Decomposition of organic pollutant in waste water using magnetic catalyst nanocomposite

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Abstract. In this study, magnetic recyclable catalyst Fe3O4/CuO/ZnO/nanographene platelets (Fe3O4/CuO/ZnO/NGP) and Fe3O4/CuO/TiO2/nanographene platelets (Fe3O4/CuO/TiO2/NGP) composites were synthesized by simple hydrothermal method. Methylene blue was used as a model of textile dye to evaluate their catalytic activities. A range of analytical techniques including X-ray diffraction, energy-dispersive X-ray spectroscopy and vibrating sample magnetometer were employed to reveal the crystal structure, composition and property of the nanocomposites. The catalytic performance was evaluated by degradation of methylene blue in aqueous solution under UV light and ultrasonic irradiation simultaneously. X-ray diffraction results revealed that cubic spinel Fe3O4, monoclinic CuO, hexagonal wurtzite ZnO and graphene platelets exist in Fe3O4/CuO/ZnO/NGP, while in Fe3O4/CuO/TiO2/NGP nanocomposites instead of hexagonal wurtzite ZnO, anatase TiO2 is observed. These results confirmed that the nanocomposites were the desired materials. In addition, all samples exhibited ferromagnetic behavior at room temperature and could be rapidly separated from aqueous solution for repeated use under external magnetic field. From the degradation of methylene blue, it is found that the as-prepared nanocomposites exhibited excellent catalytic activity compared with nanocomposite synthesized without nanographene platelets. The nanocomposites still retain the 100% of the initial activity after it has been used four times repeatedly.

1. Introduction

Recently, great interest has been stimulated in the treatment of dye-contaminated household wastewater and industrial effluents through photocatalytic and sonocatalytic methods, since these methods can effectively and efficiently destruct the hazardous dyes completely [1-2]. The metal oxide semiconductors such as ZnO and TiO2 are generally used as catalyst to remove organic pollutants due to their photosensitivity, strong oxidizing ability, non-toxic nature, favorable band gap energy and excellent chemical and mechanical stability [3-5]. In addition, ZnO and TiO2 nanocatalyst are also environmental friendly and relatively inexpensive [6-7]. Unfortunately, the light response of ZnO and TiO2 nanocatalyst are limited due to its large band-gap and high recombination of electron and hole is very fast [8-9]. Therefore, several methods have been employed to reduce recombination of charge carrier by coupling ZnO and TiO with other metal oxide to form heterogeneous semiconductor catalyst [10]. Apart from this strategy, recently carbon-based nanomaterials such as graphene has been...
investigated to be the effective material that can support coupled metal oxides to minimize charge carrier recombination [11]. It is reported that as a new kind of two-dimensional carbon materials constructed by a single layer of carbon atoms, graphene is an excellent supporting and electron-transport materials compared with other carbon materials in the process of photo and sonocatalytic [11-12].

In this study, we attempt to synthesize \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2 \) coupled with nanographene platelets (NGP) using simple sol-gel method [13-15] followed by hydrothermal method [16] in order to obtain synergetic effect towards the degradation of organic pollutant model, methylene blue. Such methods are inexpensive and are among the versatile approaches that allow the synthesis of a great variety of crystalline metal oxides at low temperature. \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) composites were used in catalytic reactions to investigate the role of graphene in the photocatalytic performance. The effect of \( \text{ZnO} \) and \( \text{TiO}_2 \) loading was also investigated.

2. Experiments

All chemical reagents were of analytical grade and were used without further purification. Iron (II) sulfate heptahydrate (\( \text{FeSO}_4 \cdot 7\text{H}_2\text{O}, 99\% \)), copper sulfate pentahydrate (\( \text{CuSO}_4 \cdot 5\text{H}_2\text{O}, 99\% \)), zinc sulfate heptahydrate (\( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}, 99\% \)) titanium dioxide (\( \text{TiO}_2, 99\% \)), sodium hydroxide (\( \text{NaOH} \)), ethanol and ethylene glycol (EG) were purchased from Merck. Nanographene platelets (NGP-N006-P) were purchased from Angstron Materials. \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2 \) nanocomposites were synthesized using a sol-gel method described in our previous study [13-15]. A series of \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2 \) nanocomposites were prepared with molar ratios of 1:1:1, 1:3:1 and 1:1:5. The \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) nanocomposites were prepared by a simple hydrothermal method based on Khalid's work [16]. 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 \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO} \) 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 \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO} \) on the graphene sheets. The resulting nanocomposite was isolated by centrifugation and dried at 70 °C for 12 h. The same procedure was also for \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) nanocomposites.

The samples were characterized by X-ray diffraction (XRD) measurements using a Rigaku Minflex 600 and monochromatic Cu-Kα (\( \lambda = 1.5 \) Å) radiation operated at 30 kV and 15 mA in the range of 10° to 80°. The instrumental broadening, including the instrumental symmetry, was calibrated using a Si powder standard. Elemental analyses and the morphology of the samples were determined using energy dispersive X-ray (EDX) spectroscopy (LEO 420). Magnetic properties were investigated using vibrating sample magnetometry (Oxford Type 1.2T). UV-Vis diffuse reflectance spectra were measured using a Shimadzu spectrophotometer with an integrating sphere and a spectral reflectance standard over a wavelength range of 200 to 800 nm.

