



Photocatalytic Degradation of Methylene Blue by Graphene Impregnated with CeO₂ Nanoparticles under Ultrasonic Irradiation

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Graphene/CeO₂ nanocomposites were synthesized in an erlenmeyer flask from hexadecyl trimethylammonium bromide, ammonium cerium nitrate and graphene. Water and ethanol were added to the mixture and stirred until complete dissolution. After exposing the solution to ultrasonic irradiation for 1 h, the colloid was filtered, washed with distilled water and dried overnight in air. The graphene/CeO₂ nanocomposites were calcinated in an electric furnace at 700 °C for 2 h. The resulting of the heated graphene/CeO₂ nanocomposites were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The photocatalytic properties of the heated graphene/CeO₂ nanocomposites in the degradation of an organic dye, methylene blue, under ultraviolet light at 254 nm were confirmed by UV-Vis spectrophotometer.

Key Words: Graphene/CeO₂ nanocomposites, Methylene blue, Photocatalytic degradation.

INTRODUCTION

Graphene is a new carbon allotrope that has attracted considerable attention owing its unique properties¹. Graphene was synthesized by the exfoliation of graphite crystals in 2004². In carbon composites³⁻⁵, graphene can serve as high performance supporters because of its ideal two-dimensional structure, excellent electrical conductivity, good chemical stability and large specific surface area⁶⁻⁸. Several metal oxide nanoparticles can be dispersed uniformly on the graphene surface and charge can be transferred by the interface of these hybrid nanomaterials, they can have a synergistic effect by a combination of the properties of each individual component. Some metal oxides have been investigated and reported to exhibit a range of enhanced properties⁹⁻¹³.

Cerium oxide is one of the most reactive rare earth materials and has been studied extensively for a range of applications including fast ion conductors, catalysis, UV blockers, oxygen storage capacitors, polishing materials and electrolytes for solid oxide fuel cells^{14,15}. CeO₂ and CeO₂-based nanocomposites are also important for environmental protection. In particular, CeO₂-based mixed oxides and supported CeO₂ are effective catalysts for the removal of organic compounds from polluted water and for the oxidation of different hydrocarbons in range of sources¹⁶⁻¹⁹.

In this paper, the impregnation of graphene/CeO₂ was performed using an ultrasonic method. The graphene/CeO₂

nanocomposites were examined as a catalyst for the photocatalytic degradation of methylene blue by UV-visible spectrophotometry²⁰. The photocatalytic effects of the heated graphene/CeO₂ nanocomposites were compared with those of unheated graphene/CeO₂ nanocomposites in methylene blue solution under irradiation with ultraviolet light at 254 nm. In addition, graphene/CeO₂ nanocomposites were characterized by XRD, SEM and TEM.

EXPERIMENTAL

Graphene was purchased from Enano Tech. Tetrahydrofuran and ethanol were obtained from Samchun Chemicals. Hexadecyl trimethylammonium bromide, ammonium cerium(IV) nitrate and methylene blue were supplied by Sigma-Aldrich.

Cerium oxide was treated under a range of conditions with ultrasonic irradiation using an ultrasonic generator (UGI 1200, Hanil Ultrasonic Co., Ltd.) with a nominal frequency 20 kHz and 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 graphene/CeO₂ nanocomposites and heated graphene/CeO₂ nanocomposites were observed by SEM (Hitachi S4700) at an accelerating voltage of 0.5-15 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 (Bruker, D8 Advance, Germany). UV-visible spectra of the samples were performed using an UV-visible spectrophotometer (Shimadzu UV-1601PC).

Synthesis of graphene/CeO₂ by an ultrasonic method:

Hexadecyl trimethylammonium bromide (12.5 g), ammonium cerium nitrate (0.2 g) and graphene (0.1 g) were placed in an erlenmeyer flask. Water (10 mL) and ethanol (10 mL) were added to the mixture, which was stirred for dissolution. After irradiating the solution ultrasonically for 1 h, the colloid was filtered, washed with distilled water and dried overnight in air. After drying, the sonochemically synthesized graphene/CeO₂ nanocomposites were heated in an electric furnace at 700 °C for 2h.

Characterization and photocatalytic activity: The photocatalytic activity of the unheated graphene/CeO₂ nanocomposites and heated graphene/CeO₂ nanocomposites were examined using methylene blue. 10 mg of each nanomaterial was dispersed in 10 mL of water containing 0.01 mM of methylene blue. All the mixed solutions were irradiated with ultra-violet light at 254 nm for 1 min with intervals. The photocatalytic degradation of methylene blue by each nanomaterial under ultraviolet light was characterized by UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1 showed SEM images of the unheated graphene/CeO₂ nanocomposites in Fig. 1(a) and heated graphene/CeO₂ nanocomposites in Fig. 1(b). The CeO₂ nanoparticles in both the unheated graphene/CeO₂ nanocomposites and heated graphene/CeO₂ nanocomposites were located above the graphene nanoparticles. After heat treatment, the graphene nanoparticles in the heated graphene/CeO₂ nanocomposites were broken into smaller particles. The CeO₂ nanoparticles in the heated graphene/CeO₂ nanocomposites showed wider dispersion than those in the unheated graphene/CeO₂ nanocomposites.

