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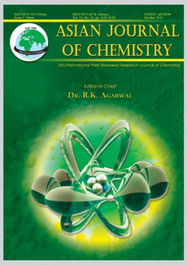

Preparation of ZnO/CNC Nanocomposite and Evaluation of Photocatalytic Activity in Various Organic Dyes

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Zinc oxide nanoparticles (ZnO) were synthesized by an aqueous alcoholic reaction between zinc nitrate and sodium hydroxide under ultrasonic irradiation at room temperature and their photocatalytic activities were examined using various organic dyes. To fabricate the ZnO/carbon nanocolloid (CNC) nanocomposite, ZnO and carbon nanocolloid were heated in an electric furnace at 700 °C for 2 h. The optical properties of the unheated ZnO/CNC (UH-ZnO/CNC) and heated ZnO/CNC (H-ZnO/CNC) nanocomposites were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The photocatalytic activities of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposites to degrade organic dyes, such as methylene blue, rhodamine B, methyl violet and methyl green under ultraviolet light at 365 nm were examined by UV-VIS spectroscopy. The heated-ZnO/CNC nanocomposite showed more efficient photocatalytic activity in the degradation of various organic dyes than the unheated-ZnO/CNC nanocomposite, especially with the degradation of methylene blue.

Key Words: ZnO, Carbon nanocolloid, ZnO/CNC nanocomposite, Photocatalytic activity, Organic dyes.

INTRODUCTION

The management, treatment and fundamentally the eradication of hazardous materials, such as organic compounds, from wastewater effluents has attracted considerable attention. Several methods for eliminating of hazardous materials have been developed, but they do not satisfy the stringent environmental quality standards. Therefore, more aggressive treatment approaches are needed. One enhanced method is advanced oxidation technologies (AOT), such as photolysis, photofenton, ozonolysis, sonolysis and photocatalysis. Advanced oxidation technologies produce high oxidizing species and radicals. Among the advanced oxidation technologies methods, photocatalysis is at the forefront due to its capacity for the total destruction of pollutants, non-selectivity and ultimately its potential to generate less harmful and more environmentally friendly products[1]. Some studies reported that nanostructured metal oxides can degrade various organic pollutants under UV light irradiation. Therefore, many kinds of metal oxides nanostructure photocatalysts, such as Bi_2O_3, Fe_2O_3, TiO_2, ZnO have been assessed for their enhanced properties and suitable application to environmental remediation[2-5]. Among these nanostructured metal oxides, ZnO and TiO_2 are promising materials as photocatalysts because of their high photosensitivity, nontoxic nature and large band gap[6-9]. ZnO is adequate suitable alternative to TiO_2 because of its similar band gap energy (3.37 eV) and low cost[10]. ZnO absorbs mainly in the UV region because of its wide band gap. Abundant studies report an improvement in the photocatalytic activity of metal oxides by doping with cations[11], anions[12], metals[13] and non-metals[14]. In terms of studying the mechanism of photocatalysis, ZnO is quite strongly luminescent, which facilitates a study of the recombination of electron-hole pairs and is a suitable way of investigating the photocatalytic activity mechanism. The emission properties of ZnO have also been used to sense the presence of organic molecules in its immediate vicinity[15].

Carbon nanocolloids are stable enough that precipitation does not occur, even after a few months. The characteristics of carbon nanocolloids include high heat and electrical conductivity as well as lubricous properties, which gives them a wide range of uses in many industries[16].

The photocatalytic properties of ZnO and the efficient conductivity of carbon nanocolloid (CNC) suggest that a combination of ZnO and CNC would show improved photocatalytic activity. This paper reports the preparation of ZnO/CNC nanocomposites. In addition, the photocatalytic activity of the unheated ZnO/CNC (UH-ZnO/CNC) nanocomposite and heated ZnO/CNC (H-ZnO/CNC) nanocomposite was examined in various organic dyes under UV light at 365 nm per 20 min.

EXPERIMENTAL

Zinc nitrate hexahydrate, ethanol, sodium hydroxide and tetrahydrofuran were purchased from Samchun chemicals. The carbon nanocolloids (CNC) were supplied by N-barotech. The organic dyes (methylene blue, rhodamine B, methyl violet and methyl green) were obtained from Sigma-Aldrich.

