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# Characterization of Metal (Cu, Zn)-Carbon/$TiO_2$ Composites Derived from Phenol Resin and their Photocataytic Effects

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**ABSTRACT**

Metal-carbon/$TiO_2$ composite photocatalysts were thermally synthesized through the mixing of anatase to metal (Cu, Zn) containing phenol resin in an ethanol solvent coagulation method. The BET surface area increases, with the increase depending on the amount of metal salt used. From SEM images, metal components and carbon derived from phenol resin that contains metal was homogeneously distributed to composite particles with porosity. XRD patterns revealed that metal and titanium dioxide phase can be identified for metal-carbon/$TiO_2$ composites, however, the diffraction peaks of carbon were not observed due to the low carbon content on the $TiO_2$ surfaces and due to the low crystallinity of the amorphous carbon. The results of a chemical elemental analysis of the metal-carbon/$TiO_2$ composites showed that most of the spectra for these samples gave stronger peaks for C, O, treated metal components and Ti metal compared to that of any other elements. According to photocatalytic results, the MB degradation can be attributed to the three types of synergetic effect: photocatalysis, adsorptivity and electron transfer, according to the light absorption between the supporter $TiO_2$, metal species, and carbon layers.

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

## 1. Introduction

Carbon/$TiO_2$ composite photocatalysis has been used to convert a variety of organic materials in conjunction with a number of processes including oxidation.[1-3] The degradation of organic pollutants in water by photocatalysis, using the wide optical band gap material, has attracted widespread attention recently.[4-6] Several researchers have shown that carbon/$TiO_2$ composite is an excellent photocatalysis that can break down most types of refractory organic pollutants, including detergents, dyes and herbicides under UV light irradiation.[7,8] However, it is also known that this type of photooxidation has a number of common defects. Given that $TiO_2$ has a high-energy band ($E_g \approx 3.2$ eV), the material can only be excited by high-energy UV irradiation with a wavelength no longer than 387.5 nm. This practically rules out the use of sunlight as an energy source for a photocatalytic reaction. A low rate of electron transfer to oxygen and the high rate of recombination between excited electrons or hole pairs results in a low quantum yield rate. Recently, a number of studies have been proposed regarding photocatalytic activity of a metal oxide-carbon/$TiO_2$ composite for the purpose of improving the photocatalytic activity of $TiO_2$.[9,10] Three-component combined photocatalysts may perhaps increase the efficiency of the photocatalytic process by increasing the charge separation and extending the energy range of photoexcitation. Generally, a high surface area, as well as excellent thermal stability is required for catalyst supports to disperse a catalyst material effectively and to increase the number of active sites of the catalyst. Another important characteristic of a metal oxide-carbon/$TiO_2$ composite is its ability as a photocatalyst, which originates from its synergistic effects derived from the adsorptivity of porous carbon,[11] the effective electron transfer by metal oxide impurities in carbon[9,10] and the semiconducting nature of $TiO_2$.[12,13] The overall rate of the photocatalytic reaction is expressed as a function of the rates of recombination and the capture of a photoexcited electron ($e^-$) and positive hole ($h^+$) by substrates adsorbed on the surface. On the basis of this finding, it can be suggested that a metal oxide-carbon/$TiO_2$ composite with adsorptivity, an effective electron transfer and semiconducting nature, leading to respectively enhancement of the capture and the suppression of the recombination, should show high photocatalytic activity. Energized electrons and holes may either recombine for the dissipating energy, or be available for a redox reaction with an electron donor or acceptor species adsorbed on the photocatalyst surface. The penetration of the length of light is a very important parameter. It is a function of the particle size and use of impurities in the composite. It also supports transparency to radiation, among metals as a light transfer, carbon as light absorptive materials and $TiO_2$ as a photocatalyst. It is not an easy task to control variables effectively with the multiplicity of variables involved given the complexity of the photocatalytic process. The major purpose of

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**Table 1.** Nomenclatures of Metal ($Cu^{2+}$, $Zn^{2+}$)-Carbon/$TiO_2$ Samples Prepared with Phenol Resin and Anatase

| Synthesis Procedure | Nomenclatures |
|---|---|
| 1) Phenol Resin (40%) in EtOH Solution, 2) 0.1 M $CuCl_2$ Soln., 3) Stirring: mixtures of 1) Soln. + 2) Soln., 4) Mixture 3) + Anatase | CRT1 |
| 1) Phenol Resin (40%) in EtOH Solution, 2) 0.5 M $CuCl_2$ Soln., 3) Stirring: mixtures of 1) Soln.+ 2) Soln., 4) Mixture 3) + Anatase | CRT2 |
| 1) Phenol Resin (40%) in EtOH Solution, 2) 0.1 M $ZnCl_2$ Soln., 3) Stirring: mixtures of 1) Soln.+ 2) Soln., 4) Mixture 3) + Anatase | ZRT1 |
| 1) Phenol Resin (40%) in EtOH Solution, 2) 0.5 M $ZnCl_2$ Soln., 3) Stirring: mixtures of 1) Soln. + 2) Soln., 4) Mixture 3) + Anatase | ZRT2 |

*Solvent reflux temperature at Step 4): ca. 378 K
**Heat treatment temperature after Step 4): ca. 973 K

this study is to find common ground for a comparison of the photocatalytic performances between metal-supported carbon-titania and unsupported carbon-titania.

In this study, to metal (Cu, Zn)-carbon/$TiO_2$ composites were prepared with mixing ratios of anatase to phenol resin using an ethanol solvent coagulation method. The roles of metal and carbon were investigated through the preparation of metal (Cu, Zn)-carbon/$TiO_2$ photocatalysts and the determination of their photocatalytic activities. The studied catalysts were characterized according to their BET surface area and by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-rays (EDX) and through the use of a UV/VIS spectrophotometer.