Fig. 2 showed TEM images of the unheated graphene/CeO₂ nanocomposites and heated graphene/CeO₂ nanocomposites. A comparison of the unheated graphene/CeO₂ nanocomposites [Fig. 2.(a)] with the heated graphene/CeO₂ nanocomposites [Fig. 2.(b)] showed that the graphene in the heated graphene/CeO₂ nanocomposites might be looked like teared smaller plane than the unheated graphene/CeO₂ nanocomposites. Therefore, the heated graphene/CeO₂ nanocomposites had a higher surface area than the unheated graphene/CeO₂ nanocomposites. In addition, the CeO₂ nanoparticles in the heated graphene/CeO₂ nanocomposites were spherical. The heated graphene/CeO₂ nanocomposites had a more pronounced photocatalytic effect on the degradation of methylene blue than the unheated graphene/CeO₂ nanocomposites.

Fig. 3 showed XRD patterns of the unheated graphene/CeO₂ nanocomposites and heated graphene/CeO₂ nanocomposites. The XRD patterns in Fig. 3(a-b) were similar. The peaks for the unheated graphene/CeO₂ nanocomposites were observed at 26.60 and 54.69 as a 2θ, as shown in Fig. 3(a), whereas the heated graphene/CeO₂ nanocomposites showed peaks at 26.51 and 54.63 as a 2θ (Fig. 3(b)). After heat treatment, the XRD peaks owing to heated graphene nanoparticles

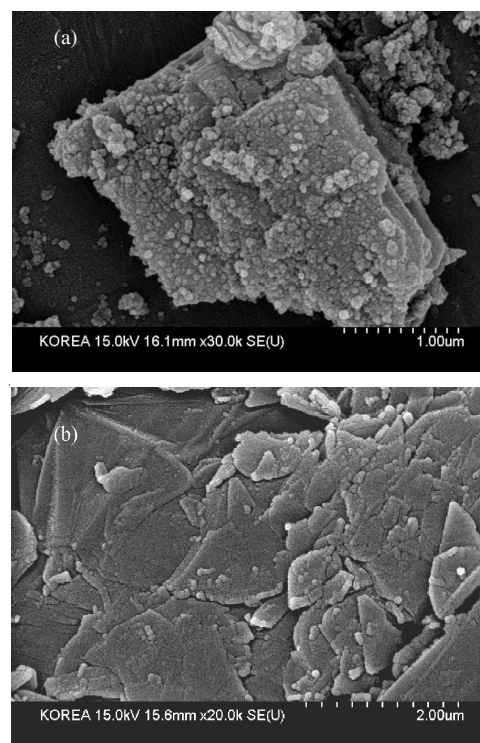


Fig. 1. SEM images of (a) unheated graphene/CeO₂ nanocomposites and (b) heated graphene/CeO₂ nanocomposites

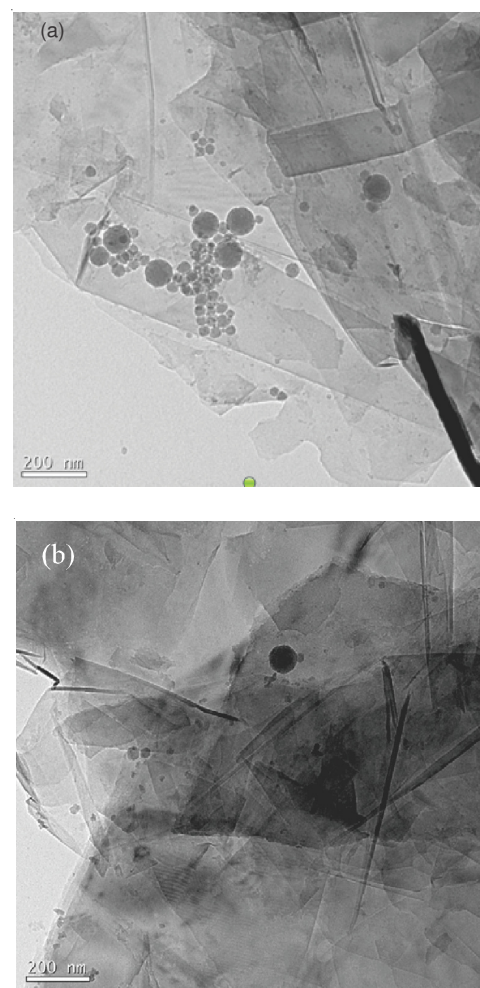


Fig. 2. TEM images of (a) unheated graphene/CeO₂ nanocomposites and (b) heated graphene/CeO₂ nanocomposites

