Enhanced UV Photocatalytic Performance of Magnetic Fe_3O_4/CuO/ZnO/NGP Nanocomposites

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Abstract
Fe_3O_4/CuO/ZnO/nanographene platelets (Fe_3O_4/CuO/ZnO/NGP) with varied ZnO loadings have been synthesized using a sol-gel method followed by hydrothermal method. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) confirmed the formation of the Fe_3O_4/CuO/ZnO/NGP composites. All of the samples showed the presence of graphene nanoplatelets incorporating Fe_3O_4, CuO and ZnO structures and exhibited ferromagnetic behavior at room temperature. The composites showed photocatalytic activity under UV irradiation, which was used to affect the degradation of methylene blue. The Fe_3O_4/CuO/ZnO/NGP composites showed superior photocatalytic activity than the Fe_3O_4/CuO/ZnO materials.

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1. Introduction

Since it was first introduced by Novoselov et al. [1], graphene, a planar sheet of sp^2−bonded carbon atoms with single-atom thickness, has attracted an enormous amount interest within material science and condensed matter physics due to its fascinating physical and chemical properties [2]. It has been recently reported that graphene can compete with carbon nanotubes as a catalyst scaffold, anchoring organic and inorganic groups [3-4]. In addition, through a chemical oxidation process, a wide variety of oxygen-containing functionalities, such as hydroxyl and epoxide groups, can be formed that alter the materials physical and chemical properties [5]. These attractive characteristics have cultivated increased interest in the development of graphene/metal oxide composites with robust photocatalytic properties in environmental remediation applications [6].

A major limitation in achieving the required photocatalytic performance is the quick recombination of photogenerated charge carriers [7]; therefore, slowing this recombination is essential. Recently, many researchers have reported reductions in the charge carrier recombination rate by coupling graphene to two or more metal oxide nanoparticles [8]. Metal oxide nanocomposites, formed by two or more distinct metal oxide nanomaterials, often yield desirable combinations of properties not found from the individual components [9-10]. The similar combination of graphene with several metal oxides photocatalyst may likewise slow the recombination of charge carriers, increasing photocatalytic performance. Therefore, in the present study, Fe_3O_4/CuO/ZnO/NGP composites were developed as photocatalysts using a sol-gel method and employed to remove methylene blue as a model of organic pollutants from water. Fe_3O_4/CuO/ZnO/NGP composites with

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different ZnO loadings were used in photocatalytic reactions to investigate the role of graphene in the photocatalytic performance. The effect of ZnO loading was also investigated.

2. Experimental

All chemical reagents (Merck) were of analytical grade and used without further purification. Nano graphene platelets (NGP) were purchased from Angstron Materials. All solutions were prepared with distilled water. CuO and Fe_3O_4 nanoparticles and Fe_3O_4/CuO/ZnO nanocomposites were synthesized using sol-gel method as described previously [11]. The Fe_3O_4/CuO/ZnO/NGP nanocomposites were prepared by a simple hydrothermal method based on Khalid's work [12]. Briefly, 200 mg of NGP was dissolved in a solution of water (80 mL) and ethanol (40 mL) through ultrasonic treatment for 2 h, followed by the addition of 2 g of Fe_3O_4/CuO/ZnO to the NGP solution and an additional 2 h of stirring to achieve a homogeneous suspension. The suspension was then heated at 120 °C for 3 h to affect the deposition of Fe_3O_4/CuO/ZnO on the graphene sheets. The resulting nanocomposite was isolated by centrifugation and dried at 70 °C for 12 h.

The samples were characterized by Field Emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD). Magnetic measurements were performed by vibrating sample magnetometer (VSM).

Methylene blue (MB) was selected as a model of organic pollutant. The photocatalytic activity was evaluated by degradation of organic pollutant in the presence of Fe_3O_4/CuO/ZnO/NGP nanocomposite in aqueous solution under 40 W UV light irradiation. In this study, organic pollutant solutions of 30 mg/L concentration were prepared and 0.3 g/L of Fe_3O_4/CuO/ZnO/NGP nanocomposite were immersed in these solutions.