## 2. Experimental Procedure

### *2.1. Materials*

Phenol resin was used as a carbon source in the preparation of the metal (Zn, Cd)-carbon/$TiO_2$ composite. Powdered phenol resin was supplied from Sumitomo Chemical Co. (Japan). Reagent-grade $CuCl_2$ and $ZnCl_2$ as impure metal sources for the synthesis of metal (Cu, Zn)-carbon/$TiO_2$ composites were purchased from Duk-San Pure Chemical Co. (Korea). The pristine $TiO_2$ was commercially available (Duk-San Pure Chemical Co., Korea). They were composed of a single phase of anatase with secondary particles that were approximately 80-150 μm aggregated from primary particles of approximately 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of approximately 98 $m^2/g$. To dissolve the phenol resin, ethanol (Dae-Jung Chemical Co., Korea) was used as solvent. After dissolving the phenol resin in the ethanol solution, 0.5 M of each metal solution was mixed with the phenol resin-ethanol solution. The slurry mixtures of metal carbon precursor with anatase were heated to 333 K for 1 h. The solvent in the mixtures was vaporized at 353 K for 6 h. The agglomerates of metal-carbon-$TiO_2$ were heated to 1023 K for 1 h at an inert atmosphere.

### *2.2. Characterization*

For the BET surface area measurements, nitrogen isotherms were measured using a BEL Sorp analyzer (BEL, Japan) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JEOL, Japan) was used to observe the surface state and structure of the metal (Cu, Zn)-carbon/$TiO_2$ modified using the metal sources and with the phenol resin treatment. X-ray diffraction patterns were obtained using an X-ray generator (Shimadzu XD-D1, Japan) with Cu Kα radiation. Elemental analyses of the metal (Cu, Zn)-carbon/$TiO_2$ composites were performed with an energy dispersive X-ray analyzer (EDX). As one of the types of analyses of the photocatalytic activity, a UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of the catalytic efficiency of the metal (Cu, Zn)-carbon/$TiO_2$ composites.

### *2.3. Photocatalytic effect*

Characterization by methylene blue ($C_{16}H_{18}N_3S$, MB) in water was done via the following procedure. Photocatalytic activities were evaluated by MB degradation in an aqueous media under ultraviolet light irradiation. For UV irradiation, a reaction tube was located axially and held in a UV lamp (20 W, 365 nm) box. The lamp was used 100 mm from the solution in a darkness box. A metal (Cu, Zn)-carbon/$TiO_2$ powdered sample of 0.05 g was suspended in an aqueous solution (ca. 70 mL) with an initial concentration ($c_0$) of $1.0 \times 10^{-5}$ mol/L in a dark atmosphere at room temperature. Before activating the irradiation, the suspension of MB solution containing the metal (Cu, Zn)-carbon/$TiO_2$ composites was stirred with an ultrasonicater in a dark condition for three minutes to establish equilibrium. The suspension was 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 centrifuge. Each concentration was measured as a function of the UV irradiation time from the amount of absorbance in a wavelength range of 300-750 nm from the MB solution as measured by a UV/VIS spectrophotometer. Additionaly, the concentration (c) of the MB solution that decomposed 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 using an extrapolation method.

## 3. Results and Discussion

### *3.1. Surface properties*

Table 2 shows the textural properties of the raw materials

**Table 2.** Textural Properties of Pristine Materials and Metal ($Cu^{2+}$, $Zn^{2+}$)-Carbon/$TiO_2$ Composite Samples

| Sample | Parameter | | | |
|---|---|---|---|---|
| | $S_{BET}$ ($m^2/g$) | Micropore Volume ($cm^3/g$) | Internal Surface Area ($m^2/g$) | Average Pore Diameter (Å) |
| As-received $TiO_2$ | 98.0 | - | - | - |
| CRT1 | 341 | 0.208 | 188 | 9.58 |
| CRT2 | 354 | 0.212 | 196 | 9.65 |
| ZRT1 | 408 | 0.217 | 201 | 9.80 |
| ZRT2 | 421 | 0.225 | 215 | 9.87 |

and metal (Cu, Zn)-carbon/$TiO_2$ composites derived from anatase and phenol resin treated with metals. The results show a slight increase in the BET surface area of the composite samples as the amount of metal increases. The surface areas were measured and calculated from analyses of nitrogen adsorption isotherms. The BET surface area of Cu-carbon/$TiO_2$ was found to be smaller than that of Zn-carbon/$TiO_2$. This was attributed to the modification of the surface by the formation of titania crystals. The surface areas depend on the metal content, which was found to change the pore structure into a phenol resin surface due to raw $TiO_2$. Generally, carbon treatment as an added material experimentally shows that the carbon assembled to most ceramic substrates from carbon precursors is highly microporous.[14] It is plausible to assume that thin carbon layers on the $TiO_2$ particles cause the increase of the BET surface area.[15,16] According to Colon *et al.*,[17] surface area values appear be correlated somewhat with the carbon and titanium source. The higher the percentage, the larger the surface area is. In the present case, this increase in the surface area is directly related with the reactivity between the metal and carbon used in the precipitation. Hence, relevant control of the metal content in the carbon assembled $TiO_2$ samples can allow the adsorbing and decomposing of a relatively large amount of organic pollutants in a liquid phase. It is believed that the increase in the porosity of carbons produced by metal as an activation agent after a heat treatment along with the increases in the surface parameters among composite series are related to the removal and decomposition efficiency of the organic dye. Regarding the metal (Cu, Zn)-carbon/$TiO_2$ composites morphologies, SEM micrographs clearly indicate homogeneity in the shapes of all samples. In Figs. 1 and 2 show selected SEM images of the metal (Cu, Zn)-carbon/$TiO_2$ composite from a different series. The morphologies of the metal (Cu, Zn)-carbon/$TiO_2$ composites prepared via the coagulation method were fairly homogeneous in shape except for the CRT1 series, as can be inferred from the SEM images. It was observed that the ZRT series particles are more homogeneous in shape compared to the CRT series. The CRT series samples (Fig. 1) show heterogeneous and more irregular morphologies, indicating that in this preparation procedure for the CRT series, this method did not lead to homogeneity along the carbon surface, but instead led to, after calcination to a material with irregular

