

Fabrication of Zn-treated ACF/TiO₂ Composites and Their Photocatalytic Activity for Degradation of Methylene Blue

Yu-Gyoung Go, Feng-Jun Zhang*, Ming-Liang Chen and Won-Chun Oh[†]

Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam 356-706, Korea

*Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture,
Anhui Hefei 230022 P. R. China

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Abstract In this paper, non-treated ACF (Activated Carbon Fiber) /TiO₂ and Zn-treated ACF/TiO₂ were prepared. The prepared composites were characterized in terms of their structural crystallinity, elemental identification and photocatalytic activity. XRD patterns of the composites showed that the non-treated ACF/TiO₂ composite contained only typical single and clear anatase forms while the Zn-treated ACF/TiO₂ contained a mixed anatase and rutile phase with a unique ZnO peak. SEM results show that the titanium complex particles are uniformly distributed on and around the fiber and that the titanium complex particles are more regularly distributed on and around the ACF surfaces upon an increase of the ZnCl₂ concentration. These EDX spectra show the presence of peaks from the C, O and Ti elements. Moreover, peaks of the Zn element were observed in the Zn-treated ACF/TiO₂ composites. The prominent photocatalytic activity of the Zn-treated ACF/TiO₂ can be attributed to the three different effects of photo-degradation: doping, absorptivity by an electron transfer, and adsorptivity of porous ACFs between the Zn-TiO₂ and Zn-ACF.

Key words TiO₂, ZnO, ACF, photocatalytic, methylene blue.

1. Introduction

Heterogeneous photocatalysis is a very promising destructive technique to complete mineralization of dye as it has already been applied with success on the degradation of different categories of organic compounds combining the low cost, the mild conditions and the possibility of using sunlight as the source of irradiation.¹⁾ TiO₂ have been proved to be an important photocatalyst for degradation of environmental contaminants.^{2,3)} However, in field applications, there are at least two obvious problems arising from using TiO₂ as a photocatalyst. Lower photonic efficiency and usually be induced only by ultraviolet light limit the application of TiO₂. In order to solve these problems, there are two ways at present. One way to improve the photocatalytic activity of TiO₂ particles is the manipulation of shape, size and surface properties of TiO₂ particles.⁴⁾ Another way to enhance the photocatalytic activity is the coating and doping of other materials, including metal ions and semiconductors, onto the surface of TiO₂ nanoparticles.⁵⁻⁷⁾

ZnO has been also conceived as a significant candidate that was reportedly known to be more efficient than TiO₂ in photooxidation of organic compounds. The band gap energies of ZnO and TiO₂ are similar to each other (approximately 3.2 eV).

In the past decade, there were a number of studies related to the photocatalytic activity of TiO₂ and ZnO.⁸⁻¹⁴⁾ They are known as low operation temperature, low cost, low energy consumption, and nontoxic and very effective semiconductor photocatalysts. The photocatalytic properties of TiO₂/ZnO composite photocatalysts remain largely unexplored although a few studies focused on TiO₂/ZnO composites. In the present work, heterojunction films composed of ZnO and TiO₂ layers were provided to improve photoelectrocatalytic properties.^{9,10)} Li and his coworkers¹¹⁾ have investigated the differences in the interaction of MnO₂ with ZnO and TiO₂ in suspension and their photocatalytic degradation. Evgenidou *et al*¹²⁾ has reported the photocatalytic oxidation of methyl parathion over TiO₂ and ZnO suspensions. Uddin *et al* have studied the influence of TiO₂ and ZnO photocatalysts on adsorption and degradation behaviour of Erythrosine.¹³⁾ The photocatalytic activity for degradation of methyl orange using the nanosized TiO₂/ZnO

[†]Corresponding author

E-Mail : wc_oh@hanseo.ac.kr (W. C. Oh).

composite catalyst has been reported by Liao *et al.*¹⁴⁾

In previous works,^{15,16)} it was found that TiO₂/ACF composite has excellent photocatalytic activity in the degradation of methyl blue (MB), which is a representative azo dye. However, the influences of ZnO on photocatalyst TiO₂/ACF in the degradation of MB, and the effect of ZnO on the photocatalytic activity of TiO₂/ACF, are not known well. Hence, the objective of this research is to (1) study the influence of ZnO on TiO₂/ACF photocatalytic degradation of MB, (2) examine the effect of ZnO on TiO₂/ACF photocatalytic degradation of MB.

