Magnetically Separable and Reusable Fe₃O₄/ZnO/Nanographene Platelets Photocatalyst for the Removal of Dye

Ardiansyah Taufik¹², Iqriah K. Susanto¹², and Rosari Saleh¹²*

¹Departemen Fisika, Fakultas MIPA-Universitas Indonesia, 16424 Depok, Indonesia.
²Integrated Laboratory of Energy and Environment, Fakultas MIPA-Universitas Indonesia, 16424 Depok, Indonesia.

*Corresponding’s author: rosari.saleh@gmail.com; rosari.saleh@ui.ac.id

Abstract. In this study, we report the sol-gel synthesis of nanocomposite Fe₃O₄/ZnO with nanographene platelets (NGP) and characterized by suitable techniques, including field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), UV-visible diffuse reflectance spectroscopy and vibrating sample magnetometer. The as-synthesized Fe₃O₄/ZnO/NGP nanocomposites materials were used for photocatalyst under UV as well as visible light irradiation to remove methylene blue as a model of organic pollutant. The XRD spectra reveal peaks that can be attributed to cubic spinel Fe₃O₄, hexagonal wurtzite ZnO and nanographene platelets structure. The FESEM images show Fe₃O₄/ZnO uniformly decorating NGP sheets. EDX analysis signifies the formation of Fe₃O₄/ZnO/NGP. The photocatalytic activity was found to be ZnO loading dependent. Higher ZnO loading lead to higher rate of photocatalytic activity under UV light irradiation, while the opposite trend observed under visible light irradiation. The addition of NGP effectively enhanced the photocatalytic performance of Fe₃O₄/ZnO nanocomposites. Separation of Fe₃O₄/ZnO/NGP nanocomposites from the solution could be achieved by applying an external magnetic field, demonstrating the magnetic properties of the nanocomposites.

1. Introduction

Oxide semiconductor-based catalyst utilizing solar energy as energy source is a promising material for environmental purification of waste water and air [1-2]. To date, among various oxide semiconductors, most of investigations have focused on TiO₂ and ZnO. Between both metal oxides, it is proved that ZnO may exhibit better efficiency than TiO₂ in photocatalytic degradation [3]. However, in practical application ZnO has not yet fully been utilized due to their wide band gap, high recombination rate of electrons and holes and the low quantum yield of photocatalytic reactions in aqueous solutions [4]. To address this issue, several strategies and approaches such as nanocomposites construction and heterostructure assembly have been studied [5].

The combining of graphene with ZnO nanoparticles to form nanocomposites has been regarded as an effective approach to promote the efficiency of photocatalysis [6]. It is believed that the two-dimensional layered structure of graphene can inhibit the recombination of photogenerated electron-
hole pairs and can also significantly enhance the adsorption of organic pollutant [7-8]. In addition, incorporating Fe$_3$O$_4$ nanoparticles with ZnO nanoparticles not only efficiently improve the separation of photogenerated electron and hole pairs but also enhances the absorption ability of ZnO nanoparticles in longer wavelength region [9]. Moreover, Fe$_3$O$_4$ nanoparticles with separation function using via external magnetic field have been proved to effective in reused [10]. Therefore, in the present study, nanocomposites comprising ZnO, Fe$_3$O$_4$ and nanographene platelets have been synthesized using sol-gel techniques followed by hydrothermal. The effects of the molar ratios of ZnO to Fe$_3$O$_4$ on the structural and magnetic properties, especially on the photocatalytic activity, are investigated systematically.

2. Experimental Method

All chemical reagents were of analytical grade and were used without further purification. Iron (II) sulfate heptahydrate (FeSO$_4$. 7H$_2$O, 99%), zinc sulfate heptahydrate (ZnSO$_4$. 7H$_2$O, 99%), sodium hydroxide (NaOH), ethanol and ethylene glycol (EG) were purchased from Merck. Nanographene platelets (N008-100) were purchased from Angstrom Materials. Fe$_3$O$_4$ nanoparticles were synthesized using sol-gel method. In a typical procedure, 0.027 mole of FeSO$_4$.7H$_2$O was dissolved in 100 ml of deionized water to produce a solution that was then vigorously stirred at room temperature. The desired amount of CH$_3$COOH and 30 ml of ethylene glycol were added to the solution while stirring continuously until a pH value of 3 was obtained. Then, 0.054 mole of NaOH in 150 ml of deionized water was added dropwise to the mixture. The final solution was maintained at 80°C with stirring for 3h to form a gel. Afterward, the gel was dried at 80°C for 4 h before it was annealed at 125°C for 8h.