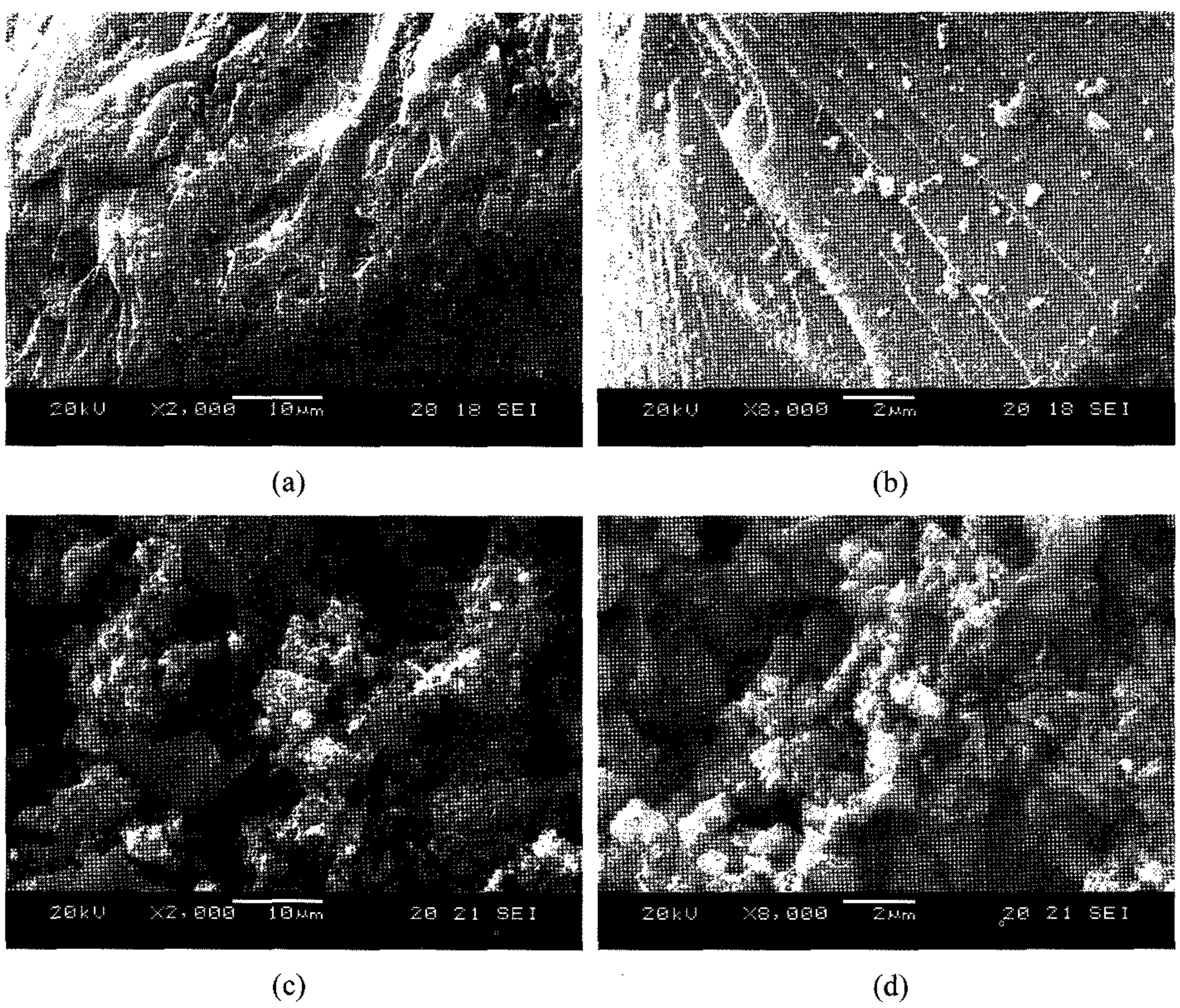


**Fig. 1.** SEM micrographs for the Cu-carbon/$TiO_2$ composites; (a) CRT1 (overall), (b) CRT1 (close-up), (c) CRT2 (overall), and (d) CRT2 (close-up).

