

Photocatalytic Effect for TiO₂/ACF Composite Electrochemically Prepared with TNB Electrolyte

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Abstract

TiO₂/ACF composites were prepared by the electrochemical method with Titanium (IV) *n*-butoxide (TNB) electrolyte under different electrochemical operation time. The BET surface area for TiO₂/ACF composites decrease with the increase of electrochemical operation time. There is a single crystal structure which is anatase in all of the samples from the data of XRD. The SEM micrphotographs of TiO₂/ACF composites show that the TiO₂ particles were well mixed with the ACF. There are O and P with strong C and Ti peaks in all samples from EDX results, and it also shows that a decrease of the C content with a increasing of Ti content with increasing of the electrochemical operation time in the over all composites. DSC cures show that the exothermic peak of all composites at 560°C represents the transformation heat of amorphous parts to anatase phase and the discontinuous grain growth of the transformed anatase particles. Finally, the excellent photoactivity of TiO₂/ACF composites (especially, ACFT10) could be attributed that the decrease of concentration of MB can be concluded to be much faster for the adsorption by ACF than for photocatalytic decomposition by TiO₂.

Keywords : Titanium (IV) *n*-butoxide (TNB), Activated carbon fiber, BET, XRD, SEM, EDX, DSC, photoactivity

1. Introduction

Activated carbon fiber (ACF) is a fibrous adsorbent which has been recently developed by an adequate carbonization and activation of fibrous precursors. ACF has an excellent adsorption capacity and show very fast adsorption/desorption rates comparison with conventional activated powder or activated granular carbons. Furthermore, ACF could be used in the form of cloth, felt, mat, and so on for adsorption and filtration, even though the physical properties of fiber were inferior to those of precursor fibers.

Activated carbon fibers as an adsorbent are a comparatively modern form of porous carbon material with a number of significant advantages over the more traditional powder or granular forms. These include a developed surface area, microporosity, thermal stability, high adsorption capacity as well as very high rates of adsorption from the gas and liquid phase. The micropore size is in general uniform and can often be controlled by adjusting the conditions of preparation of the fibers or by post-preparation modification like metal treatment. For ACF, the characteristics of their inner and outer surfaces play also a signification role in their primary application. Considerable effect has been devoted to characterize, and to comprehend the chemical properties of carbon surfaces, as well as their microstructure [1, 2]. It is well known that activated carbon and cokes have been recognized as excellent adsorbents for SO₂ and catalysts for reduction of

NO_x with NH₃ [3]. However, Mochida [4] reported pitch based activated carbon fibers had high activity for the conversion of NO to NO₂ at room temperature, and have better pore structures than activated carbon for adsorption and desorption. Mochida et al. showed that PAN-ACFs have high activity for the NO reduction in the temperature range between 150°C and 350°C [4] and NO oxidation at room temperature [5]. Kim and Hong have reported PAN-ACFs activated with KOH showed high efficiency for SO_x removal [6].

Titanium dioxide has also been extensively studied as a promising material for environment protection for the past few decades. Especially, anatase-type TiO₂ has attracted great attention because of its excellent photocatalytic activity [7, 8]. Numerous studies have shown their unique performance in photodegradation of toxic components in wastewater, such as phenols, herbicides, pesticides, dyes and surfactants, etc [9, 10]. According to our former studies [11-14], carbon-TiO₂ composites had a high surface area, porous texture distribution and showed an excellent photoactivity.

In the present work, we have prepared TiO₂/ACF composites though the electrochemically method with TNB electrolyte and ACF electrode. TNB rather than the commonly employed TiO₂ powder was chosen as the precursor to increase the mixing rate of TiO₂ and activated carbon fiber. The developed composites were characterized by N₂ adsorption, X-ray diffraction (XRD), scanning electron microscope

(SEM), energy dispersive X-ray (EDX), and thermogravimetry analysis (DSC). The catalytic efficiency of the developed composites was evaluated by the photodegradation of an azo compound, methylene blue (MB, $C_{16}H_{18}N_3S \cdot Cl \cdot 3H_2O$).