To synthesize Fe$_3$O$_4$/ZnO nanocomposites, 0.0125 mole of ZnSO$_4$.7H$_2$O was dissolved in 30 ml of distilled water with magnetic stirring. Then, 0.025 mole of NaOH in 65 ml of deionized water was added dropwise to the solution. This solution was designated as solution A, which was then stirred and heated at 80°C. The synthesized Fe$_3$O$_4$ nanoparticles were dispersed in 30 ml of ethanol and were designated as solutions B. Subsequently, solutions B was added to solution A, and the mixtures were stirred continuously at 80°C for 2h. These mixtures were then centrifuged and washed several times with ethanol and distilled water to remove residual and unwanted impurities. Afterward, the final product was allowed to stand overnight at room temperature and was then heated at 100°C for 1h under vacuum. A series of Fe$_3$O$_4$/ZnO nanocomposites were prepared with molar ratios of 1:1:1 and 1:1:5. The Fe$_3$O$_4$/ZnO/NGP nanocomposites were prepared by a simple hydrothermal method based on Khalid's work [19]. Briefly, 200 mg of NGP was dissolved in a solution of water (80 mL) and ethanol (40 mL) through ultrasonic treatment for 2h, followed by the addition of 2g of Fe$_3$O$_4$/ZnO nanoparticles to the NGP solution and an additional 2h of stirring to achieve a homogeneous suspension. The suspension was then heated at 120°C for 3h to affect the deposition of Fe$_3$O$_4$/ZnO on the NGP sheets. The nanocomposite was isolated by centrifugation and dried at 70°C for 12h.

The samples were characterized by X-ray diffraction (XRD) measurements using a Rigaku Miniflex 600 and monochromatic Cu-Ka ($\lambda = 1.54060$ 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. The X-ray diffraction patterns were analyzed by means of the MAUD program using Rietveld whole profile fitting to determine the crystal structure and lattice parameters. Elemental analyses and the morphology of the samples were studied with energy dispersive X-ray (EDX) spectroscopy and field emission scanning electron microscope (FESEM). The UV-Vis diffuse reflectance spectrum was measured using a Shimadzu spectrophotometer with an integrating sphere and a spectral reflectance standard over a wavelength range of 200-800 nm. Magnetic characteristics were measured by Oxford Type 1.2T vibrating sample magnetometer.

Methylene blue was selected as a model of organic pollutant. The photocatalytic activity was evaluated by degradation of organic pollutant in the presence of Fe$_3$O$_4$/ZnO/NGP nanocomposites in aqueous solution under UV and visible light irradiation. The photocatalytic experiments were performed using the same method described in our previous work [11]. The photocatalytic activities were then controlled, by adding different radical-scavengers into the solution of organic pollutant.
Ammonium oxalate, natrium sulfate, and tert-butyl alcohol were used as scavenger for photogenerated holes, photogenerated electrons and hydroxyl radical species, respectively. In the experiment the 10 mM of scavenger was added to the solution of organic pollutant and the same measurements as above are performed. To evaluate the photostability of the nanocomposites, a recycled photocatalytic activity measurement was performed. Typically, after the reaction of the first run under light irradiation, a permanent magnetic bar was used to separate the liquid and nanocomposites. The fresh organic pollutants, namely, methylene blue was mixed with the used nanocomposites to perform photocatalytic activity measurements for the second run. The experiment was repeated four times under identical conditions.

