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In situ synthesis of iron oxide nanoparticles in a styrene-divinylbenzene copolymer

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Summary

Magnetic iron oxide nanoparticles were prepared by *in situ* within a sulfonated styrene-divinylbenzene copolymer. The magnetic nanocomposite was characterized by X-ray diffraction, transmission electron microscopy and vibrating sample magnetometry. The size distribution of the nanoparticles was relatively narrow with good distribution within the copolymer. Nearly spherical nanoparticles, 7 nm in diameter, were identified as $CoFe_2O_4$ and had a well-defined crystalline structure. Magnetic measurements revealed that the magnetic nanocomposites are superparamagnetic.

Introduction

The design and synthesis of materials with nanoparticles has been subject of intense research. These materials display novel chemical, electronic, optical, and magnetic properties, which differ considerably from those of bulk materials [1]. Magnetic nanoparticles can be synthesized by different methods. They have been obtained from sol-gel [2], chemical coprecipitation [3] and microemulsion [4] among others. However, the tendency of the magnetic nanoparticles to form aggregates during the synthesis had represented a critical obstacle for size control. This problem can be avoided using an inert matrix; magnetic nanoparticles have been obtained in a variety of matrix materials such as silica [5], zeolites [6] and polymers [7]. The choice for the most suitable method will depend on the application wanted for the material. A good way to control the size and size distribution of magnetic particles is to make use of copolymer templates. Copolymer templates have been efficiently used to host chemical reactions, not only avoiding nanoparticle clustering but also providing stable frameworks against chemical degradation [8]. Copolymer templates have been used in the synthesis of iron oxide nanoparticles as: maghemite (γ-Fe_2O_3) [9], cobalt ferrite ($CoFe_2O_4$) [10] and magnetite (Fe_3O_4) [11, 12].

In this work, a sulfonated styrene-divinylbenzene (Sty-DVB) copolymer template was used to produce iron oxide nanoparticles. X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM) were used to characterize the magnetic nanocomposite.

Experimental

Materials

Styrene and divinylbenzene (Aldrich) were vacuum distilled. Deionized water was used as diluent. The initiator benzoyl peroxide (J.T. Baker) was used as received. Cobalt nitrate hexahydrate and ferric nitrate nonahydrate were purchased from Aldrich and were used without further purification.

Synthesis of the copolymer

Beads of styrene-divinylbenzene copolymers were synthesized by suspension polymerization in the presence of deionized water as diluent. The polymerization was carried out in a chemical reactor fitted with mechanical stirrer, thermometer and condenser. The percentage in weight between monomers and deionized water used in the reaction was of 1:2. The percentage used for divinylbenzene was of 7% wt with respect to styrene. The initiator concentration used was 1.5% mol in relation to the monomers. The solution containing the monomers and initiator was poured into the reactor containing the aqueous phase at room temperature. The temperature was then raised to 89 ± 1°C and stirring speed of 400 rpm kept constant during the reaction time (4 h). The copolymer beads were then separated and washed with ethanol to remove the diluent. The beads were finally sieved, washed with ethanol and vacuum dried at 50°C for 24 h. The copolymer was sulfonated using concentrated sulfuric acid (2 g of copolymer / 20 ml of sulfuric acid), to do this, the copolymer beads were suspended in dichloroethane (40% in volume with respect to sulfuric acid), after that the sulfuric acid was added slowly and the temperature was maintained at 70°C for 3 h. Finally the copolymer beads were washed with water until neutral pH and vacuum dried at 50°C for 24 h in air.

Magnetic composite preparation

Magnetic composites were obtained as follows: the sulfonated copolymer beads were immersed in aqueous solution of Fe(III) and Co(II) nitrates (molar ratio 2:1) by 12 h, followed by thorough washings to remove excess physisorbed ions. The copolymer was then exposed to a 1.2 N aqueous solution of NaOH at 80°C by several hours, which causes precipitation of the corresponding hydroxide. After that an aqueous hydrogen peroxide solution was added dropwise over a period of 15 min. The reaction mixture was kept at 80°C for 2 h, for the conversion to oxide. After stirring, the copolymer was thoroughly washed with deionized water to neutral pH and dried. The above-described procedure (reaction cycle) was performed three times in order to obtain composite samples with increasing amount of magnetic material.

