Makara J. Sci. 17/2 (2013), In Press
doi: 10.7454/mss.v17i2.xxxx

Synthesis of Fe_3O_4 Nanoparticles from Ironstone Prepared by Polyethylene Glycol 4000

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Abstract

This study reports the modification of the preparation method of Fe_3O_4 nanoparticles, which consists of two stages, beginning with the destruction and separation of iron ore from ironstone. Then, the Fe_3O_4 nanoparticles are synthesized using the coprecipitation method with magnetite (Fe_3O_4). Polyethylene glycol (PEG) 4000, a readily available chemical, was introduced in varying amounts into the reactions. The ratio of Fe_3O_4 powder and PEG 4000 is 1:3, 1:4, and 1:5, respectively, and the effects of the PEG 4000 on the morphology, crystalline size, and magnetic properties of the products were studied. It was shown that the particle and crystalline sizes decreased when the concentration of PEG 4000 increased. Additionally, the smallest Fe_3O_4 nanoparticles were around 50-60 nm, and semispherical nanoparticles were formed. The reduction of the crystalline size with the increase in PEG 4000 was shown by using XRD patterns, with the crystalline size being about 30 nm at a ratio of 1:5 Fe_3O_4 and PEG 4000, respectively. The hysteresis loop showed low coercivity, indicating that all products were soft magnetic.

Abstrak

Sintesis Nanopartikel Fe_3O_4 dari Batuan Besi dibantu oleh Polietilen Glikol 4000. Pada penelitian ini dilakukan modifikasi metode pembuatan nanopartikel Fe_3O_4. Sintesis nanopartikel Fe_3O_4 terdiri atas dua tahap, diawali dengan destruksi dan pemisahan biji besi dari batuan besi yang terdiri dari unsur-unsur lain selain besi (Fe). Selanjutnya nanopartikel Fe_3O_4 disintesis menggunakan metode kopresipitasi. Polietilen Glikol 4000 (PEG 4000) yang mudah diperoleh, digunakan sebagai cetakan pada sintesis nanopartikel Fe_3O_4. Variasi penggunaan PEG 4000 terhadap serbuk Fe_3O_4 adalah 1:3, 1:4, dan 1:5. Ukuran partikel dan ukuran kristal menurun dengan peningkatan jumlah PEG 4000. Ukuran partikel terkecil sekitar 50-60 nm, dan partikel berbentuk semi bulat. Ukuran kristal menurun dengan peningkatan jumlah PEG 4000 yang terlihat pada pola difraksi XRD, dengan ukuran kristal terkecil sebesar 30 nm pada perbandingan serbuk Fe_3O_4 dengan PEG 4000 yaitu 1:5. Berdasarkan kurva hysteresis yang diperoleh, medan koersivitas untuk semua nanopartikel Fe_3O_4 cukup kecil, hal tersebut mengindikasikan bahwa nanopartikel Fe_3O_4 bersifat magnetik lemah.

Keywords: coprecipitation, Fe_3O_4, ironstone, nanoparticles, PEG 4000

1. Introduction

Ferrite iron (Fe_3O_4) is a traditional magnetic material used in magnetic storage media, solar energy transformation, electronics, ferrofluids, biomedicine and catalysis [1-4]. During the last decade, significant research was done in the field of nanosized magnetic particles, due to their potential for biomedical applications, such as improving the quality of Magnetic Resonance Imaging (MRI), drug delivery systems [1,5], and recent research interests in manipulating cell membranes [2-3]. Several methods have been published for synthesizing Fe_3O_4 powders, and several research studies have reported the successful preparation of nano- or microscale Fe_3O_4. Using different methods, such as the ultrasonic chemical coprecipitation method [2] and the solvothermal method [4], Hai *et al*. 2010 [6] reported the synthesis of nanoparticle Fe_3O_4 in organic solvent, and Cuyper *et al*. 2003 [7] successfully fabricated magnetic Fe_3O_4 covered with a modifiable phospholipid coat. Of these methods, chemical coprecipitation was reported to be the most promising because of its simplicity and productivity [8-10].

The physics of nanoscale magnetic materials has been a vivid subject for researchers within the last few decades, and the exploration of iron sand from beaches or rivers to prepare magnetic materials in nanoscale has been reported in some studies [11]. In this paper, magnetic materials from ironstone mining in Pasaman Barat West Sumatera were investigated, and it was found that ironstone in that area contained 12.462 ppm of iron (Fe), with a susceptibility magnetic value of 888.81 x 10^{-8} m^3/kg by using an atomic absorption spectrophotometer and magnetic susceptibility meter. For these reasons, these materials have the potential to be developed and cultivated as raw materials for magnetite (Fe_3O_4). Although there have been many significant developments in the synthesis of magnetic nanoparticles, the stability of these particles without agglomeration or precipitation is an important issue. Polyethylene glycol 4000 (PEG 4000), a readily available chemical, was introduced into the reactions to prevent agglomeration.