3. Results and discussion

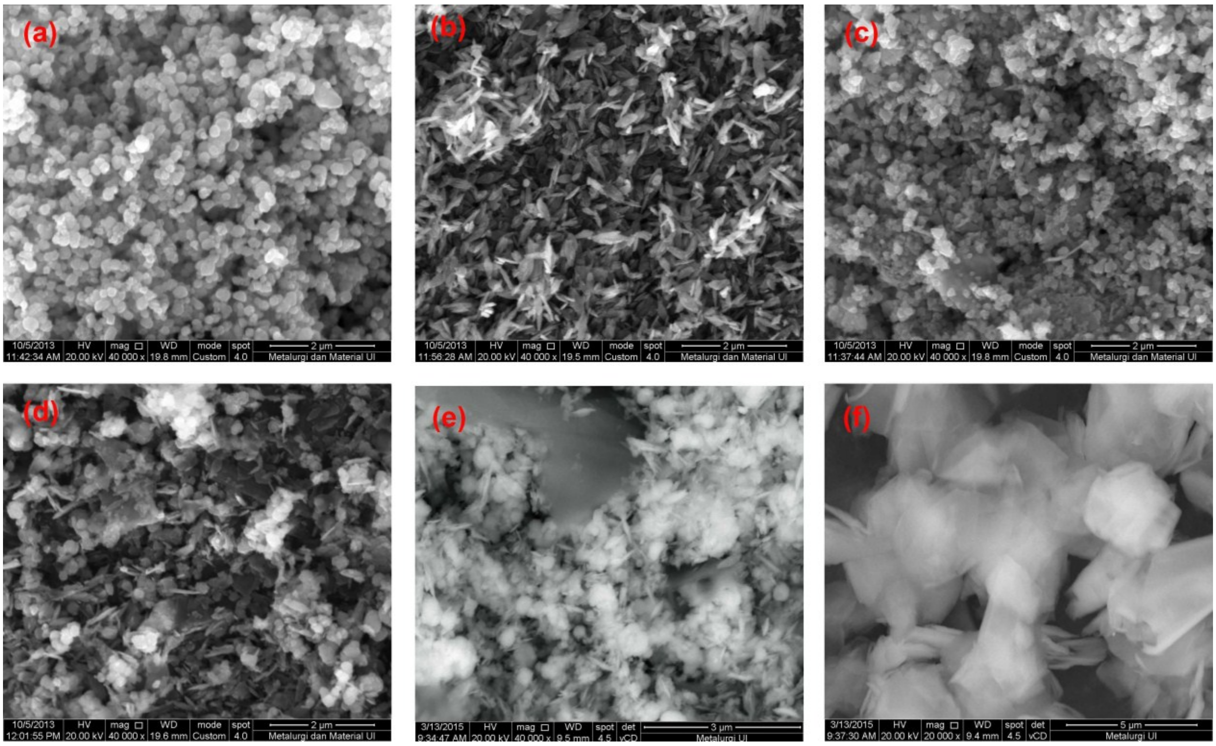

Figure 1. FESEM image of (a) Fe_3O_4, (b) CuO, (c) ZnO nanoparticles, (d) Fe_3O_4/CuO/ZnO nanocomposites and (e) Fe_3O_4/CuO/ZnO/NGP nanocomposites, (f) NGP.

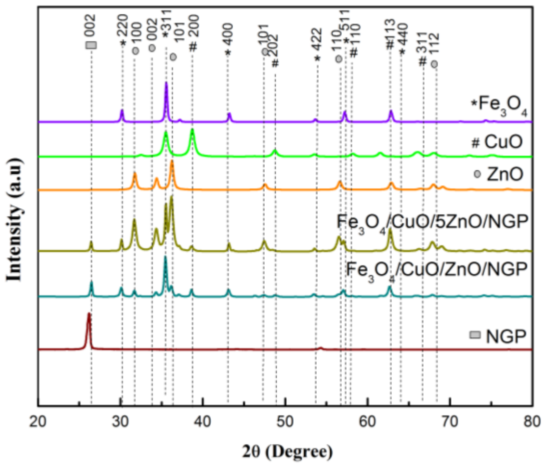

Figure 2. XRD pattern of Fe_3O_4, CuO, ZnO nanoparticles and Fe_3O_4/CuO/ZnO/ NGP nanocomposites.

