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High Photocatalytic Performance of Magnetic CoFe2O4-Graphene Nanocomposite for Organic Dye Removal

Cheewita Suwanchawalit

Department of Chemistry, Faculty of Science, Silpakorn University, Sanam Chandra Palace Campus, Nakornpathom, Thailand 73000

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ABSTRACT

In this study, magnetic CoFe2O4-graphene nanocomposites have been prepared via a facile one-pot hydrothermal method. It is notable that the combination of CoFe2O4 nanoparticles with the graphene sheet results in a marked increase in the efficiency for the degradation of methylene blue (MB). The CoFe2O4-graphene nanocomposites were characterized by XRD, SEM, TEM, FT-IR, DRS and VSM techniques. The CoFe2O4 nanoparticles were found to have a size of ca. 15 nm and were spread out on the graphene sheet. Magnetic studies revealed that the CoFe2O4-graphene nanocomposites can be easily separated from the solution by an external magnetic field.

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INTRODUCTION

Environmental problems have emerged as global concerns and are associated with industrialization. he utilization of solar energy by semiconductor photocatalysis to solve environmental problems and the energy risis has attracted wide attention (Fujishima and Honda, 1972; Kamat, 1993; Li *et al*., 2011). Nano-semiconductor photocatalysts offer an extremely convenient route for the elimination of various organic pollutants under UV or solar light irradiation in the presence of these photocatalysts (Fujishima and Honda, 1972; Kamat, 1993; Zheng *et al*., 2008). The major problem of using nano-semiconductors is the difficulty to separate the small sized photocatalysts from the suspensions. In order to overcome this separation problem, magnetic photocatalysts offer an advantage since they can be recovered by applying an external magnetic field. Among various semiconducting materials, cobalt ferrite (CoFe2O4) is a class of semiconductors with narrow bandgaps, exhibits characteristics of visible-light response, possesses good photochemical stability, as well as favorable magnetism. It is well known that bivalent cation (Co2+) and trivalent ferric ion (Fe3+) can distribute at both tetrahedral and octahedral sites and the type of cationic distribution affects the magnetic properties of spinel ferrite (Zi, *et al*., 2008; Cao and Gu, 2005). The presence of CoFe2O4 magnetic nanoparticles fairly enhances the efficiency of the degradation of organic contaminants and can be easily separated from the solution by applying an external magnetic field.

It is well known that the major hindrance for enhancing the photocatalytic efficiency of pure semiconductor photocatalysts is the fast recombination of photogenerated electron–hole pairs (Sun *et al*., 2009; Huang *et al*., 2009). One of the effective strategies to address this problem is to prepare semiconductor nanocomposites, which will facilitate the charge migration (Huang *et al*., 2009). Among various nanocomposites materials, graphene, the two-dimensional (2D) crystal of hybridized carbon with a large specific surface area, remarkable electrical conductivity, excellent adsorptivity, and high chemical and thermal stability, has attracted a great deal of interest in the field of photocatalysis (Zhang *et al*., 2010).

In this study, magnetic CoFe2O4-graphene nanocomposites were synthesized by the hydrothermal method using graphite powders, FeCl3•6H2O and CoCl2•6H2O as precursors. The microstructure, optical properties, and magnetic properties of the synthesized CoFe2O4-graphene nanocomposites were investigated. The photocatalytic activity of the as-prepared CoFe2O4-graphene nanocomposites was evaluated using methylene blue as a model pollutant.

Experimental Detail:

Preparation of graphene oxide:

Graphene oxide (GO) was synthesized using the Hummers method through oxidation of graphite

Corresponding Author: Cheewita Suwanchawalit, Department of Chemistry, Faculty of Science, Silpakorn University, Sanam Chandra Palace Campus, Nakornpathom, Thailand 73000

powder (Hartono *et al*.2009; Bradder *et al*., 2010). Briefly, 1.0 g of flake graphite was added to 250 ml concentrated sulfuric acid. After stirring for 24 h at room temperature, 0.5 g of NaNO3 and 3 g of KMnO4 were added in succession with continuous stirring. Subsequently, the mixture was heated at 40□ C for 30 min. Then, a certain amount of water was slowly added, and the mixture was continuously stirred for another 15 min. The reaction was then terminated by the addition of 140 ml water followed by 10 ml of 30% aqueous H2O2 solution. The resulting solid product was separated by centrifugation. The collected precipitate was mixed with 150 ml of water and bath sonicated for 20 min. Finally, a brown homogeneous supernatant was obtained after centrifugation.