2. Experimental

2.1. Materials

TNB (Titanium (IV) n-butoxide, 99.9%) was purchased from Acros organics Co., Ltd, USA. ACF was purchased from EAST ASIS Carbon Fibers Co., Ltd, AnShan, China. Table 1 shows the properties of ACF. The MB was used as analytical grade which was purchased from Dukan Pure Chemical Co., Ltd. It was selected because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines. For the comparative experimental, the TiO_2 photocatalysts was commercially available (Duk-San Pure Chemical Co., Korea), which was composed of a single phase of anatase with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm .

2.2. Samples preparation

In this experiment, TNB was used as electrolyte. ACF was used as electrode, which was connected with sources of electricity. The counter electrode of same size was artificial graphite (TCK, Korea). After two electrodes were complete-

ly put into TNB, electricity was run between the two electrodes in the solution. The ACFs of test electrodes was consist of the size of $40 \times 15 \times 3$ mm felt typed ACFs. The pristine concentrations of 50 mL of TNB were used as an electrolyte. The condition of electro-chemical reaction for the measurements and the preparation of TiO_2/ACF composites was 0.5 mAcm^{-2} at room temperature. The applied voltage was set to 4.5 V. The ACF was exchanged by 10 min, 20 min, 30 min, 40 min and 50 min. The electrochemical reaction mechanism was explained to earlier study [15]. These samples prepared from electrochemical operation were heat treated at 873 K for 1 h and then crushed at auto miller. The preparation conditions and the sample code used in the present paper are listed in Table 2.

2.3. Characterization

Nitrogen isotherms were measured using an ASAP 2010 (Micrometrics) at 77 K. Before the experiment the samples were heated at 473 K and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa to a constant pressure. XRD was used for crystal phase identification and estimation of the anatase-to-rutile ratio [16]. XRD patterns were obtained at room temperature with a diffractometer Shimata XD-D1 (Japan) using $CuK\alpha$ radiation. SEM was used to observe the surface state and pore structure of the TiO_2/ACF composites were carried out using a JSM-5200 JOEL electron microscope (Japan). EDX was used to measure the elemental analysis of the TiO_2/ACF composites. DSC were carried out in a Schimahzu thermoanalyzer TG-50 under dry nitrogen, using platinum crucibles and a constant heating rate $10^\circ C/min$ up to $1000^\circ C$, Fine alumina powder was used as a reference substance. UV-VIS spectra for the MB solution obtained from degradation by TiO_2/ACF composites dispersion under UV ray irradiation were recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.4. Photocatalytic Decompositions

The photocatalytic decomposition was tested by TiO_2/ACF composites powder and an aqueous solution of MB in a 100-mL glass container and then irradiating the system with 20W UV light at 365 nm, which was used at the distance of 100 mm from the solution in darkness box. The same amount of TiO_2/ACF composites (0.05 g) was suspended in 75 mL of 5.0×10^{-5} mol/L MB solution. The photocatalytic activities of the TiO_2/ACF composites were investigated using the photodegradation rate of MB, which was measured for 10 min, 30 min, 40 min, and 50 min. The blue color of the solution faded gradually with time duo to the adsorption and decomposition of MB. And 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.

Table 1. The properties of ACF

Physical properties	Units
Density	1.53~1.75 g/mL
Electrical Resistivity	$5.2 \times 10^{-3} \sim 6.8 \times 10^{-3} \Omega \cdot cm$
Diameter	12~15 μ
Tensile Strength	$4 \sim 6 \times 10^8$ Pa
Tensile Modulus	$3 \times 10^{10} \sim 4 \times 10^{10}$ Pa
Elemental carbon	≥ 95 wt%

Table 2. Nomenclatures of TiO_2/ACF Composites Prepared with Different Electrochemical Operation Time to Activated Carbon Fiber

Carbon matrix	Preparation method		Nomenclatures
	Electrolyte	Electrochemical Operation Time	
Activated Carbon Fiber	Titanium n-butoxide (TNB, 99.9%)	10 min	ACFT10
		20 min	ACFT20
		30 min	ACFT30
		40 min	ACFT40
		50 min	ACFT50

Table 3. Textural Properties of Pristine Materials and TiO₂/ACF Composites Prepared with Different Electrochemical Operation Time 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 AC	1842	0.2401	6.22
ACFT10	1268	0.1452	5.36
ACFT20	1132	0.1225	5.12
ACFT30	1025	0.1232	4.81
ACFT40	989	0.1189	4.88
ACFT50	978	0.1128	4.79