In this study, the photocatalytic degradation of MB has been investigated using non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ as catalysts. Titanium iso propoxide (TIP) rather than the commonly employed TiO₂ powder was chosen as the precursor to increase the mixing rate of TiO₂ and ACF. The prepared composites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX). The catalytic efficiency of the prepared composites was evaluated by the photodegradation of MB.

2. Experimental Procedure

2.1 Materials

Activated Carbon Fiber (ACF) was purchased from EAST ASIS Carbon Fibers Co., Ltd, Anshan, China. Table 1 shows the properties of ACF. Titanium iso propoxide (TIP, 97%) as a titanium source for the preparation of TiO₂/ACF composites were purchased from Kanto Chemical Company (Tokyo, Japan). Zinc chloride (extra pure reagent, ZnCl₂) as the zinc source for ZnO was purchased from Daejung Chemical & Metal Co., Ltd, Korea. The MB was used as analytical grade which was purchased from Duksan Pure Chemical Co., Ltd, Korea. It was selected because it can be readily under anaerobic conditions to produce potentially more hazardous aromatic amines.

2.2 Preparation of samples

In this experimental, at first, 10 g ACF power was added into 50 mL 0.1 M HCl solution and stirred 2 hours and dry at 378 K. Then the pretreated ACF was put into the different concentration of ZnCl₂ solution and stirred 30 minutes, after heat treated at 773 K, we obtained the Zn-ACF materials. The Zn-ACF was put into the mixing solution of TIP and benzene. Then the solutions were homogenized under reflux at 343 K for 5 hours using a magnetic stirrer in a vial, and then the stirring solutions were transformed to one kind of gels, and these gels were heat treated at 973 K for 1 hour. And then the Zn-treated ACF/TiO₂ composites were prepared. In this state, zinc ions can be formed as salts combined with functional groups on the ACF surfaces. The nomenclatures of prepared samples are listed in Table 2.

2.3 Characteristics and investigations of the samples

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 Cu K α radiation. SEM was used to observe the surface state and porous structure of the non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites using a JSM-5200 JOEL electron microscope (Japan). EDX was used to measure the elemental analysis of the non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites. UV-VIS spectra for the MB solution degraded by non-treated ACF/TiO₂ and Zn-

Table 1. The properties of activated carbon fiber (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	$\geq 95 \text{ wt}\%$

Table 2. Nomenclatures of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites.

Preparation method	Nomenclatures
ACF + Titanium iso propoxide	AT
0.1M HCl + ACF + Titanium iso propoxide	AT1
0.05 M ZnCl ₂ + 0.1M HCl + ACF + Titanium iso propoxide	ZAT1
0.1M ZnCl ₂ + 0.1M HCl + ACF + Titanium iso propoxide	ZAT2
0.5 M ZnCl ₂ + 0.1M HCl + ACF + Titanium iso propoxide	ZAT3

treated ACF/TiO₂ composites dispersion under different conditions was recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.4 Photocatalytic decomposition

The photocatalytic decomposition was performed by using non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites in a 100 mL glass container and then irradiating the system with 20W UV light at 365 nm. The initial MB concentration was chosen 1.0×10^{-5} mol/L. 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 hours, 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, 300 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-vis spectrophotometer. The blue color of the solution faded gradually with time due 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.