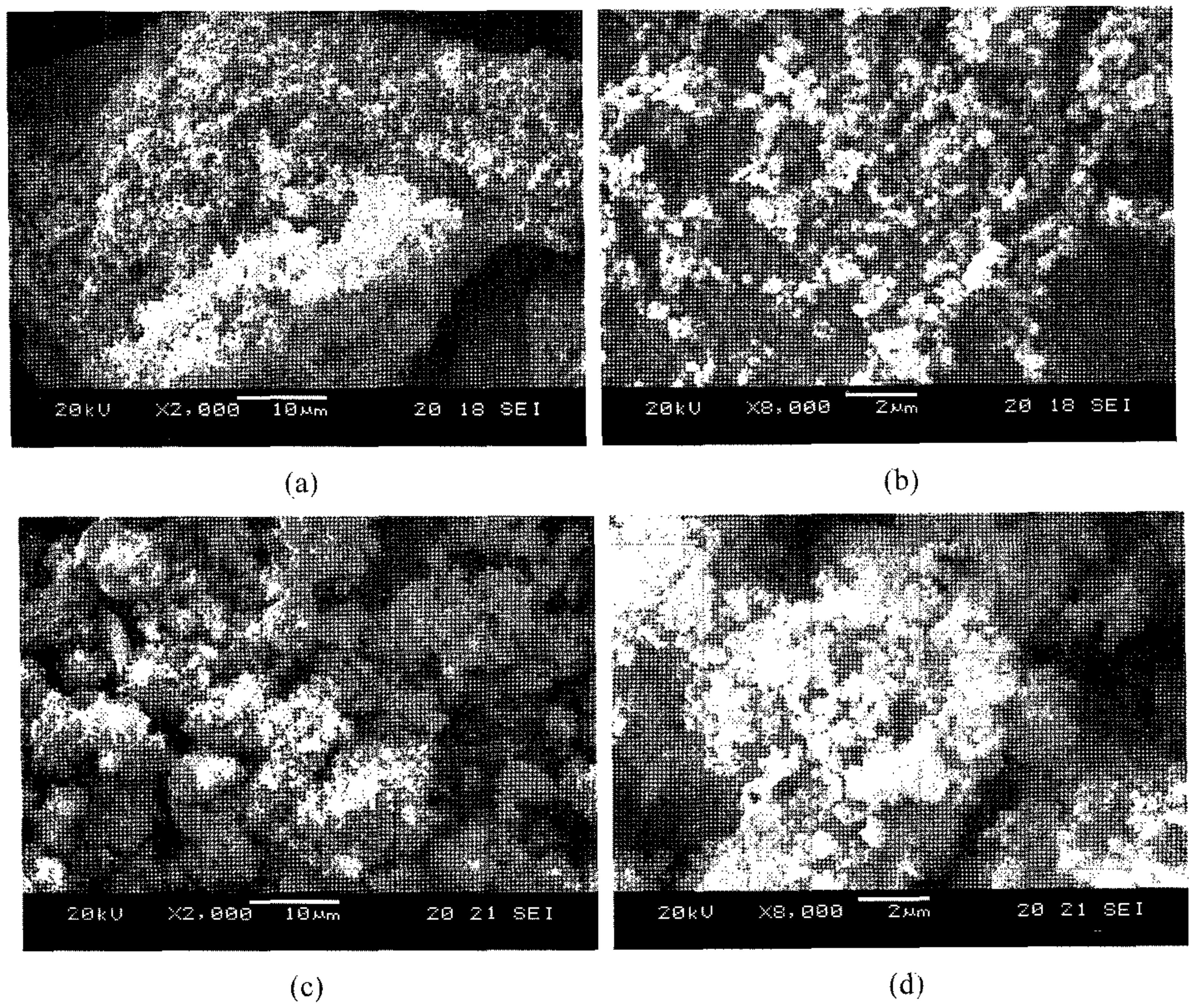


**Fig. 2.** SEM micrographs for the Zn-carbon/$TiO_2$ composites; (a) ZRT1 (overall), (b) ZRT1 (close-up), (c) ZRT2 (overall), and (d) ZRT2 (close-up).

morphology. In the case of the CRT series, small clusters were found largely covering the $TiO_2$ particles. It was considered that a good dispersion of small particles may provide additional reactive sites for the reactants compared to the use of aggregated particles. Generally, graphene layers in carbon in these composite particles can lead to high light-absorption effects. This can participate in the surface photochemical processes, resulting in the oxidation of the adsorbed substrate. The excited state processes of titania composite materials have been investigated in earlier studies.[18,19] Accordingly, a high photocatalytic yield can be expected with a homogenous and small $TiO_2$ particle distribution.

### *3.2. Structural and elemental analysis*

The XRD analysis of metal (Cu, Zn)-carbon/$TiO_2$ composites prepared with two types of metals showed that the anatase phase was dominant at 973 K. The XRD analysis results for the catalysts samples are shown in Fig. 3. In the XRD patterns for all of the metal (Cu, Zn)-carbon/$TiO_2$ composites, the diffraction peaks of carbon were not observed due to the low crystallinity as amorphous carbon and also due to the low carbon content of the materials. However, crystalline $TiO_2$ was clearly detected. The patterns of these composites showed narrow diffraction peaks, reflecting that, after the calcinations, the $TiO_2$ particles underwent transformation of rutile phase, with the exception of ZRT2. The main crystalline phase showed the rutile characteristics of (101), (103), (112), (105), (211), (204), (116) and (220). In the case of ZRT2, however, the relative content of the anatase or rutile phase not found, and zincite and zinc titanium oxide phase were the primary types on the sample. The XRD patterns of $TiO_2$/carbon composites from Maldonado-Hodar *at. al.*[2] showed a 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. In this case, the addition of metallic salts in the carbon sources in the carbonization process can catalyze the phase transformation from the anatase phase to the rutile phase at low temperatures. In former studies of the formation of $TiO_2$ from organometallic titanium sources,[20] XRD results showed that the anatase phase wil disappear depending on the temperature and the preparation process. It was considered that several preparation factors, such as an increase in the heat treatment temperature and changes in the mixing ratio of the solvents in the sol-gel methods, influence the phase transformation from pure anatase phase to rutile phase.

A quantitative microanalysis of C and Ti as major elements for the metal (Cu, Zn)-carbon/$TiO_2$ composites was performed by EDX. The EDX spectra of metal (Cu, Zn)-carbon/$TiO_2$ composites are shown in Fig. 4. Carbon-coated solid particles and composite-type carbon for the elemental analyses have been reported with various types of titania.[5,6] In this study, the spectra showed the presence of major elements of C and O with strong Ti peaks. Interesting correlations can be established between the SEM morphology and the carbon content in the metal (Cu, Zn)-carbon/$TiO_2$ series.

