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Magnetite nanoparticles prepared by co-precipitation method in different conditions

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HIGHLIGHTS

- Magnetite nanoparticles were prepared in two different conditions.
- Specific surface area of sample prepared in water- ethanol mix is higher than the sample prepared in water.
- Both samples are magnetically homogeneous.
- The sample prepared in aqueous solution present zero-field absorption.

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ABSTRACT

Magnetic nanoparticles (MNPs) of pure magnetite (Fe_3O_4) were prepared in an aqueous solution (sample M–I) and in a water-ethyl alcohol mixture (sample M–II) by the co-precipitation method. The structure and magnetic properties of both samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), magnetic (M–H) and microwave measurements (FMR). The mean average particle diameter and particle size distribution was evaluated by the Dynamic Light Scattering (DLS) and Brunauer- Emmett-Teller techniques (BET). The Quantitative chemical analysis of iron was performed by Inductively Coupled Plasma (ICP)- Atomic Emission Spectroscopy (AES) technique. The MNPs prepared in aqueous solution show a higher grain than those prepared in the water-ethyl alcohol mixture. The type of phase structure in both cases can be defined as "defective spinel". The shape of the majority of M–I MNPs is octahedral. The shape of the majority of M–II MNPs is cubic. The specific surface area of MNPs was as high as 14.4 m^2/g for M–I sample and 77.8 m^2/g for sample M–II. The obtained saturation magnetization values of 75 emu/g (M–I) and 68 emu/g (M–II) are consistent with expected values for magnetite MNPs of observed sizes. Ferromagnetic resonance (FMR) measurements confirmed that MNPs of both types are magnetically homogeneous materials. FMR lines' position and line widths can be understood by invoking the local dipolar fields, deviations from sphericity, magnetocrystalline anisotropy and stresses. M–I sample shows sizeable zero field microwave absorption which is absent in the M–II case. The differences in microwave behaviour of M–I and M–II MNPs can be used in the design of microwave radiation absorbing multilayers.

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1. Introduction

Studies of nanoscale materials have captured significant scientific and industrial interest in recent years, as well as in the fields of environmental protection and biomedicine [1–4]. The development of nanosized magnetic materials is a subject of considerable

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importance both for understanding their fundamental properties and new technological applications, including clinical needs [4–6]. Careful studies are essential in order to determine the influence of preparation techniques, surface effects and shape on functional properties of magnetic nanoparticles (MNPs) and their biocompatibility [5,6].

High electrical resistance and reasonably high saturation magnetization are the characteristics of soft ferrites [4,6,7]. Ferrites are widely used in microwave devices, insulators, circulators, phase shifters due to very high electrical resistivity, flexibility in tailoring magnetic properties, and the existence of well established techniques of preparation [3,4,7–9]. Ferrite MNPs with controlled sizes and morphology can be prepared by electric explosion of wire, laser target evaporation, biomineralization [10–13], but wet chemical methods like sol–gel and co-precipitation are still the most used techniques [14–16]. Other applications of the ferrite MNPs are magnetic biosensing, hyperthermia and thermal ablation – promising forms of cancer therapy, toxic metals adsorption, microwave absorption and electromagnetic interference (EMI) [1,3,6,17,18]. These different applications have their specific requests such as narrow size distribution for biomedical applications and particular shapes and anisotropy features for controlled microwave absorption and EMI. For example, iron oxide polymer-composites could be employed as frequency selective materials or electromagnetic field absorbers with smaller dimensions comparing to the dimensions of conventional protectors [19].

It was also shown that the amount of MNPs in a polymer matrix (fractions of 0%–30% of the iron oxide MNPs were studied) is responsible for the permeability and permittivity behaviour of the polymer: both dielectric and ferromagnetic resonances of the composites were affected by the presence of the MNPs. The possibility of such composites to be optimized for specific applications requiring absorption of electromagnetic radiation from the MHz up to the GHz range were also discussed [20]. These examples of the recently imaged area of applications are related to composite materials consisting of polymer matrix with embedded ferrite MNPs. The composites are an excellent example of smart nanostructures with potential for application such as biosensors, flexible electronic, electromagnetic shielding, magnetic inks and adhesives, etc. [21]. Another simple example of such a functional material is the commercially available magnetic Dynabeads® widely used for magnetic separation [22,23]. The Dynabeads® M-450 are magnetisable superparamagnetic polystyrene beads of 4.5 microns in diameter consisting of nanometer-sized iron oxide particles embedded in a polymer matrix. It was also shown previously [9,24] that magnetite (Fe_3O_4) MNPs can appear in a polymer soluble and a polymer insoluble state depending on the particular synthesis condition for the case of polyaniline based magnetic composites, including magnetic field assisted synthesis [25]. The magnetic and transport properties of the PANI/Fe_3O_4 composites prepared by casting were explained by the presence of MNPs agglomerates which have mixed properties corresponding to both the properties of the dipolar chains and the separate particles, i.e. aggregation/de-aggregation features were shown to be very important.