3. Results and Discussion

3.1 Structure and morphology of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂

The XRD analysis results for the catalyst are shown in Fig. 1. Diffraction peaks corresponding to anatase and rutile phases have been marked with 'A' and 'R', respectively; diffraction peaks corresponding to ZnO phase has been marked with 'Z'. XRD patterns of the composites showed that the non-treated ACF/TiO₂ composite contained only a typical single and clear anatase forms while the Zn-treated ACF/TiO₂ contained a mixing anatase and rutile phase. For the non-treated ACF/TiO₂ composite, after the heat treatment at 973K for 1hour, the main crystalline phase is not transformed to the rutile structure. The major peaks at 25.3, 37.8, 48.0,

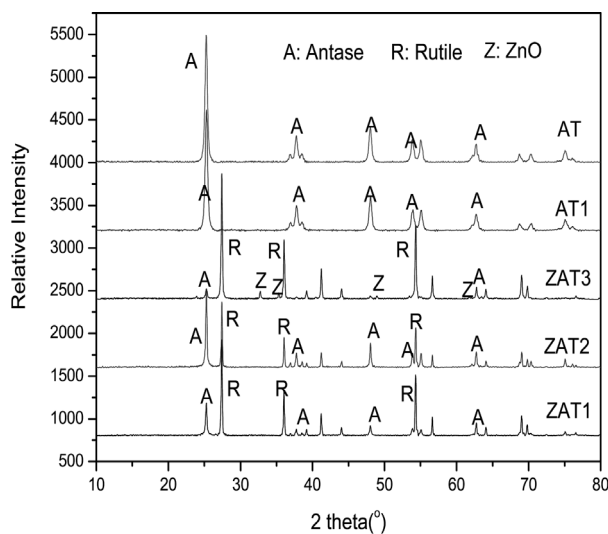


Fig. 1. XRD patterns of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites.

53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the prepared non-treated ACF/TiO₂ composites existed in anatase state. According to the former study,¹⁷⁻²⁰ it is well known that the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature. The result is in accordance with references.^{15,16}

However, for the Zn-treated ACF/TiO₂ composites, the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200) and (204) planes of anatase, indicating the developed CNT/TiO₂ composites existed in anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. Therefore, it can be concluded that the developed Zn-treated ACF/TiO₂ composites had a mixing structures of anatase and rutile crystals. As we known, the anatase phase formed below 773 K starts to transform to rutile-type structure above 873 K and changed into single phase of rutile at 973 ~ 1173 K.²¹ It is evident, from these studies, that zinc treatment induces the phase transformation from anatase to rutile. The inducement in the phase transition with Zn²⁺ doping is attributed to the oxygen vacancies in the structure caused by doping; essential for charge compensation of lower valent cations. These vacancies enhance the transport of atoms required for phase transition from anatase to rutile.²² This is exactly the reverse phenomenon reported in the doping of higher valent cations, where phase transition has been

expected to be retarded by forming interstitial Ti³⁺ cations that suppresses atomic transport in the anatase phase.²³⁾ Therefore, the effect of Zn²⁺ doping is to introduce oxygen vacancies in the TiO₂ structure which enhances the diffusion of atoms in the system. This mechanism is supposed to be responsible for the phase transition of Zn-treated ACF/TiO₂ as compared to non-treated ACF/TiO₂.

Moreover, in the curve of ZAT3, we can clearly find the peaks of ZnO, but for ZAT1 and ZAT2, we could not observe characteristic peaks of ZnO in the XRD patterns. This implies either zinc was incorporated in the crystallites of TiO₂ or ZnO was very small and highly dispersed, which was further supported by observation via SEM and EDX elemental microanalysis of Zn-treated ACF/TiO₂. The similar phenomena can be observed in the references.²⁴⁾ The photodecomposition for dye in liquid reaction was enhanced over Zn-incorporated TiO₂ compared with pure TiO₂.²⁵⁾

Fig. 2 shows the SEM surface morphology of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites. It shows that TiO₂ particles uniformly covered 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.¹⁵⁾ Moreover, for Zn-treated ACF/TiO₂ composites, the titanium complex particles more regularly distributed on and around the ACF surfaces with the increase of ZnCl₂ concentration. It was considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. Accordingly, a Heterogeneous TiO₂ particle distribution was expected for a high photocatalytic yield.¹⁾ Therefore, the higher photocatalytic activity of the Zn-treated ACF/TiO₂ composite prepared might be attributed to chemical degradation by the

homogenous distribution of titanium complexes including TiO₂, ZnO and physical adsorption by the activated carbon fiber.