Characterization

The magnetic phase in the nanocomposite was identified using an X-ray diffractometer Siemens D-5000 (25 mW, 35 kV, Cu K_α). The particles size and morphology of the magnetic nanoparticles inside the polymer matrix were studied using a JEOL JEM 1200EXII transmission electron microscope operated at 100 kV. The magnetic properties of the nanocomposites were measured using a vibrating sample magnetometer Lakeshore 7300 with a maximum field of 15 kOe.

Results and discussion

In order to identify the magnetic phase by X-ray diffraction, the magnetic nanocomposite was heated at 500°C under a nitrogen atmosphere for 8 h to degrade the polymer matrix. In agreement with a similar work [7], this temperature is sufficient so that they are not carried out a growth of nanoparticles due to solid state reactions. The nitrogen flow was of 20 ml/min and this permit to carry out the treatment in an oxygen free atmosphere. Once the polymer matrix was removed, the diffraction pattern from the iron oxide particles was collected as shown in Figure 1. The position and intensity of all the peaks coincided with the characteristics peaks of standard $CoFe_2O_4$ phase [13], insert as bars in the figure. Also the lattice spacings, *d*, obtained from x-ray diffraction were in agreement with the reported values [13] for $CoFe_2O_4$ as shown in Table 1. No diffraction lines of other phases can be observed.

For TEM measurements the magnetic nanocomposite was grounded to fine powder. The powder obtained was dispersed in ethanol and droplets of the dispersion were placed on top of copper grid coated with carbon film. Figure 2 displays a transmission electron micrograph of the magnetic nanocomposite subjected to three reaction cycles. This figure shows that the $CoFe_2O_4$ nanoparticles with good distribution within the

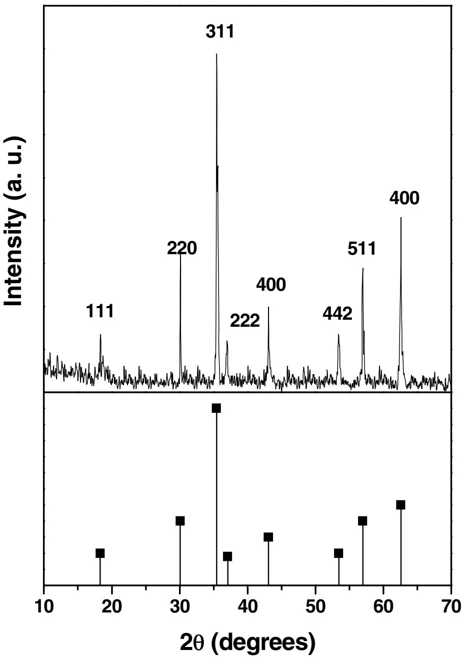

Figure 1. X-ray diffraction pattern of the magnetic nanocomposite after heat treatment.

Table 1. Diffraction data for the iron oxide synthesized within St-DVB copolymer.

hkl	***d* (experimental), Å**	***d* (JCPDS data[13]), Å**
111	4.838	4.847
220	2.966	2.968
311	2.530	2.531
222	2.427	2.424
400	2.097	2.099
442	1.714	1.713
511	1.615	1.615
400	1.482	1.483

polymer matrix. The particles show a nearly spherical morphology with diameters ranging between 5–10 nm. The particle size distribution (Figure 3) was obtained by measuring the diameter D_i of all the particles from different parts of the grid for an average number of particles close to 400. The particle size histogram in Figure 3 was curve fitted using the log-normal probability function [14]:

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

Where D is the particle diameter, D_m is the average particle diameter and σ is the standard deviation. From which the average particle diameter and standard deviation were $\langle D \rangle = 7$ nm and $\sigma = 1.09$ nm, respectively.

