Research Article

Synthesis and Properties of Magnetic-Luminescent Fe$_3$O$_4$@ZnO/C Nanocomposites

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A Fe$_3$O$_4$@ZnO/C nanocomposite with a core-shell structure was synthesized using the co-precipitation method. To prevent the aggregation of the Fe$_3$O$_4$ magnetic particles, polyethylene glycol (PEG) was added. The X-ray diffractometer (XRD) results confirmed the formation of Fe$_3$O$_4$ and ZnO phases, with Fe$_3$O$_4$ having a cubic crystal system and ZnO having a hexagonal crystal system. Carbon in Fe$_3$O$_4$@ZnO/C had no effect on the crystal structure of Fe$_3$O$_4$@ZnO. Images from transmission electron microscopy (TEM) and scanning electron microscopy (SEM) revealed that the nanocomposite formed a core-shell structure. The Fourier transform infrared (FTIR) spectra verified the presence of bonds among ZnO, Fe$_3$O$_4$, and carbon. The appearance of the stretching vibration of the C≡C bond on the Fe$_3$O$_4$@ZnO/C sample revealed the nanocomposites’ carbon coupling. Photoluminescence (PL) spectroscopy was used to characterize the optical properties of the nanocomposites. Based on the results of the PL, the sample absorption of visible light was in the wavelength range of 400–700 nm. The photoluminescence of Fe$_3$O$_4$@ZnO differed from that of the Fe$_3$O$_4$@ZnO/C, especially in the deep-level emission (DLE) band. There was a phenomenon of broadening and shift of the band at a shorter wavelength, namely, in the blue wavelength region. Magnetic properties were characterized by vibrating-sample magnetometry (VSM). Based on the VSM results, the sample coupled with carbon exhibited a decrease in magnetic saturation. The presence of carbon changed photon energy into thermal energy. So, this material, apart from being a bioimaging material, can also be developed as a photothermal therapy material.

1. Introduction

Fe$_3$O$_4$ nanoparticles are considered a potential candidate for application as magnetic bioimaging materials, by making Fe$_3$O$_4$ nanoparticles covered by biocompatible materials [1–3]. Magnetic nanoparticles made of Fe$_3$O$_4$ have a high surface-to-volume ratio and a high surface energy. As a result, the magnetic nanoparticles tend to agglomerate to reduce the surface energy. In addition, these nanoparticles are highly reactive and easily oxidized which decrease their magnetic properties and dispersibility. Various strategies are further being developed by researchers to solve these problems. These strategies include doping Fe$_3$O$_4$ and surface coating of magnetic nanoparticles with organic molecules (such as surfactants, polymers, and biomolecules) or non-organic materials (such as SiO$_2$ and Au). The coating material for magnetic nanoparticles must be compatible and maintain the stability of the magnetic nanoparticles [4–6]. Several coating materials for Fe$_3$O$_4$ have been proposed, including polymers (such as dextran, albumin, polyethylene glycol, polyvinylpyrrolidone [7], folic acid [8, 9], chitosan [10], and silica [11]).

Combining magnetic and luminescent materials, such as lanthanide [12, 13], carbon/graphene [14, 15], and semiconductor [16, 17], produces materials with unique properties for different applications. Several researchers combined Fe$_3$O$_4$@ZnO nanocomposites with other materials to be utilized for antibacterial application [16], photodegradation of organic pollutants [18], and targeted drug delivery [19]. However, only a few studies have developed Fe$_3$O$_4$@ZnO nanocomposites as bioimaging materials. The main advantage of such nanocomposites for biological
applications is nontoxicity and biocompatibility. The surface modification must not significantly change the biocompatibility, photoluminescence, and magnetic properties. One of the materials that can be employed as a combiner for Fe₃O₄@ZnO is carbon. Carbon can also transfer the generated heat by the electron recombination process on the ZnO surface. Therefore, this material has multiple functions in biological applications, such as bioimaging and photothermal therapy of cancerous cells [20, 21].