Fig. 3 shows the results of elemental analysis by EDX spectra of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites. These spectra show the presence of peaks from the C, O and Ti elements. For the Zn-treated ACF/TiO₂ composites, we observed the peaks of the Zn element. 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 composite series are listed in Table 3. From the table, it is shown that carbon and Ti are present as major elements in the composite series. As expected, it was observed that the Zn contents of Zn-treated ACF/TiO₂ composites show an increase with an increase of ZnCl₂ concentration.

3.2 Photocatalytic activity

The UV/VIS absorbance spectra of MB concentration at 1.0×10^{-5} mol/L against the non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composite series are shown in Fig. 4. In Fig. 4 the absorbance values decreased with an increase in UV irradiation time. 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⁾ However, it is shown that the absorbance of AT and AT1 is lower than that of ZAT1, ZAT2 and ZAT3. It was considered that potential transformation of the structural phase to rutile was shown to reduce the photocatalytic activity of carbon/TiO₂ catalysis, similar results have also been observed by Chen et al.¹⁷⁾ Fig. 5 shows changes in relative concentration (c/c_0) of MB under UV light irradiation in the solution. MB removal with non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ 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 relative concentration

Table 3. EDX elemental microanalysis of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites.

Sample	C	O	Ti	Zn
AT	40.70	27.42	31.56	0
AT1	53.84	21.79	23.90	0
ZAT1	48.67	21.12	28.03	1.17
ZAT2	48.25	22.28	27.08	1.47
ZAT3	47.74	21.51	27.54	2.13

