

Tunnel Magnetoresistance in Self-Assemblies of Exchange Coupled Core/Shell Nanoparticles

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Abstract

We report the precise control of tunneling magnetoresistance (TMR) in devices of self-assembled core/shell $\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles ($0 \leq x \leq 1$). Adjusting the magnetic anisotropy through the content of Co^{2+} in the shell, provides an accurate tool to control the switching field between the bistable states of the TMR. In this way, different combinations of soft/hard and hard/soft core/shell configurations can be envisaged for optimizing devices with the required magnetotransport response.

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I. INTRODUCTION

The possibility to manipulate the electrical resistive state of magnetic/non-magnetic multilayers by an external magnetic field (giant magnetoresistance, GMR) was demonstrated already 30 years ago.[1, 2] The strong coupling between the electron spin and charge degrees of freedom and the development of the tools for their manipulation, triggered the growth of a new field called spintronics.[3, 4] The fabrication of magnetic tunnel junctions (MTJ) constitutes one of the most important advances in this field since then.[5, 6] A MTJ is composed of two layers of ferromagnetic conductors separated by an insulating tunneling barrier, typically of ≈ 1 nm. The different density of states at the Fermi level, $N(E_F)$, of the spin up/down subbands of the ferromagnetic metals imply a spin-dependent tunneling probability. Therefore, the electrical resistance of the device switches between high/low resistance states as the magnetic field changes the relative orientation of the magnetizations of the two magnetic layers (tunneling magnetoresistance, TMR). The MTJ devices present high versatility and a great degree of functionalization, allowing to combine electrodes and barriers of different nature, where large tunneling magnetoresistance, up to hundreds of percents at room temperature, was obtained [7, 8]. However their fabrication is a challenge, involves advanced thin film deposition techniques and complex microfabrication procedures. Tunneling magnetoresistance has also been studied in simpler nanostructures as granular or disordered single films [9, 10], where the grain boundaries act as tunnel junction barriers. However, the characteristic of the barrier cannot be controlled in these nanostructures and lower TMR values are obtained.

On the other hand the spectacular advances of the chemical synthetic methods produced over the last few years, offer an affordable route for the synthesis of complex nanostructures, with a precise control of their chemical composition, shape and size. [11] These can be assembled in crystal-like structures over large areas, in which the organic capping layer or a non-magnetic shell protecting the particles acts as a tunneling barrier that controls the electronic transport. [12–17] Spin-dependent electrical transport and large magnetoresistance was also observed in devices formed by assembling of conducting magnetic nanoparticles (MNPs)[14, 18, 19] or binary nanoparticles superlattice [20–22].

However, an important challenge that must be addressed in this field is the design of strategies to tune the switching field of the TMR devices, which is entirely determined

by the anisotropy of the magnetic material.[9, 10, 23–26] Therefore, a good handling over the coercivity of the magnetic nanoparticles would allow the control over the TMR of the assemblies, in a similar approach as that used in multilayers. [27]

In this regard, an exciting possibility is the fabrication of devices based on self-assemblies of exchange coupled core/shell MNPs with tailored magnetic properties.[28] The coercive field in these systems can be finely modified through the interface magnetic coupling[29–34], the core size and shell thickness,[35–37] or the magnetic anisotropy of the components.[23, 38–40] Devices of this type should provide a way to manipulate at will the characteristic switching field of TMR by controlling the magnetic coupling across the core/shell interface. In this way, core-shell nanoparticles combine the properties of multilayered based tunnel junctions and granular or disordered thin films, offering very high versatility with a simple fabrication process.

Here we report the precise control of the TMR in self-assemblies of half metallic ferrimagnetic Fe_3O_4 nanoparticles encapsulated in ferrimagnetic electrical insulator $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$). Progressive replacement of Co^{2+} by Zn^{2+} in the shell reduces the magnetic anisotropy and shifts the maximum of the TMR of the self-assembled device in a perfect correlation with the magnetic response. These results demonstrate the feasibility of tuning the TMR switching field in self-assembled devices formed by magnetic core/shell nanoparticles.

II. EXPERIMENTAL PROCEDURE

$\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ core/shell nanoparticles were fabricated by seed mediated high temperature decomposition of metal-acetylacetonates in benzyl ether assisted by oleic acid and oleylamine, based on the method described in Refs. [39, 41, 42]. Initially monodisperse Fe_3O_4 seeds were obtained by mixing 12 mmol of Fe(III) acetylacetonate ($\text{Fe}(\text{acac})_3$) with 24 mmol of 1,2-octanediol, 210 mmol benzyl ether, 8 mmol oleic acid, and 40 mmol oleylamine into a three neck flask, under N_2 flow. The mixture was slowly heated up to the reflux temperature (295 °C) and held for a total time of 120 minutes. Then the solution containing the nanoparticles was separated in five portions in order to overgrow the spinel ferrite shell. At this point 0.6 mmol of Co(II) acetylacetonate ($\text{Co}(\text{acac})_2$) and Zn(II) acetylacetonate ($\text{Zn}(\text{acac})_2$) were added to the mixture, according to a nominal molar ratio $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, together with $\text{Fe}(\text{acac})_3$ (1.2 mmol), 1,2-octanediol (3 mmol), oleic acid (3 mmol), oleylamine

(3 mmol) and benzyl ether (210 mmol), and the heating procedure was repeated. Five samples with Zn nominal concentration $x=0.00, 0.25, 0.50, 0.75$ and 1.00 were synthesized. The samples were washed by adding ethanol and centrifuged, followed by the addition of acetone, and magnetically separated. Finally the MNPs were dispersed in hexane. The nanoparticle composition were determined with an Inductively Coupled Optical Emission Spectrometer (ICP-OES) brand Agilent model 5110. To perform the measurements the samples were processed with a Berghoff microwave digester model SW4 in an acid mixture with $HNO_3 : HCl$ 4 : 1.

