



Research articles

Unusual variation of blocking temperature in bi-magnetic nanoparticles



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ABSTRACT

Ferrite nanoparticles with bi-magnetic layered structure were synthesized by a seed-mediated coprecipitation technique. The strategy of growing a second magnetic layer enhanced the magnetic saturation (M_s) of the nanostructures, with a very small increase in their blocking temperature (T_B). In contrary to the common magnetic nanostructures of 10–15 nm size range, which manifest blocking temperatures around room temperature (≈ 300 K), the measured T_B values of the bi-magnetic nanostructures are much lower. The experimental T_B values of the bi-magnetic nanostructures are much lower than their theoretically predicted ones. Moreover, the T_B of the nanoparticles varies unusually, decreasing with particle size beyond a certain value. The low blocking temperature and high M_s of the fabricated bi-magnetic nanoparticles indicate the seed-mediated coprecipitation is an effective method for designing magnetic nanostructures suitable for biomedical applications such as in magnetic hyperthermia treatment, where nanostructures of low T_B and high M_s are required.

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1. Introduction

Magnetic nanoparticles (MNPs) are attractive because of their many potential practical applications such as in magnetic storage, biomarkers, contrast agents, biomolecule separation, sensors, and for advanced clinical treatments [1–4]. In many of those applications; particularly for biomedical applications, it is desirable that the MNPs are superparamagnetic, to avoid aggregation in body fluid systems [3]. However, the MNPs often lose their superparamagnetic state and enter into a spin blocked regime even with sizes well-below of 20 nm. Although the critical size below which the MNPs remain superparamagnetic depends on their compositions, the dependence is not very significant [4–6]. Spin blocking occurs when the thermal energy (T_E) is less than the energy barrier (E_B) needed to produce the inversion of the spins ($E_B = K_{eff}V$). Since this E_B is proportional to the volume of the nanoparticles and the anisotropy of the spin-orbit coupling [7], increasing the size of nanoparticles increases the E_B [8,9]. That is the reason that most of the

MNPs cannot be in a superparamagnetic regime above a certain size.

Many strategies have been utilized to control the blocking temperature (T_B) of magnetic nanomaterials. Most of them are based on the use of a diamagnetic material such as organic polymers and ceramic materials as a coating layer. The most common organic polymers used as coatings are polyols, dextran, oleic acid, carbohydrates chains, etc. [10–12]. These organic coatings also serve to stabilize the nanomaterials in suspension and induce additional functionalities to their surfaces. Common ceramic materials used as coatings for MNPs are SiO_2 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and several other porous ceramic matrices [13–15]. Separation of disaggregation of MNPs reduces the anisotropy produced by interparticle interactions, i.e., dipole-dipole interactions. Since the energy of a magnetic dipole depends directly on its magnetic moment and inversely to the cubic distance between the poles ($E_D = \mu_0 \cdot \mu^2 / 4\pi d^3$) [9], this approach has given good results [14]. Although separating or disaggregating the MNPs helps to reduce their T_B , sometimes the use of a diamagnetic shell decreases the magnetic saturation (M_s) to less than 10 emu/g, due to the increase of non-magnetic mass.

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Decreasing the M_s of MNPs may also reduce their efficiency in the desired applications. Often MNPs of high M_s are desired to improve their performance in hyperthermia treatments or as MRI contrast agents [16,17]. In hyperthermia treatment, the magnetic spins align with respect to an alternating magnetic field. So, the MNPs with high M_s values generate more friction and hence higher amount of heat [18]. On the other hand, in the use of MNPs as MRI contrast agent, high M_s values strongly affects the precession movement of hydrogen atoms [19]. An advantage of using a diamagnetic shell around/over MNPs is that it may lower the toxicity of the MNPs. The toxicity of some magnetic materials like ferrites, in particular, magnetite (Fe_3O_4), has been extensively studied [20–23] and most of the results reported no alteration in the normal behavior of the cells used to test the toxicity, suggesting good biocompatibility even at high doses. Contrast agents based on magnetite nanoparticles are also commercially available for clinical use.

It is difficult to compare the reported T_B values of MNPs due to the versatility of the conditions used to obtain their zero-field cooled (ZFC) curves, the synthesis procedure, the used coating materials, etc. However, for ferrites such as magnetite, the values are in the range of 10–280 K for nanoparticles of 4–14 nm size range. For cobalt ferrite (CoFe_2O_4), the common values are over 200 K, even for sizes around 4 nm, due to the high anisotropy of cobalt ions [24]. On the other hand, the reported T_B values for manganese ferrite (MnFe_2O_4) are very disperse. For the nanoparticles smaller than 10 nm, the reported values are often less than 150 K [25]. However, for nanoparticles larger than 12 nm, the value increases rapidly to more than 250 K [26]. Finally, the T_B values for reported core-shell structures like $\text{MnFe}_2\text{O}_4@ \text{CoFe}_2\text{O}_4$ of 6–9 nm size range have been reported to vary between 130 and 270 K [27], and for $\text{CoO}@ \text{CoFe}_2\text{O}_4$ nanoparticles of 5–11 nm size range, it varied from 167 to 388 K [28]. Although it is difficult to compare the reported T_B values of MNPs due to the reasons stated above, one thing remains clear, that for all the materials the T_B of MNPs always increases with their size.