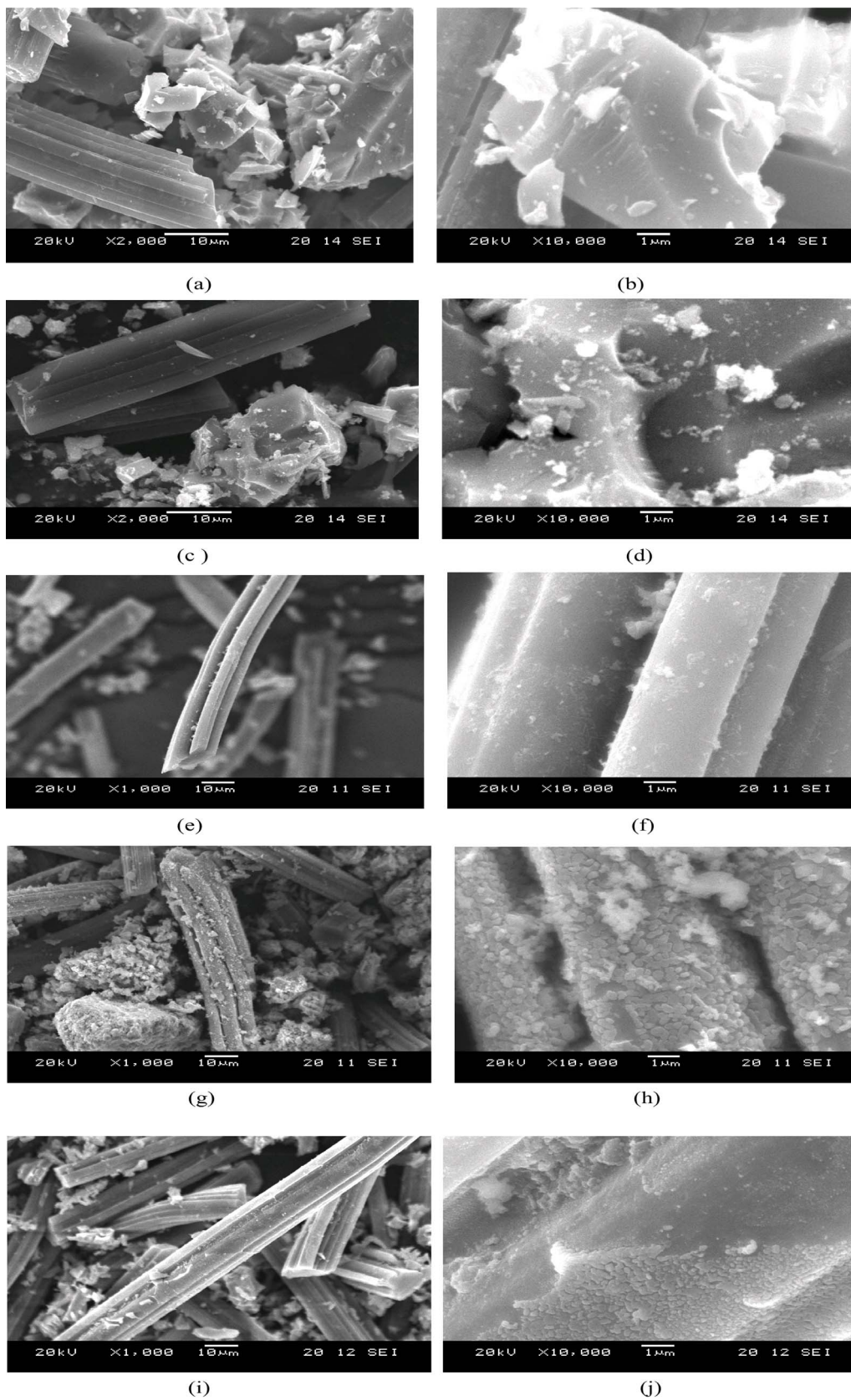


Fig. 2. SEM images of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites: (a) AT(over-all scale), (b) AT (close-up), (c) AT1 (over-all scale), (d) AT1 (close-up), (e) ZAT1(over-all scale), (f) ZAT1 (close-up), (g) ZAT2 (over-all scale), (h) ZAT2 (close-up), (i) ZAT3 (over-all scale), (j) ZAT3 (close-up).

