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Room Temperature Synthesis of Magnetite Particles by an Oil Membrane Layer-Assisted Reverse Co-Precipitation Approach

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Abstract. Reverse co-precipitation (RCP) in ambient atmosphere is one of the strategies to produce magnetite nanoparticles in a rapid, simple, and cost-effective synthesis route without applying temperature surfactants or inert gases. However, RCP of ferrous/ferric blended salt in sodium hydroxide (NaOH) solution in an oxidizing medium produced of maghemite as a dominant phase rather than magnetite because of the oxidation of Fe^{2+} to Fe^{3+} happened. Based on this background, an oil membrane layer-assisted reverse co-precipitation approach has been examined to synthesis of magnetite in ambient atmosphere at room temperature. The result showed that although addition of benzene as an oil membrane layer was effective to prevent oxidation of magnetite to maghemite, but the magnetite particle size for the samples from the oil membrane layer-assisted reverse co-precipitation method was much larger than that from a reverse co-precipitation method without addition of oil membrane layer.

Introduction

It is well known that the magnetite (Fe_3O_4) nanoparticles investigation has gained particular interest during a decades ago concerning the capability of these materials in a many relevant field and because of its high magnetization and generally high biocompatibility [1]. Some of the parameters that strongly influence the properties and applications of these magnetite nanoparticles are their size and narrow size distribution. The size strongly determines the magnetic properties of magnetite particles. The saturation magnetization can be no doubt influenced by the spin disorder layer that increase with a reduction in crystallite size [2]. Synthesis strategies to control the size of the nanoparticles have become a significant challenge among researchers, mainly to acquire close-hypothetical value for large scale production [3].

It is also well known that thermodynamically magnetite is unstable in the aerobic atmosphere, but kinetically the oxidation rate of bulk natural magnetite in an oxidizing environment is very slow. On the other hand, synthetic magnetite nanoparticles are either fast oxidized to other iron oxides during the synthesis process or storage in the ambient atmosphere because of its very high surface area [4]. Generally, the reaction of magnetite synthesis is carried out under an inert gas (N_2 or Ar) for avoiding oxidation of Fe^{2+} into Fe^{3+} during the synthesis process.

Recently, a wide assortment of synthetic procedure to create magnetite nanoparticles with any alluring molecule size is reported. Among the different procedures for magnetite production, the co-precipitation technique is an advantageous method to production magnetite nanoparticles. In a typical co-precipitation framework, an alkaline solution is dropped into the mixture of iron salts and pH increments gradually. When reaching the pH to 3, Fe^{3+} ions are precipitated as ferrihydrite, which at that point reacts with the Fe^{2+} ions in the arrangement structure for magnetite formation. It was assumed that the electron transfer between Fe^{2+} and Fe^{3+} plays a significant role in the crystallization mechanism [5]. Generally, the co-precipitation processes are performed at 70–80 °C under an inert gas [6]. However, this technique usually yields particles with a wide size distribution, most likely due to the high possible arrangement of pathways that lead to the development of magnetite structure [7].

The factors of the complicated aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion chemistry and the fluctuating magnetic in co-precipitation process make controlling the exact reaction route is not easy, obtaining particles with narrow size distribution and high magnetization become be a challenging.

In this paper we present the preparation of magnetite nanoparticles by reverse co-precipitation approach in the ambient atmosphere at room temperature. In this reverse co-precipitation method, the magnetite nanoparticle was synthesized by directly dropwise addition of iron salts solution into an alkaline solution. Aono *et al.* [8] showed that the crystal diameter for the samples from the reverse co-precipitation technique was smaller than that from an ordinary coprecipitation technique. Although the heating property in AC magnetic field for the product of the reverse co-precipitation technique improved with the increasing of the synthesis temperature, but the crystal diameter increased with an increasing the synthesis temperature.