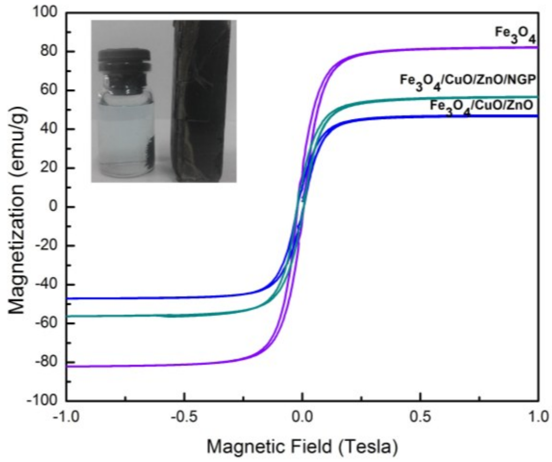

Figure 3. VSM curve of Fe_3O_4 nanoparticles, Fe_3O_4/CuO/ZnO nanocomposites, and Fe_3O_4/CuO/ZnO/NGP nanocomposites.

Table 1. Magnetic Saturation of Fe_3O_4 nanoparticles, Fe_3O_4/CuO/ZnO, Fe_3O_4/CuO/ZnO/NGP, and rate constant of Fe_3O_4, CuO, ZnO nanoparticles, Fe_3O_4/CuO/ZnO nanocomposites and Fe_3O_4/CuO/ZnO/NGP nanocomposites.

Sample	Magnetic Saturation (emu/g)	Rate Constant (k(min^{-1}))
Fe_3O_4	82	0.0029
CuO	-	0.0052
ZnO	-	0.0147
Fe_3O_4/CuO/ZnO	46	0.0059
Fe_3O_4/CuO/ZnO/NGP	57	0.0070
Fe_3O_4/CuO/5ZnO	17	0.0176
Fe_3O_4/CuO/5ZnO/NGP	27	0.0249

Figure 1 depicts the FESEM images of Fe_3O_4/CuO/ZnO/NGP composites. The FESEM images of Fe_3O_4, ZnO, and CuO nanoparticles as well as Fe_3O_4/CuO/ZnO composites and NGP were also observed [11]. It can be seen that the particle morphology of pure Fe_3O_4 and ZnO is generally spherical while the CuO nanoparticles consist of clew-like shapes and the Fe_3O_4/ZnO/CuO hybrid is a combination of spherical and clew-like shapes. Morphology of Fe_3O_4/CuO/ZnO/NGP shows the dispersion of Fe_3O_4/ZnO/CuO in nanographene materials.

Figure 2 shows the XRD patterns of the Fe_3O_4/CuO/ZnO/NGP with different ZnO loadings. The XRD patterns of pure Fe_3O_4, CuO, ZnO nanoparticles and NGP are given as well. The diffraction patterns exhibited a series of peaks characteristic for crystalline cubic spinel Fe_3O_4, monoclinic CuO, hexagonal wurtzite ZnO structures, as well as for NGP. The Fe_3O_4 peaks are very sharp, indicative of their greater crystallinity than found for CuO and ZnO. Moreover, the intensities of the ZnO peaks linearly increased with increasing ZnO loading in the composites. The absence of mixed Fe_3O_4, CuO and ZnO diffraction peaks in the spectra confirmed that the nanocomposites were the desired Fe_3O_4/CuO/ZnO/NGP materials.

