Effect of Template on Structural and Band Gap Behaviors of Magnetite Nanoparticles

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Abstract. Magnetite nanoparticles (MNNPs) were prepared via the coprecipitation-sonochemical route. Polyethylene-glycol as a template was employed with volume variations of magnetite/polyethylene-glycol of 1:0; 2:1; and 1:1. The structural and band gap characters of the samples were studied using XRD, SEM, FTIR spectrometer, and UV-Vis spectrometer. The data analysis presented that the magnetite formed spinel structure with particle size ranging from 20 to 23 nm. This result was confirmed by SEM characterization showing a particle size of lower than 25 nm in a spherical form. The FTIR spectra presented that the samples had vibrational peaks originating from the magnetite particles at wavenumbers in the range of 445 to 600 cm⁻¹. Furthermore, the data of the UV-Vis characterization showed band gap values of 2.52–2.61 eV for respective samples. It can be concluded that the polyethylene-glycol was effective to produce the magnetite nanoparticles via the coprecipitation-sonochemical route.

Keywords: Magnetite, template, nanoparticle, spinel, coprecipitation-sonochemical route.

1. Introduction
Magnetite is a material with a unique magnetic characteristic since its bulk form has a ferrimagnetic property while its reduced size to a nanometric order would have a superparamagnetic property [1]. The superparamagnetic phenomenon of magnetite could be seen when the particle is in a single domain. Hence, the morphology and particle size of magnetite could be controlled by a synthesis method that is appropriate for specific applications.

To date, several synthesis methods for producing magnetite nanoparticles have been developed. For example, ball milling [2], hydrothermal [3], coprecipitation [4], microwave [5], sonochemical [6] method, and so on. Each of the developed methods has its advantages and disadvantages. The previous research showed that the coprecipitation-sonochemical method, which is a combination of coprecipitation and sonochemical methods, is useful for reducing magnetite particle size until it reaches below 10 nm and it has a single domain character [7].

A single-domain particle shows a high magnetic response when induced by an external magnetic field. However, the particle’s tendency to agglomerate would be higher due to the van der Walls force among the magnetic particles. Therefore, it is necessary to employ a method to control the particle size such as using a polymer-based template. One of the polymers that could be utilized to form while
controlling particle size and distribution is polyethylene-glycol [8]. In this case, polyethylene-glycol functions to prevent the formation of a more extensive particle aggregation to enable the production of uniform magnetite particles. Nonetheless, right molecule length and number are necessary for the polyethylene-glycol to function.

In their research, Radoń et al. utilized polyethylene-glycol polymer, PVP, and dextrin to form uniform and water-soluble magnetite particles and citrate as a template to form a soluble surface in an organic acid solution [9]. The polyethylene-glycol polymer is biocompatible, and an active layer that has a hydrophilic property contained in the particle surface enables the particle to disperse in water efficiently [10]. Thus, magnetite particle layering with polyethylene-glycol is excellent for further applications such as water-based ferrofluid fabrication for various biomedical applications. The research trend in the past one year presented several uses of polyethylene-glycol in producing biocompatible particles for biomedical applications such as preclinical imaging [11], MRI and cancer ablation [12], drug delivery [13], MRI contrast agent [14], photocatalyst [15], and so forth.

Based on the explanation above, the magnetite nanoparticles in this research were synthesized via coprecipitation-sonochemical method using polyethylene-glycol as a template. The magnetite nanoparticles with different polyethylene-glycol volumes were characterized by XRD to identify its crystal structure, by FTIR to know its functional group, by SEM to analyze its morphology, size, and particle distribution, and by UV-VIS to identify its structural and energy band gap ($E_g$).

2. Materials and Methods

Iron sands extracted by a permanent magnet were dissolved in HCl through a stirring process using a magnetic stirrer. The solution was then filtered to produce FeCl$_2$ and FeCl$_3$ contents. Such processes were in accordance with our previous studies [16–18]. The polyethylene-glycol solutions in water with 0.75 and 15 ml compositions were added into the FeCl$_2$ and FeCl$_3$ solutions while stirred by using a magnetic stirrer and wisely dropped by NH$_3$OH. After that, the solution produced by such coprecipitation method was sonicated at 40 kHz frequency for 1 hour to produce black sediment. Next, the sediment was washed with distilled water until it reached a neutral pH and continued by the final process of sediment heating at 100 °C for 1 hour in order to obtain magnetite particles.