In this study, a new route in the preparation of Fe_3O_4 nanoparticles is reported. It began with the destruction of ironstone and the separation of iron ore from high purity stone. Fe_3O_4 nanoparticles were synthesized by using the coprecipitation method of magnetite, then the effects of PEG 4000 on the morphology and magnetic properties of the products were analyzed.

2. Experiment

In this paper, the experimental techniques of Fe_3O_4 nanoparticle preparation, and its characterization, will be discussed. Two steps of preparing samples have been investigated in this research. The first step is the physical preparation method, in which ironstone was pulverized to obtain a powder of 200 mesh in size. Then a permanent magnet was used to obtain the iron ore. In the second step the iron ore powders were prepared by the chemical coprecipitation method, and the Fe_3O_4 properties were investigated by adding different amounts of PEG 4000.

In a typical coprecipitation synthesis procedure, 10 g Fe_3O_4 powder and 20 ml HCl (12 M) were mixed at 90 ^oC for 60 minutes. The solutions were filtered and then 25 ml NH_4OH (90%) was added to the filtrate. The black precipitates were collected and washed with de-ionized water and ethanol three times. PEG 4000 was melted at 40 ^oC for 15 minutes, and then the black precipitates and PEG 4000 solution were mixed and heated to 400 ^oC for 2 hours. The solution was cooled at normal room temperature. The ratios of Fe_3O_4 powder and PEG 4000 varied at 1:3, 1:4, and 1:5, respectively.

The structure and crystallite size were investigated by using X-ray diffraction (XRD). The XRD patterns of the samples were recorded on a Rigaku D/max 2550 V diffractometer equipped with a Cu KR (1.5418 A) X-ray source. Information on the morphology of the samples was characterized by Scanning Electron Microscopy (SEM, JEOL JSM-6360LA). The magnetic properties of these samples were determined by using a Vibrating Sample Magnetometer (VSM, Oxford VSM1.2H).

3. Results and Discussion

The product obtained was a black powder, which was then collected by using a permanent magnet, and finally characterized using the XRD, SEM, and VSM.

The XRD pattern of the Fe_3O_4 sample obtained in the experiment is shown in Figure 2. All peaks can be identified as face centered cubic Fe_3O_4, which is very similar to the reported data (JCPDS 85-1436). No characteristic peaks of impurities could be detected. As shown in Figure 2, the products display several relatively strong diffraction peaks in the 2Ɵ region of 25^0 to 65^0.

The average size of the Fe_3O_4 nanoparticles was deduced from Scherrer's formula [12-16]:

$$D = \frac{K\lambda}{B\cos\theta_B} \quad (1)$$

Figure 1. Magnetic Black Powder

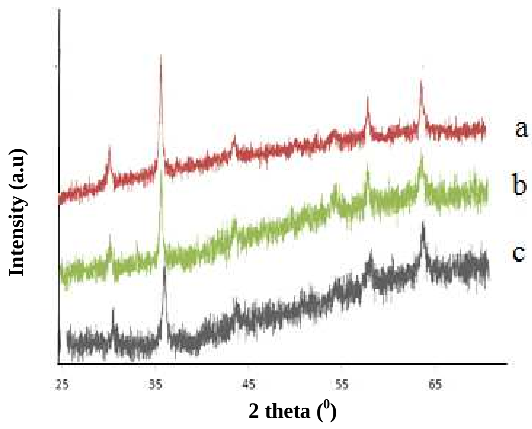

Figure 2. XRD Patterns of Fe_3O_4 Samples with Different Ratios of Fe_3O_4 and PEG 4000: (a) 1:3, (b) 1:4, and (c) 1:5

Where, D is the crystallite size, λ is the wavelength of the X-ray radiation (CuKα = 0.15406 nm), K is a constant taken as 0.94, θ_B is the diffraction angle, and B is the line width at half maximum height (FWHM). The size of the crystallites obtained in the powder is a function of the PEG 4000 amount, and becomes smaller as the amount of PEG 4000 becomes larger (Table 1).

The morphology of the sample was examined using the SEM, and Figure 3 is a typical SEM image of the product. After examining numerous SEM images of the samples, it appeared that almost all of the nanoparticles had a semispherical shape, with an average size of 50-110 nm.