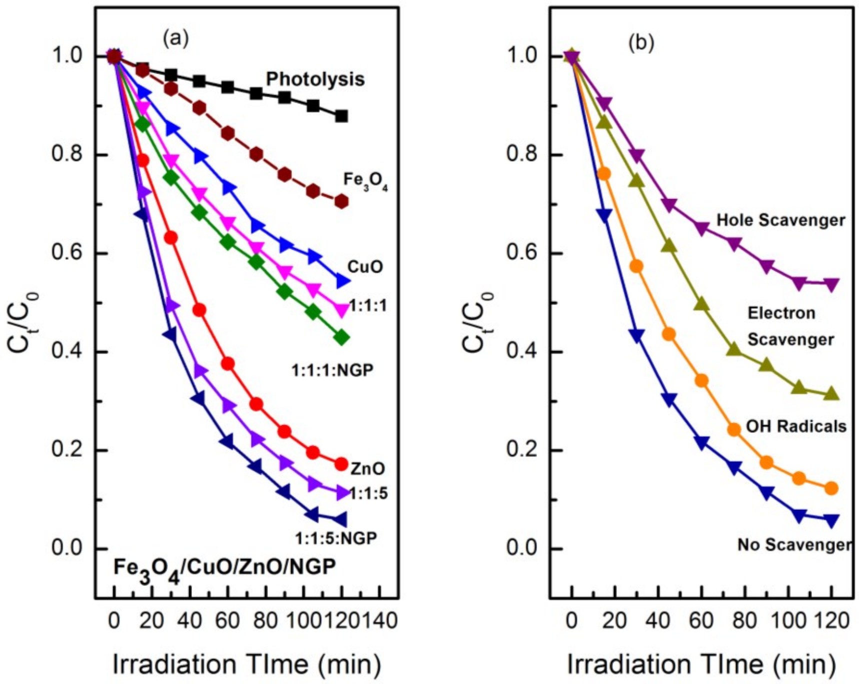

Figure 4. (a) Photodegradation of methylene blue (b) Effect of adding scavenger on photodegradation methylene blue under UV irradiation.

Magnetic hysteresis curves of Fe_3O_4/CuO/ZnO/NGP composites with different ZnO loading are presented in Figure 3. For comparison magnetic hysteresis curves of pure Fe_3O_4 nanoparticles and nanocomposites Fe_3O_4/CuO/ZnO were also measured. The corresponding saturation magnetization values are tabulated in Table 1. All of samples exhibited ferromagnetic behavior. It is found that the value of saturation magnetization decrease as Fe_3O_4 is coupled with CuO and ZnO nanoparticles. However, the incorporation of NGP in nanocomposites Fe_3O_4/CuO/ZnO showed the enhancement of saturation magnetization. According to the literature [13], this might be due to Fe_3O_4 nanoparticles attached to the surface of the NGP materials acting as defects and creating a stable NGP-based magnetic material. To study the magnetic separability of the material, a magnetic bar was placed near the sample holder supporting the Fe_3O_4/CuO/ZnO/NGP composites in water. As seen in the inset of Figure 3, this test demonstrated that the Fe_3O_4/CuO/ZnO/NGP composites can be separated from a suspension by use of a magnetic bar.

The photocatalytic capacity of the Fe_3O_4/CuO/ZnO/NGP composites was tested through the degradation of MB in aqueous solution (Figure 4). Direct photolysis resulted in a ~12 % degradation of MB, while the use of Fe_3O_4/CuO/ZnO composites with molar ratios of 1:1:1 and 1:1:5 removed approximately 52% and 87% of MB, respectively, under UV light irradiation for 2 h. It is indicated that the incorporation of Fe_3O_4/CuO/ZnO nanocomposites could enhance the photoreduction of methylene blue by oxidation process. The removal efficiencies were enhanced to 57% and 93% when NGP was incorporated into the Fe_3O_4/CuO/ZnO composites. It was found that Fe_3O_4/CuO/ZnO composites with molar ratios of 1:1:1 and 1:1:5 showed lower photocatalytic activities than the Fe_3O_4/CuO/ZnO/NGP composites with the same molar ratios. The photocatalytic performances obtained with the Fe_3O_4/CuO/ZnO and Fe_3O_4/CuO/ZnO/NGP composites with different ZnO loadings are plotted in Figure 4a, demonstrating that increased ZnO loading resulted in progressive increases of photocatalytic efficiency. Provided that the photocatalytic reaction follows pseudo-first order kinetics, the apparent reaction rate constants (k) for the degradation of MB could be calculated (Table 1). The values of k for the Fe_3O_4/CuO/ZnO/NGP samples are higher than those of the Fe_3O_4/CuO/ZnO composites, demonstrating that the presence of NGP enhances the photocatalytic performance, possibly due to