3. Results and Discussion

Figure 1 exhibits the XRD patterns of magnetite nanoparticles with polyethylene-glycol composition variations. The data identification shows some diffraction peaks at the angle of 2θ namely 30.2895°; 35.7527°; 43.4787°; 53.7999°; and 57.4081°, respectively in accordance with the hkl fields of (220), (311), (422), (511), and (440) based on AMCS model code 0002402. The hkl field indicates that the sample has a cubic-spinel structure as reported by Baltazar et al. [19]. The XRD patterns obtained in this research also provide information of the magnetite nanoparticle crystallinity and the absence of a new phase that can cause impurities. It evidenced that magnetite nanoparticles with a high level of purity have been successfully synthesized through coprecipitation-sonochemical method. The highest intensity peaks of all samples were found at (311) hkl field. A quantitative analysis of the (311) hkl field via Scherer equation produced particle sizes ranging from 21.3 – 25.7 nm. The diffraction peak intensity of the crystal field qualitatively related to the crystallinity level of the particles. An addition in the polyethylene-glycol volume resulted in an increasing number of polyethylene-glycol layers on the magnetite surface. Thus, the peak intensity value of the (311) hkl field was decreasing since polyethylene-glycol is a polymer with an amorphous characteristic [20].
Figure 1. XRD patterns of the magnetite particles with polyethylene-glycol content of (a) 0 ml, (b) 7.5 ml, and (c) 15 ml

Figure 2. SEM images of the magnetite particles with polyethylene-glycol content of (a) 0 ml, (b) 7.5 ml, and (c) 15 ml

Figure 2 provides information about the particle morphology based on the SEM test. The qualitative analysis via SEM image observation showed that the particles have spherical forms with different shapes and sizes in accordance with the polyethylene-glycol variations. The SEM test results were analyzed using ImageJ software resulting in different particle sizes ranging from 22.5–27.3 nm of all polyethylene-glycol variations. The morphology of all of the samples is spherical resulting from the nucleation rate per unit between isotopes on the surface of the magnetite nanoparticles.
Figure 3. Particle size distribution of the magnetite particles with polyethylene-glycol content of (a) 0 ml, (b) 7.5 ml, and (c) 15 ml

Complete information about the particle size homogeneity is analyzed based on the histogram fitting of particle size distribution in Figure 3. Such histogram fitting provides information of the magnetite particle size distribution with polyethylene-glycol volume variations shown by the value of the inhomogeneity level obtained from the size deviation towards the average value in percentage unit [21]. It is known that the level of particle size inhomogeneity decreased along with the addition of polyethylene-glycol volume. It was possible due to the polyethylene-glycol percentage that significantly affects the polyethylene-glycol chain’s ability to bind and to cover the magnetite nanoparticles [22]. Hence, the chain ability to wrap would be higher, and the homogeneity of the particle size and shape will be uniform. The average size was smaller compared with the previous research where the polyethylene-glycol-200 produced 128 nm particle size [23]. Meanwhile, a single reaction polyol method employed on 80 ml polyethylene-glycol produced magnetite nanoparticles in the size of 32.3 nm [24]. It indicated that the employment of the coprecipitation-sonochemical synthesis method via polyethylene-glycol-1000 as the template has successfully produced smaller-sized particles and an addition of polyethylene-glycol composition resulted in more uniform magnetite particle sizes.

Table 1 presents different particle sizes based on the results of XRD and SEM analysis. The particle size analysis using Scherrer approach resulted in a lower value than SEM. It was due to the inhomogeneity strain and instrumental effect that have an insignificant effect on the value of the diffraction peaks during the calculation using Scherrer’s equation [25] and the thin polyethylene-glycol layer on the particle surface resulted in different particle sizes via Scherrer approach and direct observation.

| Sample               | Particle size (nm) | Inhomogeneity level (%) |
|----------------------|--------------------|-------------------------|
|                      | Scherrer equation  | SEM                     |
| Polyethylene-glycol  | 21.3               | 22.5 ± 1.9              | 8.4                    |
| (0 ml)               |                    |                         |                       |
| Polyethylene-glycol  | 23.6               | 22.5 ± 1.8              | 8.0                    |
| (7.5 ml)             |                    |                         |                       |
| Polyethylene-glycol  | 25.7               | 27.3 ± 0.8              | 2.9                    |
| (15 ml)              |                    |                         |                       |