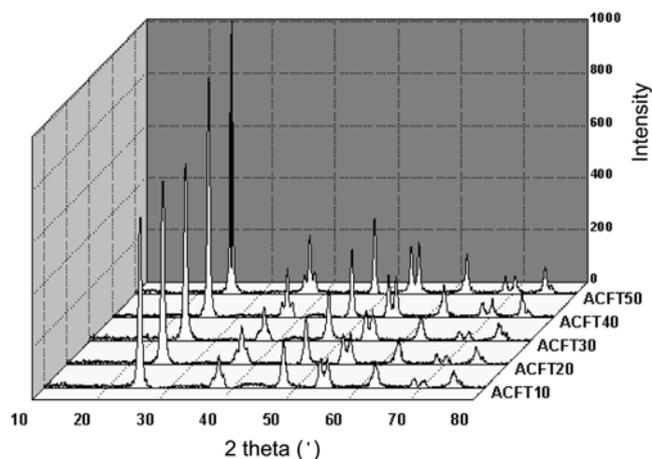
3. Results and Discussion

3.1. Structure and morphology of TiO₂/ACF composites

The values of BET surface area of TiO₂/ACF composites are shown in Table 3. As the results of Table 3, it demonstrates that there markedly decrease in the BET surface area of the TiO₂/ACF composites with the increase of the electrochemical operation time. However, almost all surface textural parameters for the composites are a considerably more decrease than that of pristine ACF. This can be attributed to the blocking of micropores by the formation of TiO₂ on the ACF surface with HTT. It is expected that the invaded Ti element can be blocked to pore in ACF. It is also noteworthy that decreases of surface parameters among the composites are related to removal efficiency of MB by adsorptivity.

According to the former study [11, 17], it is well known that the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature. Fig. 1 depicts XRD patterns of TiO₂/ACF composites prepared with different electrochemical operation time to activated carbon fiber heat-treated at 873 K for 1 h. 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 TiO₂/ACF 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 concluded that the developed TiO₂/ACF composites have a single and clear crystal structure, just is anatase.

The SEM microphotographs of TiO₂/ACF composites prepared with different electrochemical operation time are shown in Fig. 2. It was observed that TiO₂ particles were penetrated into the ACF. Contrast with the former studies [11-14], it was considered that TiO₂/ACF composites could have much more activity because the TiO₂ particles were mixed well with the ACF. So the TiO₂/ACF composites

**Fig. 1.** XRD patterns of TiO₂/ACF composites prepared with different electrochemical operation time to activated carbon fiber heat-treated at 873 K for 1 h.

would show an excellent photocatalytic activity. From the results of Fig. 2, it was also seen that the amount of the TiO₂ particles was increased with increasing of the electrochemical operation time (ascertained with EDX microanalysis).

Fig. 3 shows the EDX spectra of TiO₂/ACF composites prepared with different electrochemical operation time. These spectra show the presence of O and P with strong C and Ti peaks. The results of EDX elemental microanalysis of TiO₂/ACF composites are listed in Table 4. All of the composites are richer in carbon and Ti metal than any other elements. It should be note that a decrease of the C contents and the increase of Ti contents with the increase of the electrochemical operation time are observed for the over all composites.

The DSC cures obtained under a N₂ flow for the TiO₂/ACF composites prepared with different electrochemical operation time and the results are shown in Fig. 4. All the TG cures exhibit similar characteristics in the temperature 120-1000°C except ACFT50. The exothermic peak of all composites at 560°C represents the transformation heat of amorphous parts to anatase phase and the discontinuous grain growth of the transformed anatase particles.