3. Results and Discussion

The magnetic properties of Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$/ZnO/NGP nanocomposites measured by VSM at room temperature are shown in Fig.1a. Saturation magnetization, remnant magnetization and coercivity values obtained from the hysteresis curves are given in Table.1. As can be seen from Fig.1a and Table. 1 all samples exhibited room temperature ferromagnetic. The decrease of saturation magnetization in order of Fe$_3$O$_4$, Fe$_3$O$_4$/ZnO =1:1 and Fe$_3$O$_4$/ZnO =1:5 is consistent with an increase of ZnO component in the nanocomposite samples, indicated that the strong ferromagnetic behavior of the nanocomposites depends on the content of the magnetic phase. It is reported that the magnetization of a ferromagnetic material was dependent on the strength of super exchange interaction between Fe$^{3+}$ cation in octahedral sites [12]. ZnO being diamagnetic reduces the super exchange interaction among Fe$^{3+}$ cation, therefore the saturation magnetization decreased. However, it was observed that the value of saturation magnetization increases as Fe$_3$O$_4$/ZnOis coupled with NGP.

Table 1. Magnetization value of Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/NGP composites

| Sample               | Magnetic Saturation (emu/g) |
|----------------------|-----------------------------|
| Fe$_3$O$_4$          | 82                          |
| Fe$_3$O$_4$/ZnO      | 78                          |
| Fe$_3$O$_4$/5ZnO     | 29                          |
| Fe$_3$O$_4$/ZnO/NGP  | 76                          |
| Fe$_3$O$_4$/5ZnO/NGP | 30                          |

Figure 1. (a) VSM Spectra of Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/ZnO nanocomposites, and Fe$_3$O$_4$/ZnO/NGP composites with two different molar ratio, (b) XRD spectra of ZnO and Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$/ZnO Nanocomposites, and Fe$_3$O$_4$/ZnO/NGP composites with two different molar ratio
Figure 1b illustrates the XRD patterns for Fe$_3$O$_4$/ZnO/NGP nanocomposite with a Fe$_3$O$_4$/ZnO molar ratio of 1:1 and 1:5. Also shown in the figure the XRD reflection intensity of pure Fe$_3$O$_4$, ZnO and NGP. The patterns of pure NGP, Fe$_3$O$_4$ and ZnO nanoparticles were marked and all peaks can be indexed as NGP, the typical cubic spinel and hexagonal wurtzite, respectively. No other diffraction peaks have been detected in the pure Fe$_3$O$_4$ and ZnO nanoparticles. In Fe$_3$O$_4$/ZnO/NGP nanocomposite, the characteristic 2θ values of the XRD patterns of the Fe$_3$O$_4$/ZnO/NGP nanocomposites all have been identified as individual structure and phase of Fe$_3$O$_4$, ZnO and NGP with no other diffraction peaks being detected in the nanocomposite. Six characteristic Fe$_3$O$_4$ peaks were observed at the 2θ diffraction angles of 30.01°, 35.36°, 43.02°, 53.33°, 56.98° and 62.48° in the nanocomposite samples. These peaks correspond to the (220), (311), (400), (422), (511) and (440) planes in the cubic spinel structures. Besides those peaks, other peaks located at the 2θ diffraction angles of 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9° and 69° were indexed to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction plane indices of the ZnO structures with hexagonal wurtzite phase, while peaks located at the 2θ diffraction angle of 26.4° has been attributed to the (200) diffraction planes in NGP structures. The diffraction analysis provides no evidence of the formation of mixed oxides in the sample. The values of crystallites' size calculated using the Scherrer formula are tabulated in Table 2.

| Sample                  | $<D>$ (nm) | <at>.% | | |
|-------------------------|------------|--------|---|---|---|
|                         | ZnO        | Fe$_3$O$_4$ | Zn | Fe | O  | C  |
| Fe$_3$O$_4$/ZnO         | 19         | -       | 60 | -  | 40 | -  |
| Fe$_3$O$_4$/5ZnO        | 17         | 38      | 55 | 14 | 32 | -  |
| Fe$_3$O$_4$/ZnO/NGP     | 16         | 35      | 24 | 23 | 39 | 14 |
| Fe$_3$O$_4$/5ZnO/NGP    | 15         | 34      | 50 | 10 | 27 | 13 |

![Figure 2](image-url) Figure 2. FESEM image of (a) Fe$_3$O$_4$ and (b) ZnO nanoparticles, (c) NGP materials, (d) Fe$_3$O$_4$/ZnO composites, (e) Fe$_3$O$_4$/ZnO/NGP composites, (f) EDX spectra of Fe$_3$O$_4$ and ZnO nanoparticles, Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$. 