Figure 3 shows that the particle size of Fe_3O_4 decreases due to the increase in PEG 4000. When the PEG is low, the SEM image shows that semispherical Fe_3O_4 nanoparticles of about 90-110 nm are obtained (Figure 3.a). However, when the PEG is increased, the SEM image shows a decrease in the size of the Fe_3O_4 (Figure 3.b), and the particle size in Figure 3.c is reduced to 50-60 nm. The effect of the PEG 4000 amounts on the morphology of the products is to reduce their tendency to agglomerate. These nanoparticles are separated due to the PEG 4000 coating on their surfaces. This result is consistent with a previous report [17] suggesting that Fe_3O_4 nanoparticles agglomerate in the presence of low amounts of polymer. The increase in PEG 4000 leads to more surface coating and the separation of the Fe_3O_4 nanoparticles from each other. These results can be compared to Fe_3O_4 nanoparticles without PEG 4000 (Figure 3.d). Figure 3.d shows the agglomeration of the Fe_3O_4 particles, and the larger particle size.

Figure 4 shows the magnetic hysteresis curves of the samples prepared by different ratios of Fe_3O_4 and PEG 4000. The hysteresis loop of the Fe_3O_4 nanoparticle exhibits ferromagnetic behavior, and the saturation magnetization (M_s) values of the products are 39 emu/g, 11 emu/g, and 45 emu/g for the ratios of Fe_3O_4 to PEG 4000. These are 1:3, 1:4, and 1:5, respectively, whereas the magnetic resonance (M_r) values are 18 Tesla, 3.5 Tesla, and 25 Tesla.

The M_s of the Fe_3O_4 nanoparticles decreases along with a decrease in the nanoparticle size. This observed decrease is attributed to the contributions originating from the magnetically disordered shell. The magnetization value increases dramatically for sample (c), and

Table 1. Crystalline Size of Fe_3O_4 Samples with Different Ratios of Fe_3O_4 and PEG 4000

Ratio of Fe_3O_4 and PEG 4000	XRD (nm)
1 : 3	104
1 : 4	34
1 : 5	30

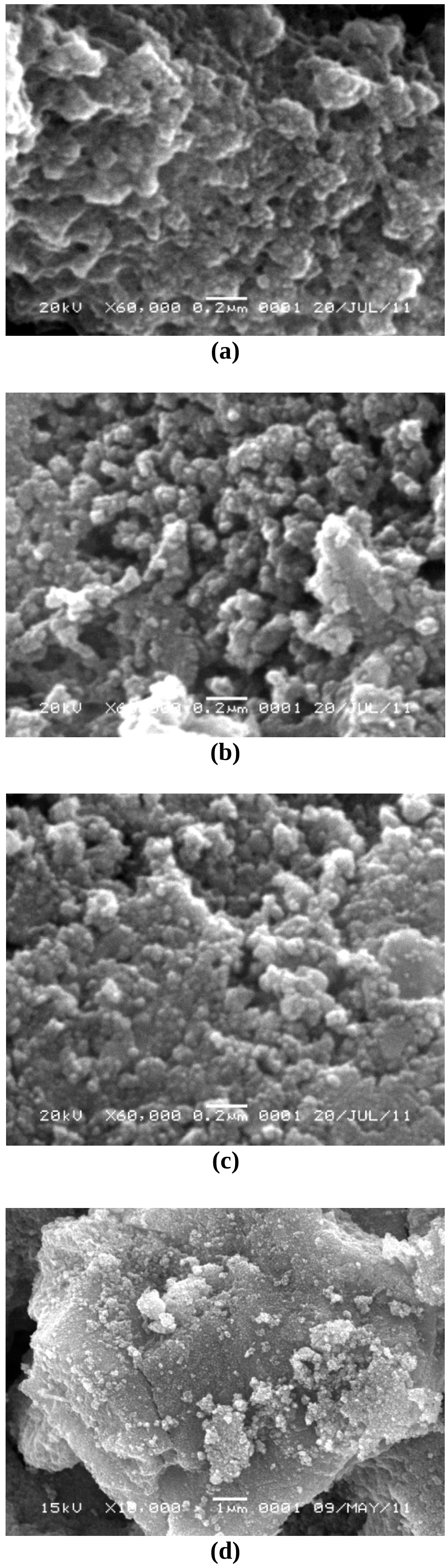

Figure 3. SEM Images of Fe_3O_4 Samples with Different Ratios of Fe_3O_4 and PEG 4000: (a) 1:3, (b) 1:4, (c) 1:5, and (d) without PEG 4000

the fact that sample (b) and sample (c) are about the same average crystallite size, the morphology and superficial effects increase the saturation of the sample (c). This is likely due to the degree of oxidation at the surface during the synthesis process. The oxygen layer causes a superexchange interaction between the iron atoms close to the surface, resulting in an increase in net magnetization [18].