3.2. Photocatalytic activity

The UV/VIS spectra of MB concentration of 5×10⁻⁵ mol/L against the TiO₂/ACF composites prepared with different electrochemical operation time under various time conditions are shown in Fig. 5. As can be seen from the spectra, the absorbance maxima of the all composites slowly decrease with the increase of UV irradiation time because of the adsorption and photoactivity of structural transformation of the sample particles into MB. According to the former studies [11-14], it implies that the transparent of the MB concentration highly increase by photocatalytic effect of

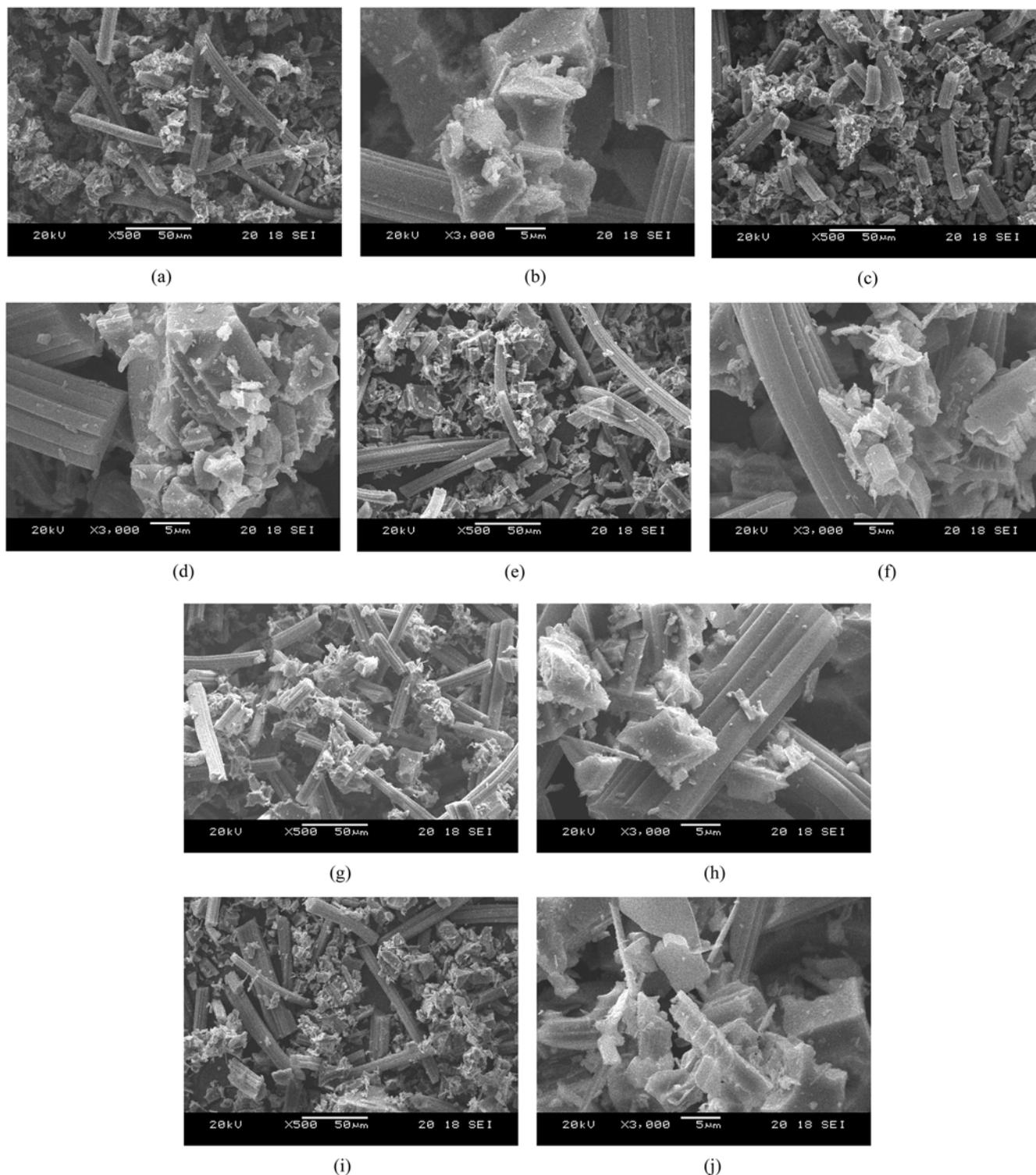
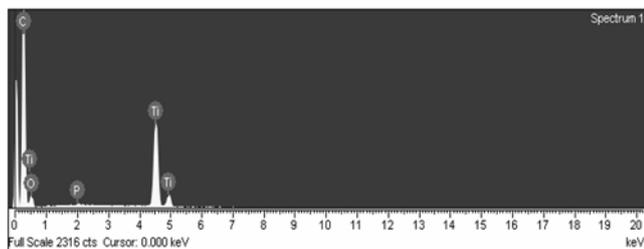


