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Research Article

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Schemes for fabrication and characterization of superparamagnetic magnetite nanoparticles via chemical coprecipitation method

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ABSTRACT

Synthesis of superparamagnetic nanoparticles of Fe_3O_4 was carried out via coprecipitation using $NH_3.H_2O$ and NaOH solutions in Ar and N_2 atmosphere. The obtained magnetic nanoparticles were characterized using X-ray diffraction, Fourier transform-infrared, scanning electron microscopy, variant strength magnetization and N_2 gas adsorption–desorption techniques. The results indicated that all samples exhibit superparamagnetic properties, although the saturation magnetization of the Fe_3O_4 nanoparticles prepared with NaOH under Ar atmosphere was higher in contrast to other samples. The crystalline structural study of different samples of Fe_3O_4 nanoparticle demonstrates the magnetite crystal with a cubic spinel structure. Morphology of the particles was uniform and semispherical shape nanoparticles were approximately in the range of 15-25 nm.

Keywords: Coprecipitation, Magnetite, Nanoparticle, superparamagnetic, Saturation magnetization.

INTRODUCTION

Studies of nanoscale materials have captured significant scientific and industrial interest in recent years [1]. Research in magnetic nanoparticles has increased due to their potential in a variety of applications [2]. Magnetic nanoparticles possess some extra ordinary physical and chemical properties and find applications in many industrial and biological fields such as medical treatment, drug delivery systems, magnetic resonance imaging (MRI), cancer therapy, and in making membranes, generating electricity, and fabricating memorizer for electronic and quantum computers [3]. Transition metal oxides have been of scientific and technological interest for many decades due to their interesting optical, magnetic and electrical properties. Iron oxides exist in many forms in nature, with magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃) being probably the most common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming afcc (face-centered cubic) closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites (Fig. 1) [5-7].



Fig. 1. Crystal structures of magnetite

Magnetite particles exhibit superparamagnetic behavior under optimum conditions of size and operating temperature. The magnetite can be synthesized by various methods, including: hydrothermal synthesis, micro emulsion, thermal decomposition and chemical co-precipitation. Thermal decomposition and co-precipitation are most commonly used [8-10]. The main advantage of the co-precipitation is that it can generate nanoparticles in large quantity and in general, the size distribution is relatively narrow. Nanoparticles can be prepared with or without a surfactant. In co-precipitation, a stoichiometric mixture of ferrous and ferric precursors in a molar ratio of 2:1, are used as an iron source, which under alkaline conditions yield superparamagnetic nanoparticles. Two methods were reported to prevent the change of the ratio caused by air oxidation. One is to conduct the reaction under an inert environment with nitrogen gas. Another is to set the initial Fe^{3+} : Fe^{2+} molar ratio less than 2:1 so that after the oxidation of Fe^{2+} to Fe^{3+} , the ratio approaches to 2:1[11,12]. During synthesis of magnetite nanoparticles by coprecipitation technique, magnetite or goethite (α -FeOOH) or mixture of magnetite-goethite is obtained depending on the process conditions. When magnetite-goethite mixtures are formed, quantification of the magnetite phase is essential for correlating with magnetic and chemical properties of synthesized nanoparticles [13]. Depending on the reaction procedure, Massart method and titration hydrolysis method are recognized. In the Massart approach, an alkaline solution, is introduced into the Fe^{2+} and Fe^{3+} iron solution. While in titration hydrolysis, the Fe^{2+} and Fe^{3+} iron solution is added gradually into the alkaline solution. Magnetite is sensitive to oxygen and in the presence of air might undergo oxidation to $Fe(OH)_3$ or to hematite phase and lose its magnetic property. On the other hand, magnetite is transformed into maghemite in the presence of H⁺. Therefore, to avoid side reactions, a careful control of pH value of reaction mixture during precipitation is necessary [14-16]. Reaction temperature also affects the particle size in that higher temperature gives larger particles. Base on the thermodynamics of the reaction, it was suggested that in order to obtaining particles of pure phase, nanoparticles should be prepared by addition of the ferrous and ferric precursor to a strong alkaline solution, e.g. NaOH, or NH₄OH at a pH value between 8 and 14. Moreover, to maintain a suitable redox potential, the ratio of Fe^{3+} : Fe^{2+} should be carefully controlled at 2:1 in a nonoxidizing environment [17].

