

SYNTHESIS AND CHARACTERIZATION OF MAGNETITE NANOPARTICLES EMBEDDED IN COPOLYMER MICROSPHERES

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INTRODUCTION: In recent years the design and synthesis of nanometer-scaled magnetic structures have been the focus of intense investigation, particularly because the unusual or enhanced properties of such materials [1]. As far as the size and size-dispersity control is concerned, the tendency of isolated magnetic nanostructures to aggregate into bigger clusters during the synthesis process, driven by particle-particle interaction (e.g. magnetic dipole and Van der Waals) and/or reduction in energy associated with the high surface-to-volume ratio, has represented a critical obstacle. Iron oxide-based nanoparticles can be conveniently synthesized and maintained as stable single units using a variety of polymer templates, though it is quite clear that the chemical route, the nature of the polymer matrix, and the polymer morphology strongly affect the composition of the end product.

Magnetic polymer-based spheres have lately been considered as an important material in the biotechnology industry, for cell separation [2] and DNA extraction [3] for example. In particular, mesoporous polymeric templates can be produced as micron-sized spheres that allow *in-situ* chemical synthesis of nanosized ferrite particles with adjustable magnetic properties and mass density [4]. Both parameters are extremely important in the composite engineering for targeting of tumor cells, among others [5]. The fine-tuning of the physical parameters, e.g. net magnetic moment and density of the composite, can be realized through several cycles (N) of chemical synthesis. Once the composite spheres are dispersed in the blood and bound to a particular biological structure the resulting complex can be efficiently trapped in a high magnetic field gradient device for later removal. In the present study Mössbauer spectroscopy (MS) and transmission electron microscopy (TEM) were used to characterize the iron oxide-based nanoparticles precipitated in mesoporous styrene-divinylbenzene (Sty-DVB) microspheres.

METHODS: Six composite samples were chemically prepared using the Sty-DVB template immersed in FeSO₄ aqueous solution (bath solution) at 30 mmol/L. The Sty-DVB copolymer used was synthesized by suspension polymerization in the presence of inert diluents. The porous structure in the dry polymer template presents an average pore diameter of about 13 nm. The swelling behavior of the copolymer in heptane indicates the presence of collapsed pores, which could not be detected through mercury intrusion porosimetry and surface area measurements. The porous structure in the swollen state can be considered to be preferentially mesoporous due the expansion of the collapsed pores. The sulfonated copolymer presented ion exchange capacity (dry resin) of about 4.8 mmol H⁺/g. The polymeric matrix was characterized through the apparent density (0.44 g/cm³), fixed pore volume (0.44 cm³/g), surface area (140 m²/g), toluene regain (1.52 cm³/g), heptane regain (1.24 cm³/g), % volume swelling in toluene (100 %), and % volume swelling in heptane (58 %).

Each chemical cycle in the composite synthesis follows a four step experimental procedure. Firstly, the mixture was first stirred for 1 hour at room temperature. Second, the iron-loaded polymer particles were separated by filtration and washed thoroughly with water until no ferrous ion was detected in the eluent. Third, the oxidation of the ferrous ion was performed in alkaline medium following the standard recipe used in the synthesis of magnetite micro-crystals from ferrous ion in aqueous solution. Fourth, the obtained black composite was filtered, washed with water until the pH of the eluent was neutral, and dried at 60 °C. The described procedure was performed up to six times in order to obtain composite samples with increasing amount of magnetic material.

Transmission electron micrographs were obtained from the dried composite samples using a Jeol 100CXII instrument. Typically, 3 mg of the composite sample was frozen in liquid nitrogen and ground to fine powder. The powder obtained was dispersed in 3 ml of n-propanol and droplets of the

dispersion were placed on top of the copper grid coated with palladium and carbon films. Transmission Mössbauer spectra were recorded at 77 and 300 K, using a MCA (256 channels) and a Wissel constant acceleration transducer coupled to a 50 mCi $^{57}\text{Co}/\text{Rh}$ source. Each plastic sample holder (1.7 cm diameter) contained 80 mg of uniformly distributed and pressed sample. The spectra were least square fitted using two sextets.

RESULTS & DISCUSSION: Typical particle size histograms obtained from the TEM micrographs are shown in Figure 1, for $N = 1, 3,$ and 5 chemical cycle composite samples. The histograms were curve-fitted using the log-normal distribution function:

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

where D_m is the mean particle diameter and s is the standard deviation.

