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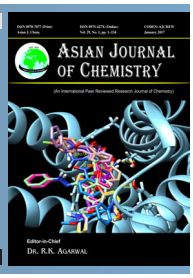

A Size Controlled Synthesis of Magnetite Nanoparticles in Pure Inorganic Medium

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An extensive research has been carried out on the synthesis of magnetite nanoparticles by co-precipitation technique. Most of the co-precipitation technique shows the improper size and size distribution of the magnetite nanoparticles. In few reports organic stabilizers were employed to control the synthesis of magnetite nanoparticle. In this work, the pure inorganic precursors were employed for the synthesis of magnetite nanoparticles. The reports showed that pure form of magnetite nanoparticles with good size distribution. Hence this is the facile approach for the synthesis of magnetite nanoparticles; which can be employed for the various biomedicine applications.

Keywords: Magnetite nanoparticles, VUSPIO, Superparamagnetic, Nanomaterials.

INTRODUCTION

A number of synthetic methods have already been reported in literatures for the preparation of magnetite nanoparticles. Among them the co-precipitation technique is possibly the simplest and most competent chemical pathway to obtain magnetite nanoparticles. The main advantage of the co-precipitation process is that it can be easily scaled up for bulk preparation. However, the control of particle size distribution is limited, because only the kinetic factors control the growth of the crystal. Size controlled magnetite nanoparticles of range 10-40 nm were prepared through co-precipitation method [1-3]. The magnetite nanorods with anisotropic property have been synthesized by reverse co-precipitation technique with the support of magnetic field. The magnetic fluid has been synthesized from magnetite nanoparticles and hydrophilic surfactant Tween 80 through co-precipitation for the applications in MRI and magnetic fluid hyperthermia. In the co-precipitation process, two stages are involved (i) a short burst of nucleation occurs when the concentration of the species reaches critical super saturation and (ii) slow growth of the nuclei by diffusion of the solute to the surface of the crystal. To produce monodisperse iron oxide nanoparticles, these two stages should be separate, *i.e.*, nucleation should be avoided during the period of growth [4-7].

The magnetite nano crystals of size 2-4 nm can be synthesized by a chemical co-precipitation method in which the particle size was controlled by the reaction temperature [7-13]. The mechanism of the first stage of formation of magnetite nanoparticle synthesized by chemical precipitation technique and the rate of nanoparticle formation is high in its initial period of time and then found decreasing due to the decrease in the number of combining molecules in the solution. Thus the rate of nanoparticle growth depends on its size because the mean size of nanoparticles depends on the physical properties of the medium (viscosity, temperature, *etc.*) [14-17]. Magnetite particles with an average size of 39 nm and good monodispersity have been synthesized by co-precipitation at 70 °C from ferrous Fe^{2+} and ferric Fe^{3+} ions by a tetra methyl ammonium hydroxide solution, followed by hydrothermal treatment at 250 °C. Further this report explains the conversion of magnetite to other iron oxide phases at elevated temperature [18,19]. Hence the above reports show that the synthesis of magnetite nanoparticles by co-precipitation technique can be achieved only by adding organic stabilizer or tedious reaction setup. In this work the pure magnetite nanoparticles were prepared by using inorganic precursors with facile chemicals.

EXPERIMENTAL

The magnetite nanoparticle is prepared by using analytical grade of iron(II) perchlorate [$Fe(ClO_4)_2$, Alfa Aesar] and iron(III) perchlorate [$Fe(ClO_4)_3$, Sigma Aldrich] as iron precursor solution in the 1:2 M ratio, respectively. Sodium hydroxide (1 M, Fisher India) is used to maintain the pH of the solution to be 9. Water utilized in the experiments was Milli-Q (Millipore) deionized water. Septum sealed twin neck 100 mL round bottom flask is employed as a reaction container and it was maintained in an inert atmosphere by an argon balloon to prevent the oxidation of magnetite to maghemite

conversion during the process. Both the iron precursor solutions were added in equal amount of 10 mL each and stirred with magnetic pellet. The colour of the solution was monitored till turns into yellow colour. The pH of the reaction is increased by adding 10 mL of 1 M NaOH dropwise using a syringe. With continuous stirring for 10 min, the solution turns into black colour colloidal which indicates the formation of magnetite nanoparticle. The black colour colloidal solution was washed with water for several times to remove the unreacted excess of alkali, carefully dried and used for further characterization. To optimize the formation of magnetite nanoparticle the process has been carried out with different temperatures such as 30, 40 and 50 °C.

