Synthesis of Fe₃O₄ Nanoparticles using PEG Template by Electrochemical Method

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Abstract. One of the nanoparticles which have been developed is magnetite. Due to its magnetism and reactivity, this particle can be used in various fields including technology, environment, and biomedical. One simple method to synthesize magnetite is electro-oxidation of iron in the water. The particle size produced by this method can be adjusted by controlling the electrochemical cell parameters. Unfortunately, this method usually releases polydispersed particles. One solution to overcome this problem is by using an in situ PEG in the synthesis process. In this research, PEG 6000 was chosen as a template, so the synthesis process was performed by electro-oxidation of iron in the dilute solution of PEG. Particles with an average diameter of 62.5 nm were obtained. The monodispersity, surface area, and crystallinity of the particles increase in this way. The specific surface area increased from 55.322 to 391.314 m²/g. The results of XRD and FTIR analysis showed that PEG acted as a template in the synthesis process. In addition, the yield obtained with PEG template was larger than without the template. This method is quite promising as a way of synthesis of magnetite nanoparticles.

Keywords: Magnetite, PEG, nanoparticle, electrochemical method, template.

1. Introduction

Today, the development of nanoparticles, including magnetite nanoparticles, is a very interesting field of research since nanoscale magnetic materials have superior physical and chemical properties [1]. Magnetite nanoparticles are widely used in many areas of technology including environmental, ferrofluid, energy storage, and medical technology (both as diagnostic and therapeutic agents) [1, 2].

To obtain the desired properties due to their specific use, various methods of synthesizing these nanoparticles have been developed, for example, coprecipitation [3], hydrothermal [4], sol gel [5], and electrochemistry [6-8]. Each method has its own advantages and limitations. The advantages of the electrochemical method, in this case, is the electro-oxidation of iron in water are environmentally friendly and the properties of the synthesized product can be set easily by controlling the parameters of electrolysis cells such as cell dimensions, electrolyte type, current density, and temperature. The disadvantage of this method is the inadequacy of the resulted product, but this weakness will be overcome by using many electrode systems and electrochemical cell parameter setting [9].

Some previous studies have obtained a pure magnetite with a fairly uniform particle size distribution and high saturation magnetization [6]. This study was intended to increase the surface area of the particles using templates in the synthesis process. The template was added to the electrolyte.
before the electro-oxidation was executed. The template acted only as a mold of the particles formed without affecting the reaction process in electrolysis. After the synthesis process ended, the template could be easily removed, for example, through heating. The release of the particles from the template would leave some pores. Thus, the in situ template-assisted electro-oxidation is expected to produce particles with a larger specific surface area and uniform size. One of the substances that meet the above requirements as a template is PEG. Non-ionic PEG will not interfere with the process of magnetite formation. PEG will decompose on the product drying process. The synthesis of magnetite nanoparticles by the other methods has also been done using PEG as a template [10]. The purpose of this study was to examine the differences in crystallinity, monodispersity, and the specific surface area between magnetite synthesized with and without PEG 6000 as an in situ templates.

2. Materials and Methods
The synthesis of Fe₃O₄ nanoparticles with and without the PEG 6000 template was performed by an electrochemical method and followed by characterization with the following equipment: XRD (Panalytical X'pert Pro), SEM (Type Inspect S50, FEI), FT-IR (Shimadzu Type FT-IR 8400S), and BET (Nova 1200, Quantachrome). The materials which were used included filter paper (Whatman-42), universal indicator (Merck), iron electrode, carbon electrode, technical FeSO₄, PEG 6000 (Merck), NaOH (Merck), and demineralized water (Hydrobath).

The synthesis of Fe₃O₄ nanoparticles began with the preparation of anode as a source of iron ion through a process of depositing of pure iron film to a commercial iron plate using a technical iron (II)sulfate solution by electroplating. The synthesis of Fe₃O₄ nanoparticles was carried out in an aqueous solution of PEG 6000 0.004 M (for particles with the PEG template) and in demineralization water (for particles without the PEG template) under DC voltage for 4 hours. Both processes produced black deposits which could be magnetized. The generated particles were then filtered, dried at 60 °C, and characterized.

3. Results and Discussion

3.1. The Mechanism of Magnetite Formation
The processes of the synthesis of magnetite nanoparticles with and without PEG were followed by observing the color change in the solution around the anode ranging from t = 0 to t = 240 minutes. The results of the observation are shown in Figures 1 and 2. Based on these two images, there was no fundamental difference between the two synthesis processes. The solution around the anode was initially colorless, then gradually turn into a light brown turbid solution, orange, dark brown, and black at the end. This phenomenon indicated that the addition of PEG in the electrolyte did not affect the reactions. The color change of solution and sediment around the anode in both processes can be explained in equation (1) to (4) and proceeded with the following process as described in equation (5), if the PEG solution was used as an electrolyte. The PEG template would decompose on a heating process, so magnetite nanoparticles would be obtained as described by equation (6).