All samples, unheated ZnO/CNC and heated ZnO/CNC nanocomposites were treated under a range of conditions by ultrasonic irradiation using an ultrasonic generator UGI 1200 (Hanil Ultrasonic Co., Ltd.) with a frequency 20 kHz and a power of 750 W. The ultrasonic generator was a horn type system with a horn tip diameter of 13 mm. An electric furnace (Ajeon Heating Industry Co., Ltd.) was used to heat the sample. A UV lamp (8 W, 365 nm, 77202 Marne La Valee-cedex 1 France) was used as the ultraviolet light irradiation source.

The surfaces of the unheated ZnO/CNC and heated ZnO/CNC nanocomposites were observed by SEM (Hitachi S4700) at an accelerating voltage of 0.5 to 15 kV. The morphology and crystallite size of the samples were examined by TEM (JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The structures of the nanomaterials were examined by XRD (Rigaku, Rigaku DMAX PSPC MDG 2000). UV-Vis spectroscopy for analyzing samples was performed by UV-Vis spectrometer (Shimazu UV -1601PC).

Synthesis of ZnO under ultrasonic irradiation: Zinc nitrate hexahydrate (1 M) and sodium hydroxide (10 M) were dissolved separately in distilled water (6 mL) at room temperature. Ethanol (15 mL) was added to each solution. The solutions were combined in a beaker and exposed to ultrasonic irradiation in a water bath at room temperature for 45 min. At the end of the reaction, the mixture had separated two phase, one is a white precipitate and the other is a transparent solution. The white precipitated particle was washed with distilled water and ethanol the eliminate the remaining ions, such as Zn^{2+}, Na^+, NO_3^- and OH^- and dried at room temperature[17].

Preparation of unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite: To prepare the unheated-ZnO/CNC nanocomposite, synthesized ZnO and CNC were placed in a vial containing tetrahydrofuran (10 mL) and stirred vigorously at room temperature for 1 h. The mixture was poured into a glass dish and dried at room temperature for 2 h. The preparation method of heated-ZnO/CNC nanocomposite was similar to the process of the unheated-ZnO/CNC nanocomposite. Synthesized ZnO and CNC were placed in a vial containing tetrahydrofuran and stirred at room temperature for 1 h. The mixture was poured into a vessel and heated in an electric furnace. The vessel was placed in an electric furnace under Ar gas at 700 ºC for 2 h and dried at room temperature for 6 h.

Evaluation of various organic dyes with unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite: The photocatalytic activities of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposites were evaluated by UV-VIS spectroscopy using various organic dyes, such as methylene blue, rhodamine B, methyl violet and methyl green under UV light every 20 min. Before evaluating the photocatalytic activities of each photocatalyst, a 0.01 mM solution of various organic dyes were prepared in a vial. 10 mg of each photocatalyst were placed into these vials. A vial of containing the organic dye and photocatalyst was exposed to UV light of 365 nm wavelength at room temperature.

RESULTS AND DISCUSSION

The crystallinity of unheated-ZnO/CNC and heated-ZnO/CNC was examined by X-ray diffraction (XRD) (Fig. 1). The XRD pattern of the unheated-ZnO/CNC nanocomposite showed peaks at 10.85, 20.47, 23.51, 27.61, 31.65, 35.16, 35.87, 45.98, 57.17, 62.85, 66.10 67.57, 68.23, 73.85, 76.42 as a 2θ. The XRD pattern of the heated-ZnO/CNC nanocomposite showed peaks at 31.98, 34.89, 36.11, 47.37, 56.86, 62.9, 66.28, 67.82, 68.95, 72.67, 76.90 as a 2θ. Most peaks of XRD were assigned to ZnO, but the peaks at < 30° as a 2θ were assigned to CNC. The XRD pattern of the unheated-ZnO/CNC nanocomposite in Fig 1(a) confirmed the synthesis of ZnO with good purity. On the other hand, CNC peaks in the XRD pattern (Fig. 1(b)) of the heated-ZnO/CNC nanocomposite showed lower intensity than those of the unheated-ZnO/CNC nanocomposite in Fig. 1(a). The CNC peaks in the XRD pattern of the heated-ZnO/CNC nanocomposite were the result of a thermal treatment. In a previous paper, high temperatures caused the transformation of carbon material structures from crystal to fragments[18].

