Synthesis of silver-coated magnetite nanoparticles

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Abstract

In this paper we describe the preparation of relatively monodisperse silver-coated Fe₃O₄ nanoparticles by a two-step procedure. Fe₃O₄ nanoparticles of 9 ± 2 nm in size were first prepared in microemulsions. They were subsequently coated with silver using glucose as reducing agent. The presence of a relatively homogeneous coating of ≈2 nm was confirmed by transmission electron microscopy and X-ray diffraction. A preliminary study of the magnetic properties shows a large decrease of the magnetization for the coated magnetite nanoparticles in comparison with the uncoated ones.

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1. Introduction

Nanometer-size metallic and semiconducting particles have been the subject of substantial research in recent years because these materials represent an ‘intermediate’ dimension between bulk materials and atoms/molecules. Among these materials, bimetallic nanocomposites having core-shell structure have received special attention because of their electronic, magnetic and optical properties [1–6].

In this paper we report the synthesis of Fe₃O₄ nanoparticles by the microemulsion method, and their coating with silver noble metal to impress optical properties to the magnetic core particles.

2. Chemical and experimental section

2.1. Synthesis of Fe₃O₄ core-Ag shell nanoparticles

Ferric (III) chloride, ferrous (II) sulfate, cyclohexane, cyclohexilamine, Brij-97, silver nitrate (99%) and d(+) glucose anhydrous, were purchased from Aldrich Chemical. Chlorhidric and nitric acids were obtained from Merck, and solution of 10% tetramethylamnonium hidroxide (TMAOH), from Fluka. All of them were used as received.

A microemulsion method was used to the synthesis of Fe₃O₄ nanoparticles and its aqueous stabilization [7,8], confirming the formation of the nanoparticles the black color acquired by the mixture.

The prepared Fe₃O₄ particles were then separately coated with silver. The amount of AgNO₃ used was calculated assuming a complete covering of the magnetic cores (of 9 nm size) with a 2 nm silver shell. For the reduction a mild reducing agent, glucose, was employed in order to ensure a controlled shell growth of silver onto Fe₃O₄.
particles and avoiding the formation of new silver nuclei. The mild conditions promote the reduction of Ag(I) ions adsorbed onto Fe₃O₄ particles. The molar ratio of AgNO₃ to glucose was 2:1 and the synthesis was carried out at room temperature. As the particles were gradually coated by silver, the black Fe₃O₄ particles turned brownish. For comparison purposes silver nanoparticles were produced in a separate batch using the same experimental conditions.

2.2. Characterization

Particle size distributions were characterized by transmission electron microscopy (TEM) with a 200 kV ultrahigh-resolution analytical electron microscope JEOL JEM-2010. UV–visible spectra were measured with a Hewlett-Packard 8452A Diode-Array Spectrophotometer.

The crystalline structure of the powders was studied by X-ray diffraction (XRD) with a Philips PW-1710 X-ray diffractometer using Cu Kα radiation with a wavelength of 1.54056 Å.

Thermogravimetric analysis was performed with a Perkin Elmer TGA-7 in order to determine the amount of Fe₃O₄ in the nanoparticle cores.

Magnetization measurements were recorded with a Quantum Design PPMS Model 6000 magnetometer.

3. Results and discussion

Fig. 1 shows a transmission electron micrograph of aqueous stabilized magnetite nanoparticles. Nanoparticles are relatively monodisperse and nearly spherical. The average size of the particles is 9 ± 2 nm.

Fig. 2 shows a TEM picture of Fe₃O₄@Ag nanoparticles. It can be seen that, as expected, the particles are now more polydisperse with a size of 13 ± 4 nm.

The UV–visible spectrum of the silver coated nanoparticles shows an absorption peak at 400 nm due to the silver surface plasmon resonance band, confirming the presence of silver in the particles.

Fig. 3 shows the XRD patterns of (a) the magnetite nanoparticles with a cubic spinel structure (space group Fd3m); (b) silver nanoparticles with a cubic close packed structure (space group Fm3m); and silver coated magnetite nanoparticles (c). The fact that the diffraction peaks from Fe₃O₄ are not observed in the XRD of Fe₃O₄@Ag is a strong evidence for a complete coverage of the oxide by Ag, supporting the formation of Fe₃O₄@Ag core-shell nanoparticles [9,10].

The average crystalline size for the Fe₃O₄@Ag nanoparticles, using the Debye–Scherrer formula for the most intense peaks is 12 ± 3 nm. This value agrees very well with the TEM measurements.

From the sizes obtained for the coated and uncoated particles, it can be concluded that the silver shell has a thickness of 2 ± 1 nm, which nicely agrees with the amount...
of silver used in the reactions. This can be taken as a proof that most of the silver is reduced onto the core particles.

Fig. 4 shows the temperature dependence of the magnetization for Fe3O4 and Fe3O4@Ag nanoparticles. The data were corrected for the presence of foreign substances in the samples (mainly salts and solvent) using the data obtained from the thermogravimetric analysis (data not shown).

A clear decrease of the magnetization (at least 20 times smaller) is found for the coated nanoparticles. This surprising result agrees with recent results for Au coated magnetite [11]. The reason for this decrease is still under study.

4. Summary

In this study it is reported the preparation of silver coated Fe3O4 nanoparticles in a two step procedure: first

a core of 9 ± 2 nm Fe3O4 by the microemulsion technique is obtained. In a second step a silver shell of 2 ± 1 nm using glucose as reducing agent is obtained. Characterization of the particles by UV, XRD, TEM and magnetometry are reported.

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