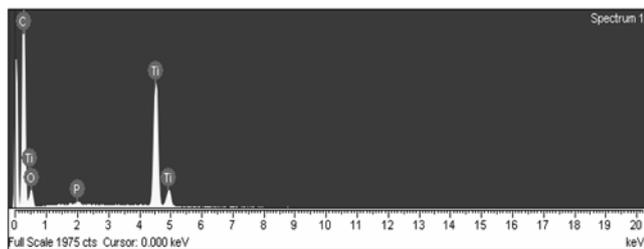
Fig. 2. SEM micrographs of the TiO_2/ACF composites electrochemically prepared from TNB; (a) ACFT10 ($\times 500$), (b) ACFT10 ($\times 3000$), (c) ACFT20 ($\times 500$), (d) ACFT20 ($\times 3000$), (e) ACFT30 ($\times 500$), (f) ACFT30 ($\times 3000$), (g) ACFT40 ($\times 500$), (h) ACFT40 ($\times 3000$), (i) ACFT50 ($\times 500$), (j) ACFT50 ($\times 3000$).

TiO_2/ACF composites. It can be also considered that two types of degradation of MB were adsorption of ACF and

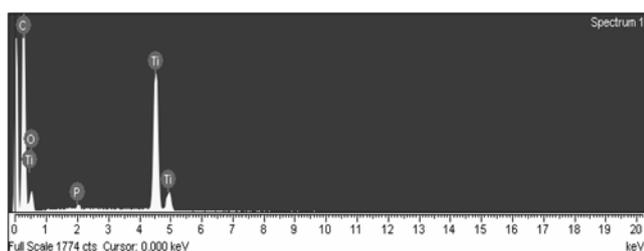
photocatalytic performance of TiO_2 . If this concentration is degraded by TiO_2/ACF composite, the concentration is very



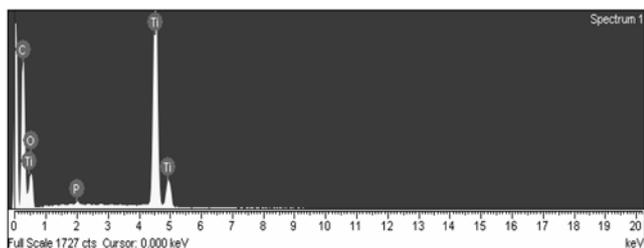
(a)



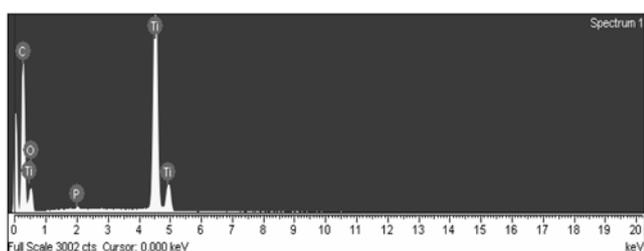
(b)



(c)



(d)



(e)

Fig. 3. EDX elemental microanalysis of the TiO₂/ACF composites prepared with different electrochemical operation time to activated carbon fiber; (a) ACFT10, (b) ACFT20, (c) ACFT30, (d) ACFT40 and (e) ACFT50.

Table 4. EDX Elemental Microanalysis of TiO₂/ACF Composites Prepared with Different Electrochemical Operation Time to Activated Carbon Fiber

Sample	Elements			
	C	O	Ti	P
ACFT10	65.5	15.4	18.9	0.22
ACFT20	50.5	17.1	23.2	0.29
ACFT30	56.9	28.4	24.3	0.36
ACFT40	42.1	27.6	30.1	0.19
ACFT50	45.6	21.5	32.7	0.23

