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 co-precipitation 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_B) 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, Ca_3(PO_4)_2OH 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 = μ_0 * μ^2/4-πd^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.
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\(_3\)O\(_4\)), 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\(_2\)O\(_4\)), the common values are over 200 K, even for sizes around 4 nm, due to the high anisotropy of \( M_s \)

2. Materials and methods

All the chemicals were purchased from Sigma-Aldrich (Toluca, México). Manganese (II) chloride tetrahydrate (MnCl\(_2\).4H\(_2\)O, >98%), zinc chloride (ZnCl\(_2\), >98%), sodium hydroxide (NaOH, >97%), iron (II) chloride tetrahydrate (FeCl\(_2\).4H\(_2\)O, >98%), iron (III) chloride hexahydrate (FeCl\(_3\).6H\(_2\)O, >97%), iron (III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\).9H\(_2\)O, >98%), hydrogen chloride (HCl, 37%) and nitric acid (HNO\(_3\), 70%) were of reagent grade and used as received with further purification. Magnetic nanoparticles (MNPs) of zinc ferrite were obtained by co-precipitation as previously reported [24]. On the other hand, the reported \( T_B \) values for manganese ferrite (MnFe\(_2\)O\(_4\)) 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 MnFe\(_2\)O\(_4@\)CoFe\(_2\)O\(_4\) of 6–9 nm size range have been reported to vary between 130 and 270 K [27], and for CoO@CoFe\(_2\)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 Zn\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4@\)Fe\(_3\)O\(_4\) core-shell nanoparticles of varied shell thickness, we discuss how these MNPs considerably increase their magnetic properties, we discuss how these MNPs considerably increase their magnetic properties.

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

ZnMn nanoparticles were prepared by adding 1 mL of a solution of ZnCl\(_2\) (1.25 \( \mu \)mol) and MnCl\(_2\).4H\(_2\)O (1.25 \( \mu \)mol) into a 5 mL solution of FeCl\(_3\).6H\(_2\)O (5 \( \mu \)mol) 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 (Zn\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4@\)Fe\(_3\)O\(_4\)) (ZnMn-Fet, \( t = 30 \) m, 1 h, 2 h, 3 h)

Previously prepared ZnMn MNPs were used as seeds for the growth of ZnMnFe\(_2\)O\(_4\) core-shell structures. Briefly, a 6 mL solution of FeCl\(_2\).4H\(_2\)O (2.5 \( \mu \)mol), FeCl\(_3\).6H\(_2\)O (5 \( \mu \)mol) and 250 \( \mu \)L 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 Fe(NO\(_3\))\(_2\).3H\(_2\)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 Cu K\(_\alpha\) radiation (\( \lambda = 1.5406 \) Å, Ni filter) in a PANalytical Empyrean diffractometer, between 15° and 80°+ of 2\( \theta \), 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 (\( \approx 300 \) 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.
3.3. Toxicity assays

For the potential toxicology evaluation of the nanostructures, mussel hemocytes cells were used. Hemocytes are the cells of the immune system of mussels, that have been extensively used in the nanotoxicological analysis. Multiple parameters of cell toxicity were evaluated including mitochondrial membrane damage, production of reactive oxygen species (ROS), cell viability, cell death and lysosome abundance, as well as soluble zinc uptake. The effects of ZnMn, ZnMn-Fe1 h, and ZnMn-Fe3 h were evaluated as representative samples. The complete description of the toxicity evaluation of the samples by this model is available in the SI section.

4. Results and discussion

4.1. Size and crystallographic results

The average size of the MNPs used as seeds (ZnMn) determined by TEM was around 8.0 ± 0.2 nm, while for the core-shell structures, the size increased to 10.0 ± 0.3, 11.5 ± 0.2, 12.3 ± 0.2 and 13.0 ± 0.3 nm for the reactions of 30 min, 1 h, 2 h and 3 h, respectively. These values were calculated by the average of more than 300 well-defined nanoparticles at different areas. The size increase of the second layer with reaction time agreed with previous reports for seed-mediated synthesis [28,33,34]. Discussion of the DLS analysis of the aqueous colloids can be found at the SI [35].