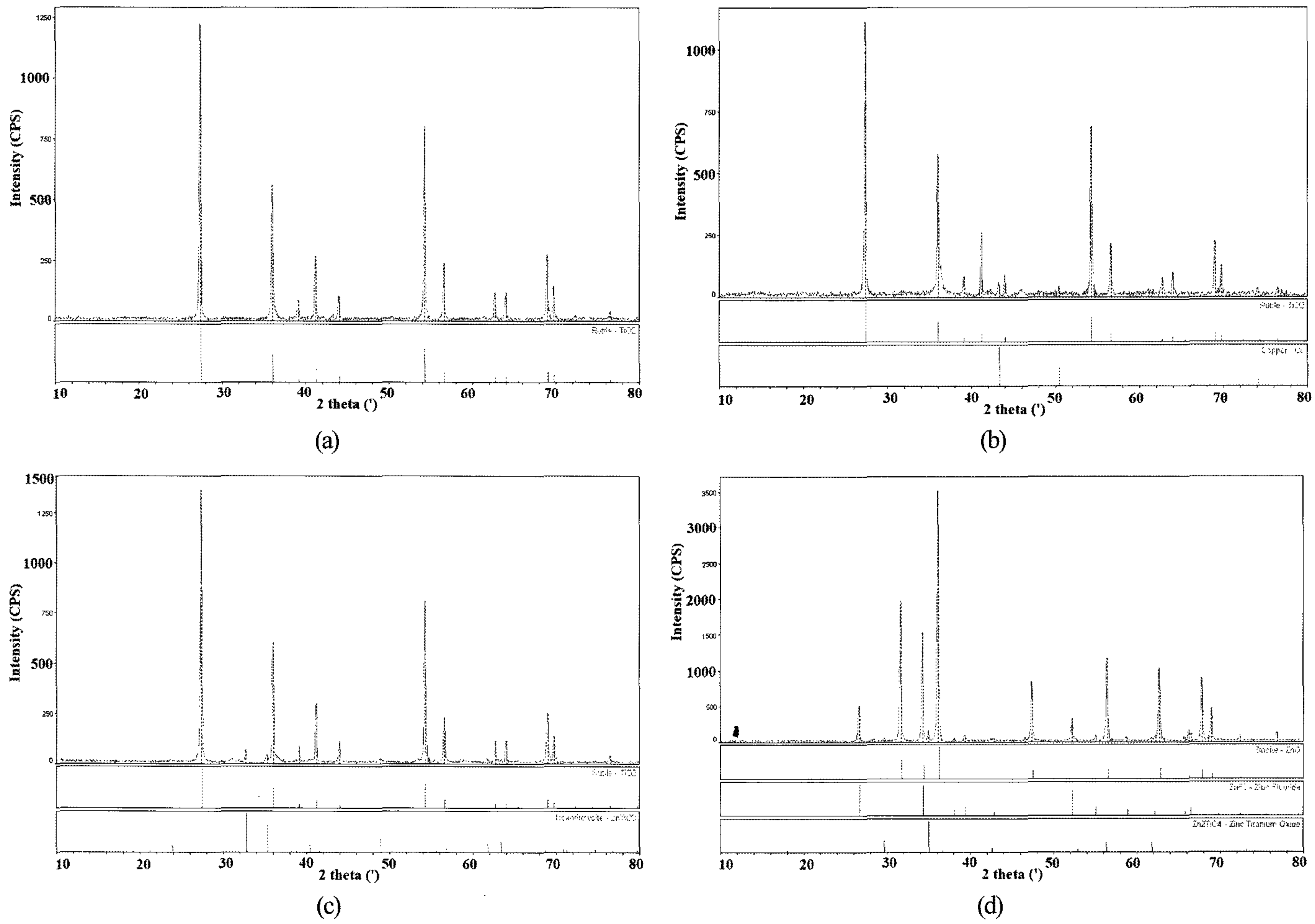


**Fig. 3.** XRD patterns of metal (Cu, Zn)-carbon/$TiO_2$ composites derived from phenol resin and anatase; (a) CRT1, (b) CRT2, (c) ZRT1, and (d) ZRT2.

