

Fabrication of Ni-AC/TiO₂ Composites and their Photocatalytic Activity for Degradation of Methylene Blue

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ABSTRACT

Activated carbon modified with nickel (Ni-AC) was employed for the preparation of Ni-activated carbon/TiO₂ (Ni-AC/TiO₂) composites. The N₂ adsorption data showed that the composites had a decreased surface area compared with pristine AC. This indicated blocking of the micropores on the surface of the AC, which was further supported by observation via SEM. XRD results showed that the Ni-AC/TiO₂ composite contained a mixed anatase and rutile phase while the untreated AC/TiO₂ contained only a typical single and clear anatase phase. EDX results showed the presence of C, O, and Ti with Ni peaks on the composites of Ni-AC/TiO₂. Subsequently, the photocatalytic effects on methylene blue (MB) were investigated. The improved decomposition of MB showed the combined effects of adsorptions and photo degradation. In particular, composites treated with Ni enhanced the photo degradation behaviors of MB.

Key words : Activated carbon, Titanium dioxide, Nickel, Photo degradation, SEM, XRD

1. Introduction

The preparation of effective catalysts is imperative for the degradation of pollutants, given the increasing environmental pollution and destruction on a global scale in modern society. Titanium dioxide (TiO₂)-based heterogeneous photocatalysis has attracted much attention due to its potential applications to the decomposition of pollutants in water and air.¹⁻⁵⁾ Owing to the use of dioxygen, light and completely mineralized organic and inorganic substrates, especially bio-recalcitrant compounds, this method is considered to be environmentally friendly as a pollution treatment. Thus, it is highly desirable that this method can be applied on a large scale for water and wastewater treatment. However, despite the many known advantages of TiO₂, its use associated with the shortcoming of lower photonic efficiency. Moreover, it is usually induced only by ultraviolet light, which prevents the large-scale application of this promising method.

Several attempts have been made to enhance the photocatalytic performance of TiO₂, such as immobilization of TiO₂ powder onto supports such as porous nickel,⁶⁾ activated carbon fiber (ACF)^{7,8)} and AC.⁹⁻²¹⁾ AC is highly adsorptive owing to its developed pore structure and high specific area; moreover the particle size of commercial AC is usually in the micro-scale range. AC must be of medium surface area

and porosity to facilitate the diffusion of pollutants and the release of products from the surface. Therefore, many authors have reported a synergistic effect of AC-supported TiO₂ systems⁹⁻²¹⁾ that included a high photocatalytic activity, photosensitivity and high adsorptive ability.

AC/TiO₂ composites are typically used to procure the combined effects of the photoactivity of TiO₂ and the adsorption of carbons. Generally, it is considered that organic molecules can be adsorbed into the carbon layer, diffused into its surface to the surface of TiO₂, and decomposed under UV light.¹⁸⁻²¹⁾ It is expected that these effects would be enhanced if the TiO₂ was well dispersed on the surface of the AC. However, simple mobilization has been found to decrease the reaction efficiency by reducing the TiO₂ dispersion and its contact with light. This also introduces a potential mass transfer limit.^{11,13)} Recently, a method for the preparation of AC/TiO₂ composites that involves the penetration of a titanium n-butoxide (TNB) solution into the AC was developed.²²⁾ This method is expected to provide a number of advantages compared to the use of liquid solvents in the coating process due to its high diffusivity, on-condensation and weak salvation properties. The concept is that the TNB can penetrate into the micropore and mesopore structures of the AC and become adsorbed in the pores as TNB molecules. The adsorbed TNB on the solid surface would then be converted to TiO₂ through thermal decomposition and hydrolysis. As another means of the improving the photocatalytic activity, reducing the recombination of holes and electrons by doping TiO₂ with transition metals has been proposed.