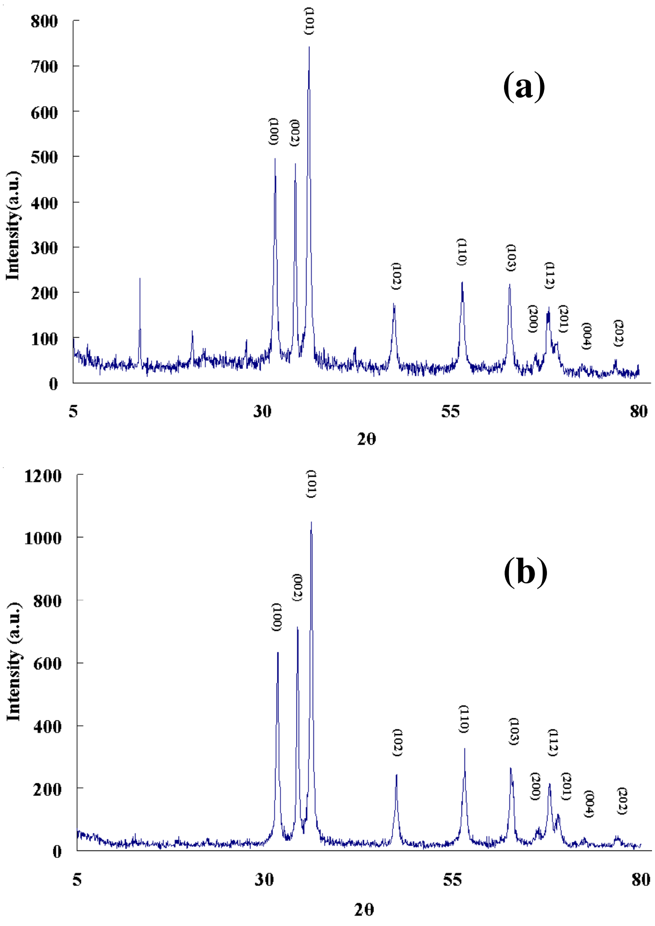
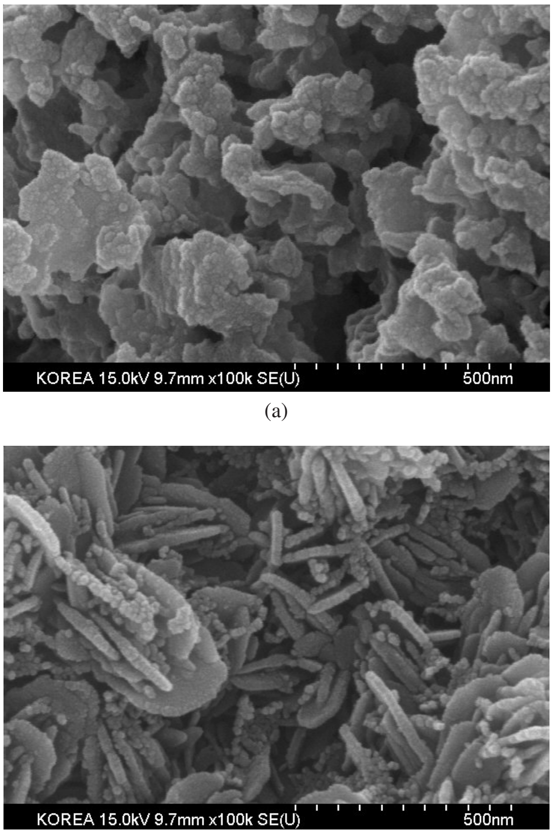


Fig. 1. XRD patterns of (a) unheated-ZnO/CNC and (b) heated-ZnO/CNC nanocomposite

The morphology and nanostructure of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite were characterized