The magnetic characterization studies were carried out at room temperature. The VSM measurements showed that the materials were superparamagnetic in character, showing no hysteresis, remanence and coercitivity. Superparamagnetic materials are easily magnetized in a magnetic field but not retain magnetization once removed from the field. The magnetization curves for the samples with different reaction cycles are shown in the Figure 4. The one reaction cycle sample reaches a maximum magnetization of about 0.8 emu/g, increasing to 3.68 emu/g for the three reaction cycle sample. As it already mentioned after each cycle the amount of magnetic material present in the copolymer increases. The magnetization values depend of the

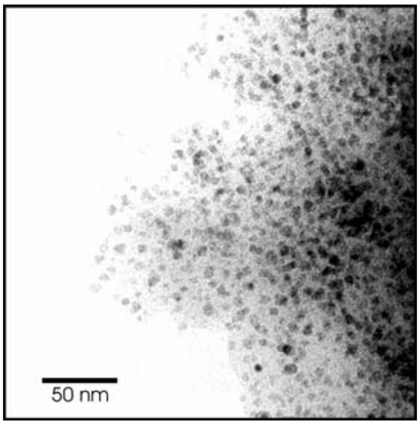

Figure 2. Transmission electron micrograph of the magnetic nanocomposite.

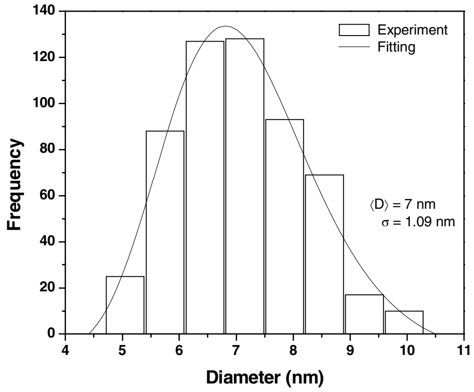

Figure 3. Particle size histogram obtained from the TEM micrograph of the Figure 2.

amount of magnetic material within the copolymer, due to this the values of magnetization increase for each cycle.

The magnetization curves of the samples with different weight percentages of $CoFe_2O_4$ in the polymer matrix and one reaction cycle are shown in Figure 5.

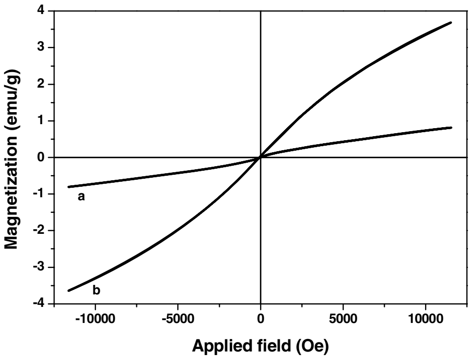

Figure 4. Magnetization curves for the magnetic nanocomposites with: a) one reaction cycle. and b) three reaction cycle.

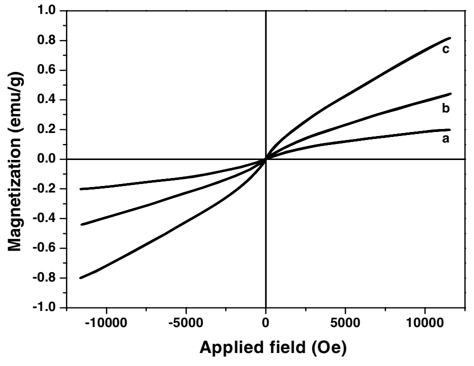

Figure 5. Magnetization curves for the magnetic nanocomposites with different percentages of $CoFe_2O_4$: a) 3.8%, b) 4.3% and c) 4.8%.

Superparamagnetic behavior is always observed for all samples. The magnetization values increase up to a maximum of 0.818 emu/g obtained for sample with 4.8% wt. of $CoFe_2O_4$. Is evident that the magnetization value of the nanocomposite increases with the increase in weight percentage of cobalt ferrite in the copolymer, as expected, since this parameter depends on the total mass of the material in the copolymer. The amount of $CoFe_2O_4$ in the copolymer, as magnetic material, is the responsible of the magnetization values in the samples.

Conclusion

As results of our investigations, cobalt ferrite nanoparticles have been synthesized *in situ* of a sulfonated styrene-divinylbenzene copolymer. The particles were found to be nearly spherical with good distribution inside the matrix, with an average diameter of 7 nm. The magnetic nanocomposites obtained are superparamagnetic. Our results suggest that the copolymer acts like a nanoreactor within which the particles of $CoFe_2O_4$ can be form at temperatures below 100°C. This copolymer is a promising route to the production of magnetic nanocomposites for advanced materials applications.

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