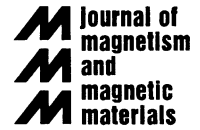




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Synthesis and characterization of size-controlled cobalt-ferrite-based ionic ferrofluids

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Abstract

Size-controlled synthesis of cobalt-ferrite nanoparticles, their passivation and peptization as stable ferrofluids are reported. Transmission electron microscopy and Mössbauer spectroscopy were used as characterization techniques. Particles with little change in size distribution, in the 10–15 nm diameter ranges, were obtained using stirring speeds between 2700 and 8100 rpm. The anomalous diffusion has been used to explain the nanoparticle size-control mechanism. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrofluids; Cobalt ferrite; Transmission electron microscopy; Mössbauer spectroscopy; Superparamagnetism; Size control; Nanoparticle synthesis

1. Introduction

The chemical synthesis of spinel ferrite-based nanoparticles and their surface passivation and stabilization as ionic ferrofluids (FFs) may represent a very important step towards the engineering of specific magnetic carriers. In particular, the capability to synthesize size-controlled cobalt-ferrite-based nanoparticles plus the possibility of using radioactive ⁶⁰Co to produce enriched FF opens new perspectives, as for instance in the targeting of cancer cells using antibody-coated nanoparticles. Size control of spinel ferrite-based nanoparticles

may be achieved by controlling the physical parameters and the chemical conditions under which the chemical condensation reaction occurs [1,2]. Furthermore, surface cation exchange may be successfully used to passivate the nanoparticle surface, thus preventing chemical transformations [3]. Finally, the control of the pH, ionic strength, and counterion nature provide the necessary conditions for the ionic FF stability [4]. Transmission electron microscopy (TEM) has been used as the most traditional technique for nanoparticle sizing of FF samples [5]. Besides the size characterization provided by the TEM data, Mössbauer spectroscopy can be used as a powerful technique to characterize several aspects, specially in iron-based materials, such as chemical composition, crystal structure, and magnetic behavior [6].

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In this study, we report the chemical synthesis of size-controlled cobalt-ferrite nanoparticles, the passivation procedure, the peptization of the nanoparticles as highly stable ionic ferrofluids, and the material characterization using TEM and Mössbauer spectroscopy. The microscopy data provide information concerning the particle-size polydispersity, which will be discussed in terms of the synthesis condition. Mössbauer spectroscopy, on the other hand, not only indicates the magnetic phase obtained but also reveals the magnetic ordering associated with the nanoparticles.

2. Experiment and discussion

Stable cobalt-ferrite-based (CoFe_2O_4) ionic FFs were obtained after performing a three-step procedure. First, cobalt-ferrite nanoparticles were synthesized by coprecipitating Co (II) and Fe (III) in alkaline medium. The starting solution containing 6 ml of concentrated nitric acid, 250 ml of aqueous solution of cobalt nitrate (0.005 mol/l), and 250 ml of aqueous solution of iron chloride (0.010 mol/l) was heated to 95°C, under vigorous stirring. Aqueous solution of sodium hydroxide (1.0 mol/l) was then quickly added to the stirring solution until pH 12 was reached. About 120 ml of the sodium hydroxide solution was required to bring the pH to about 12. Three different samples were prepared using different stirring conditions, namely, S13, S23, and S33, respectively, at 2700, 5400, and 8100 rpm. After removing the aqueous solution, nitric acid (2.0 mol/l) was added to the precipitate until pH 3 was reached. Then, the precipitate rested overnight on top of a magnet. Second, passivation of the nanoparticle surface was achieved by Fe (III) enrichment, after treatment with ferric nitrate. Samples S13, S23 and S33 were treated with 10 ml of hot ferric nitrate (0.5 mol/l) under stirring, during about 3 min. Third, peptization of the nanoparticle was obtained by controlling the surface charge density while reducing the ionic strength of the aqueous medium. An aqueous triethylamine (0.1 mol/l) solution was added dropwise to the acid precipitate until pH 6 was reached. The precipitate was then washed through several cycles with acetone and deionized water to reduce the ionic strength of the

medium. Finally, perchloric acid was added to the precipitate until pH 2 was reached at which point peptization occurred.