X-ray diffraction patterns of the samples revealed typical spinel structure of ferrites (Fig. S2, supplementary information). The XRD pattern of the Fe3O4 coated bi-magnetic NPs looks noisy with respect to the obtained pattern of the ZnMn nanoparticles. The noise could be attributed to a disordered layer of Fe3O4 [29].

4.2. Magnetometry measurements

Magnetization curves of the samples recorded at 300 K (Fig. 1a) show an increase in $M_s$ for bi-magnetic structures, as compared to the core ZnMn MNPs. The $M_s$ of the ZnMn ferrite is about 42 emu/g, while for ZnMn-Fe30 m it is about 49 emu/g (16% increase). For ZnMn-Fe1 h, $M_s$ increases to 56 emu/g (33% increase). For ZnMn-Fe2 h and ZnMn-Fe3 h, the $M_s$ values were 53 and 52 emu/g, respectively, which are higher than the values obtained for ZnMn and ZnMn-Fe30 m, but lower than the $M_s$ value of ZnMn-Fe1 h. This decrease might be associated to the mass ratio between ZnMn and Fe3O4 in the bi-magnetic system. If the mass fraction of ZnMn is considerably higher than the mass fraction of Fe3O4, then the magnetic properties of the bi-magnetic nanoparticles should be more like the ZnMn core. However, if more Fe3O4 is present, then the magnetic contribution of Fe3O4 to the total magnetization should be higher. The results presented above indicate that there is a limit on the thickness of the second magnetic layer, up to which $M_s$ increases. Below and above that limit, the contribution of one of the components (core or the shell) becomes greater than the other one. Thus, the whole system starts to behave more like the component (material) more abundant.

Although all the $M_s$ values of the bi-magnetic Fe3O4 coated MNPs were significantly greater than the values of the ZnMn nanoparticles at 300 K, the determined $M_s$ at 10 K (Fig. 1b) show considerable differences. At 10 K, the sample with highest $M_s$ was ZnMn-Fe1 h, with a value of 82 emu/g, which was also the sample with the largest $M_s$ at 300 K. However, ZnMn had the second largest $M_s$ value at 10 K (77 emu/g), followed by ZnMn-Fe30 m with a $M_s$ of 74 emu/g. Finally, ZnMn-Fe2 h and ZnMn-Fe3 h presented the lower values with $M_s$ of 73 and 70 emu/g, respectively.

These results appear incoherent since the samples with lower $M_s$ values at 300 K had the second and third largest values at 10 K. However, the XRD patterns of the core-shell structures suggest that the Fe3O4 shell layers have different crystallographic orientations than the ZnMn core. At temperatures around 300 K, the thermal energy should be enough to overcome the $E_B$ [36], and the spins of the Fe3O4 layer can align with the magnetic field increasing the $M_s$ value. However, at low temperatures (e.g. 10 K), the thermal energy is not enough to overcome the $E_a$, and the Fe3O4 spins remain randomly oriented [37], reducing the $M_s$ value of the entire structure.

A close-up of the remanent magnetization area in the hysteresis loops is presented in Fig. 2. It can be seen that at room temperature (Fig. 2a), the samples have negligible coercivity ($H_C < 50$ Oe), suggesting superparamagnetism below 300 K with low anisotropy. However, at 10 K (Fig. 2b), the hysteresis loops are wider, although the $H_C$ remained low ($H_C < 300$ Oe).

4.3. Blocking temperature determination

The $T_B$ values for all the MNPs were determined from the maximum of their ZFC curves [38–41] obtained for a 100 Oe applied field. The maximum of ZFC curves can be used to determine the $T_B$ because the samples were cooled in absence of any magnetic field, and then a small magnetic field was applied to measure the
polarization of their spins aligned to the magnetic field [42]. On slowly increasing the temperature, the thermal energy increases, and the spins of the MNPs, which have a low $E_B$, get aligned in parallel to the applied magnetic field. The unaligned spins also get aligned later at higher thermal energy, increasing the magnetization until the point where most of the spins are unblocked, and that is when the ZFC curve reaches its maximum. By increasing further the temperature, the thermal energy also increases and it may become high enough to slightly misalign the spins with respect to the magnetic field, inducing a decrease on the magnetization [43,44].