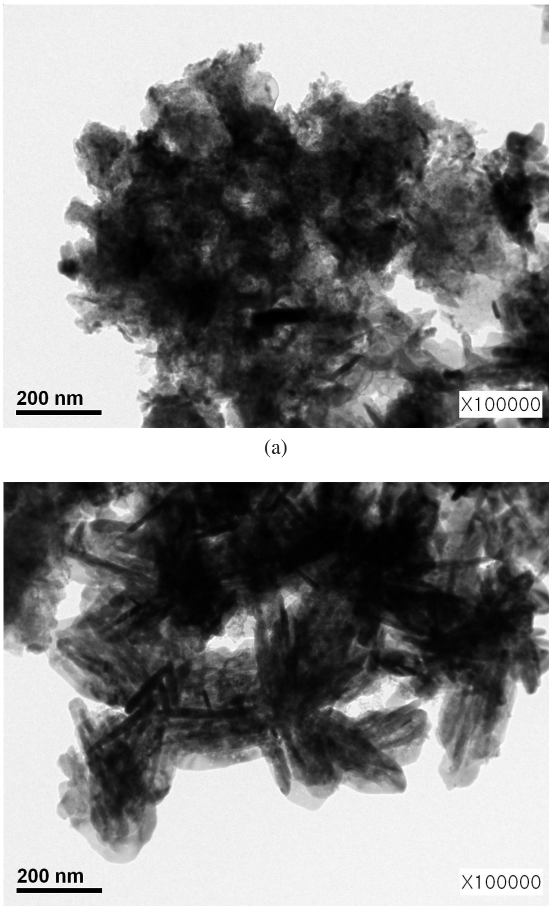
(a)

(b)

Fig. 2. SEM images of (a) unheated-ZnO/CNC and (b) heated-ZnO/CNC nanocomposite

by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2 shows SEM images of (a) unheated-ZnO/CNC and (b) heated-ZnO/CNC nanocomposite. SEM of unheated-ZnO/CNC nanocomposite (Fig. 2(a)) revealed plate-like structures of CNC and fragments of ZnO on the CNC structure. Fig. 2(b) shows the transformation of each nanostructure of ZnO and CNC by thermal treatment. ZnO was aggregated and grown like a flake type. This indicates an increase in the concentration and crystallinity of ZnO. In the case of the CNC shown in Fig. 2(b), there was an increase in surface area because the structure of CNC had fragmented from a plate-like structure. TEM was used to examine the microstructure of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposites (Fig. 3) to provide information on the transformation of ZnO and CNC after the thermal treatment. In Fig. 3(a), the structure of ZnO was unclear because CNC had agglomerated. On the other hand, Fig. 3(b) shows that the thermal treated structure of ZnO had transformed from fragments to a flake-type structure. In addition, the CNC structure was located on the ZnO surface.

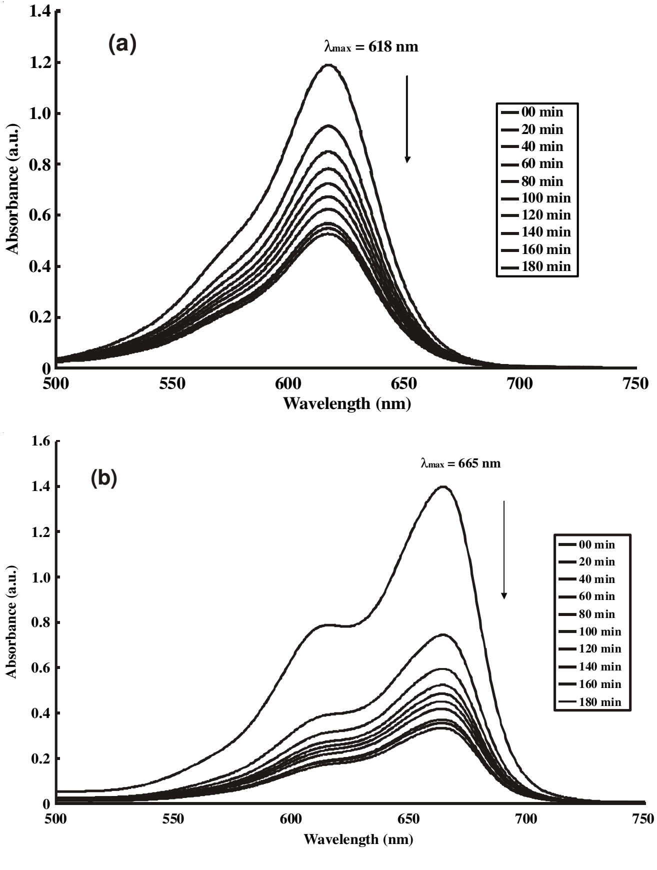
Figs. 4 and 5 show the photocatalytic activity of unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite in degrading organic dye, such as (a) methylene blue, (b) methyl green, (c) methyl violet and (d) rhodamine B. The initial concentration of each organic dye was 0.01 mM and they were exposed to UV light at 365 per 20 min. In Fig. 4, the unheated-ZnO/CNC nanocomposite did not show good photocatalytic performance in the degradation of each organic dye under UV light at 365 nm. Most of the organic dye was degraded by the unheated-