Table 2. Grain Size, atomic percent and band gap energy of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/NGP composites
The surface morphology and elemental analysis of pure NGP, Fe$_3$O$_4$ and ZnO nanoparticles as well as Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/NGP nanocomposites has been studied by FESEM and EDX measurements and represented in figure 2. FESEM images revealed that pure Fe$_3$O$_4$ and ZnO have sphere-like shapes. It is also observed that the sphere-like shape is retained in Fe$_3$O$_4$/ZnO nanocomposite. The EDX analysis shows that the sample is composed of Fe, Zn, O and C atoms. It is shown that as the ZnO loading increased the atomic ratio of Zn/Fe was also increased. It is found that the stoichiometry in the composite samples, in the final product is nearly the same as in starting. The compositions of these samples were displayed in Table 2.

The band gap energies can be calculated from the diffuse reflectance spectra by performing a Kubelka-Munk analysis [13]. The values of the band gaps of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/5ZnO were 2.91 eV and 3.31 respectively. These band gap were lower than ZnO nanoparticles band gap (3.37 eV). It can be due to the 4s orbital of Fe may be mixed with the 4s orbital of Zn that results in formation of conduction band of ZnO at lower energy [14].

To evaluate the photocatalytic performance of Fe$_3$O$_4$/ZnO/NGP nanocomposites, the reduction of methylene blue in aqueous solution was investigated. Figure 3 shows UV-vis spectra of methylene blue in the presence of Fe$_3$O$_4$/ZnO/NGP nanocomposite under UV (figure 3a) and visible light (figure 3b) irradiation. The intensity of the characteristic absorption peak around 635 nm gradually decreased with irradiation time and reaches maximum of 98 % and 76 % after 120 minutes, for UV and visible light irradiation, respectively. Moreover, the apparent rate constant of photocatalytic degradation of methylene blue in the presence of Fe$_3$O$_4$/ZnO/NGP was obtained from the slope of the plot between ln C0/Ct and irradiation time as shown in figure 4, by assuming that photocatalytic activity followed the first-order kinetic equation: ln (Ct/C0) = - kapp x t, where Ct is the reaction concentration of methylene blue with irradiation time t and C0 is the initial concentration at t = 0. For comparison, the degradation of methylene blue in the presence of Fe$_3$O$_4$/ZnO was also plotted in the figure. The apparent rate constant, kapp is displayed in the Table 2. It is seen from figure 4 and table 2, coupled NGP with Fe$_3$O$_4$/ZnO nanocomposites results greatly improvement in the photocatalytic performance.

The stability of Fe$_3$O$_4$/ZnO/NGP with respect to degradation of methylene blue as an organic pollutant model was examined in four consecutive runs. The results are shown in figure 5. After four cycles, photodegradation efficiencies of 85 % and 72 % were obtained for methylene blue under UV and visible light, respectively. The stability of Fe$_3$O$_4$/ZnO was also shown in the figure. Compared with Fe$_3$O$_4$/ZnO, it suggested that Fe$_3$O$_4$/ZnO/NGP appears to be more stable and can be reused without loss in photocatalytic activity.

![Figure 3](image-url)  
Figure 3. (a) Absorbance spectra of Fe$_3$O$_4$/5ZnO/NGP under UV light Irradiation, (b) Absorbance Spectra of Fe$_3$O$_4$/ZnO/NGP under Visible light irradiation
Figure 4. (a) Degradation rate of photocatalytic activity for all sample under (b) UV light irradiation and visible light irradiation.

Figure 5. (a) Reusability of Fe₃O₄/ZnO and Fe₃O₄/ZnO/NGP under UV light irradiation, (b) Reusability of Fe₃O₄/ZnO and Fe₃O₄/ZnO/NGP under UV light irradiation.