The functional group of the magnetite nanoparticles with polyethylene-glycol variations was characterized by using FTIR via electromagnetic wave radiation ranging from 400 – 4000 cm⁻¹ as shown in Figure 4. The functional group of the metal oxide at the octahedral position refers to the diffraction peak with a value of ~445 cm⁻¹ [26]. Meanwhile, the bonds at the wavenumbers of ~587 cm⁻¹ and ~1290 cm⁻¹ were metal oxide bonds in a tetrahedral position [27]. There was a large reduction of the peak at the wavenumbers of ~1620 cm⁻¹ and ~3460 cm⁻¹ that were bending and stretching bonds from the hydroxyl [28]. A very weak spectrum was found at ~2350 cm⁻¹ was –CH₂ stretching vibration group by
polyethylene-glycol [10]. The results of this research showed that the polyethylene-glycol wrapped the magnetite particles although it was heated at a temperature of 100 °C. Similar results were shown by the research conducted by Jayanti et al. stating that the polyethylene-glycol layer stayed on the surface of the magnetite particles after being heated up to 120 °C [10].

Figure 4. FTIR spectra of the magnetite particles with polyethylene-glycol contents of (a) 0 ml, (b) 7.5 ml, and (c) 15 ml

Figure 5 presents the UV spectrum patterns from the UV-Vis analysis on the magnetite nanoparticles. The absorption spectrum of the magnetite nanoparticles was measured on the particle sizes ranging from 420-800 nm. Hence, the magnetite nanoparticle spectra peak was only found at the wavelength ranging 430-550 nm. The UV-Vis spectroscopy provided information about the band gap, particle size distribution, and absorption spectrum so that the absorption spectrum shows the optical property and band gap of the magnetite nanoparticles. Figure 5 illustrates that the spectra peak moved to a higher wavelength along with the increasing polyethylene-glycol concentration used. Lambert-Beer law was employed to identify the absorbance value. According to the Lambert-Beer law, the absorbance value of a dissolved material is directly proportional to the path length passed by the monochromatic light and concentration of absorbing molecules [30]. Hence, the absorbance value showed the maximum wavelength that could be absorbed by the material. The higher the absorbance value of the magnetite nanoparticles, the higher the monochromatic wavelength that could be absorbed [27].
Figure 5. Band gap of the magnetite particles with polyethylene-glycol content of (a) 0 ml, (b) 7.5 ml, and (c) 15 ml

UV-Vis characterization results were analyzed using the Tauc plot model to identify the direct band gap value of the samples. It is possible since the given treatment is not in the forms of doping or annealing process that could change the crystal structure and lattice strain value [31]. The use of polyethylene-glycol as a template on magnetite particles has an insignificant effect on the direct band gap values changes, namely starting from 2.52, 2.57, and 2.61 eV for 0, 7.5, and 15 ml polyethylene-glycol concentrations. In general, such changes in values could relate to the magnetite particle size. A similar tendency was shown in the research performed by Deotale et al. stating that both the direct and indirect band gap values increased along with the increase in particle size [32]. Meanwhile, the same energy gap was presented in the results of a study conducted by Gopal et al. that employed polyethylene-glycol molarity variations where the optical linear character of the material shown by the energy gap value did not show any significant changes [33].

4. Conclusion
The magnetite nanoparticles synthesis via coprecipitation-sonochemical method assisted by polyethylene-glycol as the template has been successfully conducted. With variations of polyethylene-glycol additions, the magnetite nanoparticles have uniform shapes. The additions of polyethylene-glycol compositions result in a larger magnetite particle size and higher homogeneity level of the particle. The crystallinity of the magnetite particles decreased due to the influence of polyethylene-glycol polymer that has an amorphous characteristic. The functional group of the metal oxide was shown at the absorption peak of ~445 cm\(^{-1}\), and metal oxide bonds in a tetrahedral position were identified at the wavelengths of ~587 cm\(^{-1}\) and ~1290 cm\(^{-1}\). Further, the optical characteristic shows that the polyethylene-glycol additions enhanced the absorption value of the magnetite nanoparticles, but it could not significantly change the direct band gap value of approximately 2.52 – 2.61 eV.

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