At the same time, to decrease the charge recombination

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Table 1. Nomenclatures of Pristine AC and Ni-AC/TiO₂ Composites Prepared with Different Concentrations of NiCl₂ to Activated Carbon

Preparation method	Nomenclatures
Activated Carbon	AC
Activated Carbon+Non (NiCl ₂)+Titanium n-butoxide (99.99%)	ACT
Activated Carbon+0.05M NiCl ₂ +Titanium n-butoxide (99.99%)	NACT1
Activated Carbon+0.1M NiCl ₂ +Titanium n-butoxide (99.99%)	NACT2
Activated Carbon+0.5M NiCl ₂ +Titanium n-butoxide (99.99%)	NACT3

and increase the TiO₂ photocatalytic efficiency, a variety of metals, including Ni,^{3, 23-26)} Zr,^{27,28)} Si,^{29,30)} Zn^{31,32)} and Ag^{33,34)} have been successfully treated with TiO₂. Chen²³⁾ studied the activity of the p-n junction photocatalyst NiO/TiO₂. *n*-type and *p*-type semiconductor gas sensors based on NiOx doped TiO₂ thin films were also reported by Wisitsoraat,²⁴⁾ and Abdel Aal et al.²⁶⁾ studied the electrocatalytic oxidation of nanostructured Ni-TiO₂ composite coatings for small organic molecules. Principally because Ni²⁺ can act as both holes and electrons shallow traps to enhance the lifetimes of electrons and holes, it is generally assumed that greater photoactivity for Ni-TiO₂ is possible in comparison with untreated TiO₂.

This study focused on the preparation and characterization of Ni-AC/TiO₂ composites involving the penetration of titanium n-butoxide (TNB) solution into the Ni-treated AC. The prepared composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX). The decomposition of pollutants from MB dye under UV light was then investigated to explore the photo degradation effects of the composites of Ni-AC/TiO₂ compared with untreated AC/TiO₂.

2. Experimental Procedure

2.1. Materials

The porous and granular AC used in this study was prepared from coconut. Coconut shell was pre-carbonized first at 773 K and was then activated by steam diluted with nitrogen in a cylindrical quartz tube at 1023 K for 30 min. This AC was washed with deionized water and dried overnight in a vacuum drier at over 683 K. 5 g of AC prepared as above was added to 100 ml of different concentrations of NiCl₂. In this case, the concentrations were 0.05, 0.1 and 0.5 mol/L. The NiCl₂ was supplied from Duksan Pure Chemical Co. (Korea). The mixture was then stirred for 1 h, clarified, and poured out of the super water. The sediments of Ni/AC were dried naturally at 373 K. 5 g powdered Ni/AC as prepared above was mixed into 20 ml of a TNB (C₁₆H₃₆O₄Ti, Acros Orgnis, USA) aqueous solution and was subsequently stirred for 5 h at 333 K. Before the heat treatment, the solvent in the mixtures was vaporized at 343 K for 1 h. The mixtures were then heated at 973 K for 1 h. The nomenclatures of the samples prepared are listed in Table 1.

2.2. Characteristics and investigations of the samples

To characterize the Ni-AC/TiO₂, the BET surface area via the N₂ adsorption method was measured at 77 K using a BET analyzer (Monosorb, USA). The morphology of the Ni-AC/TiO₂ composites was examined via SEM (JSM-5200, Japan). The crystalline phases were determined using XRD (Shimadzu XD-D1, Japan) with Cu K α radiation. For the elemental analysis of the Ni-AC/TiO₂ composites, EDX was employed. Characterization of Methylene blue (C₁₆H₁₈N₃S, MB) in water was determined using the following procedure. A Ni-AC/TiO₂ powdered sample of 0.05 g was dispersed in an aqueous solution at a concentration of 1.0 \times 10⁻⁵ mol/L in a dark atmosphere at room temperature. Each concentration was measured as a function of the UV irradiation time from the absorbance in the MB wavelength range of 200~550 nm, as measured by a UV/VIS spectrophotometer.

2.3. Photocatalytic activity

For the MB, the initial concentration was set as approximately 1.0 \times 10⁻⁵ mol/L. Each of the 0.05 g composite photocatalysts (as listed in Table 1) was then used to decompose the MB. For the UV irradiation, a UV lamp (20 W, 365 nm) was used at a distance of 100 mm from the solution in a darkness box. After irradiation at 0 min, 30 min, 90 min, 150 min, and 300 min, the samples were examined to test the change of the MB concentration to compare the different photocatalytic effects between the Ni-AC/TiO₂ composites. Specifically, by sampling 3mL of solution after the removal of the dispersed powders using a centrifuge, the concentration of MB in the solution was determined as a function of the irradiation time from the absorbance change.