To detect the main active oxidative species responsible for the degradation of methylene blue, tert-butyl alcohol, ammonium oxalate and Na₂S₂O₈ scavenger for hydroxyl radicals, holes and electrons, respectively, was added and displayed in figure 6. It can be seen that the addition of ammonium oxalate scavenger for holes inhibits the photocatalytic removal of methylene blue, suggested that the photocatalytic activities of methylene blue are driven by holes under UV and visible light irradiation.

According to the above results, the photocatalytic degradation mechanism is summarized in figure 5. The photogenerated electrons (e) and holes (h) were produced when Fe₃O₄/ZnO/NGP was illuminated. Narrow light-response range of UV can be improved by coupled ZnO nanoparticles with Fe₃O₄ and adding NGP. From figure 5, it can be seen that the photo-excited electrons are transported to NGP instead of going back to the holes. NGP with delocalized π structure could efficiently transfer electrons, which can easily migrate for the inner region to the surface to take part in the surface reaction to form radical such as •O₂⁻ by reacting with O₂ adsorbed on the surface. Due to higher separation efficiency of electron and hole resulting in the increase of the number of holes participating in the photo oxidation process, and generating •OH radicals and degrade the target pollutant.
4. Conclusion

In summary, Fe$_3$O$_4$/ZnO/NGP photocatalysts were prepared by sol-gel followed by hydrothermal process. The obtained photocatalyst were characterized by XRD, EDX, FESEM, diffuse reflectance spectroscopy- and VSM method. The influence of NGP and ZnO loading were investigated by measuring the photocatalytic performance for degradation of methylene blue under UV and visible light irradiation. The Fe$_3$O$_4$/ZnO/NGP with a molar ratio of Fe$_3$O$_4$/ZnO is 1:1 exhibited enhanced photocatalytic activity for degradation of MB under visible light irradiation, while enhancement of photocatalytic activity under UV light irradiation was observed for photocatalyst with a molar ratio of 1:5. Compared with photocatalysts with the same molar ratio under identical condition, it can be concluded that incorporation of NGP resulted in an enhancement of photocatalytic efficiency. Moreover, the photocatalyst can be easily removed from the treated water and showed a better stability compared to the one synthesized without NGP.

References

[1] Qi K, Cheng B, Yu J, Ho W 2017 *Journal of Alloys and Compounds* 727 792–820.
[2] Archana B, Manjunath K, Nagaraju G, Sekhar K B C, Kottam N 2017 *International Journal of Hydrogen Energy* 42 5125–5131
[3] Kumaran N N, Muraleedharan K 2017 *Journal of Water Process Engineering* 17 264–270
[4] Chen F, Tang Y, Liu C, Qian J, Wu Z, Chen Z 2017 *Ceramics International* 43 14525–14528
[5] Samadi M, Zirak M, Naseri A, Khorashadizade E, Moshfegh A Z 2016 *Thin Solid Films* 605 2–19.
[6] Cai R, Wu J, Sun L, Liu Y, Fang T, Zhu S, Li S, Wang Y, Guo L, Zhao C, Wei A 2016 *Materials and Design* 90 839–844.
[7] Zhu L, Liu Z, Xia P, Li H, Xie Y 2018 *Ceramics International* 44 849–856
[8] Zhao D, Gao X, Wu C, Xie R, Feng S, Chen C 2016 *Applied Surface Science* 384 1–9
[9] Ghanbarnejhada S, Baghshahia S, Nematib S, Mahmoodi M 2017 *Materials Science in Semiconductor Processing* 72 85–92
[10] Wang J, Yang J, Li X, Wang D, Wei B, Song H, Li X, Fu S 2016 *Physica E* 75 66–71
[11] Taufik A, Kalim I, Saleh R 2015 *Materials Science Forum* 827 37–42
[12] Xie T, Xu L, Liu C, Wang Y 2013 *Applied Surface Science* 273 684-691
[13] Hapke B, Theory of Reflectance and Emittance Spectroscopy, University Press, Cambridge, 1993.
[14] Mirzaie R A, Kamrani F, Firooz A A, Khodadadi A A 2012 *Materials Chemistry and Physics* 133 311