In this study, a class of multifunctional nanocomposites is presented that combines superparamagnetic Fe₃O₄, ZnO, and surface modification of Fe₃O₄@ZnO with carbon. Fe₃O₄@ZnO/C is the core-shell structure of Fe₃O₄-based nanocomposite materials. The co-precipitation method was used to create a Fe₃O₄@ZnO nanocomposite. To prevent Fe₃O₄ agglomeration, polyethylene glycol (PEG) was used as a coating material. The carbon shell acted as a protective shell making it stable, free from external environmental influence, and biocompatible. XRD (Bruker D8 Advance) was utilized to determine the phase and crystal structure. The qualitative phase analysis of the XRD characterization’s diffraction pattern will be compared to established crystallographic databases, including the International Center for Diffraction Data (ICDD). To investigate optical properties, photoluminescence (PL, Horiba MicO Photoluminescence Microspectrometer) was used. SEM (SU3500) and TEM (FEI Tecnai G2 20 S-Twin) were used to examine the morphology and particle size of the samples. The chemical bonds formed were determined using FTIR (FTIR, Nicolet iS50 FTIR). In addition VSM (VSM250) was used to examine the magnetic properties of materials, which were then represented as a hysteresis curve.

2. Materials and Methods

2.1. Synthesis of Fe₃O₄@ZnO Nanocomposites. The synthesis of nanocomposite Fe₃O₄@ZnO/C begins with the synthesis of Fe₃O₄ nanoparticle combined with ZnO by the co-precipitation method [12, 22, 23]. A modified co-precipitation method was used to create Fe₃O₄@ZnO nanoparticles as done by Astuti et al. [24].

2.2. Synthesis of Fe₃O₄@ZnO/C Nanocomposites. In 25 mL of distilled water, 2 g of PEG was dissolved. Following that, 1 g of glucose was added, stirred for 30 minutes, heated in an oven at 300°C for 1 hour, and then dissolved in 10 mL of distilled water. Fe₃O₄@ZnO (0.1 g) and 5 mL of carbon solution were mixed, stirred, and then heated in the furnace at 250°C. The resulting powder was named Fe₃O₄@ZnO/C nanocomposite.

3. Results and Discussion

XRD analyzed the crystal structure, phase, and purity of the nanomaterials (Figure 1). Measurement results for Fe₃O₄ match the ICDD code 01-071-6339. Fe₃O₄ lattice parameters were \( a = b = c = 8.3153 \) Å, according the cubic system of Fe₃O₄ nanoparticles. The crystalline peaks of Fe₃O₄ observed at 2\( \theta \) values of 30.4593°, 35.7909°, 43.3784°, 53.9629°, 57.3681°, 63.2529°, and 90.5352° can be assigned to the planes with Miller indices of (220), (311), (400), (422), (511), (440), and (731).

Fe₃O₄ and ZnO were present in the Fe₃O₄@ZnO sample, and they had simple cubic and hexagonal wurtzite crystalline structures, respectively. The Fe₃O₄ phase had a cubic crystal structure with lattice parameters of \( a = b = c = 8.3761 \) Å, according to the ICDD code 01-076-7171. ZnO crystal structure has lattice parameters of \( a = 3.2525 \) Å, \( b = 3.2525 \) Å, and \( c = 5.2111 \) Å and is depicted in ICDD 01-075-7917. The crystalline ZnO peaks were observed at the 2\( \theta \) values of 31.7748°, 34.4273°, 36.2561°, 47.5718°, 57.3681°, 63.2529°, and 95.3214° which can be, respectively, assigned to the planes with Miller indices of (100), (002), (101), (102), (112), (201), and (211). The formation of the core-shell structure of Fe₃O₄@ZnO can be seen from the emergence of peaks (311) in Fe₃O₄ and (101) in ZnO, while the sample Fe₃O₄@ZnO/C showed similar peaks and crystal structure to Fe₃O₄@ZnO. This result shows that the presence of carbon has no effect on the crystal structure of Fe₃O₄@ZnO. The FTIR results confirm XRD measurements, indicating the presence of carbon in the Fe₃O₄@ZnO/C nanocomposite.