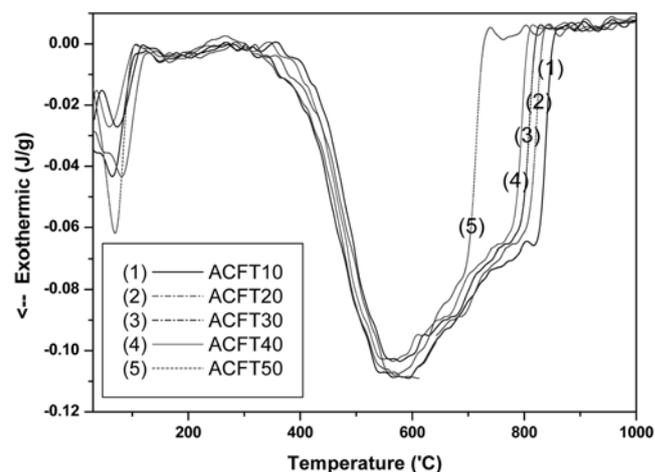


Fig. 4. DSC curves of the TiO₂/ACT composites prepared with different electrochemical operation time to activated carbon fiber.

low. Generally, the wavelength maxima are 660 nm for the visible active region. But, if the concentration degraded by photocatalysis is very low, the maxima can not be found out the solution from Beer-Lambert law. Fig. 6 shows the changes in relative concentration (c/c_0) of the pristine TiO₂ and the TiO₂/ACF composites prepared with different electrochemical operation time in MB concentration of 5×10^{-5} mol/L under UV irradiation in the aqueous solution. From the present results in Fig. 6, it can be seen that the relationship was shown approximately linearity. Because the present the TiO₂/ACF composites had an adsorptivity, as above mentioned, it is considered that decrease of MB concentration in the aqueous solution can be occurred in two physical phenomena such as adsorption by ACF and photocatalytic decomposition by TiO₂. As the result of EDX, the ACFT10 has the most content of carbon and ACFT50 has the most content of Ti. However, the photoactivity of ACFT10 was much better than that of ACFT50, which was also better than that of other samples. So it indicates that the decrease of MB can be concluded to be much faster for the adsorption by ACF than for photocatalytic decomposition by TiO₂.

