

# Photocatalytic Oxidation for Organic Dye using Phenol Resin-based Carbon-titania Composites

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## ABSTRACT

Carbon/TiO<sub>2</sub> composite photocatalysts were thermally synthesized with different mixing ratios of anatase to phenol resin through an ethanol solvent dissolving method. The XRD patterns revealed that only anatase phase can be identified for carbon/TiO<sub>2</sub> composites. The diffraction peaks of carbon were not observed, however, due to the low carbon content on the TiO<sub>2</sub> surfaces and the low crystallinity of amorphous carbon. The results of chemical elemental analyses of the carbon/TiO<sub>2</sub> composites showed that most of the spectra for these samples gave stronger peaks for carbon and Ti metal than that of any other elements. The BET surface area increases to the maximum value of 488 m<sup>2</sup>/g with the area depending on the amount of phenol resin. From the SEM images, small TiO<sub>2</sub> particles were homogeneously distributed to a composite cluster with the porosity of phenol resin-based carbon. From the photocatalytic results, the MB degradation should be attributed to the three kinds of synergetic effects, such as photocatalysis, adsorptivity, and electron transfer by light absorption between supporter TiO<sub>2</sub> and carbon.

**Key words :** Carbon, Titanium dioxide, XRD, SEM, EDX, Photocatalysis

## 1. Introduction

Titania (TiO<sub>2</sub>) is considered the most common photocatalyst employed in the oxidation of organic materials in the aqueous and gas phase in various industries. Due to its good physical and chemical properties, it has been used as a catalyst as well as a catalyst support, and has been used as well in electronic devices, cosmetics, pigments and filler coating in many fields of application.<sup>1)</sup> Recently, titania-based solid composites have attracted much attention as advanced materials due to their unique properties; for example, it has been found to be suitable for use as a photocatalyst for the decomposition of organic pollutants. The technique for combined carbon with ceramic particles through a simple thermal pyrolysis of a powder mixture of ceramics and carbon precursors has been used as a general method. Absorber coating with titania is another important and advanced applications in this area. The use of carbons is appealing because the carbons have highly absorption properties for light as well as pollutants due to their large surface area. In addition, carbon materials lend interesting optical properties to composites. One of the most common techniques used to synthesis carbonaceous materials is the aqueous polycondensation of resol with formaldehyde or the thermal pyrolysis of pitch and polymer.<sup>2-4)</sup> The introduction of a second component in the network structure can stabilize the textural properties upon the thermal treatment,

which modifies the distribution of active sites and in general enhances the catalytic properties of pure metal oxides.<sup>5,6)</sup> These composite materials have many potential applications, such as catalysts, porous supports, or adsorbents<sup>7,8)</sup> in electrode preparation processes.<sup>9)</sup> Efforts to control various factors have also been made to improve the photocatalytic activity of titania itself. Thus far, a number of studies have focused on the relationship between the chemical, crystallographic and morphologic properties of titania as well as its photocatalytic activity.<sup>10-14)</sup> In addition, other studies have been made to improve the photocatalytic activity by adding another component to titania; these efforts are associated with shifting the absorption band gap edge to the red in order to enhance activity in the visible portion of the spectra.<sup>15)</sup> For the carbon/TiO<sub>2</sub> composite, a composite photocatalyst is typically used to obtain the combined effects of the photoactivity of TiO<sub>2</sub> with the adsorptivity of carbons. It is expected that these effects would be enhanced if the carbon phase was well dispersed on the titania surfaces. Carbon/TiO<sub>2</sub> composite catalysts can be used for this, depending on their application, with very different carbon contents. Thus, the objective of this work is to study the change in the surface properties and carbon dispersion of several carbon/TiO<sub>2</sub> composites with different carbon contents.