3. Result and Discussion

3.1. The surface characteristics

The Ni-AC/TiO₂ catalysts prepared with different concent-

Table 2. Specific BET Surface Areas of Pristine Material and Ni-AC/TiO₂ Composite Samples

Sample	S _{BET} (m ² /g)
As-received AC	1083
NACT1	158.2
NACT2	148.3
NACT3	192.3

rations of Ni component are denoted as NACT1, NACT2 and NACT3. The BET surface area of the original AC was 1083 m²/g, which decreased considerably to approximately 150 m²/g when the Ni-AC/TiO₂ composites were formed. These BET surface areas are summarized in Table 2. It is clear that a large change occurred in the micropore size

distribution of the Ni-AC/TiO₂ composites compared to the change of the corresponding AC. This result indicated that the total surface area decreased after the formation of the TiO₂ particles by the TNB treatment. It is considered that the TNB can penetrate into the micropore and mesopore structures of the AC and become adsorbed in the pores as

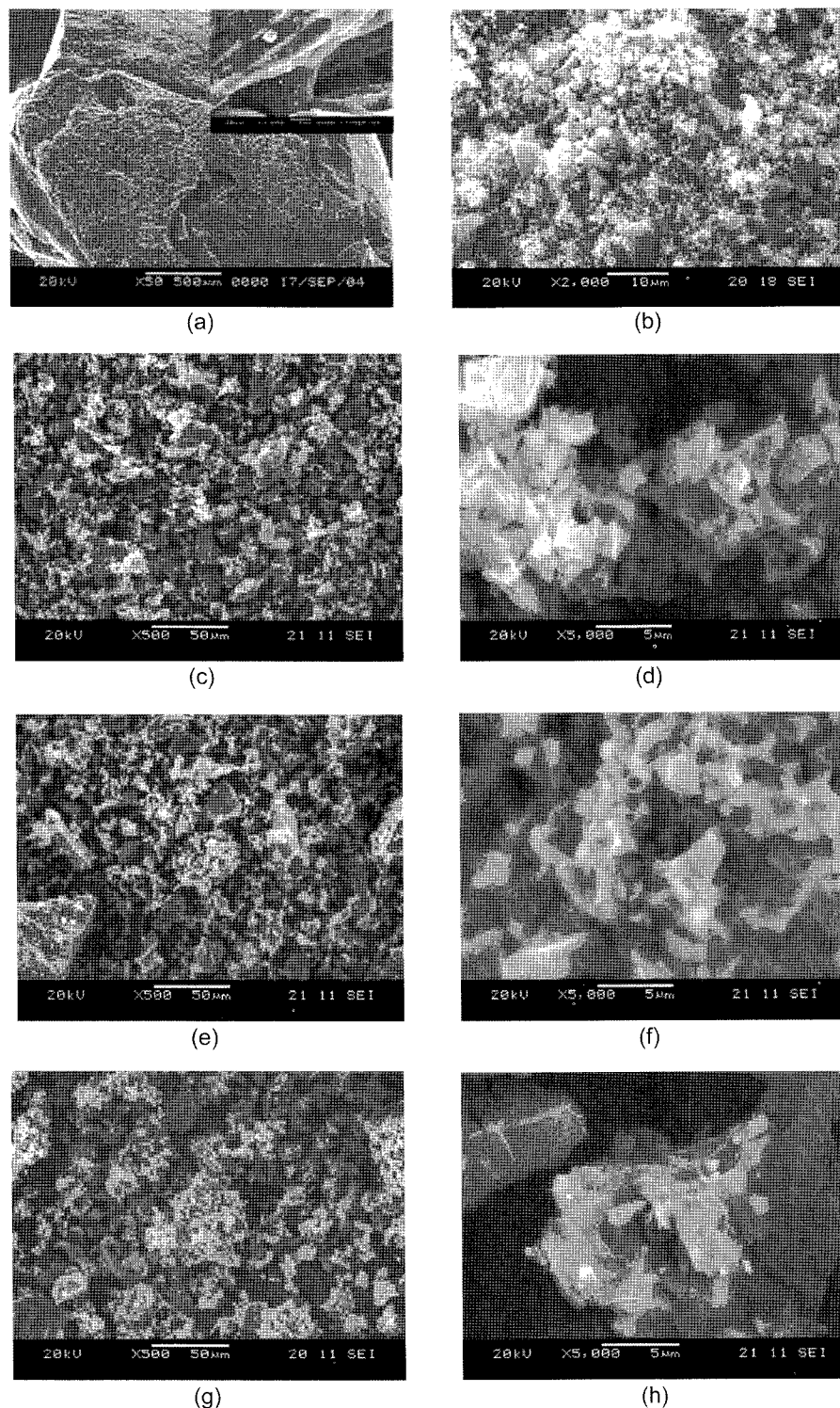


Fig. 1. SEM images of AC, AC/TiO₂ and powdered Ni-AC/TiO₂ composites: (a) AC; (b) AC/TiO₂; (c), (d) NACT1; (e), (f) NACT2, and (g), (h) NACT3.