(a)

(b)

Fig. 3. TEM images of (a) unheated-ZnO/CNC and (b) heated-ZnO/CNC nanocomposite.



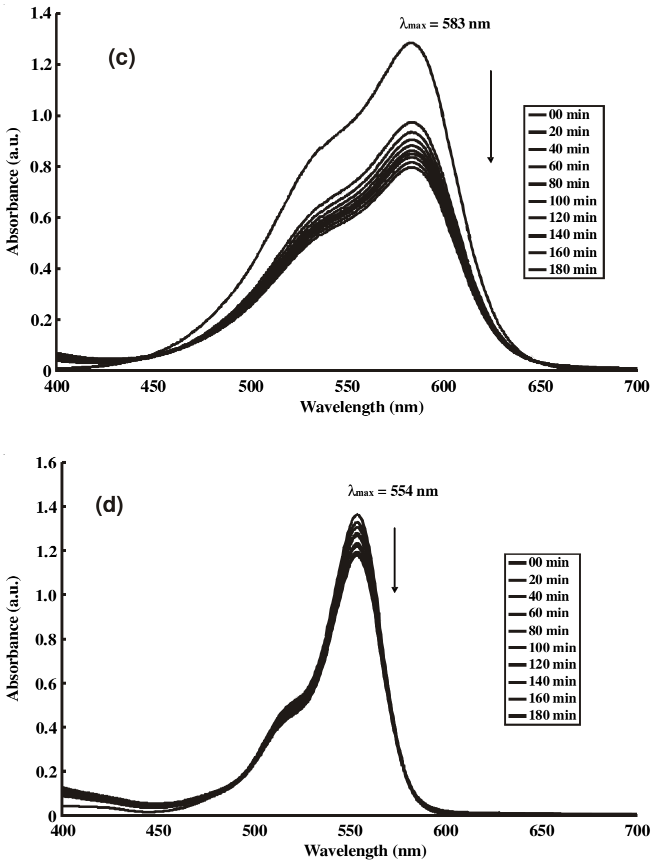
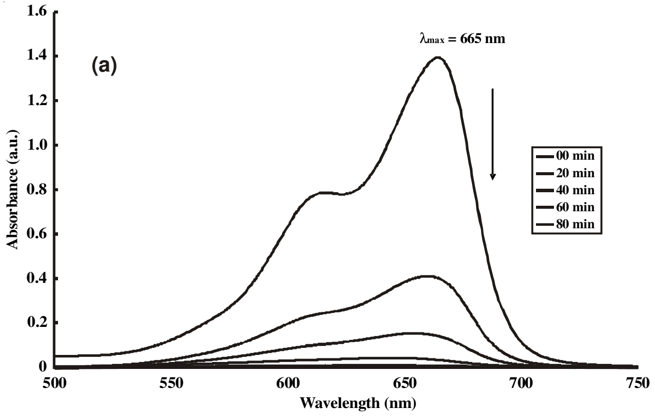


Fig. 4. UV-vis spectra of various organic dyes; (a) methylene blue, (b) methyl green, (c) methyl violet and (d) rhodamine B with unheated-ZnO/CNC nanocomposite under UV light at 365 nm

ZnO/CNC nanocomposite and UV light required considerable time to convert the dye to water and carbon dioxide. On the other hand, heated-ZnO/CNC nanocomposite produced enhanced degradation of the organic dyes, as shown in Fig. 5, because the thermal treatment caused activation as well as an increase in surface area. Methylene blue showed the fastest conversion rate of all the dyes examined, requiring 80 min to convert all the methylene blue.

