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Tuning the magnetism of ferrite nanoparticles



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ABSTRACT

The importance of magnetic interactions within an individual nanoparticle or between adjacent ones is crucial not only for the macroscopic collective magnetic behavior but for the AC magnetic heating efficiency as well. On this concept, single-(MFe₂O₄ where M=Fe, Co, Mn) and core-shell ferrite nanoparticles consisting of a magnetically softer (MnFe₂O₄) or magnetically harder (CoFe₂O₄) core and a magnetite (Fe₃O₄) shell with an overall size in the 10 nm range were synthesized and studied for their magnetic particle hyperthermia efficiency. Magnetic measurements indicate that the coating of the hard magnetic phase (CoFe₂O₄) by Fe₃O₄ provides a significant enhancement of hysteresis losses over the corresponding single-phase counterpart response, and thus results in a multiplication of the magnetic hyperthermia efficiency opening a novel pathway for high-performance, magnetic hyperthermia agents. At the same time, the existence of a biocompatible Fe₃O₄ outer shell, toxicologically renders these systems similar to iron-oxide ones with significantly milder side-effects.

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1. Introduction

Magnetic particle hyperthermia (MPH) is an anti-cancer therapeutic scheme able to deliver severe thermal shocks to targeted cancer sites. MPH was initially proposed in the 1950s [1] and is still under development in an effort to increase its efficiency benefiting from its non-invasive character when compared to current methodologies [2]. Magnetic nanoparticles (MNPs) generate heat under an alternating magnetic field as a result of various pathways strongly correlated with their morphological, structural and magnetic profile [3,4]. The produced heat is naturally delivered to cell surroundings and is used as an external factor triggering different cell routes, namely apoptosis or even necrosis especially if combined with the co-delivery of anticancer drugs or photodynamic therapy [5]. The current development of magnetic particle hyperthermia is mainly focused on two aspects, namely the nanoparticles themselves where reproducibility, scalability together with atomistic control of the electronic properties are the prerequisites, and secondly, the instrumentation required to quantify the effects of such small entities when exposed in an AC magnetic field *in-vitro*, *ex-vivo*, and *in-vivo* [6].

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Within all these years, as synthetic methodologies are continuously improving their controls even at atomic scale, various designations of MNPs are proposed as alternative MPH mediators in place of the widely used iron-oxides [7,8]. Among these studies, cubic ferrite MNPs together with their facile fabrication, chemical stability and magnetic tuning [9] show great potential in biomedical applications in general, with emphasis on MRI contrast agents [10,11] and drug carriers [12]. Cobalt ferrite (CoFe₂O₄), when compared to magnetite [13], represents a typical hard magnetic material while manganese ferrite (MnFe₂O₄) is also one of the most promising magnetic nanomaterials that exhibits a higher saturation magnetization (M_s) and low coercivity (H_c) accompanied by good chemical stability and biocompatibility facilitating its action as a powerful negative MRI contrast agent [14].

As shown in previous studies [15,16] magnetic particle hyperthermia efficiency may be enhanced by controlling the core-shell morphology in mixed-ferrites when compared to single-phase counterparts. Thus, the tuning of the structural and magnetic parameters allows the designation of mixing and matching the proper MNPs ingredients to optimized heat transfer [17].

However, unlike iron oxide nanoparticles, other spinel ferrite (e.g. CoFe₂O₄) are in principle not considered as biocompatible and their application in tissues may cause significant side-effects due to their toxicity [18,19]. In order to overcome this issue, a Fe₃O₄

shell grown around the core is a pathway for improved chemical stability and biocompatibility [9,20,21].

In this work, we report on Fe₃O₄-coated ferrite core-shell nanoparticles for magnetic hyperthermia applications and compare their records with their single-phase counterparts. The core-shell configuration is initially responsible for the tuning of magnetic anisotropy on these systems while simultaneously biocompatibility is guaranteed due to the presence of Fe₃O₄ in contact to the biological environment, thus the toxic Co ions are safely restricted solely to the MNPs central region (*i.e.* core). Under this prism, core-shell nanoparticles are synthesized with a widely-used thermal decomposition route in an organic environment at two stages initiating from single-phase Fe, Co and Mn ferrite nanoparticles. At the second stage, the single-phase MNPs synthesized initially serve as seeds for the growth of Fe₃O₄ surrounding core. This combines the positive effect of internal nanoscale magnetic interfaces for AC-field heating losses and the presence of a biocompatible cover layer.

2. Experimental

Ferrite nanoparticles were prepared by thermal decomposition of metal precursors following a route described elsewhere [16]. In particular, single-ferrite nanoparticles MFe₂O₄ (M=Co, Mn, Fe) were produced by the coprecipitation of Co²⁺, Mn²⁺ or Fe²⁺ ions, respectively, together with Fe³⁺ ions from the corresponding acetate (Co(CH₃COO)₂, Mn(CH₃COO)₂, Fe(CH₃COO)₂) and acetylacetonate (Fe(acac)₃) precursor salts. In a typical procedure, 3 mmol Fe(CH₃COO)₂ and 6 mmol of Fe(acac)₃ were dissolved together with excess of oleic acid (5 mL) in 30 mL of octadecane into a three-necked spherical flask, heated up to 300 °C and kept at this temperature for 20 min in order to evaporate side-products and moisture. Afterwards, the temperature was increased to 315–320 °C to achieve reflux conditions, and let the reaction proceed for another 30 min. Then, the solution was cooled down to room temperature. All the experiments were performed under a continuous argon flow and using magnetic stirring at around 750 rpm.

