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Electro-precipitation of Fe_3O_4 nanoparticles in ethanol

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ABSTRACT

The preparation of superparamagnetic magnetite (Fe_3O_4) nanoparticles by electro-precipitation in ethanol is proposed. Particle average size can be set from 4.4 to 9 nm with a standard deviation around 20%. Combination of wide-angle X-ray scattering (WAXS), Electron energy loss spectroscopy (EELS) and Mössbauer spectroscopy characterizations clearly identifies the particles as magnetite single-crystals (Fe_3O_4).

1. Introduction

The prospect of a new generation of materials and devices based on nanoparticles (NPs) is a major driving force in the rapidly emerging field of nanoscale research. Magnetic NPs, and more particularly magnetite (Fe_3O_4) and maghemite (γFe_2O_3), have been widely used for biomedical applications such as cell targeting, cell separation, drug delivery, hyperthermia [1,2], or in environmental sciences, for metal separation from wastewater [3]. Due to their magnetic moment, magnetic NPs can be driven by an applied magnetic field into specific regions of the human body for *in vivo* applications. For *in vitro* diagnosis or for metal separation, magnetic separation and selection can be done. For these applications, magnetic NPs have to become magnetized at low magnetic field. However, in order to avoid any agglomeration phenomenon, the magnetic NPs must not present magnetic remanence, i.e. must have a zero magnetization in the absence of an applied magnetic field. This particular behavior is achieved with superparamagnetic NPs. Typically, magnetite Nps become superparamagnetic at sizes below ~15 nm.

Chemical synthesis of colloidal magnetite has been known for a long time: aqueous mixture of ferric and ferrous salts is mixed with an alkali in order to induce the precipitation of magnetite particles (maghemite can then be obtained by soft oxidation of magnetite) [4]. The average diameter of particles can be tuned between 5–100 nm by varying experimental conditions (concentration, temperature, nature of alkali, ionic strength, agitation, etc.) but the system is always polydispersed in size [5,6] due to the Oswald ripening mechanism (the large particles will grow at the cost of the small ones) [7]. Organized assemblies or complex structures have been used as nanoreactors (microemulsion, vesicle, polymer matrix media synthesis) in order to obtain nearly monodispersed ultrafine iron oxide NPs. Readers interested by these methods can have a look on the excellent review written recently by Gupta and Gupta [8].

In practice, even if better control can actually be done over the size and the size distribution of NPs, progress in the use of superparamagnetic NPs depends on the improvement of synthetic methods. In this paper we propose a completely new process based on electro-precipitation of magnetite in ethanol media, which yields NPs with a controlled distribution avoiding the use of nanoreactors.

2. Experimental part

This electrochemical method used for magnetite (Fe_3O_4) NPs precipitation needs two carbon cylinders (5.0 cm long and 0.5 cm of diameter) which are used as a pair of electrodes in an electrochemical bath of 100 ml. During the experiment, the solution was stirred using a magnetic bar. Electrical current was

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Table 1
Synthesis conditions, and average size of Fe_3O_4 nanoparticles

Sample	$Fe(NO_3)_3 \cdot 9H_20$ (mol/l)	Current density (mA/cm^2)	Synth. time (h)	Average size (nm)	Standard deviation (nm/%)
S1	$\mathbf{10^{-2}}$	**5**	12	4.4	0.7/16
S2	$\mathbf{2 \times 10^{-2}}$	**30**	12	6.15	1.15/18
S4	$\mathbf{4 \times 10^{-2}}$	**80**	12	8.1	1.44/18
S8	$\mathbf{8 \times 10^{-2}}$	**110**	12	8.5	1.5/18
S8b	8×10^{-2}	**30**	12	7.3	1.9/26
S8c	8×10^{-2}	110	**2**	8.9	1.9/21
S16	$\mathbf{1.6 \times 10^{-1}}$	**220**	12	?	$>100\%$

Bold characters highlight the parameters modified between successive syntheses.

provided by an ISO-Tech Laboratory DC Power Supply model IPS-1630D. A 90 ml of 0.01–0.16 mol/l $Fe(NO_3)_3 \cdot 9H_2O$ ethanol solutions were used as iron precursor and the electrode area immersed was equal to 4 cm^2 (for each electrode). During the procedure the voltage between electrodes was kept constant at 62 V whereas the current could fluctuate slightly ($\approx 10\%$) especially during the first hour. Current densities reported in Table 1 are values noted after 1 h of electrolysis. Magnetite particles where collected on the cathode as black magnetic macroscopic platelets and washed with ethanol before to be dried under air at room temperature.

The size, the morphology and the crystalline structure of the particles were studied by transmission electron microscopy (TEM) on a Philips CM12 microscope at 120 kV (0.3 nm resolution). Particle size was determined by measuring at least 200 NPs taken on five different photos. Electron energy loss spectroscopy (EELS) chemical analysis was performed on a 200 kV Tecnai microscope using a GIF tridiem post-column energy filter.