Fig. 3 shows the ZFC curves for all the MNPs fabricated in this work. The sample with lowest $T_B$ is ZnMn ($T_B \approx 100$ K), which was used as seed particles for fabricating core-shell nanostructures. All the bi-magnetic nanoparticles revealed higher $T_B$, depending on their shell thickness. The increase of $T_B$ in bi-magnetic core-shell structures might be due to: a) their bigger sizes, and b) magnetic anisotropy ($K_{eff}$) between the core and the shell layers. Although the $T_B$ of all the core-shell bi-magnetic nanoparticles increased to some extent, the ZnMn-Fe1 h sample revealed highest $T_B$, which is around 150 K. However, the value is considerably lower than the previously reported $T_B$ values for any magnetic nanoparticle larger than 10 nm.

Although the $T_B$ of the MNPs suffered only a slight increase after the formation of Fe$_3$O$_4$ shell layer, their $M_s$ values increased significantly (inset of Fig. 4). Such low $T_B$ and high $M_s$ values of the bi-magnetic nanoparticles make them very attractive for biomedical applications such as in magnetic hyperthermia, where superparamagnetic nanostructures of low $T_B$ with high $M_s$ values are required [45].

4.4. Comparison of the experimental values with calculated $T_B$ values obtained from the blocking temperature formula

To compare the results of our bi-magnetic nanostructures with previously reported models, we calculated their $T_B$ by using the Eq. (1) [43]:

$$T_B = \frac{VK_{eff}}{k_B \ln(\tau_m/\tau_0)}$$

Fig. 3. ZFC curves of the MNPs used to estimate their $T_B$, arrows show the blocking temperature measured. The inset shows the hysteresis curves of ZnMn (black line) and ZnMn-Fe1 h (green line) recorded at 300 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Variation of calculated (filled circular data points connected with a continuous line) and experimental (square points connected with a dotted line) $T_B$ values for MNPs with particle size.

Fig. 2. Amplified low-field sections of the hysteresis loops of the samples showing their coercivity at a) 300 K and b) 10 K.
where $k_B$ is the Boltzmann constant (1.38 x 10^{-23} \text{J/K}), \tau_0$ the attempt time (with a value between 10^{-8} and 10^{-12} s), and $\tau_m$ the time of the measurement, which is the inverse of the measurement frequency. $T_B$ is strongly dependent of the frequency, because if the spin changes its direction during the time window of the measurement, the material should appear as superparamagnetic, while in the case that the spin does not change its direction at the time window, the material would appear as blocked [46].

To obtain the relationship between the size and blocking temperature of the MNPs, first we estimated the $K_{\text{eff}}$ of ZnMn MNPs from Eq. (1), utilizing their experimentally obtained volume and $T_B$ values. The calculated value of the logarithmic function in the denominator of Eq. (1) ($\ln \tau_m/\tau_0$) was 25.16, which agrees with the commonly reported values around 25 [39,47]. By keeping the calculated $K_{\text{eff}}$ value of ZnMn MNPs fixed, we varied the volume ($V$) of the nanoparticles from 1 to 14 nm to obtain their $T_B$ for different sizes (Fig. 4). As can be seen from Fig. 4, MNPs of 12–14 nm size range should have a $T_B$ close to 300 K (continuous line) if they follow the $T_B$ equation (Eq. (1)), agreeing with most of the reported $T_B$ values. However, the estimated $T_B$ values of the bi-metallic MNPs fabricated in this work (plotted in Fig. 5 with squares and dotted line) do not follow the same trend, indicating a clear disagreement with calculations.

Although the increasing trend of $T_B$ was followed up to a certain particle size, the trend is opposite after a critical size. This decreasing trend of $T_B$ for bigger MNPs is probably due to the higher mass fraction of Fe$_3$O$_4$ in the bi-metallic particles. The Fe$_3$O$_4$ layer, on its own, should have a lower $T_B$ value than that of ZnMn particles. Increasing the size or the thickness of the Fe$_3$O$_4$ layer diminishes the magnetic properties of the whole nanostructure such as its $M_s$ (as shown in Fig. 1) and $T_B$, as it measures the average properties of the whole system.