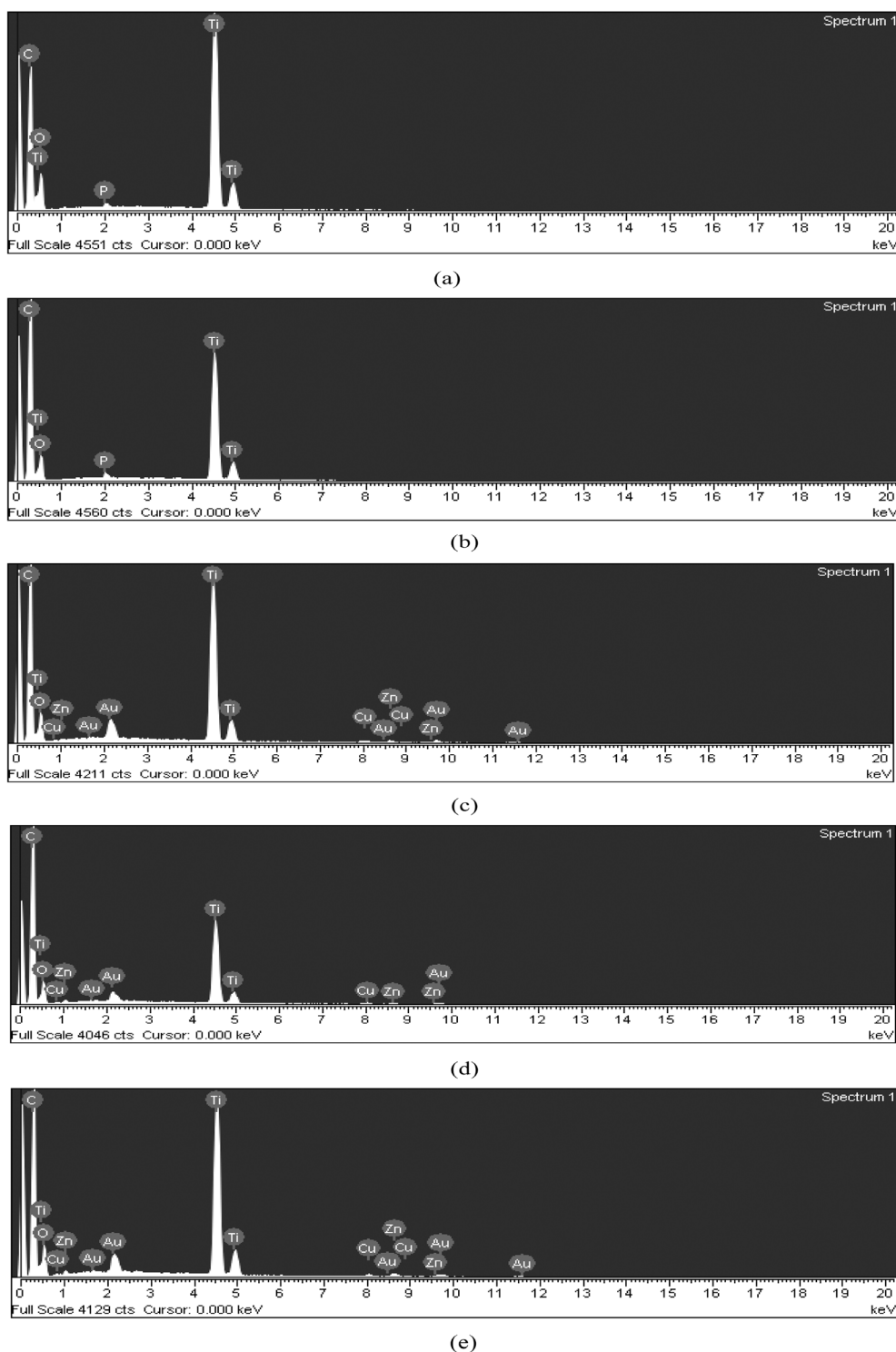


Fig. 3. EDX elemental microanalysis of non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites: (a) AT, (b) AT1, (c) ZAT1, (d) ZAT₂ and (e) ZAT3.

of MB for ZAT1, ZAT2 and ZAT3 is lower than that of AT and AT1 before turning on UV lamp, probably because the removal of MB is the main adsorption of ACF, for Zn-treated ACF/TiO₂ composites, the titanium

complex particles more regularly distributed on and around the ACF surfaces with the increase of ZnCl₂ concentration, which decrease the surface area of the composites. Moreover, the relative concentrations of MB