Figure 2 shows the results of FTIR measurements in the wavenumber range of 400–4000 cm⁻¹. Several absorption peaks in the sample Fe₃O₄@ZnO were observed, namely, the wavenumber 3352.34 cm⁻¹ related to the vibration of the -OH (hydroxyl) group. The absorption peaks illustrated the formation of PEG in the C-O and C-C vibrations of the sample, namely, at 1247.00 cm⁻¹, 1087.87 cm⁻¹, and 940.31 cm⁻¹. There were vibrations of tetrahedral Fe-O and octahedral Fe-O bonds at wavenumbers of 545.86 cm⁻¹ and 484.14 cm⁻¹, respectively, and Zn-O bonds at 424.35 cm⁻¹ [25]. Apart from the same absorption peaks, Fe-O, Zn-O, C-H, and C-O, no differences were found in the Fe₃O₄@ZnO/C sample. However, no absorption peak was found in the Fe₃O₄@ZnO sample, namely, the C≡C bond. Wavenumbers of 2086.05 cm⁻¹ and 2860.48 cm⁻¹ indicated C≡C bonds and
C-H bonds formed in the sample, respectively. The absorption peaks at wavenumbers of 1713.78 cm\(^{-1}\), 1599.98 cm\(^{-1}\), and 1348.27 cm\(^{-1}\) corresponded to bond stretching vibrations (C=O). The appearance of the stretching vibration of the C=C bond on the Fe\(_3\)O\(_4\)@ZnO/C sample resulted from carbon demonstrating the sample coupling with carbon. Besides, a more substantial shift and enhancement of absorption peaks of Fe\(_3\)O\(_4\)@ZnO/C were detected compared to Fe\(_3\)O\(_4\)@ZnO which can be possibly due to the bond between the C and O atoms in ZnO or Fe\(_3\)O\(_4\). This result shows that the synthesis of Fe\(_3\)O\(_4\)@ZnO/C using the co-precipitation method was successful.

As shown in Figure 3(a), TEM characterization was performed to determine the core-shell structure of the sample represented by Fe\(_3\)O\(_4\)@ZnO. The morphology of Fe\(_3\)O\(_4\) nanoparticles depicts a spherical shape with an approximate size of 15 nm. These clusters resemble a chain-like structure due to magnetic dipole interactions between nearby Fe\(_3\)O\(_4\) particles. Based on Figure 3(a), it can be seen clearly that the black Fe\(_3\)O\(_4\) is coated by the gray ZnO, which confirms the core-shell structure of the sample. These results were also in good agreement with the literature [17, 26]. Figure 3(b) shows a TEM image of the Fe\(_3\)O\(_4\)@ZnO/C nanocomposite. Based on the analysis of the diffraction pattern, it was found that Fe\(_3\)O\(_4\) and ZnO, had a particle size of less than 20 nm, while carbon was in the form of nanorods composed of Fe\(_3\)O\(_4\)@ZnO particles.

The SEM images of the Fe\(_3\)O\(_4\)@ZnO sample demonstrate aggregated spherical particles with sizes ranging from 50 to 100 nm (Figure 4), which can be distinguished from the white color assigned to ZnO nanoparticles covering the Fe\(_3\)O\(_4\) particles. In the preparation steps, the dispersion of Fe\(_3\)O\(_4\) in Zn\(^{2+}\) can lead to the adsorption of Zn\(^{2+}\) ions on the Fe\(_3\)O\(_4\) surface. The growth of this bound ZnO nanoparticle can be caused by Zn\(^{2+}\) ions from nearby Fe\(_3\)O\(_4\) surfaces and the freely available Zn\(^{2+}\) ions. This can also result in the attachment of a specific portion of every ZnO particle to the Fe\(_3\)O\(_4\) particles.

