Synthesis and characterization of Fe-doped ZnO/Graphene nanocomposites and their photocatalytic efficiency to degrade methyl orange

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Abstract. Various amounts (3, 5, and 10 wt.%) of graphene were coupled with Fe-doped ZnO nanoparticles by the co-precipitation method. The Fe:ZnO/G nanocomposites structural and vibration modes were studied using X-ray Diffraction (XRD), Raman, and Fourier Transform Infrared (FTIR) spectroscopies. The spectra showed that the intensity of graphene increased with its amount. The thermal stability of the nanocomposites was examined by the Differential Thermal/Thermogravimetric Analysis (DTA/TGA). The DTA curves indicated that increasing graphene’s loading could increase their thermal stability. Their photocatalytic activities were also checked under UV light irradiation where methyl orange was used as the model of organic pollutant.

Keywords: Graphene, methyl orange, photocatalytic

1. Introduction
Various attempts had been applied to enhance the photodegradation of organic pollutant to solve water problem in the environment. These attempts had been conducted to inhibit the recombination of photogenerated electron and hole pairs, which cause photocatalytic efficiency to be reduced. They doped semiconductor catalysts with transition or noble metal [1, 2], forming composite with other materials and/or adsorbents [3, 4], or combination of the two mentioned [5–7]. Many materials had been kept developed to perform better photocatalytic activity.

Carbon materials are popular in the recent years, especially reduced graphene oxide. They have superior features in the photocatalytic application such as high specific surface area, high conductivity, unique two-dimensional (2D) single monolayer, excellent optical properties, and ability to accelerate charges transfer from photocatalyst to solid-liquid interface in meaning to perform reduction-oxidation reaction prior to degrade organic pollutants [8–10]. Researches had paid attention to graphene/photocatalysts composites for the remediation of environment.

Fe-doped ZnO nanoparticles had been coupled with natural zeolites and montmorillonite and their photocatalytic activity had been studied on our previous study with various dopant concentration [5]. In this study, we would like to examine Fe:ZnO/graphene nanocomposites’ photocatalytic activity to
degrade methyl orange (MO). The samples were prepared by the co-precipitation method with various loadings of reduced graphene oxide towards Fe:ZnO: 3 wt.% (0.03G), 5 wt.% (0.05G), and 10 wt.% (0.1G). Some measurements will be done to characterize the physical properties. Additional scavengers were also added to obtain the main active species.

2. Experimental details

2.1. Materials
Iron(II) sulfate heptahydrate (FeSO₄·7H₂O), Zinc(II) sulfate heptahydrate (ZnSO₄·7H₂O), sodium hydroxide (NaOH), methyl orange (MO) were purchased from Merck. Reduced graphene oxide was purchased from Angstrom Materials. Since the synthesis used the analytical grade reagents then no purification of the reagents were carried out. Distilled water was used to prepare the solutions in the experiment.

2.2. The Fe:ZnO/G nanocomposites preparations
The synthesis of nanoparticles of Fe:ZnO using co-precipitation method has been presented in earlier study [1]. The Fe:ZnO/0.03G, Fe:ZnO/0.05G, Fe:ZnO/0.1G nanocomposites were then carried out using the co-precipitation method by the following steps: the required amount of graphene was mixed in a solution of ethanol and water in a beaker. The mixture was then treated using an ultrasonic bath for 2h to form graphene dispersion. After that, the Fe:ZnO nanoparticles were added into it and stirred magnetically for 2h. Next, the mixture was heated under temperature 120 °C for 3 h and then centrifuged. At last, the precipitation was dried for 12 h in vacuum.

2.3. Characterization
The Fe:ZnO/G nanocomposites morphologies were studied using X-ray Diffraction (XRD) and Raman spectroscopies. The thermal stability and behavior of the nanocomposites were examined by the Differential Thermal/Thermogravimetric Analysis (DTA/TGA).

2.4. Photocatalytic examination
The nanocomposites with required dosage was put into 100 mL aqueous solutions of MO in glass beakers. Prior to be irradiated with UV light, the solutions were kept in the dark for 30 min to reach adsorption-desorption equilibrium. Then, the solutions were irradiated with 40 W UV light for 2 h. At given time interval, the degradation of MO was examined using UV-Vis spectrophotometer HITACHI UH5300. The effect of electron (e⁻), hole (h⁺), and hydroxyl radical (OH•) scavengers in the photocatalytic activity was also checked.