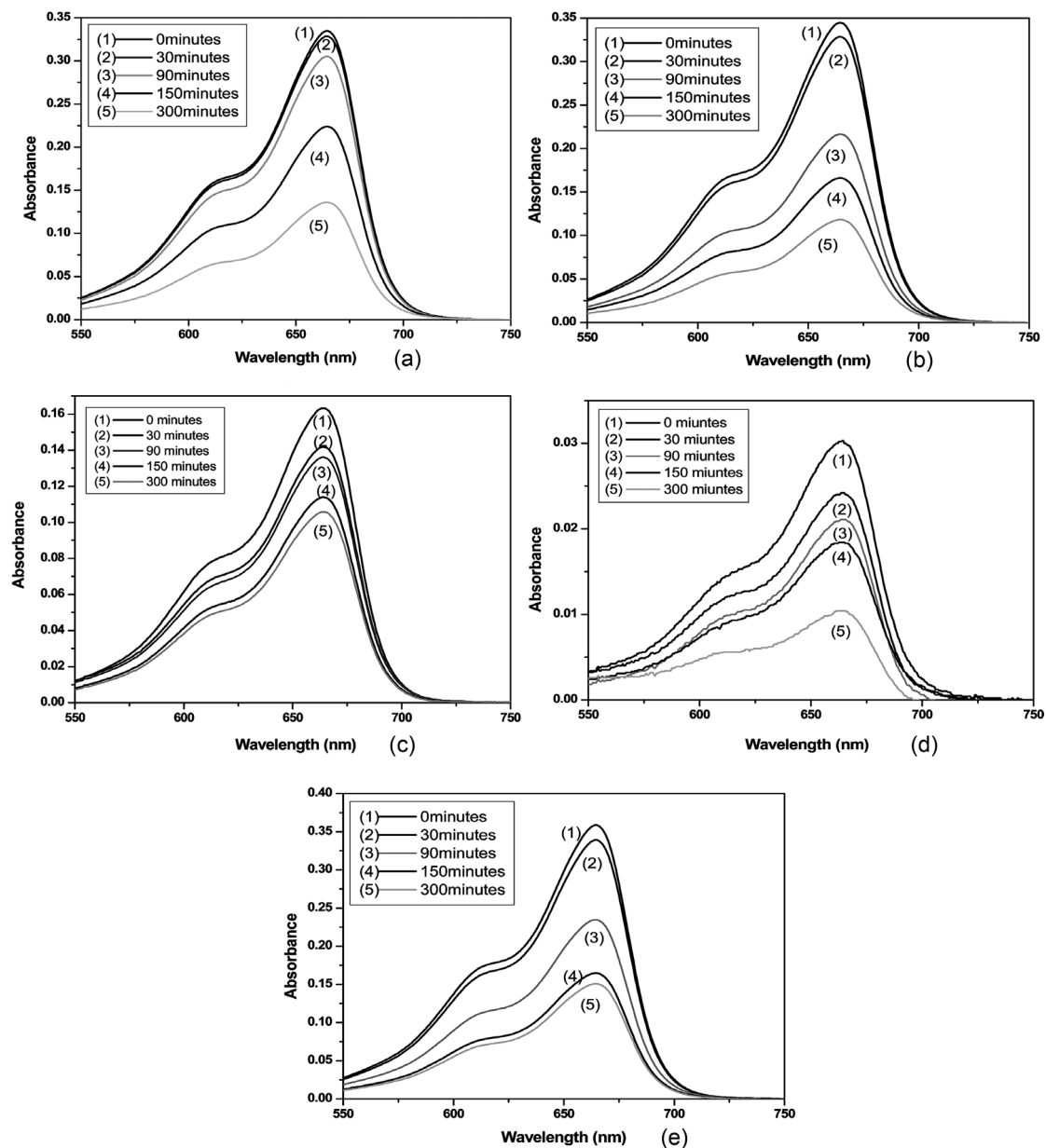


Fig. 4. UV/Vis spectra of MB concentration against non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites as time function: (a) AT, (b) AT1, (c) ZAT1, (d) ZAT2 and (e) ZAT3.

for AT is lower than that of AT1, 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.¹⁶⁾ It indicates that the HCl pretreated composites are in favor of adsorption of MB. However, adsorption-desorption equilibrium to be reached, under UV light, the decaying speeds of relative concentration for ZAT1, ZAT2 and ZAT3 series are steeper than that of AT and AT1. It is considered that photodegradation of Zn-treated ACF/TiO₂

is the main form of the removal of MB. Moreover, the photodegradation of Zn-treated ACF/TiO₂ is higher with the increase of ZnCl₂ concentration.

According to the intrinsic semiconducting characteristics of TiO₂ and ZnO, TiO₂ is an indirect band gap semiconductor but ZnO is a direct band gap semiconductor.^{9-10,26)} Theoretically, when p-type semiconductor ZnO and n-type semiconductor TiO₂ form p-n junction, the inner electric field will be formed in the interface.²⁷⁾ At the equilibrium, the inner electric field

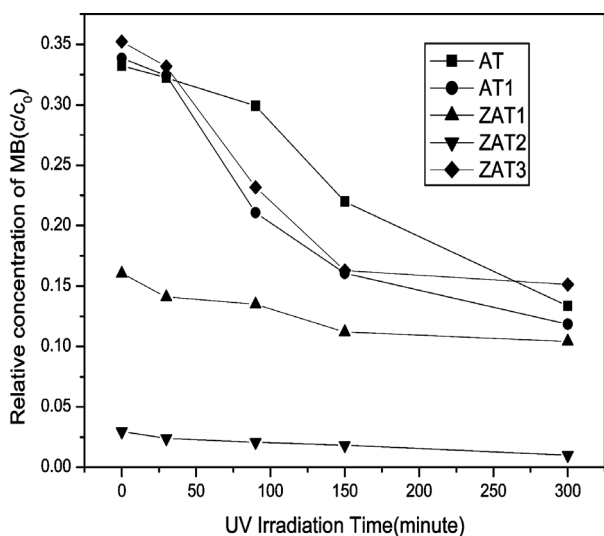


Fig. 5. Dependence of relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation for the non-treated ACF/TiO₂ and Zn-treated ACF/TiO₂ composites.

makes p-type semiconductor ZnO region have the negative charge, while TiO₂ region have the positive charge. Under near UV illumination, electron-hole pairs may be created, and the photogenerated electron-hole pairs are separated by the inner electric field. The holes flow into the negative field while the electrons move to the positive field. As a result, the photogenerated electrons and holes are separated efficiently, and the photocatalytic activity is enhanced.