Preparation of CoFe2O4:

A 4 mmol of FeCl3•6H2O solution was mixed with 0.078 M glycerol under stirring. After mixing well, an aqueous solution of 2 mmol of CoCl2•6H2O was slowly added to the above mixture to give a uniform solution. The pH was then adjusted to 10 by dropwise addition of 6 M NaOH aqueous solution. Then the mixture was transferred to a Teflon-lined autoclave and kept at 200 °C in a furnace for 6 h. Finally, the precipitate was collected, centrifuged and washed several times with distilled water, then dried at 100 °C for 6 h.

Preparation of CoFe2O4-graphene nanocomposites:

1000 mg of GO was dispersed into 50 mL of distilled water with sonication for 1 h before 200 mg CoFe2O4 suspension was added and the mixture stirred for 30 min at room temperature to produce a CoFe2O4-GO dispersion. The resulting mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated to 200 ◦C for 5 h under autogenous pressure. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed five times with distilled water and dried in a vacuum oven at 60 ◦C for 12 h.

Fig. 1: Typical procedure of CoFe2O4-graphene nanocomposite preparation by the hydrothermal method.

Characterizations:

The crystal structure and crystallite size were identified by X-ray diffraction (XRD) patterns recorded on a Rigaku MiniFlex II X-Ray diffractometer with Cu Kα radiation (1.5406 Å) from 20□ to 70□ (2θ). The particle morphologies and microstructure were investigated using a scanning electron microscopy (SEM, JEOL model JSM-5410LV and TEM, JEOL, JEM-2010). Fourier-transformed infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum Bx spectrophotometer in the range 400-4000 cm-1 using the KBr pellet technique. Optical absorption property and band gap energy were determined using a Shimadzu UV-2401 spectrophotometer. The magnetic hysteresis loops of samples were measured by a vibrating sample magnetometer (VSM, LakeShore Model 7404) at room temperature (300 K).

Photocatalytic activity test:

The photocatalytic performances of the prepared CoFe2O4-graphene nanocomposites were evaluated by the photocatalytic degradation of methylene blue under visible light using fluorescence light 18W as a visible light source (Suwanchawalit *et al*., 2012). The photocatalytic experiments were performed at room temperature. A 0.05 g of CoFe2O4 sample was added to 50 mL methylene blue solution. The suspension was stirred in the dark for 1 h to allow adsorption equilibrium of the dye onto the surface of the CoFe2O4-graphene nanocomposites.

At given irradiation time intervals, samples were collected and centrifuged to separate CoFe2O4-graphene nanocomposites. The residual concentration of methylene blue was monitored by the change in absorbance of the dye at 664 nm using a UV-Vis spectrophotometer (Analytik Jena GmbH).

RESULT AND DISCUSSION

Structure and morphology of CoFe2O4-graphene nanocomposite:

The CoFe2O4-graphene nanocomposite was synthesized by a facile one-pot hydrothermal route at 200□ C for 5 h. The XRD diffraction patterns of the as-prepared CoFe2O4- graphene nanocomposites, pure CoFe2O4, graphene and graphene oxide (GO) are shown in Fig. 1. It can be seen that almost all the diffraction peaks of CoFe2O4-graphene may be assigned to the spinel-type CoFe2O4 (JCPDS 22-1086) (Li *et al*., 2011). The characteristic peaks of graphite oxide and graphene exhibit (001) and (002) are found around 2θ = 10.8 and 24.4 degrees, respectively. During the hydrothermal reaction, crystal growth of CoFe2O4 between the interlayer of GO destroyed the regular layer stacking, leading to the exfoliation of GO and the disappearance of the (0 0 1) diffraction peak.