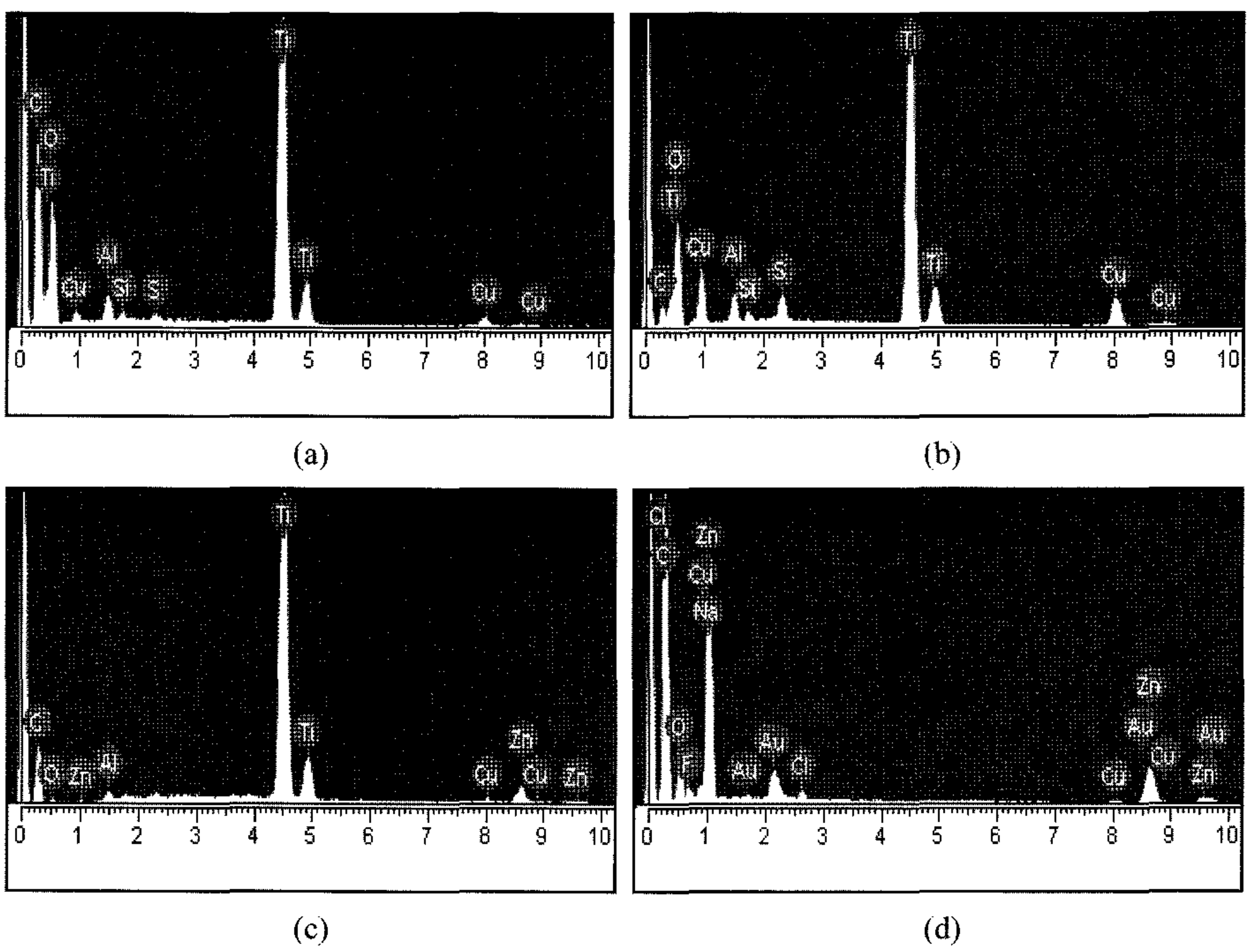


**Fig. 4.** EDX elemental microanalysis of the metal (Cu, Zn)-carbon/$TiO_2$ composites derived from phenol resin and anatase; (a) CRT1, (b) CRT2, (c) ZRT1, and (d) ZRT2.

**Table 3.** EDX Elemental Microanalysis of Metal ($Cu^{2+}$, $Zn^{2+}$)-Carbon/$TiO_2$ Composites

| Sample (wt%) | C | O | Zn | Ti | Cu | Others |
|---|---|---|---|---|---|---|
| CRT1 | 30.4 | 32.9 | - | 25.0 | 8.32 | 3.38 |
| CRT2 | 39.6 | 4.63 | - | 38.1 | 17.35 | 0.32 |
| ZRT1 | 28.3 | 15.5 | 10.6 | 42.7 | 2.00 | 0.88 |
| ZRT2 | 31.4 | 10.1 | 14.8 | 43.1 | - | 0.60 |

Additionally, it is clear that for ZRT samples with higher titanium contents, they present significantly smaller carbon content compared to those of the CRT samples. These results show a relationship between the catalytic effect 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 metal (Cu, Zn)-carbon/$TiO_2$ series are shown in Table 3. Here, it can be observed that the amounts of O decrease as the metal content in the pentration procedure increases. Accordingly, the amount of Ti decreased as the phenol resin content in the series of the metal (Cu, Zn)-carbon/$TiO_2$ composites increase.

### *3.3. Photocatalytic effect of MB*

Photocatalytic studies showed that both CRT and ZRT samples could photocatalyze the degradation of MB. Changes of the absorbance after a color removal process in the relative MB degradation concentration of the composites under UV light irradiation are shown in Fig. 5. Organic dye (MB) degradation with metal (Cu, Zn)-carbon/$TiO_2$ was used to measure the UV light photolysis effect. In this procedure, measurement of the $\lambda_{max}$ value in the 300 nm to 750 nm region with degraded MB products was done as a function of the degradation time for the metal (Cu, Zn)-carbon/$TiO_2$ composites. It was found that the $\lambda_{max}$ values showed a lower absorbance region with an increase of the irradiation time. As shown in earlier studies,[21-24] if the concentration of organic dyes used is higher, the intensity of the absorbance maxima ($\lambda_{max}$) values cannot be estimated by the photoproduct that forms as a function of the irradiation time. The formation of $\lambda_{max}$ was proportional to the concentration decrease of the transient formed after UV light excitation. Although the formations of the $\lambda_{max}$ values for the MB decomposed by the CRT samples was larger than that of the MB decomposed by the ZRT samples, the differences very small. The sharp decrease in the $\lambda_{max}$ values of absor-