Mössbauer measurements were obtained on a constant-acceleration conventional spectrometer with a 25 mCi source of ^{57}C (Rh matrix). The absorber was a powdered sample enclosed in a 20 mm diameter cylindrical, plastic sample-holder. Variable temperature spectra were obtained in the 4.4–300 K range, by using a MD 306 Oxford cryostat, the thermal scanning being monitored by an ITC4 Oxford servocontrol device (0.1 K accuracy).

The magnetic ac susceptibility was recorded at increasing temperatures and selected frequencies in the 1–852 Hz range, after an initial cooling from RT down to 4.5 K in the absence of the field (ZFC procedure); on a superconducting quantum interference device (SQUID)) magnetometer model MPMS2.

Wide angle X-ray scattering (WAXS) has been commonly applied by several authors [9] and may be one of the most powerful techniques to study the medium range order (0–4 nm) in nanometric materials. The experimental reduced radial distribution function (RDF), which reveals the distribution of the interatomic distances, was calculated similarly as given in another paper [9a]. Theoretical models were built up from the crystallographic growth of one bulk unit cell, with eventual parameters adjustment. The theoretical reduced RDF was calculated for these structural models as reported elsewhere [9a].

3. Results and discussion

Synthesis conditions and average size of Fe_3O_4 NPs are regrouped in Table 1 whereas Fig. 1 shows the TEM images.

For low $Fe(NO_3)_3 \cdot 9H_2O$ concentration ($<4 \times 10^{-2}$ mol/l) the solution remains clear during the electrolysis and magnetite particles can be collected on the cathode or from the bath as black magnetic macroscopic platelets. For higher iron (and also water content) concentration the solution becomes rapidly turbid during the electrolysis (probably due to a co-precipitation of an amorphous iron hydroxide) and pure black magnetite sample can be collected only on the cathode. For S16 sample (0.16 mol/l of $Fe(NO_3)_3 \cdot 9H_2O$), even on the cathode, the sample shows a black-brownish color indicating that magnetite is polluted. By the same way, TEM picture shows several big spherical magnetite particles (>10 nm) embedded inside an undefined amorphous matrix. Similarly, an addition of 1 ml of water in the S1 bath causes the same effect: pure magnetic particles are not formed. Consequently, we can suggest that for collecting pure magnetite particles we need a relatively water-free bath. However, the role played by water is not only negative. Indeed, as we can see on Table 1, iron nitrate increase, and consequently water increase, allowed to reach a high current density.

The electro-precipitation process leading to Fe_3O_4 NPs is not yet totally understood. However, we can suggest that the local increase of the pH at the vicinity of cathode causes $Fe(OH)_3$ precipitation. The pH increase probably comes from hydroxide ions production resulting from the nitrate and water reduction: $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [10,11]. The reduction of nitrate (NO_3^-) is confirmed by nitrite (NO_2^-) formation, verified by a simple qualitative analytical test (colorimetric test) whereas hydrogen production is clearly observed on the cathode. Finally, the iron (III) hydroxide is reduced to magnetite (Fe_3O_4) following the global reaction: $3Fe(OH)_3 + 2OH^- + e^- \rightarrow Fe_3O_4 + 4H_2O$. Note that this last reaction regenerates the water consumed in nitrate and water reduction. The H^+ consumed in the process should come from the ethanol oxidation at the anode ($CH_3CH_2OH + \frac{1}{2}O_2 \rightarrow 2H^+ + 2e^- + CH_3COOH$). Fig. 2 summarizes this general scheme of the magnetite electro-precipitation process.

The analysis of Table 1 shows that particle size can be adjusted from 4.4 nm to almost 9 nm, by increasing the $Fe(NO_3)_3 \cdot 9H_2O$ concentration from 10^{-2} to 8 10^{-2} mol/l and the current density from 5 to 110 mA/cm^2 . Probably higher concentration and current density leads to larger particles, however, those particles are contaminated rendering size measurements impossible (Fig. 1(f)).

Because iron, water content, and current density are correlated parameters, we have synthesized sample S8b where only the current density decreases compared to S8 sample. This experiment indicates that a smaller current density leads to slightly smaller particles. On the contrary, electrolysis time (S8c sample) does not have a significant effect.

X-ray diffraction is the method of reference for the structural study of crystalline materials. However, as the size of crystallites decreases, diffraction peaks get broader, making structure interpretation in the reciprocal space ambiguous. WAXS analysis, i.e. recording of the complete scattering pattern followed by Fourier transform, allows retrieval of the remaining structural information and its representation in the simpler real space as a RDF. Fig. 3 shows the RDF obtained from S1 Fe_3O_4 NPs. It very well matches the RDF computed from the spinel structure. However, since this spinel structure occurs in both magnetite and