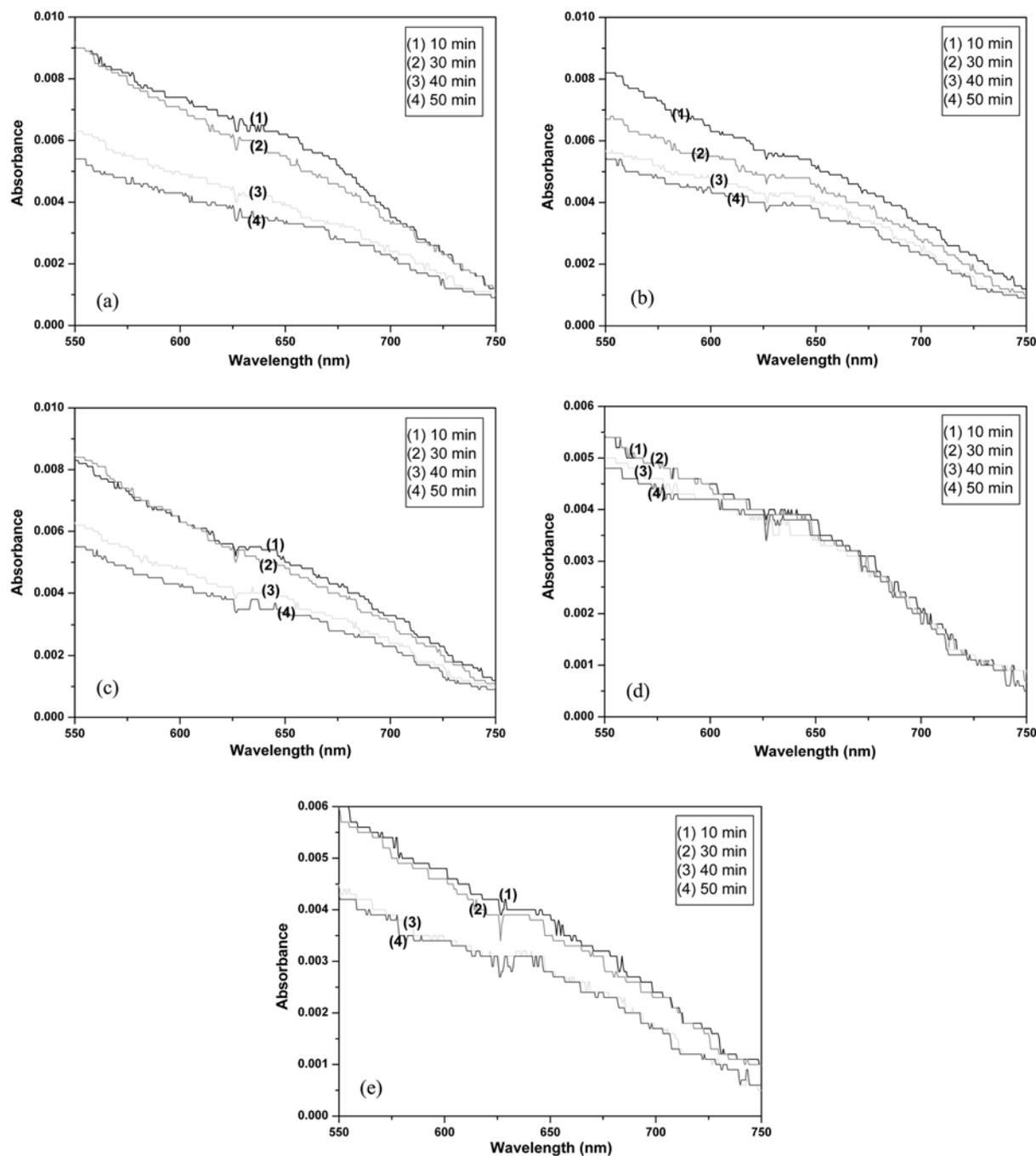


Fig. 5. UV-VIS diffuse reflectance spectra of TiO₂/ACF composites prepared with different electrochemical operation time to activated carbon fiber on methylene blue (MB) solution concentration of 5.0×10^{-5} mol/L; (a) ACFT10, (b) ACTF20, (c) ACFT30, (d) ACFT40, (e) ACFT50.

4. Conclusions

In this study, the properties of TiO₂/ACF composites are investigated through the preparation from the different electrochemical operation time to ACF with TNB electrolyte. The BET surface area for TiO₂/ACF composites is decrease with

increasing of electrochemical operation time. There is a single crystal structure which is anatase in all of the samples from the data of XRD. The SEM micropictures of TiO₂/ACF composites show the TiO₂ particles were mixed well with the ACF. There are O and P with strong C and Ti peaks in all samples from EDX results, and it also shows that a

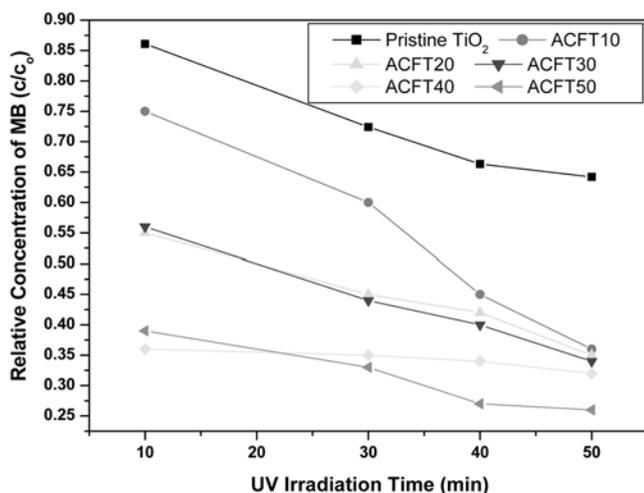


Fig. 6. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the TiO₂/ACF composites prepared with different electrochemical operation time to activated carbon fiber; the concentration of MB: 5.0×10^{-5} mol/L.

decrease of the C content with a increasing of Ti content with increasing of the electrochemical operation time in the over all composites. DSC cures show that the exothermic peak of all composites at 560 represents the transformation heat of amorphous parts to anatase phase and the discontinuous grain growth of the transformed anatase particles. Finally, the excellent photoactivity of TiO₂/ACF composites (especially, ACFT10) could be attributed that the decrease of MB can be concluded to be much faster for the adsorption by ACF than for photocatalytic decomposition by TiO₂.

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