Conclusion

This paper reports the synthesis of ZnO, unheated-ZnO, and heated-ZnO as well as characterization of photocatalytic activity. The photocatalytic activity of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite was evaluated in various organic dyes under UV light at 365 nm. The physical properties of the unheated-ZnO/CNC and heated-ZnO/CNC nanocomposite were characterized by XRD, SEM and TEM. UV-VIS spectroscopy was used to measure the concentration of the organic dyes degraded by the photocatalyst and UV light at 365 nm. heated-ZnO/CNC as a photocatalyst was applied to the degradation of various organic dyes, such as methylene blue, methyl green, methyl violet and rhodamine B, to water and carbon dioxide under UV light at 365 nm. Further studies of these nanomaterials as a photocatalyst for the decontamination of waste water are currently underway.



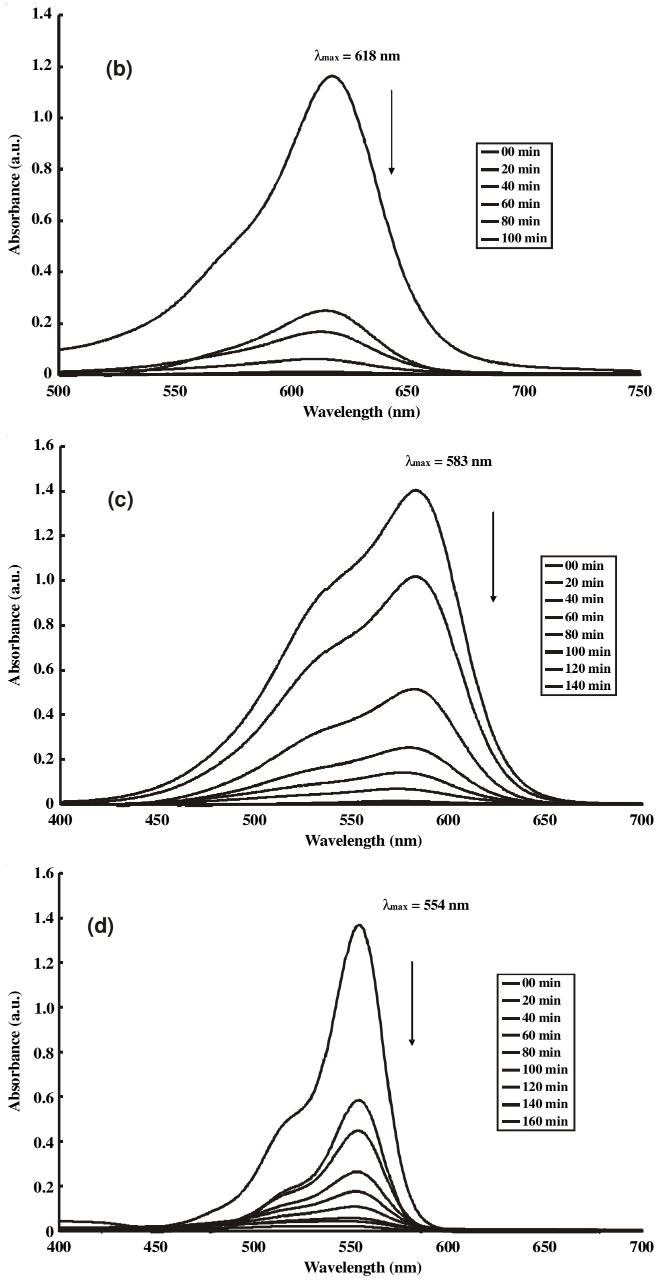


Fig. 5. UV-vis spectra various organic dyes; (a) methylene blue, (b) methyl green, (c) methyl violet and (d) rhodamine B with heated-ZnO/CNC nanocomposite under UV light at 365 nm

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