PL spectroscopy and VSM were used to investigate the room-temperature luminescence and magnetic properties, respectively. The PL spectrum of Fe\(_3\)O\(_4\)@ZnO (Figure 5) shows a UV emission peak at 381.86 nm for Fe\(_3\)O\(_4\)@ZnO and 382.49 nm for Fe\(_3\)O\(_4\)@ZnO/C, as well as a broad visible emission peak ranging from 400 to 800 nm. The visible photoluminescence emission centers in the Fe\(_3\)O\(_4\)@ZnO sample are determined by ZnO vacancies and surface defects. Although the PL mechanism of the visible ZnO band is unknown, a photoluminescence mechanism can be proposed. According to Figure 5, emissions in the 400 nm to 800 nm range are commonly referred to as “deep-level emissions” (DLEs). The DLE is caused by levels allowed inside the ZnO band gap. Transitions with energy in the visible range of the spectrum are produced by the allowed levels. The band broadness presumably resulted from a superposition of many different deep levels (yellow peak, green peak, and blue peak) emitting simultaneously [27, 28]. The presence of a strong and broad emission peak in the visible region indicates that ZnO has a higher concentration of defects. The most common surface defects reported in ZnO are oxygen vacancies, and the intensity of the green emission depends on the concentration of the oxygen vacancies. The difference between the DLE of Fe\(_3\)O\(_4\)@ZnO and Fe\(_3\)O\(_4\)@ZnO/C is visible. There is a broadening of the DLE band in Fe\(_3\)O\(_4\)@ZnO/C, and there is a shift in the band to a shorter wavelength, namely, in the blue wavelength region caused by the presence of carbon atoms. Carbon has two significant peaks at 450 nm and 510 nm attributing to the sp\(^2\) domain’s \(\pi-\pi^*\) transition and the \(n-\pi^*\) transition of the surface functional group, respectively. Interstitial oxygen cause yellow emission in ZnO which can be reduced by the presence of C atoms resulting in a shift in the blue region emission. The green and yellow peaks were observed in the Fe\(_3\)O\(_4\)@ZnO sample. Besides, the blue shift was observed in the Fe\(_3\)O\(_4\)@ZnO/C sample. Free exciton (FE) emissions dominated the UV emission band which is generally ascribed to the band-to-band transition.

Furthermore, a slight decrease in the intensity of photoluminescence of the Fe\(_3\)O\(_4\)@ZnO/C sample was identified compared to that of the sample Fe\(_3\)O\(_4\)@ZnO. A reduction in the intensity of the Fe\(_3\)O\(_4\)@ZnO/C photoluminescence is closely related to the recombination of the electron-hole pairs. It can be concluded that the weaker the PL intensity, the slower the recombination of photogenerated electron-hole pairs.

The results of measuring the magnetic properties of Fe\(_3\)O\(_4\), Fe\(_3\)O\(_4\)@ZnO, and Fe\(_3\)O\(_4\)@ZnO/C nanocomposites are shown in Figure 6. The coercivity values (\(H_{c}\)) of Fe\(_3\)O\(_4\), Fe\(_3\)O\(_4\)@ZnO, and Fe\(_3\)O\(_4\)@ZnO/C were calculated as 0.0031 T, 0.0037 T, and 0.0038 T, respectively, while the saturation magnetization (\(M_{s}\)) values were different, as shown in Table 1.