In this present, carbon/TiO<sub>2</sub> composites with different mixing ratios of anatase to phenol resin were prepared through a method involving the dissolving of an ethanol solvent. The role of carbon derived from phenol resin was investigated through the preparation of carbon/TiO<sub>2</sub> photocatalysts from different phenol resin contents and the determination of their photocatalytic activity. The studied

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**Table 1.** Analytical Result of Phenol Resin Used as a Carbon Precursor

Type	Melting point (°C)	Fluidity (cps)	Curing time (sec)
Solid (Powder)	80-90	27-39	48-58

**Table 2.** Nomenclatures of Carbon/TiO<sub>2</sub> Samples Prepared with Phenol Resin and Anatase

Synthesis Procedure	Nomenclatures
Phenol Resin (20%) in EtOH Solution + Anatase	PRT20
Phenol Resin (30%) in EtOH Solution + Anatase	PRT30
Phenol Resin (40%) in EtOH Solution + Anatase	PRT40
Phenol Resin (50%) in EtOH Solution + Anatase	PRT50

**Table 3.** Textural Properties of Pristine Materials and Carbon/TiO<sub>2</sub> Composite Samples

Sample	Parameter			
	S <sub>BET</sub> (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)	Internal Surface Area (m <sup>2</sup> /g)	Average Pore Diameter (Å)
As-received TiO <sub>2</sub>	98.0	-	-	-
PRT20	423	0.232	236	10.39
PRT30	456	0.238	238	10.55
PRT40	452	0.240	240	10.49
PRT50	488	0.243	253	10.97

catalysts were characterized by their BET surface area and by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and through the use of a UV/VIS spectrophotometer.

## 2. Experimental

### 2.1. Materials

The phenol resin was used as a carbon source for the preparation of the carbon/TiO<sub>2</sub> composite. The powdered phenol resin was supplied from Sumitomo Chemical Co. (Japan). The analytical result of the phenol resin was listed in Table 1. The pristine TiO<sub>2</sub> was commercially available (Duk-San Pure Chemical Co., Korea); which was composed of a single phase of anatase with secondary particles ranging of about 80-150 μm aggregated from primary particles ranging of about 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of approximately 98 m<sup>2</sup>/g. For the dissolve phenol resin, ethanol (Dae-Jung Chemical Co., Korea) was used as a solvent. After dissolving the phenol resin in an ethanol solution, TiO<sub>2</sub> powder was mixed with the phenol resin-ethanol solution. The slurry mixtures with different mixing ratios of anatase to carbon precursor were heated at 333 K for 1 h. The solvent in the

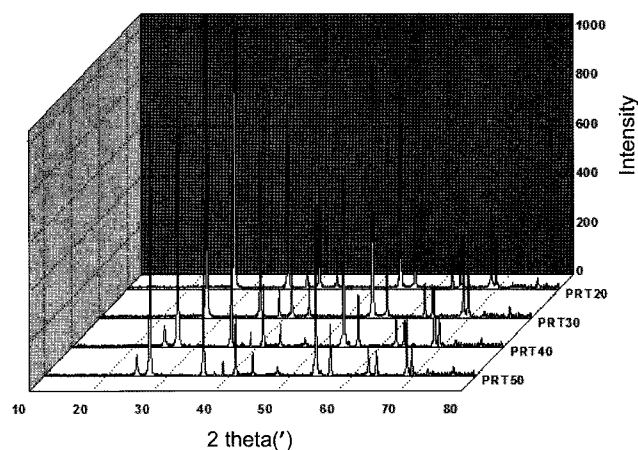
mixtures was vaporized at 353 K for 6 h. The agglomerates of carbon/TiO<sub>2</sub> were heated at 1023 K for 1 h at an inert atmosphere. The nomenclatures of the prepared samples were listed in Table 2.

### 2.2. Characterization

For the BET surface area measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JEOL, Japan) was used to observe the surface state and structure of carbon/TiO<sub>2</sub> that had been transformed through the phenol resin-treatment. X-ray diffraction patterns were taken using an X-ray generator (Shimadzu XD-D1, Japan) with Cu Kα radiation. For the elemental analysis of carbon/TiO<sub>2</sub>, energy dispersive X-ray analysis (EDX) was also used. As one type of the analysis of photocatalytic activity, a UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of catalytic efficiency of the carbon/TiO<sub>2</sub> composite.