TNB molecules. The absorbed TNB would be converted to TiO_2 through a heat treatment. As another means of improving the photocatalytic activity, reducing the recombination of holes and electrons by doping TiO_2 with transition metals has been proposed. Generally, the BET surface area is thought decrease due to the blocking of the micropores through the surface complexes introduced through the formation of the AC/ TiO_2 composites.²⁰ The variation of the surface parameters was most likely caused by the TiO_2 and Ni compounds. Similar phenomena were also observed in the literature.^{35,36}

SEM images of AC, AC/ TiO_2 and Ni-AC/ TiO_2 catalysts are shown in Fig. 1. According to Fig. 1, the TiO_2 particles are fine and agglomerated on the surface of the AC but are not uniform. Particularly, the development of the pores on the AC surface can be observed, which was consistent with the N_2 adsorption experiment. Upon introducing different concentrations of Ni into AC, no significant differences were observed. Generally, it is considered that good particle dispersion can produce high photocatalytic activity. In previous studies,³⁷ a nitric acid treatment of AC/ TiO_2 composites enhanced the homogenous and uniform distribution of TiO_2 particles.

3.2. The composition of AC/ TiO_2 composites

The XRD analysis results for the catalyst are shown in Fig. 2. Diffraction peaks corresponding to anatase and rutile phases are marked with an 'A' and an 'R', respectively, and diffraction peaks corresponding to the nickel phase are marked with an 'N'. XRD patterns of the composites showed that the Ni-AC/ TiO_2 composite contained a mixed anatase and rutile phase, whereas the untreated AC/ TiO_2 contained only a typical single and clear anatase phase.

For the untreated AC/ TiO_2 composite (sample ACT), after a heat treatment of 973 K for 1 h, the main crystalline phase was not transformed into the rutile structure. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the

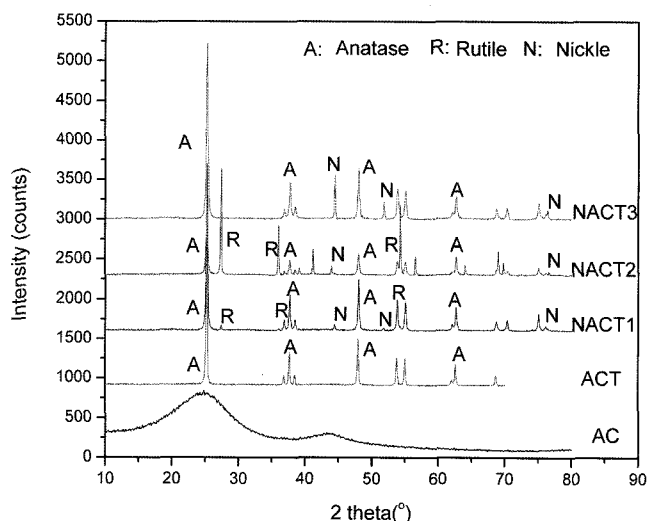


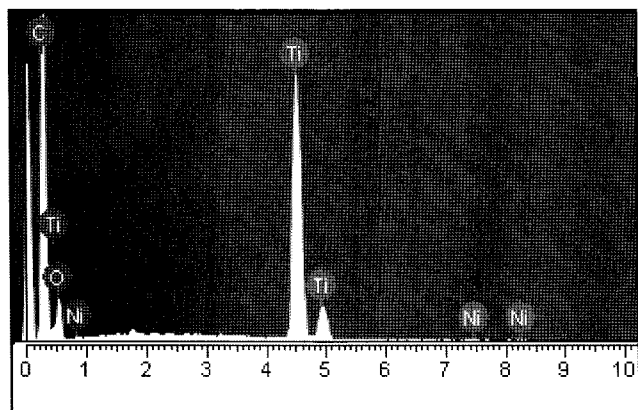
Fig. 2. XRD patterns of the pristine AC and powdered Ni-AC/ TiO_2 composites.

