New Finding on Magnetite Particle Size Reduction by Changing Temperature and Alkaline Media Concentration

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Abstract

By controlling of two significant parameters mainly alkaline media concentration and temperature, magnetite nanoparticles were produced via coprecipitation method. Effect of named parameters on the particle size, size distribution and magnetic behaviour of particles were analyzed by means of X-ray diffraction spectroscopy (XRD), transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM). To the best of our knowledge, there is no report on evaluation of sample preparation at room temperature and then post stirring at higher temperature on particle size and its magnetic properties. Results show the particles synthesized at elevated temperature (70°C) and lower alkaline concentration (0.9 M) have highest saturation magnetization, about 68 emu/gr at 70°C, compared with 63 emu/gr at 25°C and smallest particle size.

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1. Introduction

High variety of iron chemistry arisen from the occurrence of two stable oxidation states begets the key role for iron oxides in the field of science[1-2]. As magnetite nanoparticles have high magnetization saturation, can easily load with biomolecules and are biocompatible, this kind of material has extraordinary position among iron oxides[3]. Magnetite has inverse spinel structure and its unite cell structure represents with

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Magnetite nanoparticles find a conceivable application in scientific fields such as magnetic memories, optics, production of pigment, electronics, activators, ferrofluids, and biomedical [3, 6]. The most significant aspect of synthesising such materials for biomedical applications is to have high saturation magnetization ($M_s$) as well as small particle size [3].

Various synthetic methods have been used to produce these kinds of nanoparticles including coprecipitation, microemulsion, laser pyrolysis, and hydrothermal synthesis [5-8]. In an alkaline medium such as ammonium or NaOH aqueous solution, coprecipitation of Fe$^{2+}$ and Fe$^{3+}$ ions which is one of the most important chemical synthesis methods is done. As this method is one of the most efficient ones and isn’t used any surfactant, many researcher attempt to optimize this magnetite production strategy [3, 9].

Some problems regarding coprecipitation method are its uncontrollability of particle size and size distribution and sometimes simultaneous presence of different iron oxide phases such as magnetite and maghemite [10-12]. There are some articles on investigation of parameters affecting the production of magnetic nanoparticles including pH, alkaline species [12-13], reaction temperature [3, 10, 14], kind of iron salts [15] and concentration of ingredients. Based on this background, we studied the effect of alkaline medium concentration and temperature on magnetite particle size and magnetic properties. As far as the authors are concerned no report in the literature was recorded regarding the effect of extra stirring time (30 minute in our case) at elevated temperature on the synthesis method.

2. Experimental

2.1. Synthesis of Magnetite Nanoparticles

Solutions of 0.012 M ferrous chloride hexahydrate (FeCl$_2$.6H$_2$O, 99%, Merck) and 0.006 M ferric sulphate heptahydrate (FeSO$_4$.7H$_2$O, 99%, Merck) used as iron source, were prepared by dissolution of proper amount of material in double distilled water. After the ferric and ferrous solution were mixed together, the mixture was then deoxygenated by bubbling N$_2$ gas and sonicated for 30 minutes to prevent from oxygenation. Ammonia solutions with 0.9-2.1 M concentration was used as alkaline source and vigorously stirred under N$_2$ bubbling at room temperature. The mixture of ferric and ferrous solution was dropwisely added to the stirring ammonia solution, the colour of reaction mixture immediately turned to black. In this experiment, group 1 and 2 are defined as the groups containing the different alkaline concentration at two different temperatures ie. 25 °C and 70°C respectively. The reaction temperature of group 1 was kept constant at 25°C for 1 hour then all the mixtures were purified. After an hour, the group 2 was transferred to 70°C water bath where the mixture was strongly stirred for 30 minutes. The next step was to purify the black mixture of both groups using a magnetic separation five times and then it was sedimented by centrifugation. The resultant material was finally dried by freeze dryer for 24 hours.

2.2. Characterization

Crystalline phase of magnetite nanoparticles was studied using x ray diffraction using Cu Kα radiation (XRD, $\lambda = 1.5406$ Å, FK60-40 X-ray diffractometer). Saturation magnetization of samples was measured by means of vibrating sample magnetometer (VSM-PAR 155) at 300 K under magnetic field up to 8 kOe. Particle size and morphology of these nanoparticles were determined by transmission electron microscopy (TEM, Philips CM-200-FEG microscope, 120 KV).
3. Results and Discussion

3.1. XRD Analysis

XRD Results obviously confirmed the formation of magnetite phase of iron oxide with inverse spinel structure (JCPDS file no.19-0629). Thermodynamic modelling represents in oxygen free environment, pH 7.5-14 and Fe\(^{2+}\):Fe\(^{3+}\) ratio equal to 1:2, precipitation of magnetite is completed as follow:

\[ \text{Fe}^{2+} + \text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 \text{(black precipitation)} + 4\text{H}_2\text{O} \]  

(1)