### 2.3. Photocatalytic effect

Characterization of methylene blue (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S, MB) in water was determined by the following procedure. Photocatalytic activities were evaluated by MB degradation in an aqueous media under ultraviolet light irradiation. For UV irradiation, the reaction tube was located axially and held in a UV lamp (20 W, 365 nm) box. The lamp was used at the distance of 100 mm from the solution in a dark box. A carbon/TiO<sub>2</sub> powdered sample of 0.05 g was dispersed in an aqueous solution (ca. 70 mL) with an initial concentration (c<sub>0</sub>) of 1.0 × 10<sup>-7</sup> mol/L in the dark atmosphere at room temperature. Before turning on illumination, the suspension containing MB and carbon/TiO<sub>2</sub> composites was stirred with an ultrasonicator in the darkness condition for 3 min to establish an adsorption-desorption equilibrium. The suspension was then irradiated with ultraviolet light as a function of the irradiation time. Samples were then withdrawn regularly from the reactor and the dispersed powders were removed using a centrifuge. Each concentration was mea-

**Fig. 1.** XRD patterns of carbon/TiO<sub>2</sub> composites derived from phenol resin and anatase.

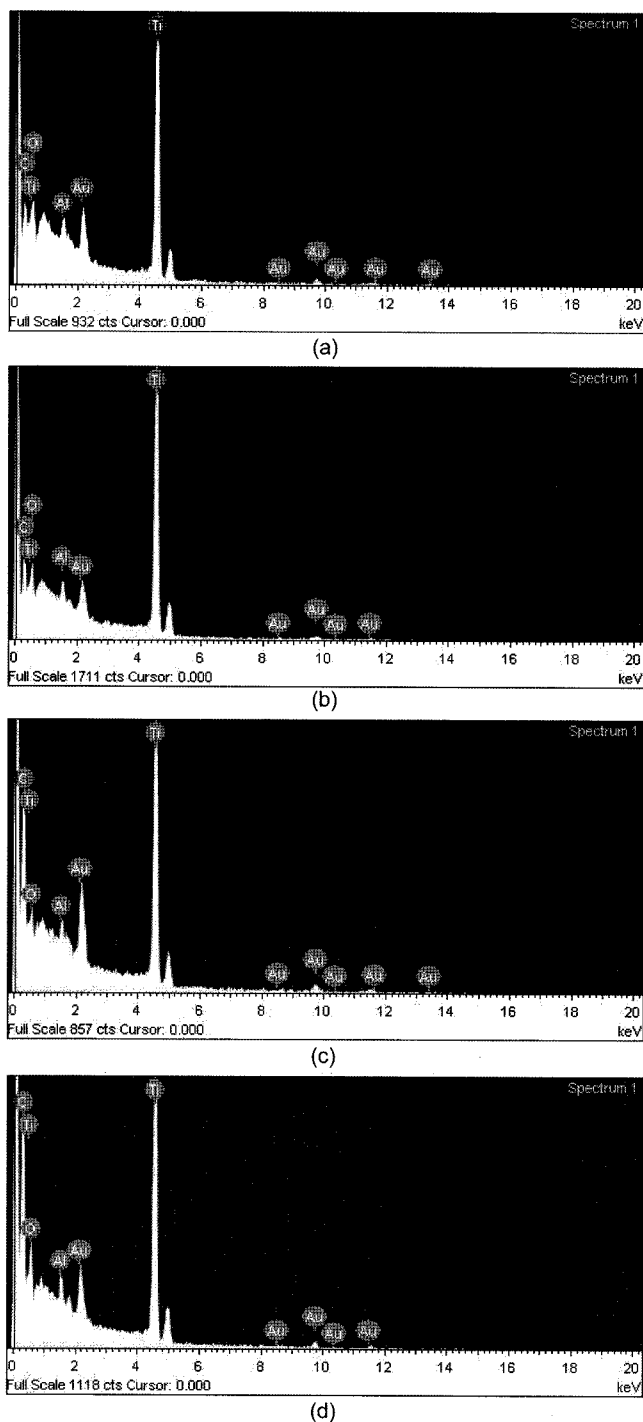


Fig. 2. EDX elemental microanalysis for the carbon/TiO<sub>2</sub> composites; (a) PRT20, (b) PRT30, (c) PRT40, and (d) PRT50.

sured as a function of the UV irradiation time from the absorbance in the MB wavelength range of 550-800 nm as measured by the UV/VIS spectrophotometer. The concentration (c) of MB in the solution after the treatment of the composite was determined as a function of the irradiation time from the absorbance region at a UV wavelength line of 660 nm. This concentration (c) was determined via an extrapolation method.