Here, apart from reporting the fabrication of bi-magnetic $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4@ \text{Fe}_3\text{O}_4$ core-shell nanoparticles of varied shell thickness, we discuss how these MNPs considerably increase their M_s with a minimum increase in their T_B . The T_B values obtained for these core-shell system does not follow any reported theory or model. After a certain optimum size, the T_B value even starts decreasing. Furthermore, *in vitro* assays (membrane integrity, production of reactive oxygen species (ROS), lysosomes abundance, cell viability, cell death, and zinc internalization) of the fabricated bi-magnetic nanoparticles have been carried out in mussel hemocytes to evaluate their potential cellular toxicity.

2. Materials and methods

All the chemicals were purchased from Sigma-Aldrich (Toluca, México). Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, >98%), zinc chloride (ZnCl_2 , >98%), sodium hydroxide (NaOH, >97%), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, >98%), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >97%), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, >98%), hydrochloric acid (HCl, 37%) and nitric acid (HNO_3 , 70%) were of reagent grade and used as received without further purification. Magnetic nanoparticles (MNPs) of zinc ferrite were obtained by co-precipitation as previously reported [29,30], followed by a seed-mediated synthesis to deposit a second magnetic layer [31].

2.1. Synthesis of zinc-manganese ferrite ($\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$) (ZnMn)

ZnMn nanoparticles were prepared by adding 1 mL of a solution of ZnCl_2 (1.25 μmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.25 μmol) into a 5 mL

solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5 μmol) in water. The mixture was added to a 2 M solution of NaOH and stirred for 30 min at 100 °C. After 30 min stirring, the obtained black precipitate was washed three times with distilled water to remove excess precursor ions. The washed black precipitate was redispersed in water and used as seeds for the fabrication of bi-magnetic core-shell nanoparticles.

2.2. Synthesis of bi-magnetic core-shell ferrite MNPs

($\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4@ \text{Fe}_3\text{O}_4$) (ZnMn-Fet, $t = 30 \text{ m}, 1 \text{ h}, 2 \text{ h}, 3 \text{ h}$)

Previously prepared ZnMn MNPs were used as seeds for the growth of $\text{ZnMn}@ \text{Fe}_3\text{O}_4$ core-shell structures. Briefly, a 6 mL solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.5 μmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5 μmol) and 250 μL of HCl (37%) were added to the previously prepared ZnMn MNPs and left stirring for five minutes. Then, 40 mL of a 2 M NaOH solution was added to the mixture and stirred for 30 min (ZnMn-Fe30 m), 1 h (ZnMn-Fe1 h), 2 h (ZnMn-Fe2 h) and 3 h (ZnMn-Fe3 h) to grow magnetite layers of different thicknesses. After that time, the black precipitate was washed 3 times with distilled water to remove the unreacted precursor ions.

2.3. Water stabilization

Stabilization of the synthesized nanoparticles was achieved by acid peptization in aqueous media to reduce their potential aggregation [26,32]. In summary, 15 mL of HNO_3 (2 M) was added to the obtained ZnMn-Fet MNPs and stirred for 15 min. After that, the supernatant was magnetically decanted and 25 mL of a 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was added and left stirring for 20 min at 100 °C. Finally, 15 mL of HNO_3 (2 M) were added under stirring. After 15 min, the supernatant was magnetically decanted and washed 2 times with acetone. The product was re-dispersed in water, obtaining a stable, water soluble ferrofluid.

3. Characterization

3.1. TEM, DLS and X-ray diffraction

Particle size and size dispersion of all the fabricated nanostructures were analyzed using a JEOL JEM1010 (JEOL USA, Inc., Peabody, MA) transmission electron microscope (Fig. S1, supplementary information). The hydrodynamic diameter of the samples was measured at room temperature using a NanoFlex dynamic light scattering (DLS) (Microtrac Inc., Montgomeryville, PA, USA) system, with a 780 nm wavelength laser of 3 mW power. X-ray diffraction (XRD) patterns of the samples were recorded using energy filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, Ni filter) in a PANalytical Empyrean diffractometer, between 15° and 80° of 2θ , at room temperature.

3.2. Magnetic measurements

Magnetic hysteresis and zero-field cooled (ZFC) curves were recorded in a Dynacool 9 physical property measurement system (PPMS, Dynacool 9, Quantum Design, USA) by placing the dry powder samples in tubular plastic sample holders. The hysteresis curves were recorded up to 5 T magnetic field at room temperature ($\approx 300 \text{ K}$) and 10 K. ZFC curves were obtained by cooling the samples up to 10 K, without applying an external magnetic field; then a magnetic field of 100 Oe was applied and heating started at a rate of approximately 0.02 K/s until a temperature of 300 K was reached.

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