Kazemzadeh *et al.* [5] have synthesized magnetite nanoparticles using reverse-coprecipitation methods with the addition of diethylene glycol (DEG) as a coating agent which prevents the agglomeration of magnetite nanoparticles. Kazemzadeh *et al.* [9] have also synthesized magnetite nanoparticles using the reverse-coprecipitation methods but with the addition of silicate as a coating agent. The results revealed that the mean particle size of magnetite diminished from 50 to under 25 nm since the covering of magnetite by silica prevent the development of hydrogen bonding among magnetite and water atoms. However, further increment in the sodium silicate concentration cause an invert impact. To this end, a reverse co-precipitation approach with the addition of an oil membrane layer is carried out to prepare magnetite nanoparticles that are performed at room temperature without a coating agent. However, to keep benzene as a layer on the top of the solution, the stirring of iron ion solution should be performed at a slower speed. There are a few studies have been carried out about the preparation of magnetite nanoparticle using the reverse co-precipitation method and the effect of lowering the stirring rate due to the benzene layer addition on the particle size distribution of magnetite are not established. The main objective of this work concerns the formation of magnetite nanoparticles with narrow size distribution by reverse co-precipitation strategy and study on the effect of lowering stirring speed due to benzene layer addition on the magnetite particle size distribution.

Experimental Procedure

Materials. All chemicals used in the experiments were analytical grades. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were supplied by Merck and used as a source of a Fe^{3+} and Fe^{2+} ions for Fe_3O_4 synthesis. All metal salts were used without further purification.

Synthesis of magnetite particles. Fe_3O_4 nanoparticles were set up by the reverse co-precipitation strategy with a Fe^{3+} and Fe^{2+} ion complex in the presence of NaOH. First, $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [$\text{Fe}^{2+}:\text{Fe}^{3+} = 1:2$] were dissolved in 130 mL distilled water that contain 5 mL HCl. The solution was added drop-wise into those NaOH solution (0.88 M). The black deposit of Fe_3O_4 nanoparticles was separated by using an external magnetic field, decanted and washed by distilled water and methanol three times. Synthesis of iron oxide by reverse co-precipitation with the addition of benzene as oil layer was done the same as the synthesis method of iron oxide by reverse-coprecipitation, but with the addition of benzene as an oil layer. A layer of benzene solution was placed on the top of the NaOH solution for preventing the oxidation of Fe^{2+} ion. The products were characterized using XRD (X-ray Diffractometer), SEM (Scanning Electron Microscope) and DLS (Dynamic light scattering).

Results and Discussion

XRD analysis has been carried out to verify the phase identification of prepared micro- and nanoparticles. Fig. 1 shows the XRD pattern of the iron oxide particle prepared using reverse co-precipitation method with (sample A) and without (sample B) the addition of benzene as an oil layer. Five characteristic peaks at 30.1° , 35.4° , 53.3° , 56.9° , and 62.6° in Fig. 1A were corresponding to the (220), (400), (422), (511) and (440) crystal planes of Fe_3O_4 (JCPDS file PDF no.79-0417) [10],

whereas four characteristic peaks at 30.2° , 35.8° , 57.3° and 62.7° in Fig. 1B were corresponding to the (220), (311), (511), and (440) crystal planes of $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS file PDF no. 39-1340) [11]. Eleven characteristic main peaks in Fig. 1A at 21.3° , 26.2° , 33.2° , 34.7° , 36.7° , 40.0° , 41.1° , 53.3° , 59.1° , 61.5° and 64.5° are equivalent to (110), (120), (130), (021), (111), (121), (140), (221), (151), (002) and (061) of goethite crystal planes (JCPDS file PDF no.29-01713) [12]. The peaks in Fig. 1A is indicating that both magnetite phase with goethite phase as impurities are detected clearly in the XRD pattern. On the other hand, the peaks in Fig. 1B is indicating that the maghemite phase is detected clearly in the XRD pattern without the goethite phase as impurities.

Table 1. The main peaks of the present samples compared with the standard JCPDS cards.

Sample	JCPDS file no.	Angle 2θ corresponding to the planes			
		220	311	511	440
		in degree			
Standard maghemite	JCPDS file no.19-0629	30.3	35.7	57.3	63.0
Standard magnetite	JCPDS file no.79-0417	30.1	35.4	56.9	62.5
Sample A	Present study	30.1	35.4	56.9	62.6
Sample B	Present study	30.2	35.8	57.3	62.7

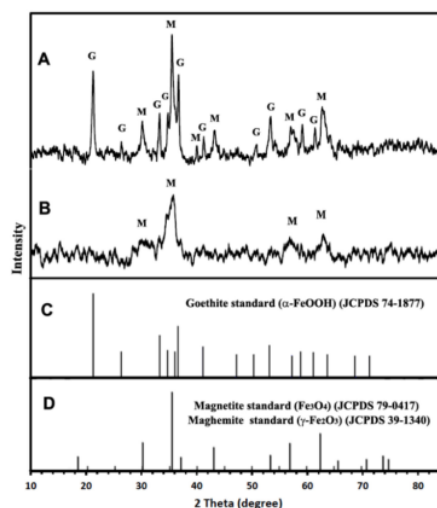


Fig. 1. X-Ray Diffraction pattern of sample A and sample B compared with the standard JCPDS cards of goethite (C) and magnetite/maghemite (D).

