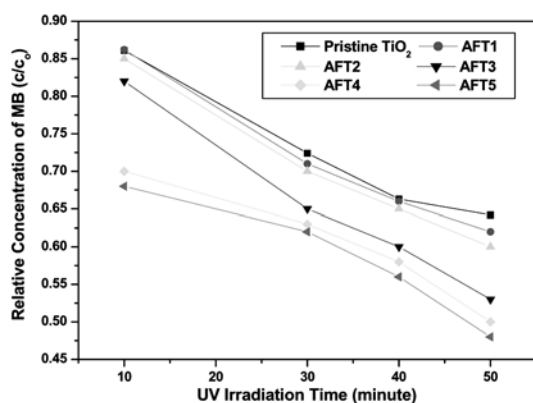


Fig. 7. Dependence of relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation for the TiO₂/ACF composites prepared with different electro-chemical operating times to activated carbon fiber.

results for relative concentration (c/c_0) reveal that the adsorbed MB is reasonably supposed to be decomposed before the MB in the solution. In Fig. 7, the changes in c/c_0 of MB in the solution with time of UV irradiation are shown for the TiO₂/ACF composites by different electro-chemical operating times in the TNB electrolyte. The relationship observed is approximately linear as reported on similar TiO₂/carbon composites samples. A combination effect has been described [15] the enhanced adsorption of the pollutants on porous carbon followed by a transfer through an interphase to titania. In our case, the prominent photocatalytic activity of the TiO₂/ACF composites could result from the

homogeneous distribution of titania complexes on the external surface during the electro-chemical process and excellent adsorptivity of activated carbon fiber by the large surface area. The formation of a surface charge of activated carbon fiber during the electro-chemical process occurs due to the acid-base character by the surface active sites transformation of the oxides. The acidic and basic active sites on the carbon surfaces can be determined by means of indirect determination, such as measurements of the catalytic activity for the degradation of MB. In this study for the removal results of MB in the solution measured periodically over 50 minutes, the increase of electro-chemical operating time results in a significant degradation effect with a remarkable decrease of c/c_0 of MB. From the results obtained with TiO₂/ACF composites prepared by an electrochemical method, the slope relationship between c/c_0 of MB and UV irradiation time were observed at ca. 1.0×10^{-4} mol/l of MB concentration. Based on these relationships, we therefore can conclude that the degree of removal of pollutants in the solution should be attributed to both the effects of photo-degradation and adsorptivity between the supported TiO₂ and the activated carbon fibers.

Conclusions

In this study, we have prepared TiO₂/ACF composite catalysts through an electro-plating method in the TNB electrolyte. The prepared composite materials were characterized by surface properties, structural crystallinity between activated carbon fiber and TiO₂, elemental

identification, thermal stability and photocatalytic activity. The conversion of Ti on the carbon surface formed by the electro-plating method to TiO_2 during heat treatment must be important for the preparation of TiO_2/ACF composites. According to the surface textural properties, both the BET surface area and the total pore volume decreases as the distribution of TiO_2 on the activated carbon fiber surfaces with the electro-chemical operating time. The XRD patterns were shown as typical anatase type on TiO_2/ACF composite prepared with an activated carbon fiber matrix by the electro-plating method in the TNB electrolyte. From the SEM results, the titanium complex particles are uniformly distributed on and around the fiber. And some large clusters were found when the electro-chemical operating time increases. The EDX results of TiO_2/ACF composites showed that most of the spectra from these samples stronger peaks in carbon and Ti metal are present than that of any other elements. From the TG results, it could be considered that the amounts of the TiO_2 components in AFT4 and AFT5 are much more than that in the AFT1, AFT2 and AFT3 with an increase in the electro-chemical operating time. Finally, the prominent photocatalytic activity of the TiO_2/ACF composites between c/c_0 and time could be attributed to both the effects of photo-degradation and adsorptivity between the supported TiO_2 and the activated carbon fibers.

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