The experimental setup and conditions used for evaluation of sonocatalytic and photocatalytic activities were identical. After dark absorption-desorption equilibrium, the solution in the presence of \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) nanocomposites were irradiated using UV light and ultrasonic irradiation simultaneously using two 40 W UV lamps and ultrasonic bath operated at fixed frequency of 40 kHz and power of 150 W. In all experiments, 0.3 g/L \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) nanocomposites were suspended in 100 mL methylene blue solution with a concentration of 20 mg/L. During the sonocatalytic as well as photocatalytic reaction, samples were collected for 2h at regular intervals. The solution was analyzed using a Dynamica UV-visible spectrophotometer with a quartz cuvette with an optical length of 10 mm.

3. Experiments

Figure 1 shows the XRD patterns of \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{ZnO}/\text{NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO}/\text{TiO}_2/\text{NGP} \) nanocomposites with different concentrations of \( \text{ZnO} \) and \( \text{TiO}_2 \). For comparison, XRD patterns of pure \( \text{Fe}_3\text{O}_4, \text{CuO}, \text{ZnO} \) and \( \text{TiO}_2 \) nanoparticles are also shown in the figure. As can be seen in figure 1 all the
reflection peaks can be readily indexed to a combination of reflection peaks that can be ascribed to cubic spinel Fe$_3$O$_4$, monoclinic CuO, hexagonal wurtzite ZnO and anatase TiO$_2$. The characteristic 2θ values in the XRD patterns of the Fe$_3$O$_4$/CuO/ZnO/NGP nanocomposites exhibited a series of characteristic diffraction peaks of Fe$_3$O$_4$, CuO, ZnO and NGP, while the XRD patterns of the Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites revealed diffraction peaks of Fe$_3$O$_4$, CuO, TiO$_2$ and NGP.

Figure 1. XRD Patterns of (a) Fe$_3$O$_4$/CuO/ZnO/NGP and (b) Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites with different concentrations of ZnO and TiO$_2$.

Table 1. Lattice Parameter of Fe$_3$O$_4$, ZnO, CuO, and TiO$_2$ nanoparticles, Fe$_3$O$_4$/CuO/ZnO/NGP and Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites

| Samples               | Lattice Parameter | Grain Size |
|-----------------------|-------------------|------------|
|                       | Fe$_3$O$_4$       | CuO        | ZnO | TiO$_2$ | Fe$_3$O$_4$/CuO/ZnO/NGP | Fe$_3$O$_4$/CuO/TiO$_2$/NGP |
| Fe$_3$O$_4$           | a=b=c             | a          | b   | c       | a=b=c   | a           | b   | c       | a=b=c   | a           | b   | c       |
| CuO                   | 8.364             | -          | -   | -       | -        | -           | -   | -       | -        | -           | -   | -       |
| ZnO                   | -                 | 4.691      | -   | 3.425   | 5.138    | -           | -   | -       | -        | -           | -   | -       |
| TiO$_2$               | 8.374             | 4.7        | 3.432| 5.136   | 5.245    | 5.214       | -   | -       | -        | 3.614       | 37  | 15      |
| NGP                   | 8.375             | 4.681      | 3.432| 5.136   | 5.245    | 5.214       | -   | -       | -        | 3.614       | 37  | 15      |

Figure 2. EDX Patterns of (a) Fe$_3$O$_4$/CuO/ZnO/NGP and (b) Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites with different ZnO and TiO$_2$ loading.
The spectra confirmed that the synthesized nanocomposites were the desired materials, \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \). The values of crystallite size calculated from Scherrer’s formula and the values of the lattice parameters refined using the Rietveld refinement are tabulated in Table 1.

To confirm the presence of corresponding components in \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites, EDX measurements were performed. Figure 2 shows the EDX spectra of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites with molar ratios of 1:1:1 and 1:1:5. The spectra of pure nanoparticles of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/TiO}_2/\text{NGP} \) are also shown in the figure. The EDX spectra indicate that \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites were successfully formed.

Magnetic hysteresis curves of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites with different ZnO and TiO\(_2\) loadings measured at room temperature are displayed in figure 3. All samples exhibited ferromagnetic behavior. For comparison the hysteresis curves of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO}, \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2 \) and pure \( \text{Fe}_3\text{O}_4 \) nanoparticles were also plotted in the figure. It is exhibited that the value of saturation magnetization decrease as \( \text{Fe}_3\text{O}_4 \) is coupled with \( \text{CuO} \) and \( \text{ZnO} \) nanoparticles. However, it is seen that due to the incorporation of NGP, the \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites show a relatively higher magnetization values compared with that of the \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2 \) nanocomposites. According to the literature [17], this might be due to \( \text{Fe}_3\text{O}_4 \) nanoparticles attached to the surface of the NGP materials acting as defects and creating a stable NGP-based magnetic material [17].