Control of the nanoparticle size happens during the first synthesis step by changing the stirring speed in the range of 2700–8100 rpm. It was found that the higher the stirring speed the smaller the average mean particle diameter. However, the standard deviation associated with the lognormal particle-size distribution did not change when the nanoparticle size increased by about 50%, as discussed below. The understanding of the nanoparticle growth mechanism through chemical condensation reaction in solution and under vigorous stirring, has not been the focus of these investigations, despite the huge impact it may have from fundamental and applied viewpoints.

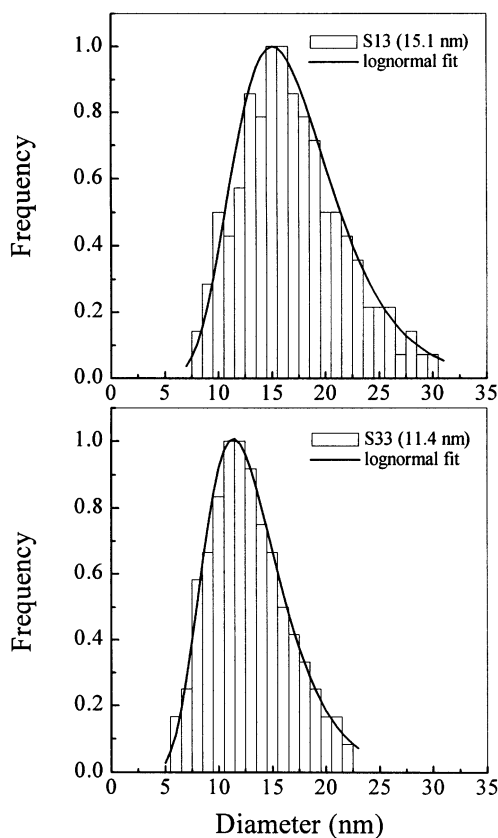


Fig. 1. Typical particle size histogram obtained from the TEM data. The solid lines represent the best fit of the data according to Eq. (1).

However, the decrease of the average particle size as the stirring speed increases may indicate that the nanoparticle growth process is mainly dominated by the nanoparticle diffusion throughout the medium instead of the diffusion of the aqueous cations into the nanoparticle surface. This seems to be an obvious conclusion, once cations are everywhere in the medium while the nanoparticles represent a small volume fraction. Nevertheless, the distinction between normal and anomalous diffusion of the nanoparticle may hold the key to understand the growth process. Under normal diffusion the nanoparticle growth process may keep the same growth kinetics along the mean-free path while under anomalous diffusion the growth kinetics may switch between two distinct paths, with very different growth velocities. The two distinct growth paths may occur along with a sequence of short flies or during the long flies, typical of the anomalous diffusion [7]. Anomalous diffusion of particles inside a turbulent fluid has been recently reported in the literature [8]. Under such a scenario, the nanoparticle growth is more likely to occur during a sequence of short flies, when space localization is higher. As the stirring speed increases, the time the nanoparticle spend during a sequence of short flies also increases, allowing the onset of a higher den-

sity of nucleation sites, with consequent reduction of the average particle size.

Fig. 1 shows the particle-size histograms of samples S13 and S33, respectively. The TEM pictures of the cobalt-ferrite nanoparticles, from where the particle-size polydispersity profiles were taken, were obtained using the Jeol 100CXII equipment. The solid line in Fig. 1 represents the best-fit curve of the particle-size histogram using the standard approach, i.e., the lognormal distribution function [9]

$$P(D) = \frac{\exp(-2\sigma^2)}{D_m \sigma \sqrt{2\pi}} \exp\left\{-\ln^2(D/D_m)/2\sigma^2\right\} \quad (1)$$

with a most probable particle diameter of $D_m = 15.1 \pm 0.1$ and 11.4 ± 0.1 nm and a standard deviation of $\sigma = 0.30 \pm 0.01$ and 0.31 ± 0.01 , for samples S13 and S33, respectively. Note that the lognormal distribution function described in Eq. (1) provides a full-width at half-maximum (ΔD) that spans from $f^{-1}D_m$ to fD_m , where $f = \exp(\sigma\sqrt{2\ln 2})$. The f factor also describes the asymmetry of the lognormal distribution function, once $f = -(fD_m - D_m)/(f^{-1}D_m - D_m)$. Therefore, from the fitting of the TEM histogram using Eq. (1) one obtains the full-width at half-maximum of