### 3. Results and discussion

#### 3.1. Structural and elemental analysis

The XRD analysis of carbon/TiO<sub>2</sub> composites prepared at various mixing ratios showed that the anatase phase was dominant at 973 K. The XRD analysis results for the catalysts samples were shown in Fig. 1. In the XRD patterns for all of the carbon/TiO<sub>2</sub> composites, the diffraction peaks of carbon were not observed due to the low carbon contents on the TiO<sub>2</sub> surfaces as well as the low crystallinity of amorphous carbon. However, crystalline TiO<sub>2</sub> was clearly detected. The patterns of these composites showed narrow diffraction peaks; thus, after carbonization the TiO<sub>2</sub> particles did not contribute to the transformation of the anatase phase. It was observed that the major peaks were diffractions from the (101), (004), (200) and (204) planes of anatase. In earlier studies of the TiO<sub>2</sub> formation from organometallic titanium sources [16,17], the XRD results showed that the anatase phase disappeared as the increasing temperature and that the rutile phase occurred at relatively high temperature. The XRD patterns of the TiO<sub>2</sub>/carbon composites in the study of Maldonado-Hodar *et al.*<sup>5)</sup> showed results that were very similar in terms of the phase transition of anatase crystallites at low temperatures. However, the patterns showed the results in mixtures of anatase and rutile structures with an increase in the pyrolysis temperature. It is believed that the increase in the temperature during the heat treatment contributed to the phase transformation from pure anatase phase to rutile phase.

The quantitative component analysis for the carbon/TiO<sub>2</sub> composite was performed by EDX. The EDX spectra of carbon/TiO<sub>2</sub> composites were shown in Fig. 2. The results were shown for the spectra of C and Ti as the major elements. According to several earlier studies,<sup>4,10,14)</sup> carbon-coated solid particles and composite-type carbon in elemental analyses have been reported for various types of titania. These results indicate a relationship between the catalytic effect