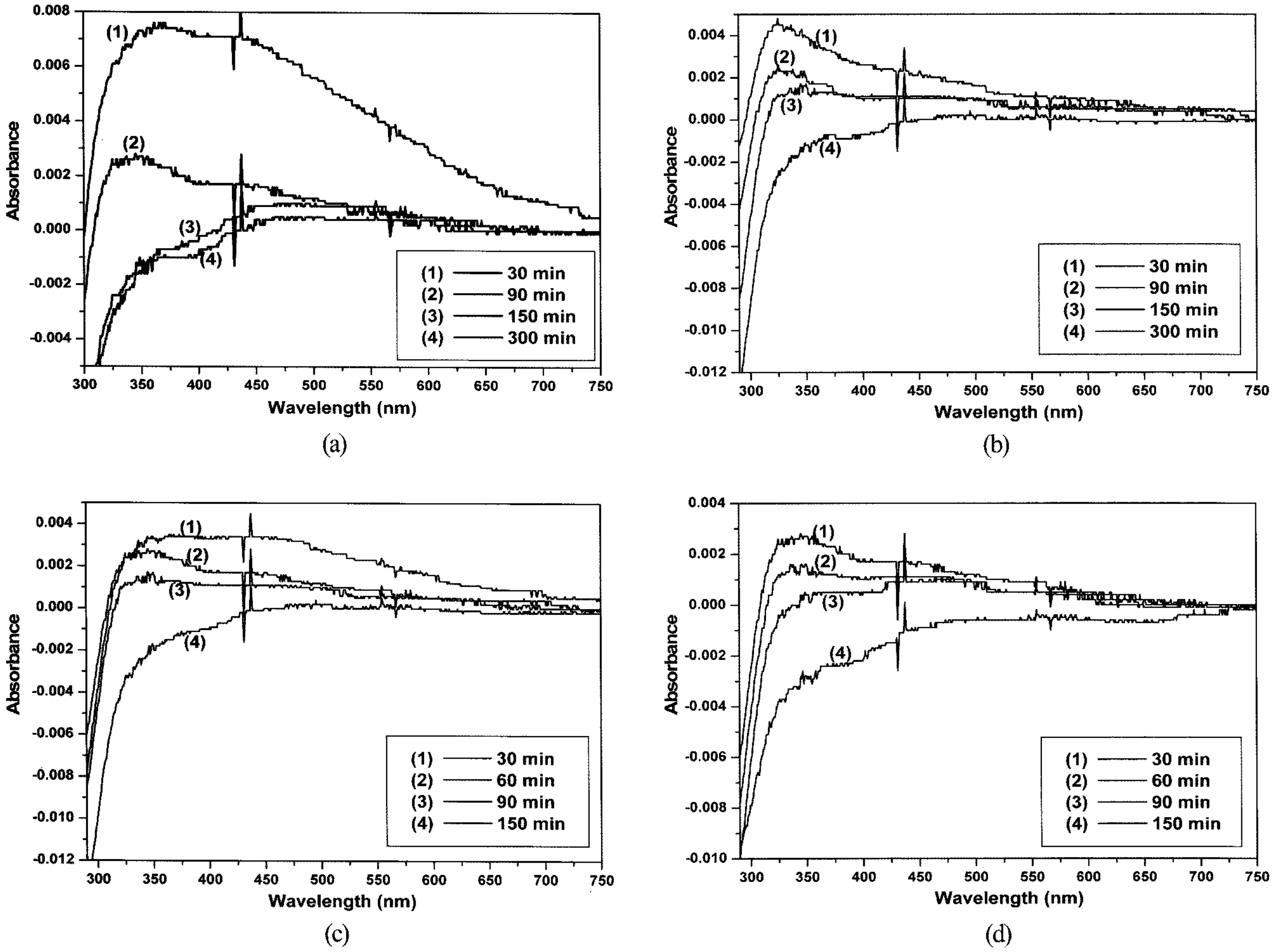


**Fig. 5.** Absorbance variation of the MB concentration against the metal (Cu, Zn)-carbon/$TiO_2$ composites derived from phenol resin and anatase; (a) CRT1, (b) CRT2, (c) ZRT1 and (d) ZRT2.