Based on Table 1 and Figure 6, the \(M_{s}\) value of Fe\(_3\)O\(_4\) nanoparticles is 68.10 emu/g. It decreased to 66.53 emu/g for the Fe\(_3\)O\(_4\)@ZnO sample. The decrease in \(M_{s}\) value of the Fe\(_3\)O\(_4\)@ZnO nanocomposite was due to the addition of nonmagnetic PEG and ZnO and also the presence of oxygen-containing groups in the matrix of Fe\(_3\)O\(_4\).
Figure 3: TEM image of (a) Fe$_3$O$_4$@ZnO and (b) Fe$_3$O$_4$@ZnO/C nanocomposites.

Figure 4: SEM image of Fe$_3$O$_4$@ZnO nanocomposite.

Figure 5: Photoluminescence spectra of the Fe$_3$O$_4$@ZnO and Fe$_3$O$_4$@ZnO/C nanocomposites.
nanoparticles which could reduce the amount of magnetic moment in the sample. The addition of carbon to the sample \( \text{Fe}_3\text{O}_4@\text{ZnO} \) caused a decrease in \( M_s \) to 44.65 emu/g. This was followed by a slight increase in the value of the coercivity field due to the presence of ZnO and C around \( \text{Fe}_3\text{O}_4 \). The three samples had high magnetic saturation values and low \( H_c \), close to zero. So, these three materials are classified as superparamagnetic. The magnetic saturation value decreases in direct proportion to particle size. The smaller the particle size, the lower the crystallinity. Therefore, reduced crystallinity decreases magnetic saturation [29]. TEM investigation indicates that the particle size of the \( \text{Fe}_3\text{O}_4@\text{ZnO} \) nanocomposite was smaller than that of the \( \text{Fe}_3\text{O}_4@\text{ZnO} \) nanocomposite. Smaller particles caused \( \text{Fe}_3\text{O}_4@\text{ZnO}/\text{C} \) nanocomposite to have a lower magnetic saturation. However, the decrease in magnetic saturation in the \( \text{Fe}_3\text{O}_4@\text{ZnO}/\text{C} \) sample was still within the proper range for biomedical applications.

### 4. Conclusion

The \( \text{Fe}_3\text{O}_4@\text{ZnO} \) nanocomposite has a cubic and a hexagonal wurtzite structure for \( \text{Fe}_3\text{O}_4 \) and ZnO, respectively. The addition of carbon increases the absorption of \( \text{Fe}_3\text{O}_4@\text{ZnO} \) UV emission. It also broadens and shifts the visible emission to shorter wavelengths. Based on the VSM results, it can be

![Figure 6: VSM measurement of \( \text{Fe}_3\text{O}_4 \) and nanocomposites.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic properties</th>
<th>( H_c ) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_3\text{O}_4 )</td>
<td>68.10</td>
<td>0.0031</td>
</tr>
<tr>
<td>( \text{Fe}_3\text{O}_4@\text{ZnO} )</td>
<td>66.53</td>
<td>0.0037</td>
</tr>
<tr>
<td>( \text{Fe}_3\text{O}_4@\text{ZnO}/\text{C} )</td>
<td>44.65</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

Table 1: Magnetic properties of \( \text{Fe}_3\text{O}_4 \) and nanocomposites.
concluded that there is a decrease in magnetic saturation of the Fe₃O₄@ZnO/C sample which is associated with a reduction of particle size based on TEM results. The presence of carbon also causes a change in photon energy into thermal energy. The addition of carbon to the Fe₃O₄@ZnO nanocomposite increases its biocompatibility as well. However, this does not significantly affect the photoluminescent and magnetic properties of the Fe₃O₄@ZnO/C nanocomposite. Therefore, these materials have the potential to be further developed as biological application materials, especially as bioimaging and photothermal therapy materials.

**Data Availability**

The data used to support the findings of the study are included within the article.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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**References**


[19] H. Qiu, B. Cui, G. Li et al., “Novel Fe₃O₄@ZnO@mSiO₂ nanocarrier for targeted drug delivery and controllable release with microwave irradiation,” *Journal of Physical Chemistry C*, vol. 118, no. 27, p. 14937, Article ID 14929, 2014.