Dang et al showed that the monodispersibility and magnetic properties of magnetite particles were improved significantly through the sonochemical synthesis under ultrasonic irradiation [18]. Faiyas et al found that the value of pH influences the reaction mechanism for the formation of Fe₃O₄, shows that while maintaining a pH value of 6 and 9 in a solution containing iron salts II and III ions produces ε -Fe₂O₃. Whereas a pH value of 11 produces magnetite phase [19]. Gnanaprakash et al. showed when the initial pH (prior to alkali addition) of the salt solution was below 5, the nanoparticles formed were 100% spinel iron oxide. The initial pH and temperature of the ferrous and ferric salt solution before initiation of the precipitation reaction are critical parameters controlling the composition and size of nanoparticles formed. As the reaction temperature was increased, maintaining a pH, the amount of goethite increased [20]. The synthesis of magnetite by coprecipitation using different precipitation agents and different atmosphere appears of interest, because there is few investigations about it. In the present investigation, magnetite nanoparticles were prepared by coprecipitation using different precipitation agents, NaOH and NH₃H₂O and different atmosphere, Ar and N₂, and were characterized by different techniques.

EXPERIMENTAL SECTION

All the reagents were of analytical purity, and were used without further purification and all of the solutions were prepared with distillated water. The experimental apparatus for preparing magnetite nanoparticles is a three-neck, 250-mL, round bottom flask equipped with a mechanical stirrer that spaced in an ultrasonic bath (Fig. 2). Solutions of ferric chloride (1 mM) and ferrous chloride (2 mM) in water with molar ratio of 2:1 were prepared and mixed together and deoxygenated by bubbling of inert gas. Initial pH of solutions was controlled about 2 with HCl 2M.

Alkaline solution was added dropwise to the suspension while the mixture was vigorously mechanical stirred under ultrasonic irradiation and inert gas atmosphere for 1 h. A moment later, a black suspension appeared, and alkaline solution was dropped into the mixture continuously and slowly until the pH value of the solution reached ~11. Then, the reaction (eq. 1 and 2) was continued for 30 min. The black samples indicate the formation of magnetite. The resulting black mixture was then collected by a magnetic field, rinsed with deionized water 4 times, and completely dried at 80°C for 1 h for characterization.

$$\begin{aligned} & \text{FeCl}_2.4\text{H}_2\text{O} + 2\text{FeCl}_3.6\text{H}_2\text{O} + 8\text{NaOH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NaCl}_3 + 20\text{H}_2\text{O} \end{aligned} \tag{1} \\ & \text{FeCl}_2.4\text{H}_2\text{O} + 2\text{FeCl}_3.6\text{H}_2\text{O} + 8\text{NH}_3.\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 20\text{H}_2\text{O} \end{aligned} \tag{2}$$

Alkaline Solution Sample Alkaline Solution Atmosphere (Volume-ml) NH₃H₂O (50%, v/v aqueous) Ar S 5 NaOH (1 M) 9 S Ar NH_{3.}H₂O (50%, v/v aqueous) S_3 N_2 5 9 S_4 NaOH (1 M) N_2 Alkaline solution Nitrogen or argon gas Sealing Ultrasound waves Ultrasound waves

Table 1. Experimental parameters for samples

Fig. 2. Apparatus for preparing magnetite nanoparticles

MPMS-5 SQUID magnetometer (Vibrating Sample Magnetometer (VSM)) used for making very high sensitivity magnetic measurements. The X-ray diffraction (XRD) with Cu K_a radiation was used to measure the crystallinity of samples by the JEOL JDX-8030 diffractometer. The FTIR (Fourier transform infrared spectroscopy) spectra were recorded in the range of 400–7,000 cm⁻¹ to study the structures of samples, utilizing a Bruker Tensor 27 spectrophotometer. Scanning electron microscopy (SEM) was applied to measure the morphology and particle size of the synthesized nanoparticles. For this purpose a gold cover was dripped onto samples then the SEM observations were carried out using a Zeiss EVO50 electron microscope. Surface area was measured by nitrogen adsorption at 77 K utilizing NanoSORD analysis instrument (SENSIRAN Co.).

RESULTS AND DISCUSSION

The magnetization curve for different synthesized magnetite nanoparticles showed in Fig.3 does not demonstrate any hysteresis behavior for any of the samples and exhibits immeasurable values of coercivity field and remnant magnetization. This confirms that the synthesized particles exhibit superparamagnetic properties. In the absence of applied magnetic field, the magnetization vectors of the magnetic particles were order-less because of thermal movement, and did not exhibit any overall magnetism[3]. However, the magnetization vectors of magnetic particles followed quickly an external magnetic field, making the particles highly magnetic. Compared to other samples, the magnetic nanoparticles prepared by coprecipitation under Ar atmosphere, showed higher saturation magnetization.