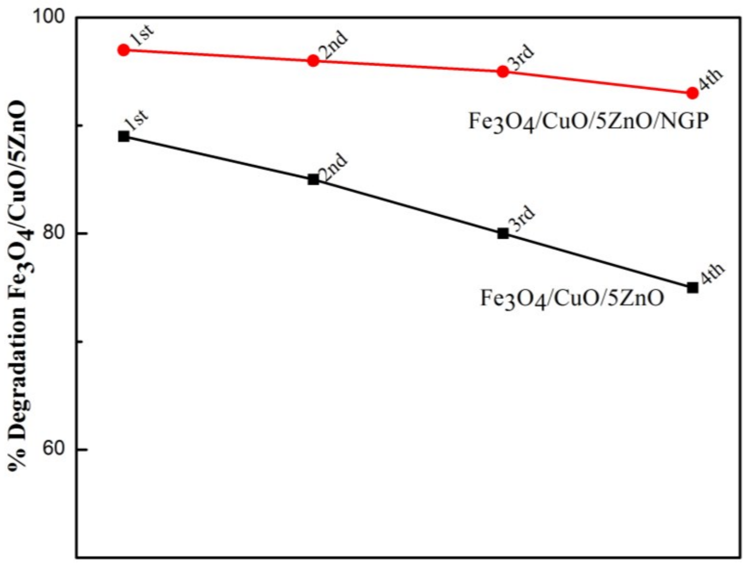

Figure 5. Photocatalytic stability of Fe_3O_4/CuO/5ZnO and Fe_3O_4/CuO/5ZnO/NGP

acceleration of the charge carriers through the conjugated π-structures of the NGP and a slowing of charge recombination [14]. The enhancement of photocatalytic performance in the presence of NGP may be caused by the involvement of radical species in the reaction. To elucidate the primary active oxidative species responsible for the degradation of MB, control experiments employing scavengers of hydroxyl radicals, holes and electrons were carried out. The photodegradation of MB in the presence of tert-butyl alcohol, ammonium oxalate, and $Na_2S_2O_8$, used for scavenging hydroxyl radicals, holes and electrons, respectively, is displayed in Figure 4b. The addition of ammonium oxalate, a hole scavenger, inhibited the photocatalytic removal of MB. The reduced photodegradation percentage suggested that the photocatalytic activity of Fe_3O_4/CuO/ZnO, as well as that of Fe_3O_4/CuO/ZnO/NGP, for the removal of MB is driven by the presence of holes.

To investigate the stability of the photocatalyst, experiments were performed with recycled Fe_3O_4/CuO/ZnO/NGP composites with a molar ratio of 1:1:5 under the same conditions used for freshly prepared composites. Four cycles were examined (Figure 5). For comparison, results for the cycling of a Fe_3O_4/CuO/ZnO composite is also plotted. The results showed that the Fe_3O_4/CuO/ZnO/NGP composites were stable after four cycles of MB photodegradation and are more stable than the composite synthesized without NGP.

4. Conclusions

Magnetically Fe_3O_4/CuO/ZnO/NGP composites have been prepared using sol-gel method for degradation of MB under UV light irradiation. The synthesized composites exhibited obviously higher photocatalytic activity in degradation of MB compared to the same composites synthesized without the presence of NGP. Based on the results of detection active species, it is concluded that the degradation of MB was driven mainly by the participation of holes. Electron and OH radicals to a lesser extent partook in this process. The Fe_3O_4/CuO/ZnO/NGP composites have good photocatalytic stability in the degradation of MB under UV light irradiation after four time cycling process.

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