diffractions of the (101), (004), (200), (105), (211) and (204) planes of anatase, respectively, indicating that the prepared untreated AC/ TiO_2 composites existed in anatase state. According to the findings of earlier studies,^{20,21} it is well known that the crystal structure of titanium dioxide is mainly determined by the heat treatment temperature. This result is in accordance with findings in the literature.^{7,8}

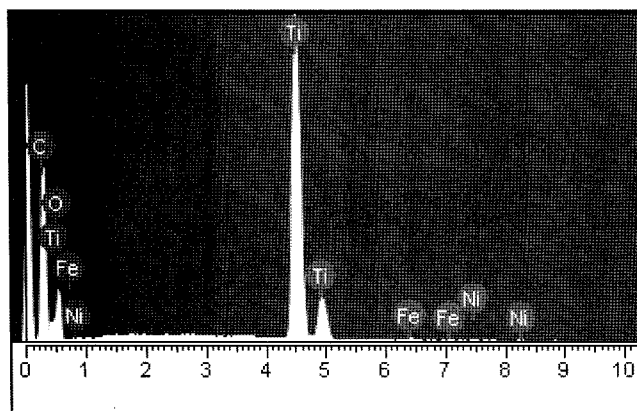
However, for the Ni-AC/ TiO_2 composites, the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of the (101), (004), (200) and (204) planes of anatase, indicating that the developed Ni-AC/ TiO_2 composites existed in the anatase state. The peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of the (110), (101), (111) and (211) rutile planes. Therefore, it can be concluded that the developed Ni-AC/ TiO_2 composites had mixed structures of anatase and rutile crystals. As is known, the anatase phase formed below 773 K starts to transform to a rutile-type structure above 873 K and changes into a single phase of rutile at 973 ~1173 K.³⁸ It is evident, from these studies, that a nickel treatment induces the temperature of the phase transformation from anatase to rutile. The increase in the phase transition with Ni^{2+} doping is attributed to the oxygen vacancies in the structure caused by doping, which are essential for charge offsetting of the lower valent cations. These vacancies enhance the transport of atoms required for the phase transition from anatase to rutile.³⁹ This is precisely the reverse phenomenon reported in the doping of higher valent cations, where the phase transition is expected to be retarded through the formation of interstitial Ti^{3+} cations that suppress the atomic transport in the anatase phase⁴⁰. Therefore, the effect of Ni^{2+} doping is to introduce oxygen vacancies into the TiO_2 structure that enhances the diffusion of atoms in the system. This mechanism is supposed to be responsible for the phase transition of Ni-AC/ TiO_2 as compared the untreated AC/ TiO_2 .

Moreover, in the curves of NACT1, NACT2 and NACT3, the peaks of nickel are clearly observable in the XRD patterns. It is also evident that the intensity of the nickel peaks increases with the increase of NiCl_2 concentration. However, for the NACT3 sample, the rutile phase of TiO_2 becomes weak, implying that the nickel concentration incorporated into the crystallites of TiO_2 affect the phase transformation from anatase to rutile.

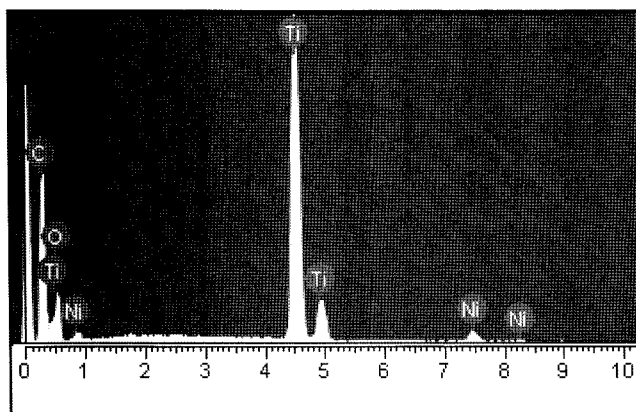
Fig. 3 shows the results of the EDX. The spectra show the presence of C, O and Ni with Ti peaks. Table 3 summarizes the specific element contents of the Ni-AC/ TiO_2 composites. As expected, the Ni element contents of the composites increased with the addition of a high amount of NiCl_2 . However, for the NACT2 sample, the Ni contents were somewhat lower than expected, and the content of Ti was higher than that of NACT1 and NACT3, which was indicative of the moderately smaller TiO_2 particles in the composites.³⁷ This might be due to the influence of Ni elements, as the content of Ni was very high in the composites. Whether this influence was present requires



(a)



(b)



(c)

Fig. 3. Typical EDX microanalyses for the Ni-AC/TiO₂ composites: (a) NACT1, (b) NACT2, and (c) NACT3.

further investigation.