Materials for specific applications requiring controlled absorption of electromagnetic radiation can be further tuned by using multilayered structures where both “polymer with MNPs” and metallic magnetic or conducting layers can be included into a multilayered structure. Iron oxide MNPs can be easily obtained with well established techniques. The slight modification of the synthesis conditions allows the fabrication of MNPs with different parameters/properties. Afterwards the batches of MNPs with specific parameters can be processed for preparation of multilayered structures “polymer with MNPs of the first type”/“polymer with MNPs of the second type”.

The aim of the present work is to study the role of different preparation conditions in the change of morphology, structure and magnetic properties of spinel iron oxide nanoparticles obtained by the co-precipitation technique. This method has advantage such as easy preparation, low cost, enough digestion to form the final structure suitable, control of particle size and shape, magnetic separation in order to obtain different particle size, pH control, maintenance of the oxidation state, sample preparation at different temperature.

We consider this study as the first important step for evaluation and development of the protocol of fabrication of Fe_3O_4/polymer multilayered composites with iron oxide nanoparticles obtained by the same cheap technique but in different conditions, MNPs having tunable properties for different layers of multilayered structure.

2. Experimental

2.1. Sample preparation

Fe_3O_4 nanoparticles of the first type (M–I sample) were prepared in an aqueous solution by the co-precipitation method. As the first step Solution 1 (Sn 1) and Solution 2 (Sn 2) were prepared respectively. For the preparation of Sn 1 previously weighed amounts of an oxidant agent KNO_3 (initial concentration 0.022 M) and KOH (initial concentration 0.15 M) were completely dissolved in distilled water (540 ml) in a condition of N_2 bubbling during 15 min at room temperature. For Sn 2 solution preparation initially weighed amounts of $FeSO_4 \cdot 7H_2O$ (initial concentration 0.27 M) were dissolved in distilled water (54 ml) and H_2SO_4 2 M (6 ml) at N_2 bubbling during 15 min at room temperature. The next step consisted in slowly additing the Sn 2 solution to Sn 1 with mechanical stirring and constant N_2 bubbling for at least 15 min at room temperature. Afterwards the system sample-reactor was kept inside a thermostatic bath at 70 °C during 210 min facilitating the formation of the iron oxide crystals. The sample was cooled down at RT during 20 h ($pH_{final} \approx 9.0$). All solid precipitates as the first step were subject to magnetic sedimentation, after which they were washed several times with distilled water, methanol, acetone and carefully centrifuged. Finally, the samples were dried 24 h in vacuum at 50 °C.

Fe_3O_4 nanoparticles of the second type (M–II sample) were prepared mixing at room temperature solutions of $FeSO_4 \cdot 7H_2O$ (Sn 1), KNO_3 (oxidant agent) and KOH (Sn 2) which had been previously flushed with N_2. The difference in this case was that distilled water was replaced by a mixture of distilled water (300 ml) plus absolute ethanol (240 ml). The products of the synthesis were washed and centrifuged with distilled water and methanol and finally were dried in vacuum. The details of the procedure are summarized in the following scheme (Fig. 1).

2.2. Characterization of nanomaterials

For structural characterization the X-ray powder diffraction patterns were collected by using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta–theta configuration, secondary monochromator with Cu-Kα radiation ($\lambda = 1.5418$ Å) and a PIXcel solid state detector (active length in 2θ 3.347°). Data were collected from 15 to 80° 2θ (step size = 0.026 and time per step = 800 s, total time 2 h) at RT. A fixed divergence and anti-scattering slit giving a constant volume of sample illumination were used. XRD diffraction data were fitted using the FULLPROF program included in WinPLOTR [18]. The profile refinement calculated the unit cell parameters *a*, peak shape (pseudo-Voigt), background, systematic 2θ shift, overall isotropic, displacement, U, V, W, half-width parameters for the profile function and

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