Maghemite contains each one of those peaks of magnetite, with the additional low-intensity peaks (<5%) of (210) and (211) crystal planes. It is interesting to confirm the phase of the present samples (A and B) in Fig. 1. We take four most intense peaks with the peak positions of the standard maghemite and magnetite tests accessible in the JCPDS records (No. 39-1340 for maghemite and No. 79-0417 for magnetite), separately. As indicated by the JCPDS record No. 39-1340 for maghemite the four most intense peaks are at 30.26° [35%, (220)], 35.66° [100%, (311)], 57.32° [24%, (511)] and 62.98° [34%, (440)], and the four most intense peaks of the standard magnetite (JCPDS record No. 19-0629) are at 30.09° [30%, (220)], 35.42° [100%, (311)], 56.94° [30%, (511)] and 62.51° [40%, (440)]. The peak positions in our present samples and that in JCPDS documents are given in Table 1 for examination. In this way, a cautious examination from this information gives proof that the peaks attribute of the present sample A is very close to those of the standard magnetite instead of standard

maghemite. At the opposite, the present sample B is very close to those of the standard maghemite instead of the standard magnetite. This method is supportive of separating between the XRD example of the maghemite and magnetite phases due to the shift at 2θ value, as reported by Kim *et al.* [13] and Bandhu *et al.* [11].

The presence of goethite as an impurity in sample A is probably due to the presence of goethite as a dominant intermediate phase, and the transformation of goethite to magnetite could not be complete yet. It is well known that magnetite nanoparticles were shaped in the coprecipitation process by the phase transformation of iron oxyhydroxides (FeOOH) instead of the immediate reaction of Fe^{2+} and Fe^{3+} . The oxyhydroxides is a polymorphism that can be formed as goethite ($\alpha\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$). These intermediate phases could be distinguished utilizing X-ray diffraction, electron microscopy, and FTIR spectroscopy, as reported by Ahn *et al.* [7].

Fig. 2 shows the SEM micrographs for solid precipitate of iron oxide particles prepared at ambient temperatures by the reverse co-precipitation method with the addition of an oil layer benzene (sample A). It can be seen from the images that the particles here appear agglomerations of numerous crystallites. Thus, SEM micrographs cannot be used to get information on the actual particle size. Based on this morphology properties, powder XRD pattern of samples that are displayed in Fig. 1 cannot also be used to estimate the particle size. Although the broadening of the peaks shows small crystal grain size of the particles and the average crystal grain size can be evaluated utilizing the Scherrer equation, it is important to understand that the Scherrer formula referred to the crystallite size, not a particle size. Thus, hydrodynamic diameters were determined with the Dynamic Light Scattering (DLS) system to measure the diameter of colloidal particles.

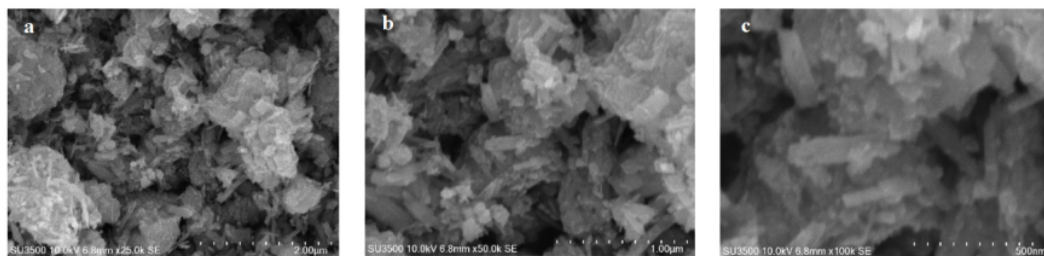


Fig. 2. SEM images of sample A with different magnifications: 25,000 \times (a), 50,000 \times (b), and 100,000 \times (c).

DLS has been broadly used to measure the hydrodynamic size of different colloidal particles. This method is very sensitive towards the system of nanoparticles [14]. Fig. 3 represents particle size distributions acquired by the DLS technique for iron oxide nanoparticles produced by the reverse coprecipitation method with and without addition of an oil layer benzene. They show distribution of particles and aggregates after 1-6 days of sample preparation.