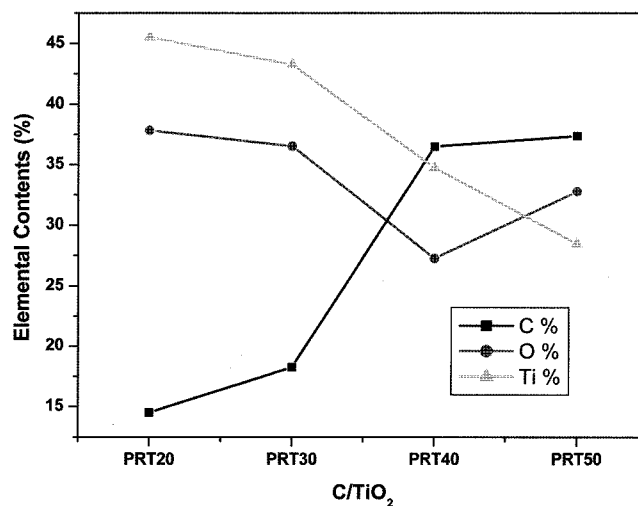
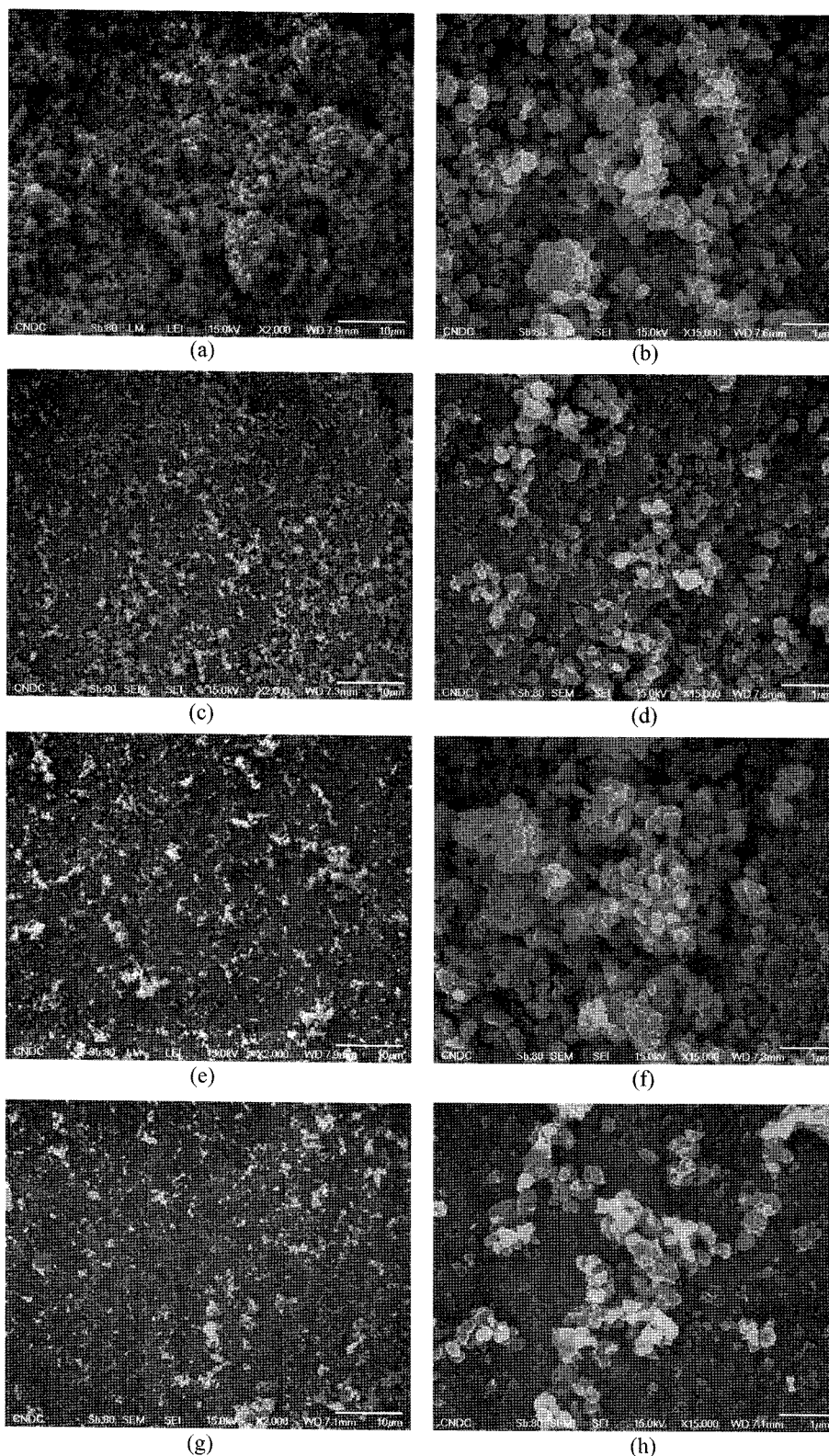


Fig. 3. Numerical elemental distributions for the EDX microanalysis (Weight %) of carbon/TiO<sub>2</sub> samples prepared with phenol resin and anatase.

and the component elements. In this study, the spectra showed the presence of the major elements of C and O with strong Ti peaks. The numerical results of the EDX quantitative microanalysis of the carbon/TiO<sub>2</sub> composite were shown

in Fig. 3. From this result, it can be observed that the amounts of C increased as the phenol resin content increased during the preparation procedure. Accordingly, the amounts of Ti decreased as the phenol resin content



**Fig. 4.** SEM micrographs for the carbon/TiO<sub>2</sub> composites; (a) PRT20 (over-all scale), (b) PRT20 (close-up), (c) PRT30 (over-all scale), (d) PRT30 (close-up), (e) PRT40 (over-all scale), (f) PRT40 (close-up), (g) PRT50 (over-all scale), and (h) PRT50 (close-up).

increased in the series of the carbon/TiO<sub>2</sub> composites.