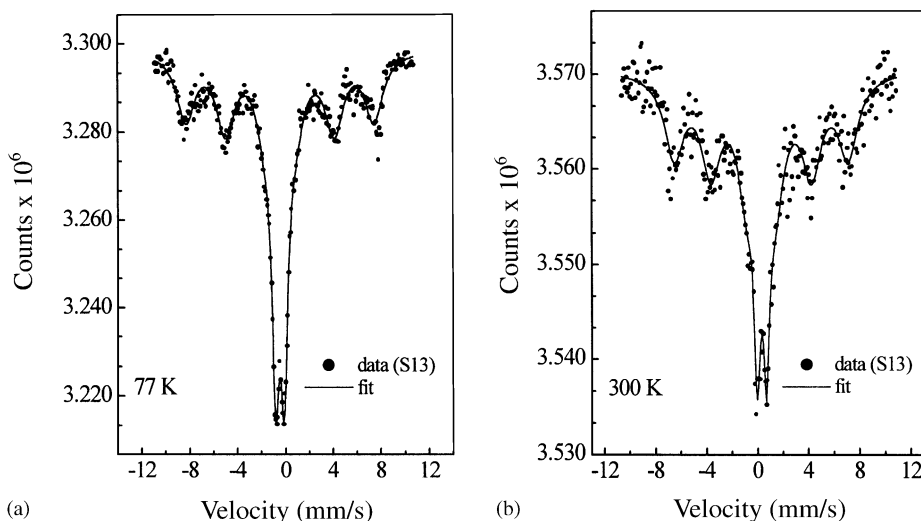


Fig. 2. Mössbauer spectra of sample S13 at (a) 77 K and (b) 300 K. Circles are the experimental data while the solid lines represent the best fit using one doublet and one sextet.

$\Delta D = 10.9 \text{ nm}$ ($\sigma = 0.30$) and $\Delta D = 8.5 \text{ nm}$ ($\sigma = 0.31$) associated to samples S13 and S33, respectively.

Figs. 2(a) and (b) show the Mössbauer spectra of sample S13 at 77 and 300 K, respectively. The Mössbauer spectra were recorded in the transmission geometry, using an MCA (256 channels) and a Wissel constant acceleration transducer coupled to a 50 mCi $^{57}\text{Co/Rh}$ source. Each plastic sample holder (1.7 cm diameter) used to record the Mössbauer spectra contained 80 mg of uniformly distributed and pressed sample. The Mössbauer spectra in Figs. 2(a) and (b) were least square fitted to a sextet and a doublet, giving parameters typical of cobalt ferrite [10]. At 77 K, the isomer shift (relative to natural iron) and the quadrupole splitting associated to the doublet are 0.47 and 0.71 mm/s, respectively. At 300 K, however, the isomer shift (relative to natural iron) and the quadrupole splitting associated to the doublet are 0.32 and 0.70 mm/s, respectively. At 77 and 300 K, the internal field associated to the sextet is 489.5 and 423.7 kOe, respectively. The collapsing of the internal field as the temperature increases from 77 to 300 K is typical of the superparamagnetic behavior of nanosized particles [11]. The Mössbauer doublet indicates cobalt-ferrite nanoparticles in the paramagnetic phase.

3. Conclusions

This work provides information concerning the synthesis of nanomagnetic particles, their passivation and peptization as stable ferrofluids. The most striking result is the possibility of controlling the nanoparticle size using different stirring speeds,

with no apparent change of the standard deviation. The anomalous diffusion of the nanoparticles under turbulent stirring may provide the best picture for the size-control mechanism. Transmission electron microscopy (TEM) data show that increasing the stirring speed from 2700 to 8100 rpm reduces the average particle diameter from 15.1 to 11.4 nm, while keeping the standard deviation around 0.30. Mössbauer spectroscopy data identified the magnetic material as superparamagnetic cobalt ferrite, in agreement with the TEM data.

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