RESULTS AND DISCUSSION

The co-precipitation technique is the simplest possible method and most competent chemical pathway to obtain magnetite nanoparticles. Magnetite nanoparticles are usually prepared by ageing a mixture of ferrous and ferric perchlorate salts in aqueous medium. In this co-precipitation process, the chemical reaction has been deduced by the following stoichiometric equation (eqn. 1) which represents the formation of magnetite nanoparticles from 1:2 mixture of Fe^{2+} and Fe^{3+}. The pH of solution is attuned to 9 by adding 1 M NaOH solution.

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O \quad (1)$$

The present work is based on the combination of iron(II) perchlorate and iron(III) perchlorate as a (precursor) formulating materials for the preparation of magnetite nanoparticles. This co-precipitation reaction is represented in eqn. 2.

$$Fe(ClO_4)_2 + 2Fe(ClO_4)_3 + 8NaOH \longrightarrow Fe_3O_4 + 4H_2O + 8Na(ClO_4) \quad (2)$$

To optimize the size and shape of the nanoparticle the co-precipitation reaction has been regulated with two different parameters like temperature and concentration of iron precursor solution.

X-ray diffraction studies: The coprecipitation reactions are carried out at different temperatures *viz.*, 30, 40 and 50 °C and the corresponding X-ray diffraction data are depicted in Fig. 1(a-c), respectively. The X-ray diffraction pattern of magnetite nanoparticle (Fig. 1b) prepared at 40 °C showed a slight variation as compared to magnetite nanoparticle prepared at 30 °C. The intensity of the peak for plane 311 is reduced for magnetite nanoparticle synthesized at 40 °C which is the typical diffraction for magnetite. The particle size of magnetite nanoparticle corresponding to the most intense peak of 311 plane (2θ = 35.43) is found to be 98 nm. The particle sizes were calculated by using Debye Scherrer equation (eqn. 3) and the result is consistent with the scanning electron microscopic results.

$$D = 0.98\lambda/\beta \cos \theta \quad (3)$$

where, $\beta = X_{diff} \times \pi/180$.

X-ray diffraction for magnetite nanoparticle prepared at 50 °C [Fig. 1(c)] showed the peak found at 2θ = 75° representing the maghemite diffraction associated with the magnetite peaks.

The result reveals that during the co-precipitation reaction, the oxidation of magnetite into the most thermodynamically stable iron oxide forms of maghemite has occurred at 50 °C.

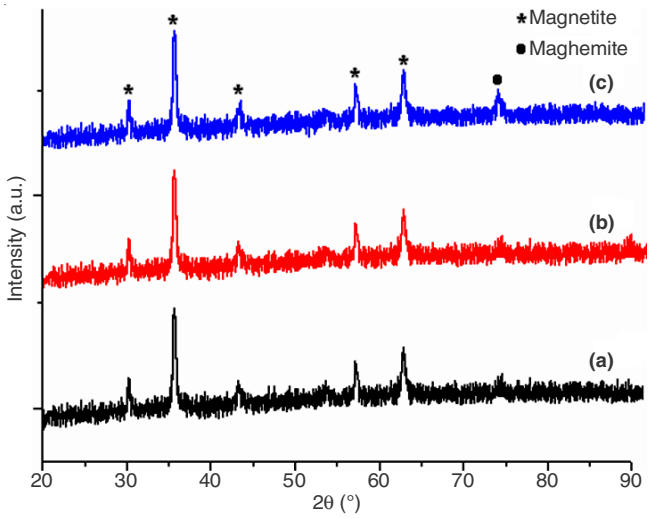

Fig. 1. XRD patterns of magnetite nanoparticle synthesized at various temperatures in 1:2 M of iron(II) perchlorate and iron(III) perchlorate (a) 30 °C, (b) 40 °C and (c) 50 °C

FT-IR spectral analysis: The FT-IR spectra of magnetite nanoparticles synthesized by co-precipitation method at different temperatures 30, 40 and 50 °C were depicted in Fig. 2a-c. The spectrum obtained for 30 °C shows the typical peak for magnetite nanoparticles (Fig. 2a). The FT-IR spectrum acquired for 40 and 50 °C show the high transmittance in the region of 1800-1200 cm^{-1} compared to the spectrum obtained for 30 °C (Fig. 2b-c). Further the peak at 50 °C appeared at 900 cm^{-1} corresponds to the other iron oxide phases like maghemite and hematite. Hence from the result it can be concluded that at higher temperature (50 °C) the magnetite could oxidize to its other iron oxide phases namely maghemite.