Anode (Fe of electroplating result): Fe→Fe²⁺+2e⁻
Cathode (commercial Fe): 2H₂O+2e⁻→2OH⁻+H₂

The reactions around the anode:
Fe²⁺+2OH⁻→Fe(OH)₂
3Fe(OH)₂+½O₂→Fe(OH)₃+2FeOOH+H₂O
Fe(OH)₃+2FeOOH→Fe₂O₄+2H₂O
Fe₂O₄+PEG→Fe₃O₄-PEG
Fe₃O₄-PEG △ Fe₃O₄
A light brown color indicated the formation of Fe(OH)$_2$ and the beginning of FeOOH formation. Orange was a typical color of FeOOH. The transition from orange to black was shown as dark brown. Black color indicated the existence of magnetite. The above reaction mechanism as written at equation (1) to (4) was corroborated by the results of the study of Lozano et al. who compared various mechanisms of magnetite formation by electrolysis method [9]. Figure 1 and 2 show the electrolyte and sediment color changes around the electrode during the electrolysis process.

![Figure 1. Solution and sediment color changes around the anode in synthesis process of magnetite without template at (A) 0, (B) 30, (C) 60, (D) 120, (E) 180, (F) 240 minutes, and (G) the final product](image1.png)

![Figure 2. Solution and sediment color changes around the anode in synthesis process of magnetite with the template at (A) 0, (B) 30, (C) 60, (D) 120, (E) 180, (F) 240 minutes, and (G) the final product](image2.png)

In addition, the yield obtained with PEG template was larger than without the template. The presence of PEG around magnetite makes magnetite seem isolated from the reacting system, thus shifting the reaction equilibrium toward the product formation. In other words, the yield will increase.

3.2. The Characteristics of the Particles

Based on the XRD analysis as shown in Figure 3, the XRD spectra of Fe$_3$O$_4$ nanoparticles with and without PEG template showed magnetite peaks at 2θ = 30.3°, 35.7°, 43.4°, 53.8°, 57.3°, 62.9°. These peaks corresponded to a typical magnetite peak in accordance with JCPDS Card No. 19-629 [6]. These spectra did not show typical PEG peaks, i.e. at 2θ: 19.41 and 23.34 according to JCPDS Card No. 49-2097 [11]. This means that the PEG acted as a particle template. The peaks of Fe$_3$O$_4$ with PEG template was higher in intensity than Fe$_3$O$_4$ without PEG. It also proved that PEG did not coat the magnetite surface, and only acted as a template. Mukhopadhyay, et al. [12] and Mahdavi, et al. [13] found that crystallinity of PEG-coated magnetite was lower than the bare one. In this study, the presence of PEG around magnetite during the synthesis process made the particles longer underwent the maturation process so that the crystallinity was higher. The heating process above PEG decomposition temperature makes the particles free from PEG.
The FTIR analysis results that are presented in Figure 4 supported that PEG acted as a template. Both synthesized magnetite spectrum showed the presence of a vibrational peak at a region of 560 cm$^{-1}$ indicating that there was a Fe-O bond of Fe$_3$O$_4$. However, the absence of the PEG 6000 vibrational peaks [14] on both magnetite spectra, i.e. C-H stretching at 2.890 cm$^{-1}$, C-O stretching at 1.110 cm$^{-1}$ and O-H stretching at 3.350 cm$^{-1}$ once again proved that PEG had become a mold on this synthesis and had been decomposed.

The specific surface area of Fe$_3$O$_4$ with and without the PEG 6000 template obtained from the BET analysis is given in Table 1. The use of PEG 6000 as a template increased the specific surface area.
Particle growth took place in a mold producing smaller particles of the size, causing a larger specific surface area. This increase was also supported by the mold release process of the particles at thermal decomposition. This process left the pores. Similar findings were also obtained by Bukit et al. which synthesized magnetite by coprecipitation methods.

Table 1. The specific surface area of the particles

| Sample                  | Specific Surface Area |
|-------------------------|-----------------------|
| Fe₃O₄ without PEG template | 55.322 m²/g          |
| Fe₃O₄ with PEG template | 391.314 m²/g          |

SEM images of magnetite with and without templates are presented in Figure 5. It appeared that the morphology of the particles produced with and without PEG was the same, spherical. The obvious difference of the image was that the magnetite with the template had a more uniform, not agglomerated and smaller size distribution. Furthermore, particles with an average diameter of 62.5 nm were obtained using PEG template process.

Figure 5. SEM image of Fe₃O₄ (b) with and (c) without template

4. Conclusion

The monodispersed magnetite nanoparticles with high crystallinity and specific surface area of 391.314 m²/g can be synthesized through an iron electro-oxidation using PEG 6000 as a template. The in situ method was conducted by using a thin solution of PEG as the electrolyte at room temperature. The yield of particles obtained with PEG template was larger than without the template. The particles with PEG showed an average diameter of 62.5 nm which was smaller than the bare particles. This method is quite promising as a way of synthesis of magnetite nanoparticles for many applications.

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