3.3. The photocatalytic activity

Fig. 4 shows the UV/VIS spectra of MB degradation as a function of the radiation time. MB treated only by AC (Fig. 4a) has a rather wide band of absorption peaks, from 250 nm to 330 nm, which indicates the variability of the structures and groups in the MB molecules. At the same time, the absorbance of MB gradually decreases with time, which shows the absorption effect of AC on MB molecules.

Table 3. EDX Elemental Microanalysis of Ni -AC/TiO₂ Composites

Sample (wt%)	C	O	Ti	Ni
NACT1	51.91	20.24	27.37	0.49
NACT2	35.99	27.99	35.18	0.43
NACT3	36.22	25.71	34.59	3.48

However, MB treated with the composites of AC/TiO₂ (Fig. 4(b)) shows a completely different result as compared to that treated by AC. There is only a sharp absorption peak at around 250 nm. This indicates that the decomposition product of MB due to the composites of AC/TiO₂ has a single and homogenous structure. The other figures show the decomposition of MB due to the composites of Ni-AC/TiO₂ (Fig. 4((c), (d), and (e))) with different concentrations of Ni. These spectra differed from those of the AC/TiO₂ composites. In addition to the peak at 250 nm, there was another small peak around 330 nm. The difference in the structures of the degradation products of MB likely demonstrates the photocatalytic selection of the Ni-AC/TiO₂ composites. As shown in Fig. 4, the absorbance maxima for all samples decrease with an increase of the UV irradiation time. This can indicate that the color of the MB solution is gradually removed; thus, the concentration of the MB solution is also gradually decreased. According to Figs. 4((c), (d), and (e)), the absorbance maxima of the Ni-AC/TiO₂ sample is shown to be decreased to a much greater extent compared to that of the ACT sample at the same irradiation time. It was considered that Ni-AC/TiO₂ will have better PC degradation of a MB solution compared to that of AC/TiO₂.

Fig. 5 shows a comparison of the photocatalytic efficiency between AC, ACT, and Ni-AC/TiO₂. As shown in the figure, from AC to Ni-AC/TiO₂, the MB degradation efficiency increases gradually. In these composites, the AC component likely absorbed the organic molecule, and the TiO₂ component subsequently degraded due to the photocatalytic reaction. It is noteworthy that the Ni-modified AC-TiO₂ considerably enhances the photocatalytic activity, although there is no significant difference between the different concentrations of Ni.

Fig. 6 shows the proposed mechanism of the photocatalytic activity of Ni-AC/TiO₂.^{17,41)} As shown in the figure, during the photo degradation process, suitable adsorption capacity is crucial for high photocatalytic activity. An important step in the photocatalytic process is the adsorption of reacting substances onto the surface of the catalyst.⁴²⁾ AC has a well-developed pore structure, a very large surface area and strong adsorption capacity; it is widely used as an adsorbent and catalyst support. The AC component likely absorbed the MB and the TiO₂ component then degraded due to the photocatalytic reaction. The Ni effect of accelerating the photocatalytic ability is due to a photo-Fenton process. In photo-Fenton reactions, the process of metal oxidation and reduction occur after each other, giving rise to OH[·] radicals, which are known to be responsi-