Fig. 3. The magnetization curve for different samples

Fig. 4 shows the IR absorption spectrum of all samples of Fe_3O_4 nanoparticles. In all samples, the FTIR band at around 3432 cm⁻¹ can be assigned to the stretching modes of H₂O molecules or OH groups on the surface of magnetite particles; the IR band at around 1625 cm⁻¹ is assigned to the H₂O bending vibrations [9,18]. Metal-oxygen band, observed at 564 cm⁻¹ corresponds to intrinsic stretching vibrations of the metal at tetrahedral site (Fe_{tetra+O}), whereas metal-oxygen band observed at 400 cm⁻¹, is assigned to octahedral-metal stretching (Fe_{octa+O}). The IR band (S₃ and S₄) at around 1422 cm⁻¹ is assigned to the hematite and maghemite formation[6,9].



Fig. 4. FTIR of different Fe₃O₄ samples

The crystalline structure of different samples of Fe_3O_4 nanoparticles, is characterized by XRD as shown in Fig. 5. The diffraction peaks of (2 2 0), (3 1 1), (4 0 0), (4 2 2) and (4 4 0) reflect the magnetite crystal with a cubic spinel structure [21]. The unit cell of cubic spinel structure consists of eight ferric ions at tetrahedral sites(A sites) each with four oxide ions nearest neighbors, and eight ferric ions and eight ferrous ions at octahedral sites (B sites) each with six oxide ions as the nearest neighbors [9]. During synthesis of magnetite nanoparticles by co-precipitation technique, maghemite or hematite phases is obtained depending on the process conditions and lose its magnetic property, which undergo in S_4 , S_3 , S_1 and S_2 , respectively (confirms the VSM and FTIR results). XRD spectra shows there are many weak but obvious peaks showing that the Fe₃O₄ nanoparticles were oxidized to hematite and maghemite (especially in S_3 and S_4). In addition, the peaks were widened, implying the small size of the particles. An estimation of the magnetite nanoparticles size has been performed from the Scherrer formula [8]:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{3}$$

where λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum (FWHM); θ is the corresponding Bragg angle; and K is the shape parameter, which is 0.89 for magnetite. Taking the highest intensity peak, namely the (3 1 1) plane, at 2 θ , and the half maximum intensity width of the peak after accounting for instrument broadening, the particle sizes are calculated (Table 2). By using the coprecipitation method over this condition at room temperature, it is easy to prepare magnetite nanoparticles with an approximate size of 20 nm, also the diameter of Fe₃O₄ nanoparticles prepared by coprecipitation using NaOH under Ar atmosphere, was the smallest.



Fig. 5. X-ray diffraction of various magnetite nanoparticle samples

Table 2. Estimation of the magnetite nanoparticles size from the Scherrer formula

sample	β	2θ	D(nm)
S_1	0.7092	35.599	22.50633
S_2	0.9700	35.497	18.0862
S ₃	0.6878	35.602	23.14608
S_4	0.6666	35.698	22.06786

Fig. 6 shows the SEM photographs of different samples. Morphology of the particles was uniform and semispherical shape nanoparticles were approximately ranging between 15 and 25 nm, which was also indicated by the previous XRD measurement. Samples show slight agglomeration, which may be due to the magnetic interaction of naked nanoparticles.



Fig. 6. Scanning electron micrographs of different Fe₃O₄ samples

The specific surface area of the magnetite nanoparticles synthesized at various conditions measured by the BET method. The samples were degassed at 423 K for 20 min, then surface area were measured by nitrogen adsorption at77 K. BET surface area (S_{BET} (m²/gr)) for S_1 , S_2 , S_3 and S_4 , measured 71.962, 68.309, 49.371 and 94.709, respectively. All of the samples had S_{BET} in similar range, but the Fe₃O₄ nanoparticles prepared by coprecipitation using NaOH under N₂ atmosphere, has larger surface area, compared with the other samples.

CONCLUSION

The following conclusions can be drawn for the present investigation. (1) The saturation magnetization of the Fe₃O₄ nanoparticles prepared by coprecipitation using NaOH under Ar atmosphere was higher compared to other samples, although any of the samples exhibit superparamagnetic properties. (2) Morphology of the particles was uniform and semispherical shape nanoparticles were approximately ranging between 15 and 25 nm. The diameter of Fe₃O₄ nanoparticles prepared by coprecipitation using NaOH under Ar atmosphere was the smallest, but agglomeration was severe. (3) The crystalline structure study of different samples of Fe₃O₄ nanoparticles, reflect the magnetite crystal with a cubic spinel structure. (4) All of the samples had S_{BET} in similar range, but the Fe₃O₄ nanoparticles prepared by coprecipitation using NaOH under N₂ atmosphere, has larger surface area, compared with the other samples.

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