

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, cyclohexylamine, 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% tetramethylammonium 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

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particles and avoiding the formation of new silver nuclei. The mild conditions promote the reduction of Ag (I) ions adsorbed onto Fe_3O_4 particles. The molar ratio of AgNO_3 to glucose was 2:1 and the synthesis was carried out at room temperature. As the particles were gradually coated by silver, the black Fe_3O_4 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 $\text{Cu K}\alpha$ radiation with a wavelength of 154056 \AA .

Thermogravimetric analysis was performed with a Perkin Elmer TGA-7 in order to determine the amount of Fe_3O_4 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 $9 \pm 2 \text{ nm}$.

Fig. 2 shows a TEM picture of $\text{Fe}_3\text{O}_4@Ag$ nanoparticles. It can be seen that, as expected, the particles are now more polydisperse with a size of $13 \pm 4 \text{ nm}$.

The UV–visible spectrum of the silver coated nanoparticles shows an absorption peak at 400 nm due to the silver

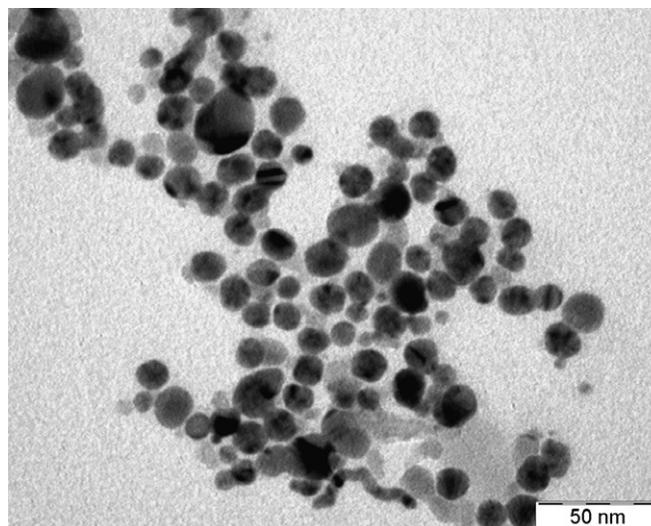


Fig. 2. Nanoparticles of $\text{Fe}_3\text{O}_4@Ag$.

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 $Fd\bar{3}m$); (b) silver nanoparticles with a cubic close packed structure (space group $Fm\bar{3}m$); and silver coated magnetite nanoparticles (c). The fact that the diffraction peaks from Fe_3O_4 are not observed in the XRD of $\text{Fe}_3\text{O}_4@Ag$ is a strong evidence for a complete coverage of the oxide by Ag, supporting the formation of $\text{Fe}_3\text{O}_4@Ag$ core-shell nanoparticles [9,10].

The average crystalline size for the $\text{Fe}_3\text{O}_4@Ag$ nanoparticles, using the Debye–Scherrer formula for the most intense peaks is $12 \pm 3 \text{ nm}$. 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 $2 \pm 1 \text{ nm}$, which nicely agrees with the amount

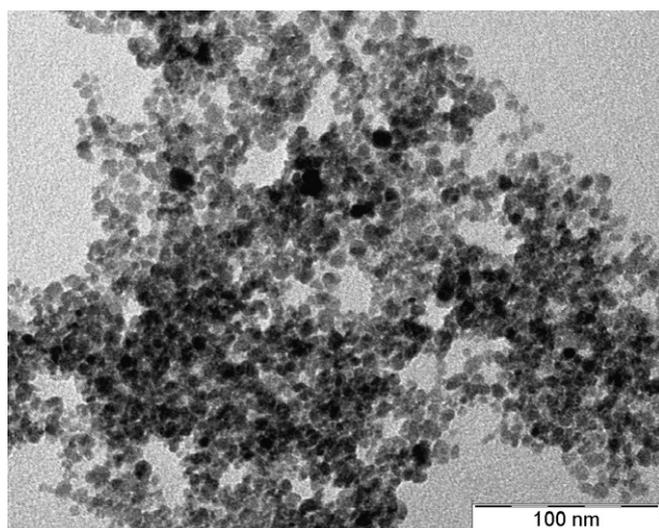


Fig. 1. Magnetite nanoparticles.

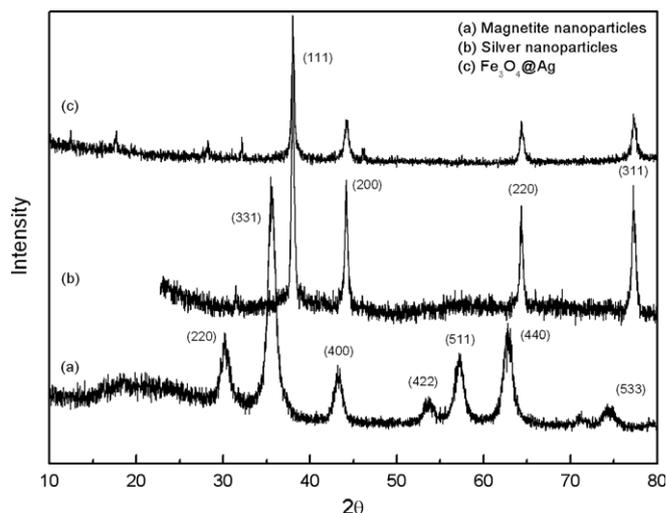


Fig. 3. X-ray diffraction patterns for the nanoparticles: (a) Uncoated Fe_3O_4 ; (b) silver nanoparticles; (c) $\text{Fe}_3\text{O}_4@Ag$.

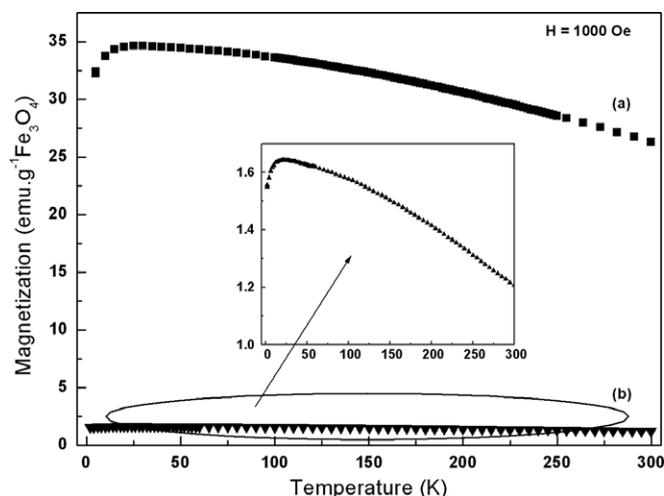


Fig. 4. Magnetization measurements of: (a) uncoated magnetite; (b) $\text{Fe}_3\text{O}_4@\text{Ag}$ at $H = 1000$ Oe.

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 Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Ag}$ 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 Fe_3O_4 nanoparticles in a two step procedure: first

a core of 9 ± 2 nm Fe_3O_4 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.

Acknowledgments

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