From other side of view, continued adsorption of MB by modified carbon surfaces has provided the substrate for the photocatalysis of TiO₂ and ZnO.²⁸⁾ Obviously, photodecomposition of adsorbed MB enhances the adsorption rate of MB by keeping the adsorptive capacity of the support unsaturated. These two mutually enhanced processes shown in Fig. 6 adsorption of the ACF and photocatalysis of the deposited TiO₂ and ZnO, have been combined as the novel properties of the Zn-treated ACF/TiO₂ photocatalyst. Based on these relationships, we therefore can conclude that the degree of removal of MB in the solution should be attributed to the three kinds of effects of photo-degradation by doping, absorptivity by electron transfer and adsorptivity of porous ACFs between the Zn-TiO₂ and the Zn-ACF.

4. Conclusions

In this study, we have prepared non-treated ACF/TiO₂

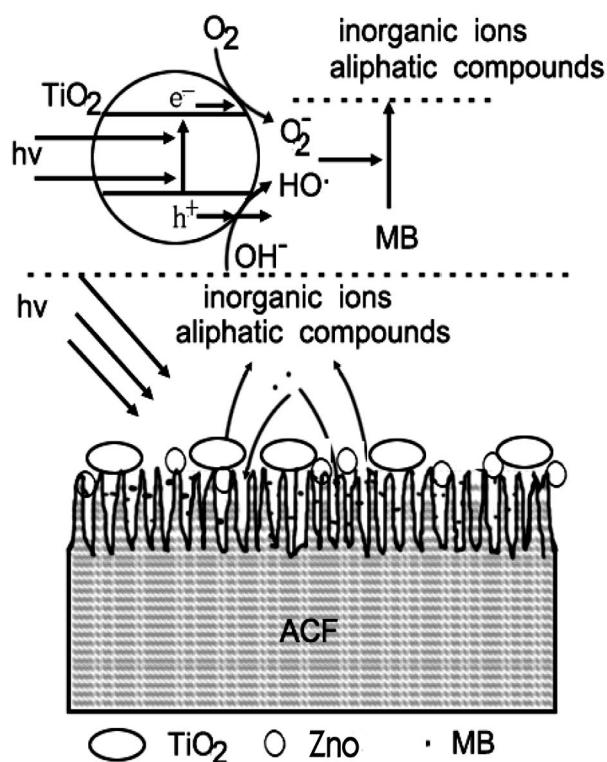


Fig. 6. Schematic diagram for the adsorption and photocatalytic degradation of MB on the Zn-treated ACF/TiO₂ composites.

and Zn-treated ACF/TiO₂ composite catalysts. The prepared composite materials were characterized by structural crystallinity between ACF and TiO₂, elemental identification and photocatalytic activity. XRD patterns of the composites showed that the non-treated ACF/TiO₂ composite contained only a typical single and clear anatase forms while the Zn-treated ACF/TiO₂ contained a mixing anatase and rutile phase. From the SEM results, the titanium complex particles are uniformly distributed on and around the fiber, and the titanium complex particles more regularly distributed on and around the ACF surfaces with the increase of ZnCl₂ concentration. These EDX spectra show the presence of peaks from the C, O and Ti elements, for the Zn-treated ACF/TiO₂ composites, and we observed the peaks of the Zn element. Finally, the prominent photocatalytic activity of the Zn-treated ACF/TiO₂ composites between c/c_0 and time could be attributed to the three kinds of effects of photo-degradation by doping, absorptivity by electron transfer and adsorptivity of porous ACFs between the Zn-TiO₂ and the Zn-ACF, and the photodegradation of Zn-treated ACF/TiO₂ depends on the ZnCl₂ concentration.

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