If this reaction takes place in oxygen containing media, the reaction condition will be ready to oxidation of \(\text{Fe}_3\text{O}_4\). Oxidation of \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\) ions \((\text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+})\) declines the effective ratio to less than 0.5 and if \(\text{Fe}^{3+}\) ions is kept on elevated pH, goethite can be produced[16-17]:

\[ \text{Fe}_3\text{O}_4 + 0.25 \text{O}_2 + 4.5 \text{H}_2\text{O} \rightarrow 3 \text{Fe(OH)}_3 \]  

(2)

As usage of strong alkaline medium (such as NaOH, KOH, and LiOH) as a hydrolyzing agent can cause formation of nonmagnetic iron components [3, 9] in order to avoid this matter, \(\text{NH}_2\text{OH}\) was used as alkaline media in present study. Also, since in this study coprecipitation reaction was performed under \(\text{N}_2\) atmosphere, the single magnetite phase without any interference of other iron oxide phase was obtained. The particle size of nanoparticles could be determined using Debye-Sherrer’s equation (eq. 3) which measures the size of particles according to broadening of the most intense peak (311) in XRD graph (Fig. 1) of prepared materials [18].

\[ D = \frac{K\lambda}{\beta\cos\theta} \]  

(3)

where \(D\) is mean diameter of particles, \(\beta\) is full width at half maximum (FWHM), \(\lambda\) is wavelength of incident X-ray and constant \(K\) is equal to 0.9. Based on this equation, particle size of samples synthesized at 25°C and 70°C were determined 10.10nm and 9.98 nm, respectively.

![XRD pattern of synthesized magnetite nanoparticles under A) 25°C  B) 70°C](image)}
3.2. TEM Analysis

Morphology and mean particle size of prepared nanoparticles at 25°C and 70°C were determined by TEM (Fig. 2). Particles are quasi sphere and have sizes ranging from 9.5 to 16 nm respect to different synthesis conditions. Polydispersity and surface aggregation of samples prepared at room temperature could be figured out from Fig. 2, this regards to small size, increased surface-to-volume ratio and thus augmented magnetic dipole-dipole interactions [19] (at synthesising conditions of prolonged time and elevated temperature, surface aggregation and polydispersity were reduced).

Fig. 2. TEM micrograph of samples prepared at A) 25°C B) 70°C

As some separate articles mentioned, in order to produce tiny nuclei, the initial temperature of this study set to 25°C and after 1 hour group 1 was purified which resulted in particles with larger size (about 11 nm). Depending on reaction time, the diffusion and growth process of samples could be completed. At elevated temperature and prolonged time, the reaction condition set to be completed and samples with less crystal defects and smaller particle size (about 9.5 nm) were produced [20-21]. With increase of ingredient (alkaline media) concentration more material is available on the growth phase and thus particles with higher diameter could be obtained (Fig. 3).

Fig. 3. Variation of particle size with alkaline media concentration and temperature measured by TEM

3.3. Magnetic Measurements

Magnetic properties of nanoparticles were determined by VSM at room temperature, results show that these materials have strong magnetic properties of 63.1 emu/gr and 67.8 emu/gr for samples synthesized at 25°C and 70°C, respectively.
Bulk material of magnetite has higher saturation magnetization, the small particle size and breaking of a large number of exchange bonds for surface atoms (pinning effect) cause this reduction [6, 22]. As figure 4 shows, complete reversibility of magnetization process confirms the superparamagnetic behaviour of prepared nanoparticles. Because of higher amount of alkali media, with increase of alkaline media concentration, the probability of non-magnetite layer production (magnetically dead layer) increased which decrease the amount of saturation magnetization (see the Fig. 5.) revealing that the positive effect of alkaline media on saturation magnetization has a limit.

Using Langevin’s equation and magnetic experimental data, the average magnetic particle diameter were calculated[2]:

$$a_M = \frac{18K_BT}{\pi\mu_0M_bM_s} \left(\frac{dM}{dH}\right)_{H \to 0} \quad (4)$$

where $a_M$ is the magnetic particle diameter, $k_B$ is Boltzmann’s constant, $\mu_0$ is the vacuum magnetic permeability, and $M_b$ is magnetization of bulk magnetite. Figures 5 and 6 represent increase of magnetic properties and slight decrease of particle size with respect to elevated temperature. Owing to prolonged reaction time and elevated temperature, synthesis reaction could be completed [18] thus particle size was reduced and because of loss of surface defects, magnetic saturation was increased.
Fig. 6. Variation of particle size with alkaline media concentration and temperature measured by VSM

4. Conclusion

This work, present the effect of changing of alkaline media concentration and temperature on copercipitation method by which the particle size could be optimized and higher magnetic properties could be obtained. The results indicate that concentration and temperature have significant effects on magnetic properties, particle size and size distribution. Increasing the alkaline concentration increased the particle size from about 9nm to 16nm and elevated temperature and prolonged synthesis time resulted in decline of surface defects and thus reduction of particle size. The saturation magnetization increased from about 63 emu/gr at 25°C to 68 emu/gr at 70°C (in the condition of lowest alkaline concentration). In this study the smallest particle size with highest saturation magnetization was obtained at alkaline media concentration of 0.9 M and prolonged synthesis time at 70°C.

References