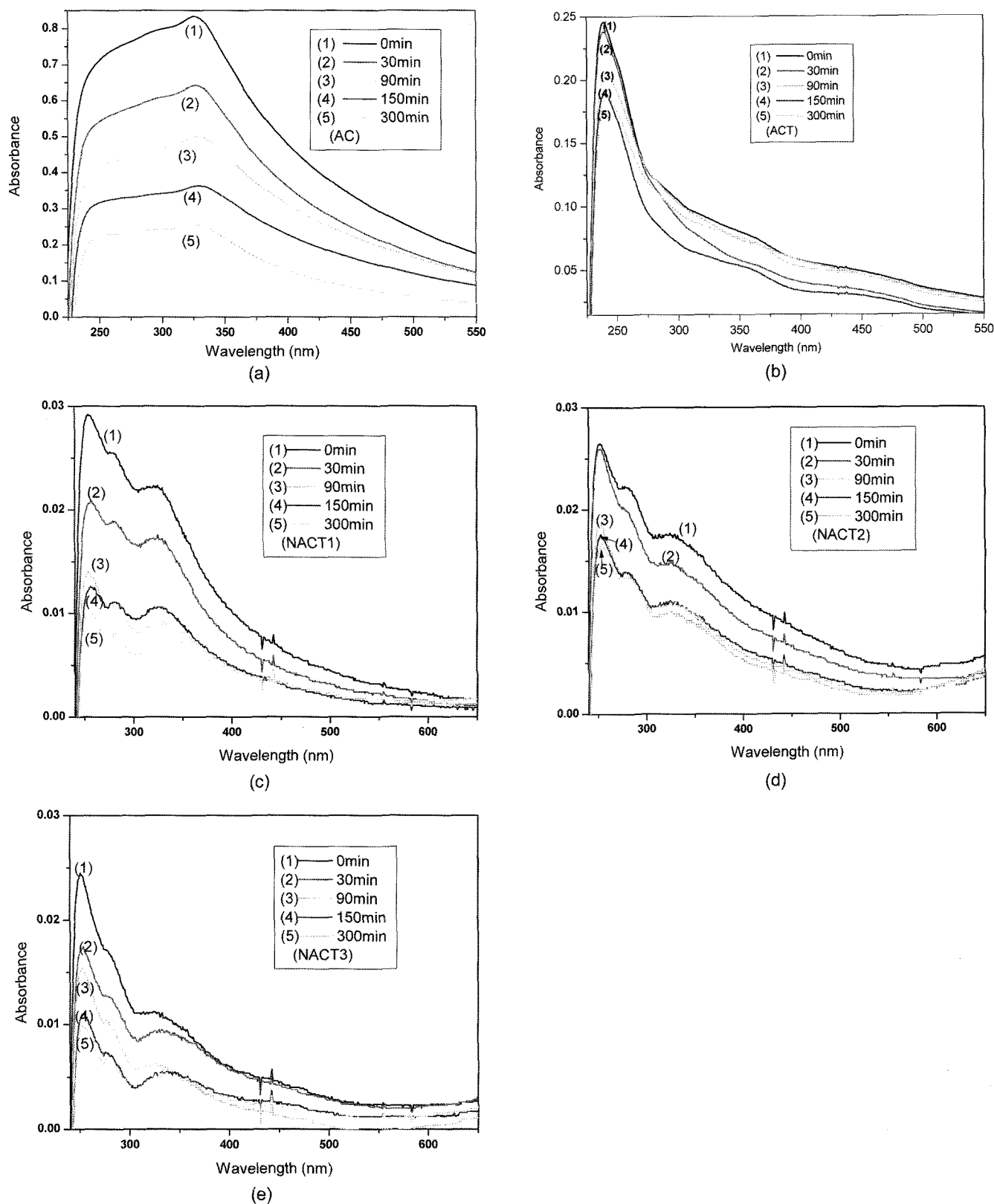


Fig. 4. UV/VIS spectra of MB concentration against a Ni-AC/TiO₂ composite under various time conditions: (a) AC, (b) ACT, (c) NACT1, (d) NACT2, and (e) NACT3.

ble for the degradation of organic compounds. In summary, the individual composites can decompose the MB to differ-

ent structural products, which reveals an interesting subject for further investigation of the degradation of Ni-

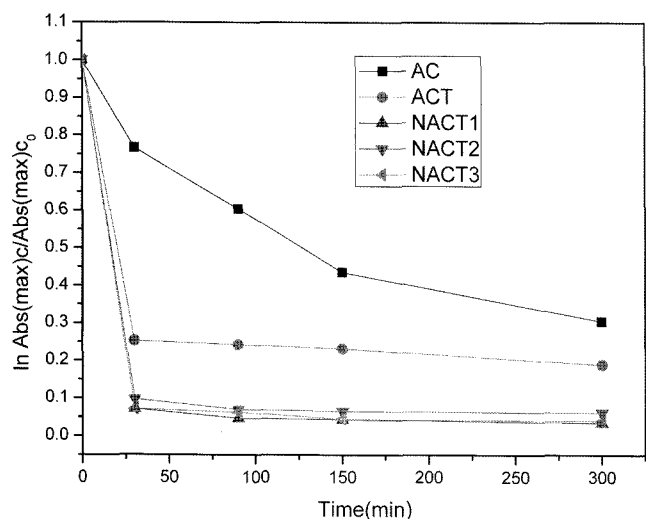


Fig. 5. Dependence of relative concentration of MB in the aqueous solution $\ln \text{Abs}_{(\text{max})c} / \text{Abs}_{(\text{max})c0}$ upon the UV irradiation time for Ni-AC/TiO₂ composites prepared from different Fe mole ratios.