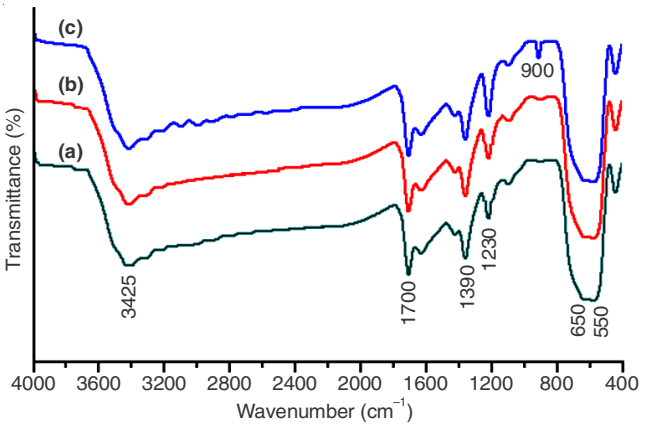

Fig. 2. FT-IR spectra of magnetite nanoparticles synthesized at various temperatures in 1:2 M of iron(II) perchlorate and iron(III) perchlorate (a) 30 °C, (b) 40 °C and (c) 50 °C by co-precipitation method

Raman analysis: The influence of temperature on the formation of magnetite nanoparticle has been evaluated by means of Raman spectroscopy and the spectra are given in Fig. 3a-c. The Raman spectrum of magnetite nanoparticle synthesized at 40 °C shows the typical Raman active bands as received magnetite. Further the increase of temperature to 50 °C leads to the formation of maghemite which is evident from the characteristic peak of maghemite at 700, 500 and 350 cm^{-1} along with the magnetite peaks. Thus elevation of

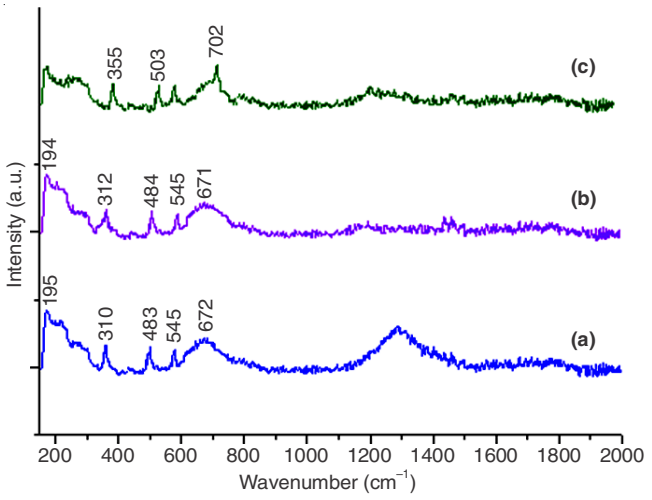

Fig. 3. Raman spectra of magnetite nanoparticles synthesized by co-precipitation method at (a) 30 °C, (b) 40 °C and (c) 50 °C

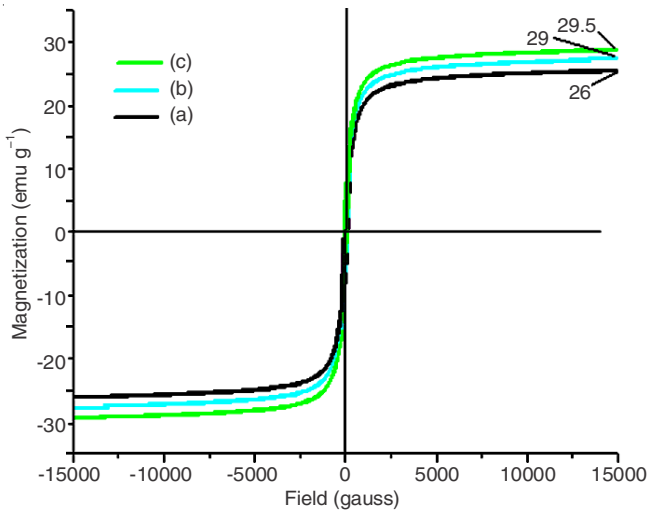

Fig. 4. VSM hysteresis curves of magnetite nanoparticles synthesized by co-precipitation method at (a) 30 °C (b) 40 °C and (c) 50 °C

reaction temperature results in the formation of maghemite. Hence it is concluded that in the co-precipitation technique, the optimum temperature for the formation of magnetite is 40 °C.