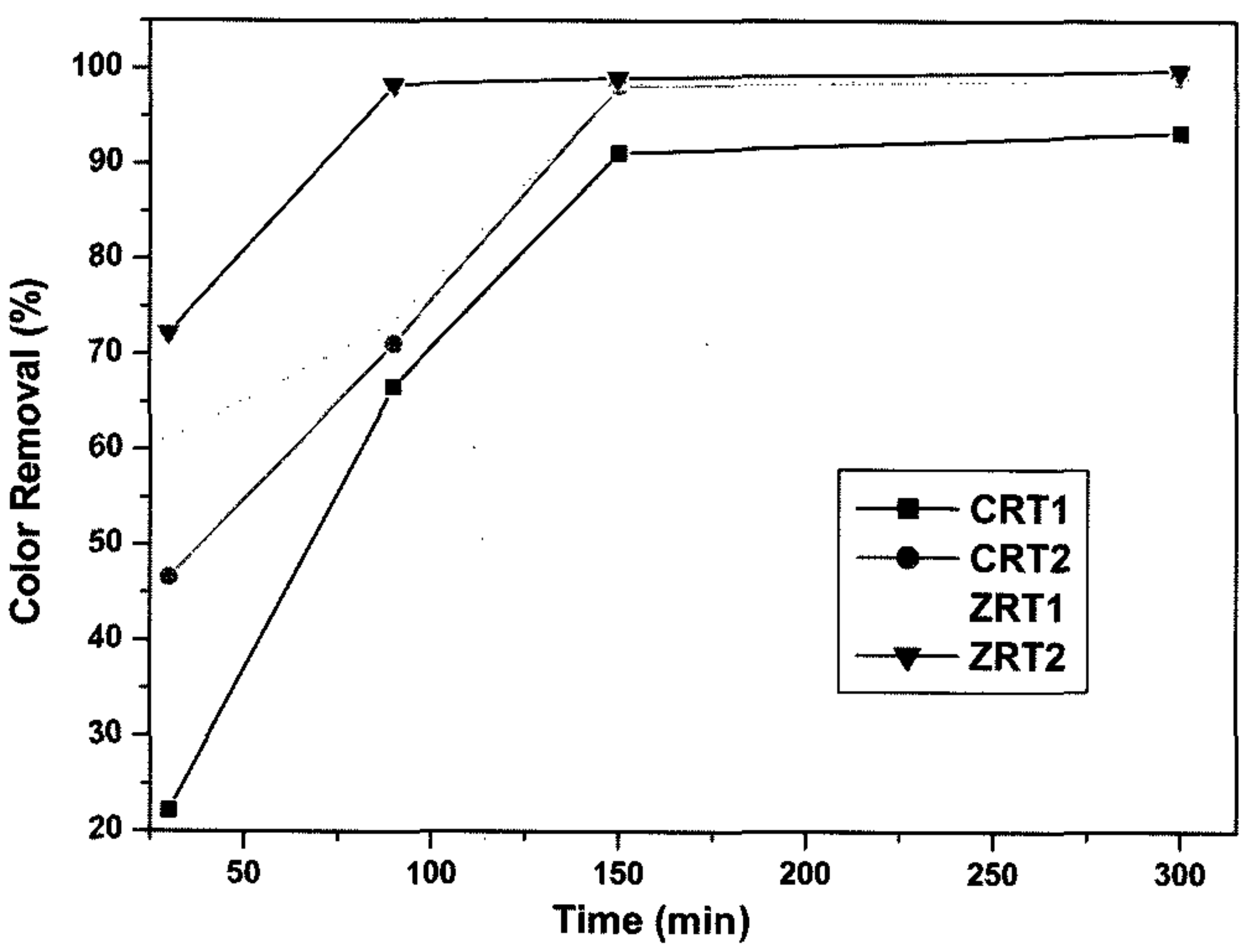


**Fig. 6.** Color removal of the MB solution under the presence of photocatalysts with time.

bance was attributed to a degradative reaction. In pristine $TiO_2$ suspensions, water molecules and hydroxyl ions act as electron donating species. Oxygen in experiments conducted in the presence of air or water act as electron accepting species.[13] In modified metal (Cu, Zn)-carbon/$TiO_2$ suspensions, an additional electron accepting species was introduced, in the form of carbon layers and metal species in the composites. The light transparency of the MB solution with an increase of irradiation time highly increases due to the photocatalytic degradation effect. The enhanced activity of metal (Cu, Zn)-carbon/$TiO_2$ particles for the formation of the carbon layer and metal species as a result of additional materials in the $TiO_2$ suspensions can be attributed to three factors: enhancements of the separation of electron and holes by absorption of the light from carbon graphene or metal species, an adsorption effect due to high porosity on the carbon surfaces and the chemical decomposition effect of the organics by the Cu and Zn species.

Plots of the decolorization effect after removal of the color with time are shown in Fig. 6. The tendencies of changes by removal of the color disappearance are presented in terms of removal percentages of the concentration of the MB that degraded in the aqueous solution. The disappearance due to the photo-degradation effect may have been due to the combination of the presence of UV light and the oxidation effect of dissolved oxygen in the suspension. In this study, it is considered that the carbon layer and Cu and Zn species in the composite can accept a photo-induced electron ($e^-$) caused by UV irradiation. Moreover, electrons in the carbon layer including the metal species can be transferred into the conduction band in the $TiO_2$ particles. When this occurs, these electrons in the conduction band may react with $O_2$, which can trigger the formation of the highly reactive superoxide radical ion ($O_2^{\cdot-}$). It was also considered that the organic dye solution is relatively unstable with variations of its concentration when irradiated under UV light with metal (Cu, Zn)-carbon/$TiO_2$ composites. As above mentioned, carbon graphene layers utilized an energy sensitizer to improve the quantum efficiency with an increase in the degree of electron transfer. As the organic molecules absorbed energy from irradiation, their delocalized electrons can shift from the bonding to the antibonding orbital.[19,24,25] The enhanced degradation of the MB as a pollutant on metal (Cu, Zn)-carbon/$TiO_2$ composites can be attributed to the combination effect of the carbon and metal species along with the $TiO_2$ followed by a transfer through an interphase to titania, at which point it is photo-degraded. As shown in earlier studies,[5,6,11] the combination effects of the degradation of MB have been attributed to the three synergetic effects: photocatalysis, adsorptivity and electron transfer by light absorption between supporter $TiO_2$ and carbon. As shown in Fig. 6, the color removal effects for the ZRT series result in a more significant degradation effect with an increase of time function of compared to that of the CRT series. The rate-determining step in photocatalytic oxidation process is believed to be the transfer of electrons derived from carbon including metal species from the $TiO_2$ surface to the oxygen molecules.

## 4. Conclusions

In this study, the preparation and characterization of metal (Cu, Zn)-carbon/$TiO_2$ composites by controlling of amount of metal species in phenol resin were investigated. The role of three component types (metal, carbon and titania) in the composite and their photocatalytic performance were investigated through structural variations, elemental analyses, surface morphology and photo-degradation. The surface textural properties were confirmed by observing SEM morphologies and BET surface parameters. The XRD patterns revealed that rutile phase and some type of metal complexes can be identified for metal(Cu, Zn)-carbon/$TiO_2$ composites. It was also observed that the diffraction peaks of carbon were absent due to the low carbon contents on the $TiO_2$ surfaces and due to the low crystallinity of the amorphous carbon. The results of the elemental analyses of the metal (Cu, Zn)-carbon/$TiO_2$ composites showed that most of the spectra for these samples showed stronger peaks for carbon, Ti and treated metal species compared to any other element. According to the photocatalytic results, a relationship exists between the absorbance and the color removal of the MB solution products regarding the concentration conversion properties depending on the time function. Finally, the enhanced degradation of the MB dye on metal (Cu, Zn)-carbon/$TiO_2$ composite was attributed to the corporation effect of the carbon and metal species in addition to $TiO_2$ followed by an electron transfer through an interphase to titania.

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