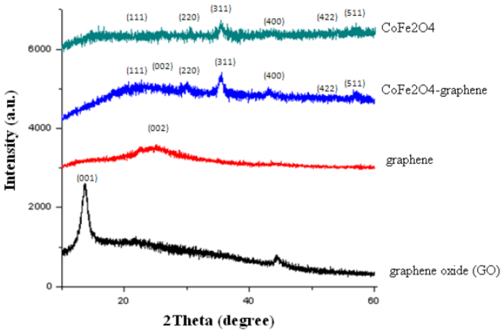


Fig. 1: XRD patterns of graphene oxide, graphene, CoFe2O4 and CoFe2O4-graphene nanocomposite.

In order to investigate the surface chemical compositions of the obtained samples, Fourier-transform infrared spectroscopy (FT-IR) was employed, and the corresponding results are shown in Fig. 2. In the FT-IR spectrum of graphene, the peaks at 3400 cm-1, 1723 cm-1, 1630 cm-1, 1370 cm-1, and 1060 cm-1 are attributed to the OH stretching vibrations of adsorbed water, C=O stretching vibrations of carboxyl or carbonyl groups, OH deformation vibrations of COOH groups, OH deformation vibrations of tertiary C-OH, and C-O stretching vibrations of epoxy groups, respectively (Li *et al*., 2011; Sun *et al*., 2013). The FT-IR bands of CoFe2O4, observed in the range 600-500 cm-1, correspond to the intrinsic stretching vibrations of the metal at the tetrahedral site Co-O stretching vibration band in CoFe2O4 and octahedral group Fe-O. The bands at 3500-3200 cm-1 and 1620 cm-1 are attributed to the stretching and bending modes of free and absorbed water on the surface of the synthesized CoFe2O4 samples. The spectrum of CoFe2O4-graphene nanocomposites exhibited the characteristic peaks due to CoFe2O4 and graphene at 536 cm-1, 3400 cm-1, and the oxygen-containing functional groups on the graphene sheet around 1370 cm-1, and 1060 cm-1, respectively.

The morphology of the CoFe2O4-graphene nanocomposites was characterized by SEM and TEM observations. Figs. 3 and 4 show the representative SEM images and the corresponding EDS spectra of the as-prepared CoFe2O4-graphene nanocomposites. In this work, the CoFe2O4 nanoparticles are well decorated on the graphene nanosheets. The EDS results showed that C, Co, Fe and O elements were clearly present in the CoFe2O4-graphene nanocomposites. In the mapping analysis, the population of color point of Co, Fe, O element in CoFe2O4-graphene nanocomposites is distinctly lower than that of the color point of Co, Fe, O element in CoFe2O4 due to the lower content of CoFe2O4 on the graphene sheet.

The typical TEM images of CoFe2O4 and CoFe2O4-graphene nanocomposites are shown in Fig. 5. It can be clearly seen that the flake-like graphene nanosheets are sparsely decorated with CoFe2O4 nanoparticles withsome formation of aggregations. The size of the CoFe2O4 nanoparticles is uniform with an average diameter ca. 15 nm.

Optical and magnetic properties:

The optical absorption property relevant to the electronic structure feature is recognized as a key factor in determining the photocatalytic activity (Sathishkumar *et al*., 2013).The optical properties of the prepared CoFe2O4 samples were investigated by the diffused reflectance UV-vis spectra (DRS) of the CoFe2O4, as shown in Fig. 5a. According to the spectra, all synthesized CoFe2O4 samples exhibited photoabsorption from UV light to visible light region, which implies the possibility of high photocatalytic efficiency of these materials under visible light. The band gap of the synthesized CoFe2O4 calculated from the plot of the transformed Kubelka-Munck function vs. the energy of light (Guo *et al*., 2014), is shown in Fig. 5b. The band gap energies of the prepared CoFe2O4 and CoFe2O4-graphene nanocomposites are 2.28 and 2.05 eV, respectively.

The magnetization measurement for the as-prepared CoFe2O4 and CoFe2O4-graphene nanocomposites was carried out using a vibrating sample magnetometer (VSM) at room temperature. Fig. 7 shows the magnetic hysteresis loops of the as-prepared CoFe2O4 and CoFe2O4-graphene nanocomposites, which demonstrates that the resulting samples exhibit a characteristic of ferromagnetic materials with the saturation magnetization of 22.0 and 3.8 emu g−1 of CoFe2O4 and CoFe2O4-graphene nanocomposites, respectively.