Vibrating sample magnetometer studies: Further the M-H analysis has been carried out for the magnetite nanoparticles synthesized by co-precipitation at different temperature 30-50 °C and the hysteresis curves have been shown in Fig. 4. M_S value for the magnetite nanoparticle synthesized at 50 °C is 29.5 emu g^{-1} and magnetite nanoparticle prepared at 40 °C is 29 emu g^{-1}. Hence increasing the temperature of the co-precipitation reaction slightly varies the saturation magnetization value compared to the reaction carried out at 30 °C. Further the existence of small coercivity confirms the ferromagnetic properties of magnetite nanoparticle.

Scanning electron microscopic analysis: The scanning electron micrographs of the magnetite nanoparticle prepared at an elevated temperature (40-50 °C) from 1 M concentration of precursor solution have been shown in Fig. 5a-b. The temperature of the reaction has remarkable influence on the particle distribution which can be evidenced by SEM micrographs. The magnetite nanoparticle synthesized at 50 °C shows the better particle distribution rather than at 40 and 30 °C.

In co-precipitation technique, the effect of concentration of iron precursors is optimized and it has been observed that 1:2 M ratio of iron(II) perchlorate and iron(III) perchlorate at 40 °C is the best among the other various conditions. Further the effect of temperature shows the better particle distribution but structural study shows the phase transformation of magnetite to magnetite maghemite at elevated temperature 50 °C. The overall SEM results show that the average size of the particles exists as randomized and in the range of 70 to 336 nm. Hence this technique is not efficient method for the synthesis of monodisperse nanoparticles.

Conclusion

The composition of iron(II) perchlorate and iron(III) perchlorate media is best precursor for the preparation of magnetite nanoparticles. The size distribution of the nanoparticles is controlled by optimizing the temperature of the reaction medium. The optimum temperature for the synthesis of magnetite nanoparticles is 40 °C. At high temperature the magnetite nanoparticles were transformed to the maghemite. It is evidenced by the Raman and FT-IR spectral studies. Further it is confirmed by the X-ray diffraction studies. Scanning electron

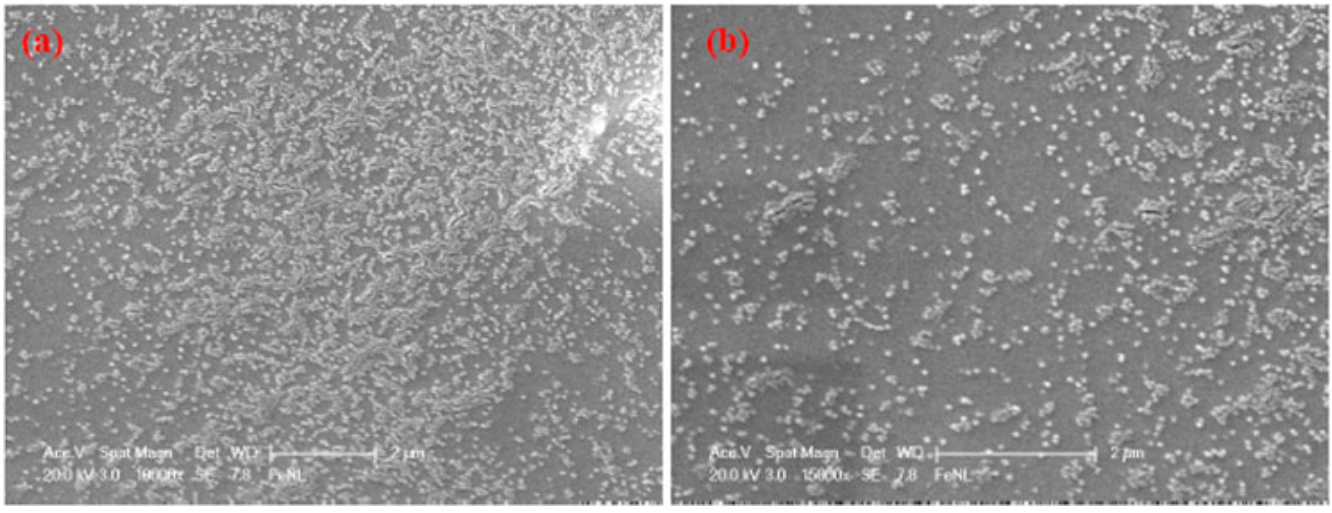

Fig. 5. Scanning electron micrograph of magnetite nanoparticle prepared in 1:2 M of iron precursors at (a) 40 °C and (b) 50 °C

microscopic analysis provides an insight on the morphological features of as-synthesized powders. The particle size has been observed in the range of 80-150 nm and they are in uniform size distribution.

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