### 3.2. Surface properties

Table 2 was shown the textural properties of raw materials and carbon/TiO<sub>2</sub> composites derived from phenol resin and anatase. The results shown in the table demonstrate that a slight increase in the BET surface area of the composite samples occurred with the increase in the amount of phenol resin. The BET surface area increases to a maximum value of 488 m<sup>2</sup>/g with the increase in the amount of the phenol resin content. The surface area depends on the phenol resin content, which was set by changing the mixing ratio of the phenol resin with the raw TiO<sub>2</sub>. Using a ceramic substrate, the carbon treatment experimentally showed that the carbon assembled on most ceramic substrates from carbon precursors was highly microporous.<sup>18)</sup> It is plausible assume that the formation of porosity in carbon surface-assembled TiO<sub>2</sub> particles contribute to the increase in the BET surface area. According to Sayari *et al.*,<sup>19)</sup> the use of pristine TiO<sub>2</sub> leads to a very small surface area (about 2 m<sup>2</sup>/g). In the present case, it was found that the surface area of the carbon layer in the sample increases as the phenol resin content increases. From this point, the present carbon-assembled TiO<sub>2</sub> samples can adsorb a relatively large amount of organic pollutants in a liquid phase. It is consid-

ered that the increase in the porosity of carbons produced by a heat treatment and the increases of the surface parameters among the composite series are related to the removal efficiency of organic dye by adsorptivity. Fig. 4 depicts SEM micrographs of carbon/TiO<sub>2</sub> composite samples derived from phenol resin and anatase. It was observed that TiO<sub>2</sub> particles were homogeneously distributed to carbon derived from phenol resin. Moreover, a number of small clusters of TiO<sub>2</sub> particles were found on large carbon cluster overall. It was considered that a good dispersion of small particles could provide additional reactive sites for the reactants compared to aggregated particles. Generally, small TiO<sub>2</sub> particle distributed on carbon clusters can be increase the photocatalytic efficiency by the light absorption effects. From the reported study,<sup>20)</sup> the quantum efficiency of the electron from the photocatalyst is responsible for carbon particles interposed to the surface as well as the recombination rate of the electron-hole pairs of the photocatalyst. Accordingly, a high photocatalytic yield was expected for a homogenous and small TiO<sub>2</sub> particle distribution. The higher photocatalytic activity of the prepared sample might be attributed to the homogenous distribution of carbon clusters.