Photocatalytic performance:

The photocatalytic degradation of methylene blue (MB, 1.0x10-5M) as a function of time using the synthesized CoFe2O4 and CoFe2O4-graphene nanocomposites was investigated under visible light irradiation, as shown in Figure 8. It can be seen that the CoFe2O4-graphene nanocomposites gave the best performance in photocatalytic degradation of methylene blue. It has been reported that the difference in photocatalytic efficiency could be related to the crystal structure, crystal size, morphology, surface area, and energy band structure (Li *et al*., 2011; Casbeer *et al*., 2012; Guo *et al*., 2014). The CoFe2O4-graphene nanocomposites gave the highest photocatalytic efficiency due to the good optical absorptions in the UV-Vis region with a lower band gap energy and a larger surface area giving rise to a higher photocatalytic performance. In addition, the graphene in the composite can act as an electron transfer channel to reduce the recombination of the photo-generated electron holes, leading to improved photo-conversion efficiency (Zhang *et al*., 2009; Wang *et al*., 2009).

The significant enhancement of the CoFe2O4-graphene catalysts in photoactivity under visible light can be attributed to the remarkable synergistic effect of the combination of CoFe2O4 and the graphene sheets, leading to the efficient separation of photogenerated carriers in the CoFe2O4 and graphene coupling system. A possible mechanism for the photocatalytic enhancement is proposed as follows and is shown in Fig. 9.

CoFe2O4 + h+→ CoFe2O4 (e - - h+) (1)
CoFe2O4 (e-) + graphene→ CoFe2O4 + graphene (e-) (2)
Graphene (e-) + O2→ O2•− + graphene (3)
CoFe2O4 (h+) + OH− → CoFe2O4 +•OH (4)
CoFe2O4 (h+) + •OH + O2•− + MB → CO2 + H2O (5)

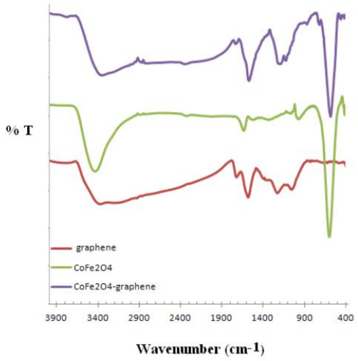
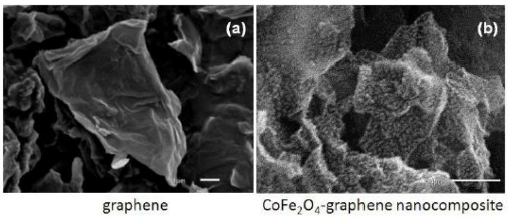


Fig. 2: FT-IR spectra of prepared graphene, CoFe2O4 and CoFe2O4-graphene nanocomposites.



graphene CoFe$_2$O$_4$-graphene nanocomposite

Fig. 3: SEM images of graphene and CoFe2O4-graphene nanocomposites.

Conclusion:

In conclusion, a magnetically separable CoFe2O4-graphene photocatalyst has been successfully prepared via a one-step hydrothermal method. SEM and TEM results indicate that graphene sheets are fully exfoliated and decorated with CoFe2O4 nanoparticles. The photocatalytic activity measurements demonstrate that the combination of CoFe2O4 nanoparticles with the graphene sheets results in a dramatic conversion of the inert CoFe2O4 into a highly active catalyst for the degradation of methylene blue under visible-light irradiation. The combination of the adsorption property of graphene sheet and the magnetic and photocatalytic property of CoFe2O4 nanoparticles makes the nanocomposites promising candidates for the solution of a variety of environmental problems.