In Sample A, particle size distribution consists of one fraction with average measurement total iron oxide particles 40.98 nm (1-2 days after preparation) and 72.93 nm (3-4 days after preparation). After 5-6 days of sample preparation, the distribution consists of two fractions: a large number of small magnetic particles with an average diameter of 77.93 nm (98.8%) and a small amount of large aggregates with an average diameter of 405.7 nm (1.2%). Formation of two peaks indicates that after four days, the nanoparticles are growing through aggregation mechanism to be a large aggregates (microparticles) after 5-6 days.

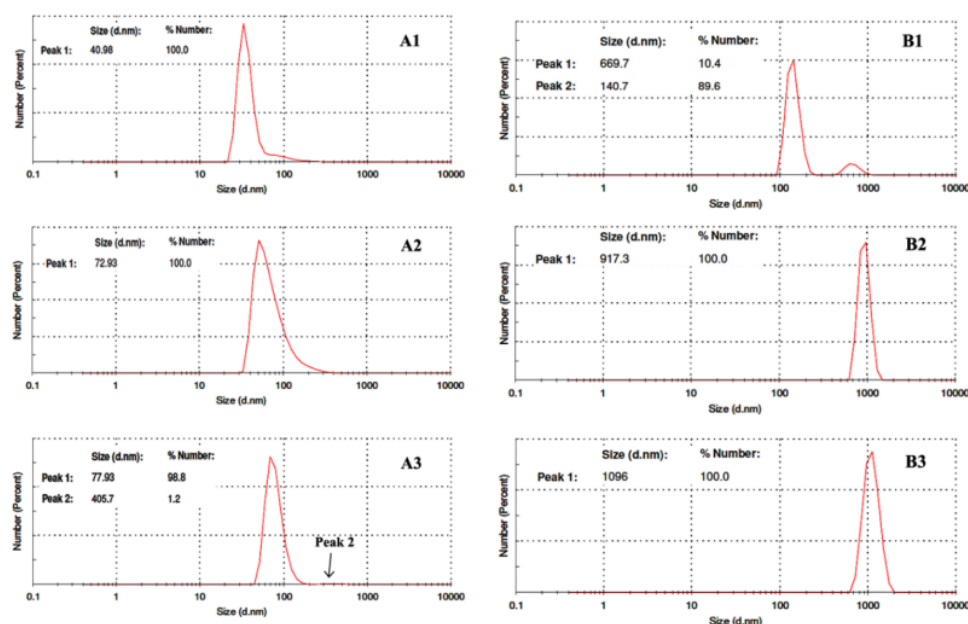


Fig. 3. Particles size distribution in Sample A (left) after about 1-2 days (A1), 3-4 days (A2) and 5-6 days (A3) of sample preparation and particles size distribution in Sample B (right) after about 1-2 days (B1), 3-4 days (B2) and 5-6 days (B3) of sample preparation.

However, in Sample B that was prepared after about 1-2 days, particle size distribution consists of two fractions: a large number of small magnetic particles with average diameter 140.7 nm and a small part number of large aggregates with average diameter 669.7 nm. These aggregates are also unstable and growth to be a larger aggregate with time. The distribution consists of one fraction and tends to more significant sums with an average diameter of 917.3 nm after about 3-4 days and 1096 nm after about 5-6 days after preparation. In this case, the small particles combine with the larger one to become a larger stable aggregate with dimensions of 900-1100 nm after three days of sample preparation.

Conclusions

The reverse co-precipitation with the addition of an oil layer benzene methods can be used to synthesis magnetite microparticle at room temperature in the ambient atmosphere without the addition of any surfactant or coating agent. The addition of benzene as an oil layer benzene is useful to prevent oxidation magnetite particles. Without the addition of benzene as an oil layer benzene, there is observed only the maghemite phase present in the product. However, a slower stirring speed as a consequence of keeping benzene as a layer on the top can cause goethite was detected as remaining intermediate due to an incomplete reaction.

Furthermore, the size of the oxide particle for the samples from the reverse-coprecipitation with the addition of the oil layer benzene method was larger significantly than that from a without the addition of the oil layer benzene method. Hence, the reverse co-precipitation with the addition of an oil layer benzene method is suitable for synthesis of magnetite in microparticles. It is necessary to find out oil membrane layer-assisted reverse co-precipitation with the faster steering speed method in order to synthesis of magnetite nanoparticle.

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