### 3.3. Photocatalytic effect of MB

Fig. 4 showed changes of absorbance by the color removal

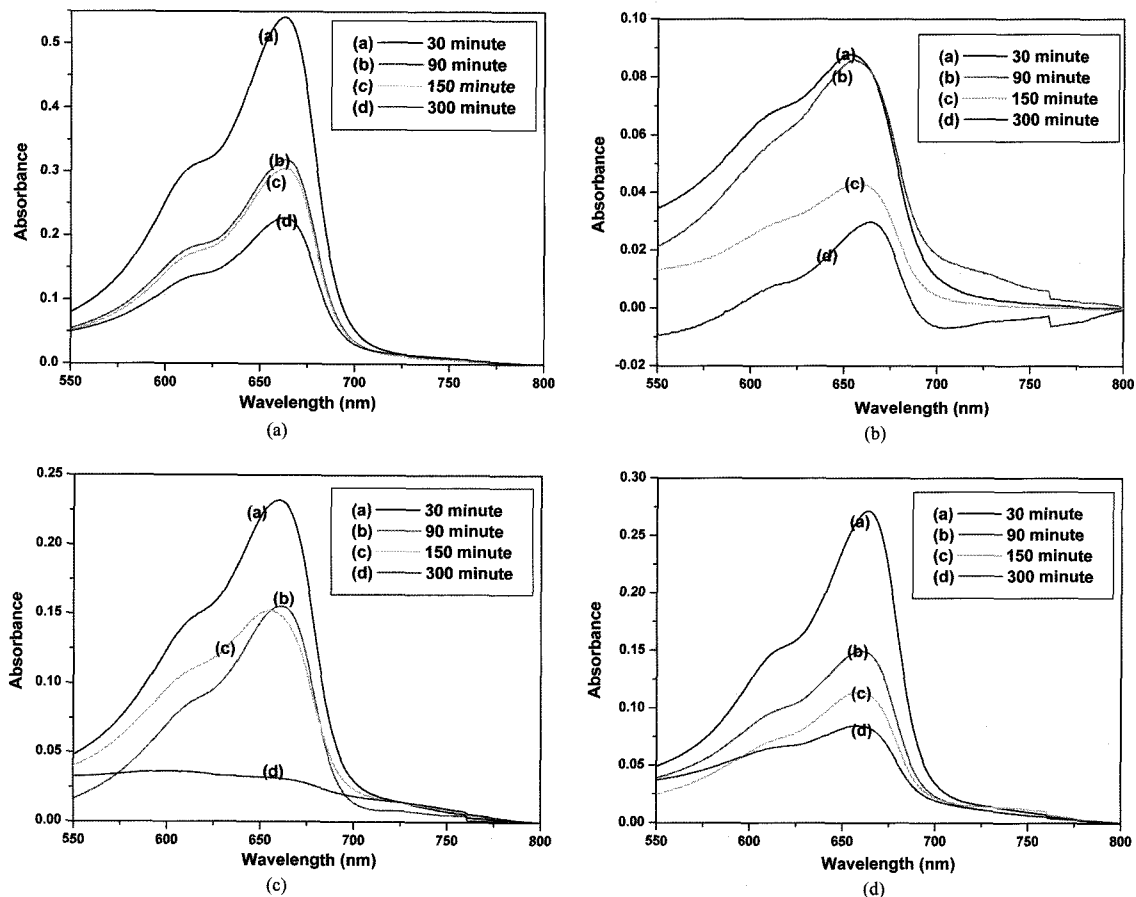


Fig. 5. Absorbance variation of MB concentration against the carbon/TiO<sub>2</sub> composite under various irradiation time conditions; (a) PRT20, (b) PRT30, (c) PRT40, and (d) PRT50.

in the relative MB degradation concentration by the composites under UV light irradiation in the solution as a function of time. MB decomposition with a carbon/TiO<sub>2</sub> composite was tested to obtain the UV photolysis effect. In pristine TiO<sub>2</sub> suspensions, the electron-donating species are water molecules and hydroxyl ions. The electron-accepting species is oxygen for experiments conducted in the presence of air or water.<sup>11</sup> In modified carbon/TiO<sub>2</sub> suspensions, an additional electron-accepting species, carbon-cluster assembled TiO<sub>2</sub> particles, is introduced. As shown in earlier studies,<sup>3,6</sup> if the MB concentration used is higher,<sup>6</sup> the intensity of the absorbance maxima ( $\lambda_{\text{max}}$ ) values cannot be estimated by the photoproduct formed as a function of the irradiation time. The formation of  $\lambda_{\text{max}}$  is proportional to the decrease in the concentration of the transient formed after UV light excitation. If the concentration is lower,<sup>10</sup> however, the  $\lambda_{\text{max}}$  values cannot be accurately estimated. However, the  $\lambda_{\text{max}}$  at the tested region decreased as the degradation time increased. In this study, the measurement of the  $\lambda_{\text{max}}$  value in the 550 nm to 600 nm region with MB products was tested as a function of the degradation time of carbon/TiO<sub>2</sub> composites. It was found that the  $\lambda_{\text{max}}$  values moved into the long wavelength area with a decrease to the lower absorbance region as the irradiation time increased. The transparent light of the MB solution with an increase of the irradiation time was increased greatly by the photocatalytic degradation effect. The enhanced activity of carbon/TiO<sub>2</sub> particles for the formation of a carbon cluster as a result of the carbon addition to the TiO<sub>2</sub> suspensions can be attributed to two factors. The first factor is the enhancement of the separation of the electrons and holes caused by the absorption of light from carbon graphene, and the second is the adsorption effect due to the high porosity of the carbon surfaces.

Fig. 5 showed the plots for the color disappearance effect by the color removal against time. The tendencies of the changes by color disappearance were presented as removal percentages of the concentration of MB that degraded in the aqueous solution as a function of the UV irradiation time. The disappearance by the photodegradation effect might be due to the combination of the presence of UV light and an oxidation effect caused by the dissolved oxygen in the suspension. According to the electron transfer properties of carbon layers, a carbon layer derived from phenol resin may accept a photo-induced electron ( $e^-$ ) by UV irradiation. It is believed that the electrons in the carbon layer transfer into the conduction band in the TiO<sub>2</sub> particles. Here, these electrons in the conduction band may react with O<sub>2</sub>, which can trigger the formation of the highly reactive superoxide radical ion (O<sub>2</sub><sup>-</sup>). The MB solution is quite unstable with variations of the concentration when it is irradiated under UV light with carbon/TiO<sub>2</sub> composites. As mentioned above, carbon graphene layers played the role of an energy sensitizer that improved the quantum efficiency with an increase in the number of electron transfers. It is considered that the photodegradation phenomena can occur in terms of two