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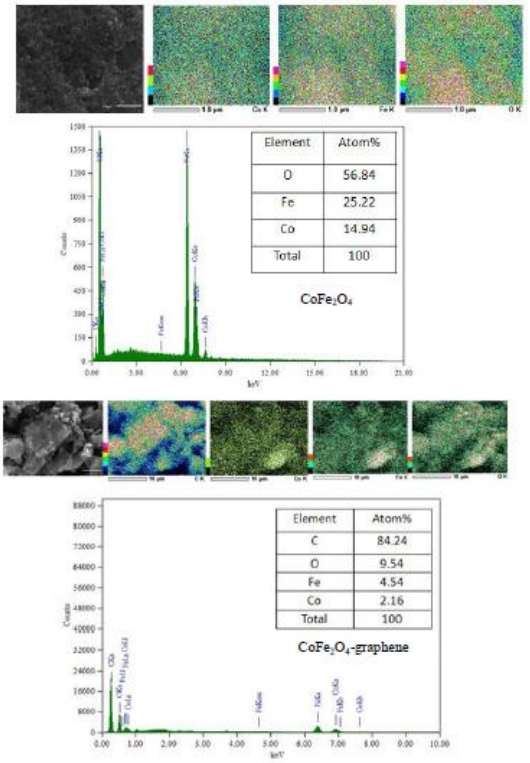

Fig. 4: EDS elemental analysis and mapping analysis of CoFe2O4 and CoFe2O4-graphene nanocomposites.

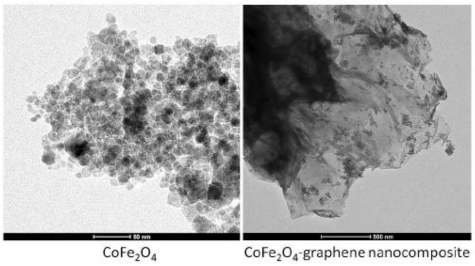

Fig. 5: TEM images of the CoFe2O4 and CoFe2O4-graphene nanocomposites.

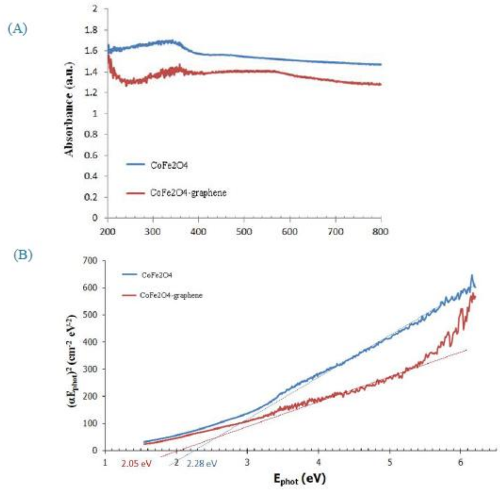

Fig. 6: DRS spectra of the prepared CoFe2O4 and CoFe2O4-graphene nanocomposite and (B) plots of (ahv)2 vs. photon energy (hv).

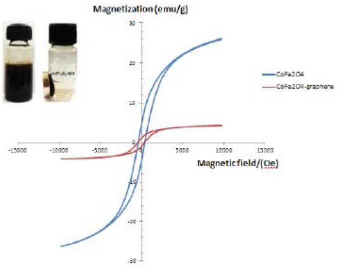

Fig. 7: Hysteresis loops of the CoFe2O4 and CoFe2O4-graphene nanocomposites. The top inset shows the magnetic separation of the CoFe2O4-graphene nanocomposites under an external magnetic field.

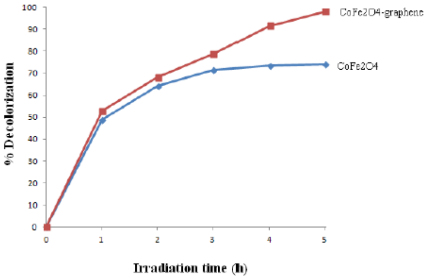

Fig. 8: Photodegradation efficiencies of methylene blue as a function of irradiation time for CoFe2O4 and CoFe2O4-graphene nanocomposite under visible light irradiation.

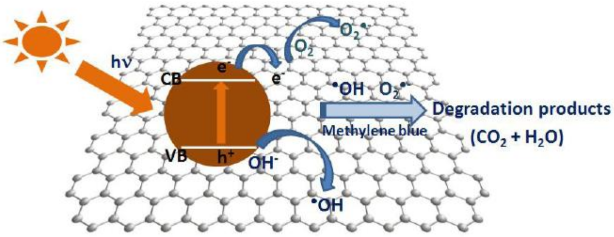

Fig. 9: Possible photodegradation mechanism of the CoFe2O4-graphene under visible light irradiation.

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