To compare our results with their reported values, some reported values of the blocking temperature for different ferrites are plotted in Fig. 5 in comparison with our calculated and experimental $T_B$ values. As can be noticed, most of the reported $T_B$ values remain close to the calculated line, but some of them are even higher than their theoretical (calculated) values. Such differences might be due to the variation of conditions used for the experiments (sample preparation and characterization). In addition, all the values reported for MNPs larger than 12 nm are blocked near room temperature, whereas, the $T_B$ of our MNPs of similar sizes are well below the room temperature.

4.5. Simulation of ZFC curves

To visualize the unusual magnetic behavior of our bi-magnetic MNPs clearly, we simulated their ZFC curves theoretically by using a simple analytical zeroth order approximation ($M_{\text{ZFC}}^0$) described by Tournus and coworkers using the Eq. (2) [39,47]:

$$M_{\text{ZFC}}^0 = M_0 e^{-\tau t} + M_{\text{eq}} (1 - e^{-\tau t})$$

where $\tau$ corresponds to the Néel relaxation ($\tau = \tau_0 \exp(E_a/k_B T)$), and $\eta = k_B T^2/|E_a|$, $M_0$ represents the blocked part ($M_0 = \mu_0 M_0 H/|E_a|$) and $M_{\text{eq}}$ the part at equilibrium ($M_{\text{eq}} = \mu_0 M_0 H/3k_B T$), both depending on the vacuum permeability ($\mu_0$) and the magnetic moment ($\mu$), which can be calculated from the $M_s$ and particle volume ($\mu = V M_s$). The particle volume $V$ was calculated from TEM results, assuming a spherical shape of the MNPs. The calculated ZFC curves are presented in Fig. 6. The magnetization values of the curves were normalized for better visualization of the shifts of the maxima of ZFC curves, i.e. between the $T_B$ values of the MNPs.

The results shown in Fig. 6 are in agreement with the calculated $T_B$ values presented in Fig. 4, where MNPs with a size around 13 nm are often in the blocked state at room temperature. However, the $T_B$ values obtained from the zeroth order expression still remains very different from the experimental $T_B$ values, as the experimental values are much lower than the calculations and present an unusual variation, which is a decrease for the largest size MNPs.

A possible explanation of the vast differences between the experimental and theoretical $T_B$ values can be attributed to the complexity of the layered structure of the MNPs. Probably, the Fe$_3$O$_4$ shell layers do not modify the size-related influence on the magnetic properties of ZnMn nanoparticles used as cores, as the Fe$_3$O$_4$ layer may just interact by a weak coupling. This coupling is the result of the different magnetic properties of the Fe$_3$O$_4$ shell with respect to the magnetic properties of ZnMn, such as lower $M_s$. Therefore, the small changes in the experimental $T_B$ values among the samples might only be through the contribution of anisotropy by dipolar interactions or a spin-orbit coupling between the layers. The shifts associated to anisotropy can be described by Eq. (3) [2]:
where $K_r$, represents the anisotropy constant of the internal layer, in this case, the ZnMn: $K_r$ represents the contribution of the anisotropy of the external magnetic layer ($Fe_3O_4$), and $D$ represents the diameter of the MNPs.

As has been stated before, the main use of these bi-magnetic MNPs with low and tunable $T_B$ might be in biomedicine. Therefore, we performed their toxicity tests in mussel hemocytes. Several parameters such as membrane integrity, ROS production, cell death or lysosome abundance and viability were evaluated. The results are presented in supporting information. The results indicate that only the viability of the hemocytes decreases for MNPs size larger than 13 nm are almost blocked at a room temperature.


F. Arteaga-Cardona, K. Rumpf, P. Granitzer, P.M. Morales, P. Poelt, M. Reissner, Variable blocking of the bi-magnetic nanostructures. As has been stated before, the main use of these bi-magnetic nanoparticles with low and tunable $T_B$ might be in biomedicine. Therefore, we performed their toxicity tests in mussel hemocytes. Several parameters such as membrane integrity, ROS production, cell death or lysosome abundance and viability were evaluated. The results are presented in supporting information. The results indicate that only the viability of the hemocytes decreases for MNPs size larger than 13 nm are almost blocked at a room temperature.