Magnetic property is of great importance to the reusable property of catalyst. To study the magnetic separability of the material, a magnetic bar was placed near the sample holder supporting the \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) nanocomposites in water. As shown in the illustration of figure 3b, the \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) catalyst can be easily separated from the aqueous solution within a few minutes and supernantant was colorless. This experiment proved that \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) possessed the required adsorption and magnetic properties and can be used also for magnetic adsorbent to remove organic pollutant in liquid phase.

The catalytic activities of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites were evaluated by degradation aqueous solution of MB under UV and ultrasonic irradiation simultaneously. The degradation of MB in aqueous solution in the presence of 20 mg of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites under both UV light and ultrasonic irradiation are presented in figure 4. Plotted is the time dependent UV-vis absorption spectra of MB in the presence of \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) (figure 4a) nanocomposites. It can be seen that after irradiation with both UV and ultrasonic for 120 min, the fraction of degradation for \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) nanocomposites is approximately 100%. The relative concentrations as a function of irradiation time is shown in figure 4b and 4c. For detailed analysis the photocatalysis kinetics of the MB degradation, the pseudo-first model was applied. The rate constants were evaluated from the data and plotted in the figure 4d for \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites. It can be seen from figure 4d, that an increase in ZnO and TiO\(_2\) loadings results in a progressive increase in catalytic efficiency. Moreover, as shown in the figure, the incorporation of NGP was able to remove approximately 99% and 99% of MB within 90 and 75 min for \( \text{Fe}_3\text{O}_4/\text{CuO/ZnO/NGP} \) and \( \text{Fe}_3\text{O}_4/\text{CuO/TiO}_2/\text{NGP} \) nanocomposites, respectively. This result indicated that ternary nanocomposites prepared with incorporation of NGP showed excellent catalytic activity under both UV and ultrasonic irradiation, which may be due to improved charge transmission between each metal oxide and NGP thus prolonging the charge carrier life time and hindering charge carrier recombination [18].
Figure 3. VSM Patterns of (a) Fe$_3$O$_4$/CuO/ZnO/NGP and Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites with different concentrations of ZnO and TiO$_2$ (b) Magnetic separation process.

Fig. 4. Time dependent UV-vis absorption spectra of MB in the presence of (a) Fe$_3$O$_4$/CuO/ZnO/NGP and Fe$_3$O$_4$/CuO/TiO$_2$/NGP, (b) Photosonocatalytic activity of Fe$_3$O$_4$/CuO/ZnO/NGP and (c) Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites, (d) the rate constants for Fe$_3$O$_4$/CuO/ZnO/NGP and Fe$_3$O$_4$/CuO/TiO$_2$/NGP nanocomposites.

In order to study the mechanism of MB removal in the photosonocatalytic activity, it is important to detect the main active oxidative species responsible in the catalytic activity. In this case, control
experiments with added different type of scavengers such as tert-butyl alcohol, ammonium oxalate and Na2S2O8 scavenger for hydroxyl radicals, holes and electrons, respectively, is deployed and the results are plotted in figure 5a and figure 5b. It can be seen that ammonium oxalate a large degree of inhibition of methylene blue, which confirmed the indispensable role of holes in the degradation process of MB.

The mode of cycling used as well as maintaining high activity of catalyst is a critical issue in catalytic activity. Therefore it is necessary to investigate the reusability and the stability of the catalyst. Fe3O4/CuO/ZnO/NGP and Fe3O4/CuO/TiO2/NGP nanocomposites in this study could be easily recovered from the solution using a permanent bar magnet as can be seen in figure 6a. To evaluate the stability of the catalyst under UV and ultrasonic irradiation simultaneously, the Fe3O4/CuO/ZnO/NGP and Fe3O4/CuO/TiO2/NGP nanocomposites with a maximum loading of ZnO and TiO2 were repeatedly used for four cycles. The results are shown in figure 6b. For comparison the stability of nanocomposite without the incorporation of NGP was also plotted. After four cycles, degradation efficiencies of 100% and 100% were exhibited for Fe3O4/CuO/ZnO/NGP and Fe3O4/CuO/ZnO, respectively, while 100% and 100%, were obtained for Fe3O4/CuO/TiO2/NGP and Fe3O4/CuO/TiO2 nanocomposites, respectively.

4. Conclusion

In this paper, Fe3O4/CuO/ZnO/NGP and Fe3O4/CuO/TiO2/NGP nanocomposites were synthesized using a two step methods, sol-gel followed by hydrothermal. The catalytic properties of the synthesized samples were investigated under UV and ultrasonic irradiations simultaneously. The results showed that the incorporation of NGP in Fe3O4/CuO/ZnO and Fe3O4/CuO/TiO2 nanocomposite showed higher catalytic efficiency compared with the same catalyst synthesized without NGP. In addition, Fe3O4/CuO/ZnO/NGP and Fe3O4/CuO/TiO2/NGP nanocomposites displayed an excellent stability during four reaction cycles, indicating that the catalysts have potential application in water purification.

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