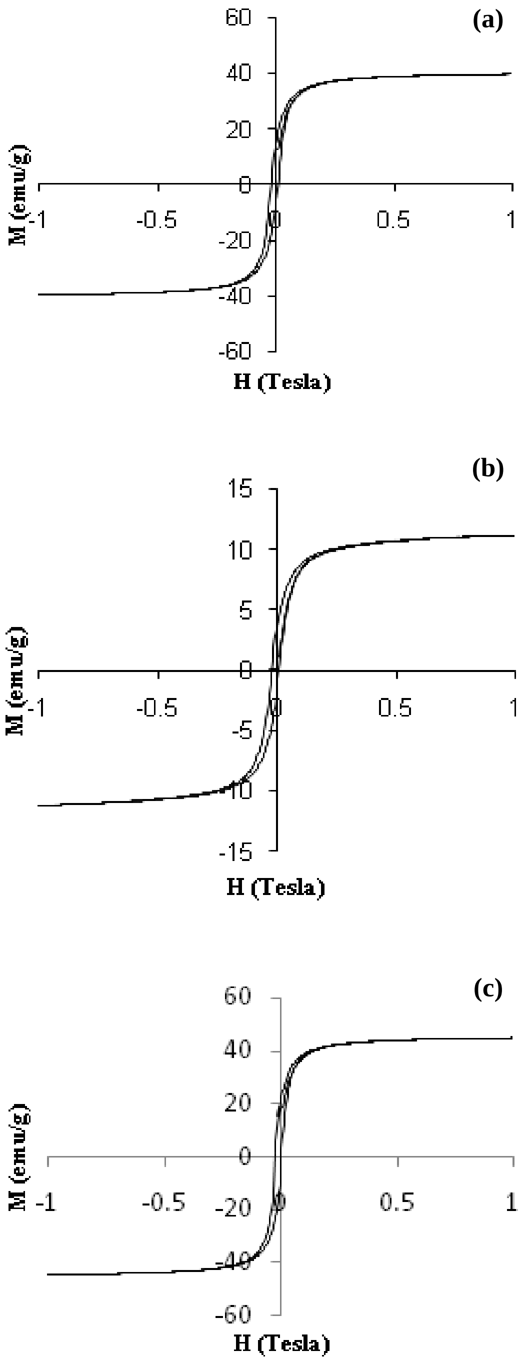

Figure 4. VSM Images of Fe_3O_4 Samples at Room Temperature (300 K), with Different Ratios of Fe_3O_4 and PEG 4000: (a) 1:3, (b) 1:4, and (c) 1:5

The hysteresis loops of all of the samples show low coercivity, meaning that the products are soft magnetic. The sphericity of the nanoparticles has a significant influence on the coercivity [19-20]. The magnetic softness of the Fe_3O_4 nanocrystalline structure is due to the opposite sign of the magnetostriction constant of the crystallites and the residual amorphous matrix, which allow the reduction and compensation of the average magnetostriction [21]. The low value of coercivity corresponds to the easy movement of the domain walls as the magnetic field changes magnitude and direction. Soft magnetic materials are used in devices that are subjected to alternating magnetic fields and in which energy losses must be low. One familiar example of this is the transformer core. For this reason, the relative area within the hysteresis loop must be small, and it is characteristically thin and narrow (Figure 4.a-c).

4. Conclusions

In summary, the Fe_3O_4 nanoparticles are synthesized in the presence of polymer PEG 4000 by using the coprecipitation method. When the concentration of the PEG 4000 increases, the nanoparticles become smaller in size and semispherical nanoparticles form. The amount of PEG 4000 plays a role in the morphology of the product, and the presence of PEG 4000 prevents agglomeration of the Fe_3O_4 particles. The smallest nanoparticle size is 50-60 nm, and similar to the XRD patterns, the crystalline size is reduced by increasing the PEG 4000. The hysteresis loop shows low coercivity, indicating that all of the products are soft magnetic. Based on this research, Fe_3O_4 nanoparticles are promising materials for applications in advanced magnetics. Soft magnetic materials can be used for the cores of transformers, generators, and motors.

Acknowledgments

The author would like to thank Mujamillah for the VSM measurements at BATAN, Serpong, Indonesia.

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