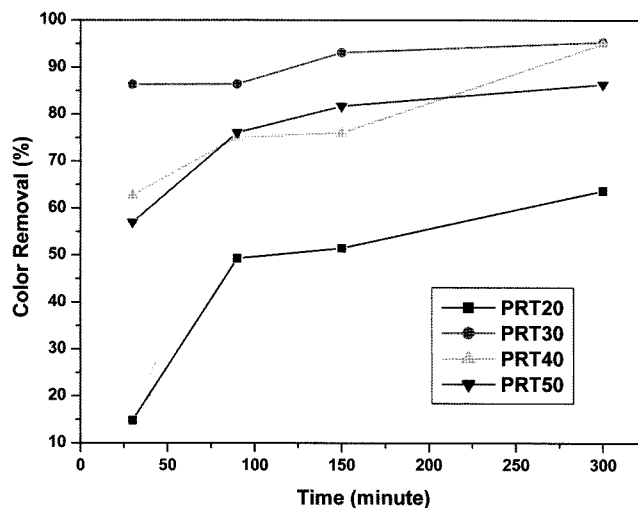


Fig. 6. Color removal of the MB solution in the presence of photocatalysts with time conditions.

physical factors by the differences of the work function: quantum efficiency by the carbon layers and photocatalytic decomposition by TiO<sub>2</sub>. As organic molecules absorb energy from irradiation, their delocalized electrons can shift from the bonding to antibonding orbital.<sup>21-23</sup> As adsorption of organics in the solution likely occurs via  $\pi$ - $\pi$  interactions between its delocalized electrons and the graphene layers, it is reasonable that shifts in its electron orbital would alter the adsorption rate.<sup>24</sup> The enhanced degradation of the MB as pollutants on the carbon/TiO<sub>2</sub> composite could be ascribed to the combination effect between carbon derived from phenol resin and TiO<sub>2</sub> followed by a transfer through an interphase to titania, where it is photo-degraded. As presented in earlier studies,<sup>11-14</sup> the combined effects of the MB degradation should be attributed to three kinds of synergistic effect such as photocatalysis, adsorptivity and electron transfer by light absorption between supporter TiO<sub>2</sub> and carbon. From the results of the degradation of the MB dye solution during 300 minutes at  $1.0 \times 10^{-7}$  mol/l of the initial MB concentration, it was shown that the color removal effects for the carbon/TiO<sub>2</sub> composites results in a more significant degradation effect with an increase of the time function compared to that of the original TiO<sub>2</sub>. In terms of the photocatalytic performance, the photodecomposition of pollutants occurs on TiO<sub>2</sub> particles, even on those coated onto carbon or aggregated in the carbon, and light absorption was active on carbon particles. The rate-limiting step in the photocatalytic oxidations is believed to be the transfer of electrons derived from carbon from the TiO<sub>2</sub> surface to oxygen molecules.

#### 4. Conclusion

In this study, we presented the synthesis and characterization of carbon/TiO<sub>2</sub> composites with different mixing ratios of anatase to phenol resin through the ethanol solvent dissolving method. The role of carbon cluster of carbon-tita-

nia composites derived from phenol resin and anatase along with their photocatalytic performance are investigated through structural variations, elemental analysis, surface morphology and photodegradation. The XRD patterns reveal that only anatase phase can be identified for carbon/TiO<sub>2</sub> composites, while the diffraction peaks of carbon are not observed due to the low carbon contents as well as the low crystallinity of amorphous carbon. The results of the chemical elemental analysis of the carbon/TiO<sub>2</sub> composites showed that most of the spectra for these samples gave stronger peaks for carbon and Ti metal than for any other element. The BET surface area increases to the maximum value of 488 m<sup>2</sup>/g, and the area depends on the amount of phenol resin. From the SEM images, TiO<sub>2</sub> particles were homogeneously distributed to carbon derived from phenol resin. According to the photocatalytic results, the relationship of the color removal of the MB solution products was shown through the color conversion properties depending on the time function under UV irradiation. Finally, the enhanced degradation of MB as a pollutant on carbon/TiO<sub>2</sub> composite be ascribed the combination effect between carbon derived from phenol resin and TiO<sub>2</sub> followed by an electron transfer through an interphase to titania.

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