3. Results and discussion
X-ray Diffraction measurement was used to study the phase structure of the nanocomposites. Figure 1 shows the diffraction peaks of reduced graphene oxide and Fe:ZnO/G nanocomposites using Retvield refinement. The graphene shows amorphous phase with its broad peak at 2θ = 24.34°. Meanwhile, the nanocomposites exhibit hexagonal wurtzite structure of ZnO with diffraction peaks at 2θ = 31.62°, 34.35°, 36.11°, 47.38°, 56.41°, 62.68°, 66.13°, 67.74°, and 68.85°. The amorphous phase of graphene was not detected in the XRD patterns of the nanocomposites due to its low concentration, as seen on the insets. The same result was also obtained by Bai et.al. [11] and Chen et.al. [7] on their ZnO/Graphene materials. The presence of graphene could be seen on Raman spectroscopy result on the next discussion. On the other hand, additional graphene on the nanocomposites could affect the crystallinity of the samples. It can be seen from the slightly decreased intensity of the diffraction peaks of the nanocomposites with the increasing graphene amount. All nanocomposites have the same value for the ratio c/a=1.60.
Figure 1. XRD patterns of graphene and Fe:ZnO/G nanocomposites.

Figure 2. Raman spectra of graphene and Fe:ZnO/G nanocomposites.

Figure 3. DTA Curves of Fe:ZnO/G nanocomposites.

Figure 4. Photocatalytic activity of Fe:ZnO/G nanocomposites to degrade MO. The inset shows their degradation percentage.

The existence of graphene could be confirmed using Raman spectroscopy with 500 nm laser light as the excitation source. The results are displayed in figure 2. The Raman shifts at 1352 and 1593 cm$^{-1}$ correspond to D and G bands, which are the characteristics of carbon elements in graphene [12]. It can be seen that the intensity of both bands increases with the graphene loading. In addition, the Fe-doped ZnO (ZnFeO) mode came out at 633 cm$^{-1}$ [13, 14] for all samples.

The thermal stability and behavior of the nanocomposites was studied using DTA/TGA measurement with aluminium as reference. Figure 3 represents the DTA curves of the nanocomposites with different loadings of graphene. Respectively, the nanocomposites with (a) 0.03, (b) 0.05, and (c) 0.1G started to lost their thermal stability at 422.2, 430, and 430.2 °C. This phenomenon pointed out that the graphene amount in the nanocomposites is proportional with the thermal stability. The increasing heat flow implies that more graphene got combusted along with the amount of graphene.

Evaluating photocatalytic activity of the nanocomposites was conducted using MO as the model of organic pollutant. Figure 4 shows the degradation of MO performed by each nanocomposites. Increasing the amount of graphene from 0.03 to 0.05 towards Fe:ZnO could enhance the degradation of MO from 46.16 to 55.03 %, respectively because the presence of graphene on Fe:ZnO nanoparticles
could increase the charge transfer from Fe:ZnO’s conduction band to graphene’s in order to interact with the dyes [12]. However, further increase of graphene to 0.1 could decrease the degradation efficiency to 51.80 %, indicating that incorporation of 0.05G is the threshold limit. The excessive graphene content could inhibit the light wave to interact with the Fe:ZnO nanoparticles, resulting in reduced active sites of the catalyst.

There are some active species in photocatalytic activity such as electrons (e⁻), holes (h⁺), and hydroxyl radicals (OH•). To find out whether the active species are, additional scavengers are needed. Tert-butanol is used as scavenger of hydroxyl radicals, whereas di-ammonium oxalate and sodium sulfate are used as scavengers of hole and electrons, respectively. Figure 5 denotes that the active species that play a major role in the photocatalytic activity is e⁻ because it yielded the lowest degradation of MO, followed by OH• and then h⁺.

We also obtained e⁻ as the main active species in our previous works for Fe:ZnO nanoparticles and Fe:ZnO/nanocomposites [1, 5, 6, 14]. These results attributed to the dopant iron that acted as the e⁻ donors in ZnO’s energy level. In this case, both photogenerated and donor electrons have very important role to react with H₂O molecules to produce super reactive OH• for degrading the dye into not harmful molecules [15, 16]. Then, the same reaction goes with h⁺ on the valence band of the catalysts [15].

4. Conclusion
The Fe:ZnO/G nanocomposites were successfully synthesized by the co-precipitation method. The XRD patterns exhibit hexagonal wurtzite structure of ZnO nanoparticles. The undetected graphene’s amorphous phase on the XRD patterns could be confirmed at the Raman shifts 1352 and 1593 cm⁻¹ by Raman spectroscopy. DTA curves indicates that graphene amount is proportional to the sample’s thermal stability. The Fe:ZnO/0.05G perfomed the best photodegradation towards MO with 55.03 %. The main active species in the photocatalytic activity of the sample is electron.

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