AC/TiO₂ as this pertains to organic pollutants. At the same time, composites modified by Ni can enhance the photocatalytic activity significantly and provide practical benefits for

industrial application.

4. Conclusion

Composites of Ni-AC/TiO₂ were synthesized by immobilizing TiO₂ particles on the surface of AC. The characteristics of the Ni-AC/TiO₂ composites were then analyzed by an N₂ adsorption experiment using SEM, EDX and XRD. Next, the Ni-AC/TiO₂ composites were used to investigate photocatalytic activity on an MB solution. The photo degradation of MB by Ni-AC/TiO₂ showed excellent photocatalytic effects. Furthermore, the MB decomposition processes confirmed the adsorption and photocatalytic reaction for the composites. Compared to composites without Ni modification, the composites of Ni-AC/TiO₂ enhanced the photocatalytic activity due to Ni assistance with the photocatalytic reaction.

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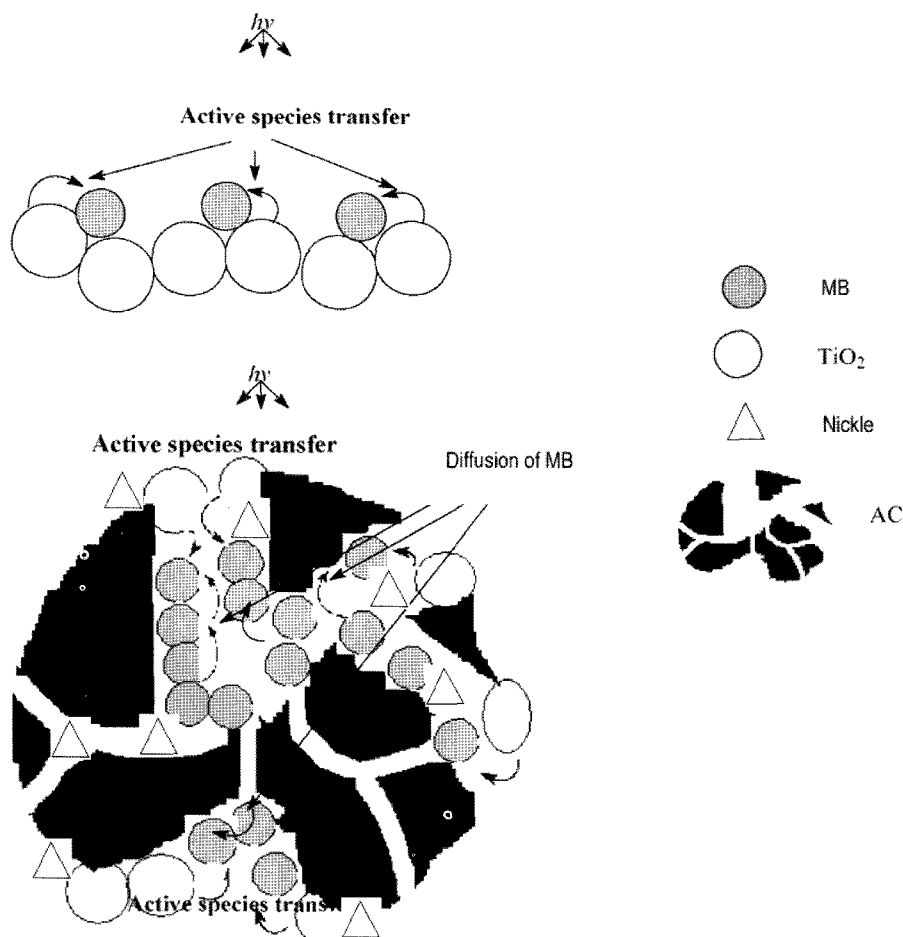


Fig. 6. Schematic diagram of the adsorption and photocatalytic degradation of MB on a Ni-AC/TiO₂ composite.

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