To collect the precipitate, around 50 mL of ethanol were added to the final solution to destabilize the nanoparticles. Finally, the particles were separated by centrifugation, washed several times with ethanol using ultrasonification and re-dispersed in n-hexane.

For the preparation of Fe₃O₄-coated CoFe₂O₄ nanoparticles, a similar synthetic procedure was used at a second stage, with Fe₃O₄ synthesis taking place by heterogeneous nucleation on dispersed Co-ferrite particle seeds.

The structural and morphological properties of the particles were investigated *ex-situ* by high resolution (HRTEM). We used a Philips Tecnai F20 Supertwin microscope operated at 200 kV with a field emission gun. Structural characterization of the synthesized nanoparticles was performed by means of selected area electron diffraction in the TEM.

The ratio of metals (Fe, Co, Mn) was determined by flame atomic absorption spectrophotometry using a Perkin Elmer Analyst 800 instrument, after dissolving the samples in concentrated HCl acid. The amount of surfactants in the dried samples was estimated by thermogravimetry (TGA) using a Perkin-Elmer STA6000 instrument under nitrogen gas flow.

The magnetic properties of synthesized samples were examined by a Quantum Design MPMS SQUID magnetometer at *T*=5 K. The heating response of nanoparticles, under a high frequency (765 kHz) AC magnetic field (30 mT), was measured using a commercial 4.5 kW inductive heater. The temperature was monitored by a GaAs-based fiber optic probe immersed in a test tube containing 1 mL of a 2 g/L concentrated particles dispersion. This temperature probe prevents erroneous temperature readings

as they would arise in a metallic thermocouple for example through inductive heating.

3. Results and discussion

3.1. Structure and morphology

The nanoparticles were prepared in the presence of a high excess of oleic acid and as a result, a large quantity of the surfactant remains bound to the particles surface after the synthesis. The amount of surfactants in each sample was determined in proportion to the weight loss during TGA measurements (Fig. 1). Magnetite nanoparticles show the highest amount of oleic acid reaching 37 wt% due to the high affinity of the molecule to iron. For the rest of the samples the surfactant content was between 18 and 26 wt% (Table 1). It is characteristic that for CoFe₂O₄ nanoparticles a sudden drop occurs at around 500 °C indicating the high percentage of weakly adsorbed oleic acid which is simultaneously released.

The mean particle diameter was determined after the number-averaged distribution derived by the TEM analysis of the samples. Fig. 2 shows representative images of the different nanoparticles systems. Single ferrite nanoparticles were found to be spherical with a mean diameter in the range of 7.4–9.1 nm (Table 1). The Fe₃O₄-coated CoFe₂O₄ nanoparticles show a lower degree of monodispersity due to the presence of homogeneous nucleated Fe₃O₄ nanoparticles formed during the second step of synthesis. Nevertheless, the size of the larger nanoparticles approaches 12 nm supporting the assumption of the formation of a core-shell structure.

The selected area electron diffraction patterns confirm the existence of the ferrite structure in all samples. In addition, chemical analysis of the nanoparticles indicates stoichiometries very close the targeted for MnFe₂O₄ and CoFe₂O₄ (Table 1).

3.2. Magnetic properties

The magnetic characteristics of the samples were investigated by SQUID magnetometry (Fig. 3). Low-temperature data are presented here to get a better understanding about the magnetism of the different specimen in their blocked state. It is obvious that among single-phase nanoparticles, the CoFe₂O₄ have the highest magnetic anisotropy with a coercive field around 1.8 T at 5 K. In

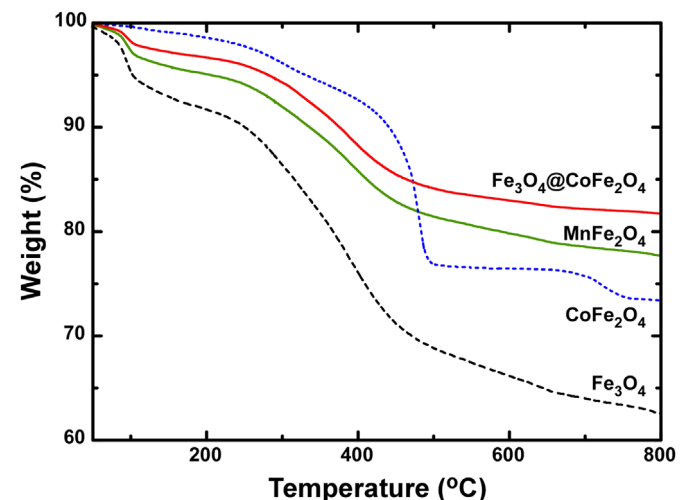


Fig. 1. Thermogravimetric analysis of nanoparticles indicating the weight loss upon heating. The relative amount of surfactants is directly measured.

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