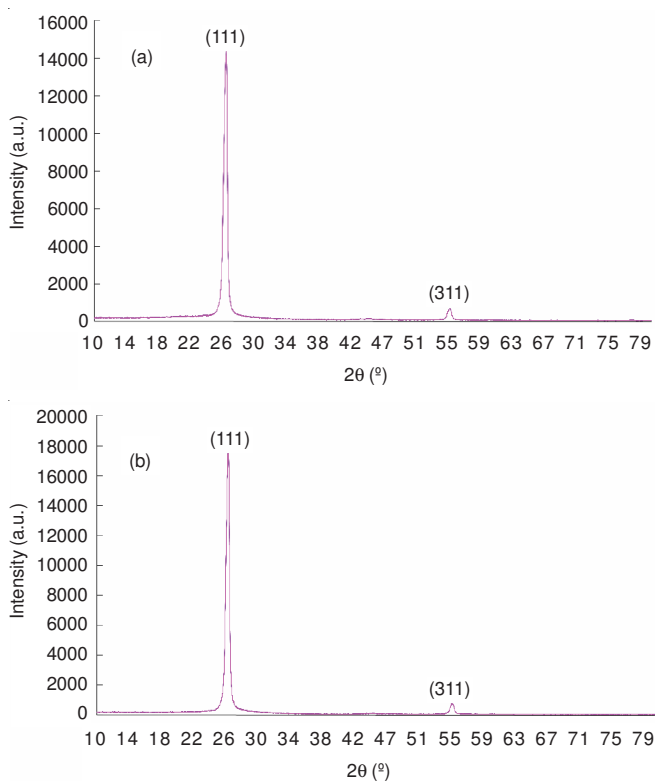


Fig. 3. XRD patterns of (a) unheated graphene/CeO₂ nanocomposites and (b) heated graphene/CeO₂ nanocomposites

in the heated graphene/CeO₂ nanocomposites had a higher intensity than those of the unheated graphene/CeO₂ nanocomposites in Fig. 3(a-b).

Fig. 4 showed the UV-visible spectra of the degradation of methylene blue with unheated graphene/CeO₂ nanocomposites in Fig. 4(a) and heated graphene/CeO₂ nanocomposites in Fig. 4(b) under ultraviolet irradiation at 254 nm. The heated graphene/CeO₂ nanocomposites were more effective on the degradation of methylene blue than the unheated graphene/CeO₂ nanocomposites. Overall, the heated nanomaterials, graphene/CeO₂ nanocomposites, showed more effective degradation capacity for methylene blue than the unheated nanomaterials, graphene/CeO₂ nanocomposites.

Conclusion

Unheated graphene/CeO₂ and heated graphene/CeO₂ nanocomposites were synthesized as a catalyst for the degradation of methylene blue under ultraviolet irradiation at 254 nm. The graphene nanoparticles in the heated graphene/CeO₂ nanocomposites were broken into smaller parts. The heated graphene/CeO₂ nanocomposites were more effective in degrading methylene blue owing to their larger surface due to the decomposition of their nanoparticles at 700 °C. Overall, the heated graphene/CeO₂ nanocomposites had better photocatalytic effect in the degradation of methylene blue under ultraviolet irradiation at 254 nm than the unheated graphene/CeO₂ nanocomposites nanomaterials.

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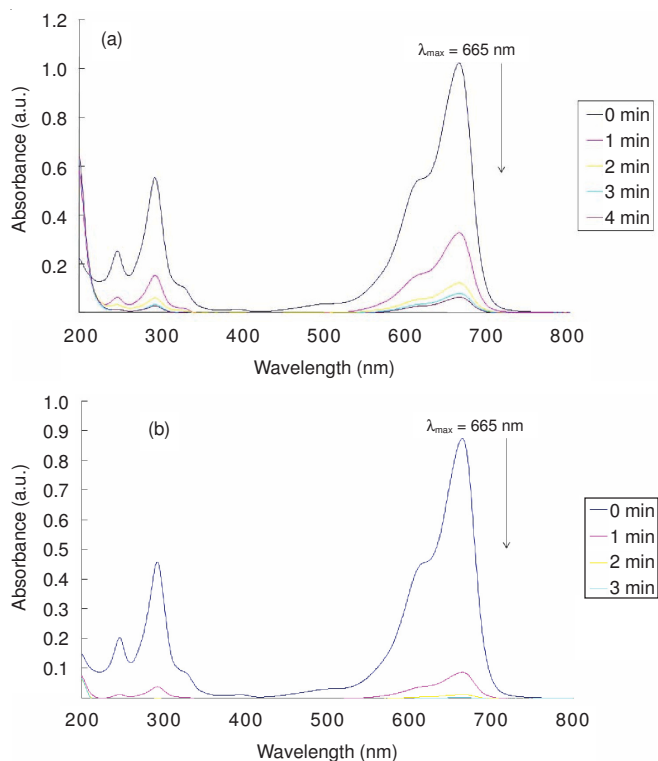


Fig. 4. UV-visible spectra of the degradation in methylene blue with (a) unheated graphene/CeO₂ nanocomposites and (b) heated graphene/CeO₂ nanocomposites

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