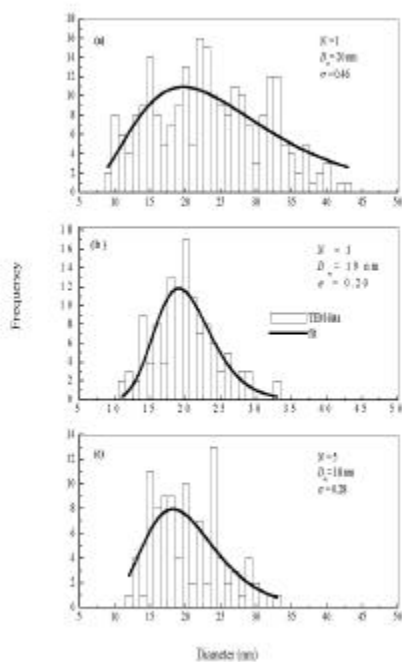


Fig. 1: Typical particle size histograms (TEM data) of magnetite nanoparticles, for (a) $N = 1,$ (b) $N = 3,$ and (c) $N = 5.$ The solid lines represent the best fit of the data using the log normal distribution function.

Whereas the mean particle diameter slightly decreases from 20 nm (1 cycle sample) down to 17 nm (6 cycle sample) the standard deviation shows a considerable decrease from 0.46 ± 0.06 (1 cycle sample) to 0.23 ± 0.02 (6 cycle sample). At the

same time, the amount of iron incorporation in the polymeric template, increases from 8.25 % (1 cycle sample) up to 29.2 % (6 cycle sample), as obtained from atomic absorption measurements (data not shown). The experimental data suggest that both template morphology and bath solution concentration determine the mean particle diameter, whereas cycling narrows the particle size distribution and increases mass incorporation.

Typical Mössbauer spectra ($N = 1, 3,$ and 5) of the synthesized black composite samples, at 77 and 300 K, are shown in Figures 2(a) and 2(b), respectively. Note that the Mössbauer spectra were curve-fitted using two sextets, as expected from bulk magnetite crystals, at 77 and 300 K. Though the curve fitting procedure is quite good for all spectra analyzed, the presence of a very small fraction of a paramagnetic phase may change the fitted values of the isomer shift with respect to the standard values.

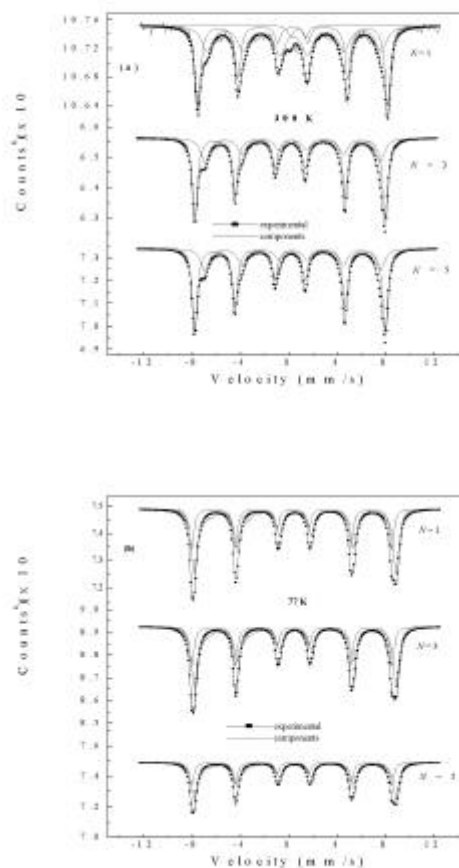


Fig. 2: Typical Mössbauer spectra of magnetic nanoparticles for (a) $N = 1, 3,$ and $5,$ at room temperature and (b) $N = 1, 3,$ and $5,$ at liquid nitrogen temperature.

Table 1 shows the Mössbauer parameters (average values), obtained from all the recorded Mössbauer

spectra, as well as the corresponding standard Mössbauer parameters from bulk magnetite [6].

Table 1. The average values of the internal fields ($H \pm 3kOe$) obtained from the composite samples ($N = 1$ through 6) and the standard magnetite data, at 77 and 300 K.

	T(K)	H (kOe) [Fe ³⁺ (Tet)]	H (kOe) [Fe ^{2+/3+} (Oct)]
Composite	77	522	509
Standard	77	514	499
Composite	300	484	458
Standard	300	493	460

CONCLUSIONS: Magnetite (Fe₃O₄) nanoparticles have been synthesized by alkaline oxidation in mesoporous sulfonated styrene-divinylbenzene copolymer template, and several iron-loading treatments of the polymer matrix to increase the amount of iron magnetic material have been used. The synthesized nanoparticles have been characterized by Mössbauer spectroscopy and transmission electron microscopy as magnetite.

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