The self-assembly of the core/shell MNPS was done at the liquid-air interface following the procedure reported in Refs. [20–22]. In the assembly process schematized in the upper panel of Figure 1, a drop of $10 \mu\text{L}$ of solution with 5 mg/mL of nanoparticles in hexane is drop-casted onto the surface of triethylene glycol in a Teflon container, which was then covered by a glass slide. In order to transfer the assemblies to a substrate, the teflon vessel of $1.5 \times 1.5 \times 1.0 \text{ cm}^3$ was designed with a 30° inclined base-plane where the substrate was located previously and was completely covered by the triethylene glycol. A self-assembled structure is formed after complete evaporation of hexane (between 10-15 min). After that the triethylene glycol was removed very slowly using a syringe in order to gently deposit the assembled film on the substrate. All the samples received a thermal treatment in a vacuum atmosphere ($\sim 10^{-3}$ Torr) in order to reduce the organic coating of the particles and to promote a closer contact between them. The decomposition temperature of the organic nanoparticle coating was determined from thermogravimetric analysis. The self-organized nanoparticles were heated from room temperature up to 400°C at heating rate of $15^\circ\text{C}/\text{min}$, kept at 400°C by 30 min and then cooled to room temperature at $15^\circ\text{C}/\text{min}$.

Structural characterization of core/shell powder samples was performed by conducting X-ray diffraction (XRD) experiments on a PANalytical X'Pert diffractometer with $\text{Cu K}\alpha$ radiation using a glass sample holder (step size 0.026° , range 15° - 90°). Transmission electron microscopy (TEM) images and electron diffraction patterns of powder samples and self assembled nanoparticles were taken in a Philips CM200 transmission electron microscope equipped with a Ultra-Twin lens operating at 200 kV and a resolution of 0.19 nm. In order to perform the structural characterization of the self-assemblies of core/shell nanoparticles, they were transferred from the triethylene glycol surface to commercial silicon nitride TEM grids followed by thermal annealing. Atomic force microscopy (AFM) measurements were

done in a Veeco (now Bruker) Dimension 3100 SPM in tapping mode using a standard tip. The $2\ \mu\text{m}$ scans were done using a scan frequency of 1Hz and after waiting 30 minutes for thermal stabilization and noise reduction. No modification of the surface was observed after the measurements.

The magnetic properties were studied using a commercial superconducting quantum interference device magnetometer (SQUID, MPMS Quantum Design). To perform the measurements the self-assembled nanoparticles were transferred from the triethylene glycol surface to glass substrate ($4\ \text{mm} \times 6\ \text{mm}$) followed by the thermal annealing. The magnetoresistive devices were fabricated by thermal evaporation of the Au/Cr electrodes on glass substrates. The Au/Cr patterns of $7\ \mu\text{m}$ channel length and $6\ \text{mm}$ channel width, were fabricated by photolithography as shown in the middle panel of Figure 1. Then, the self-assembled of core/shell nanoparticles floating on the triethylene glycol surface were transferred to the prepatterned glass substrates, and the obtained films were thermally annealed. The magnetotransport measurements were performed using a Keithley 4200 source-measure unit in a two probe configuration, with a maximum applied field of $\pm 12\ \text{kOe}$.

III. RESULTS AND DISCUSSION

Figure 2 compares the morphology and size, measured by TEM, of Fe_3O_4 nanoparticles seeds with a representative core/shell system, $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$, both samples were subjected to the same thermal annealing at $400\ ^\circ\text{C}$ in vacuum atmosphere. From the size histograms, fitted with a Gaussian function, the mean particle sizes ($\langle D \rangle$) were calculated, resulting $7.7\ \text{nm}$ and $9.6\ \text{nm}$, for core and core/shell systems, respectively. From high resolution TEM (HRTEM) image it is noticed that the core is monocrystalline and the shell growth epitaxial over the core for most of the nanoparticles. Moreover different crystalline orientations for core and shell can be observed for most of the nanoparticles as noticed in Figure 2(d) where the (044) and (222) crystalline planes of spinel phase are signaled for core and shell, respectively. The core/shell structure is confirmed by dark field, as shown in Figure 2(e) where the TEM image was recorded with a small objective aperture positioned on the (113) brighter electron diffraction ring of the spinel phase. In this way the bright contrast in the reconstructed image corresponds to the spinel grains with the selected crystallographic orientation as schematically drawing in Figure S1(d-e) (see Supplemental Material). From

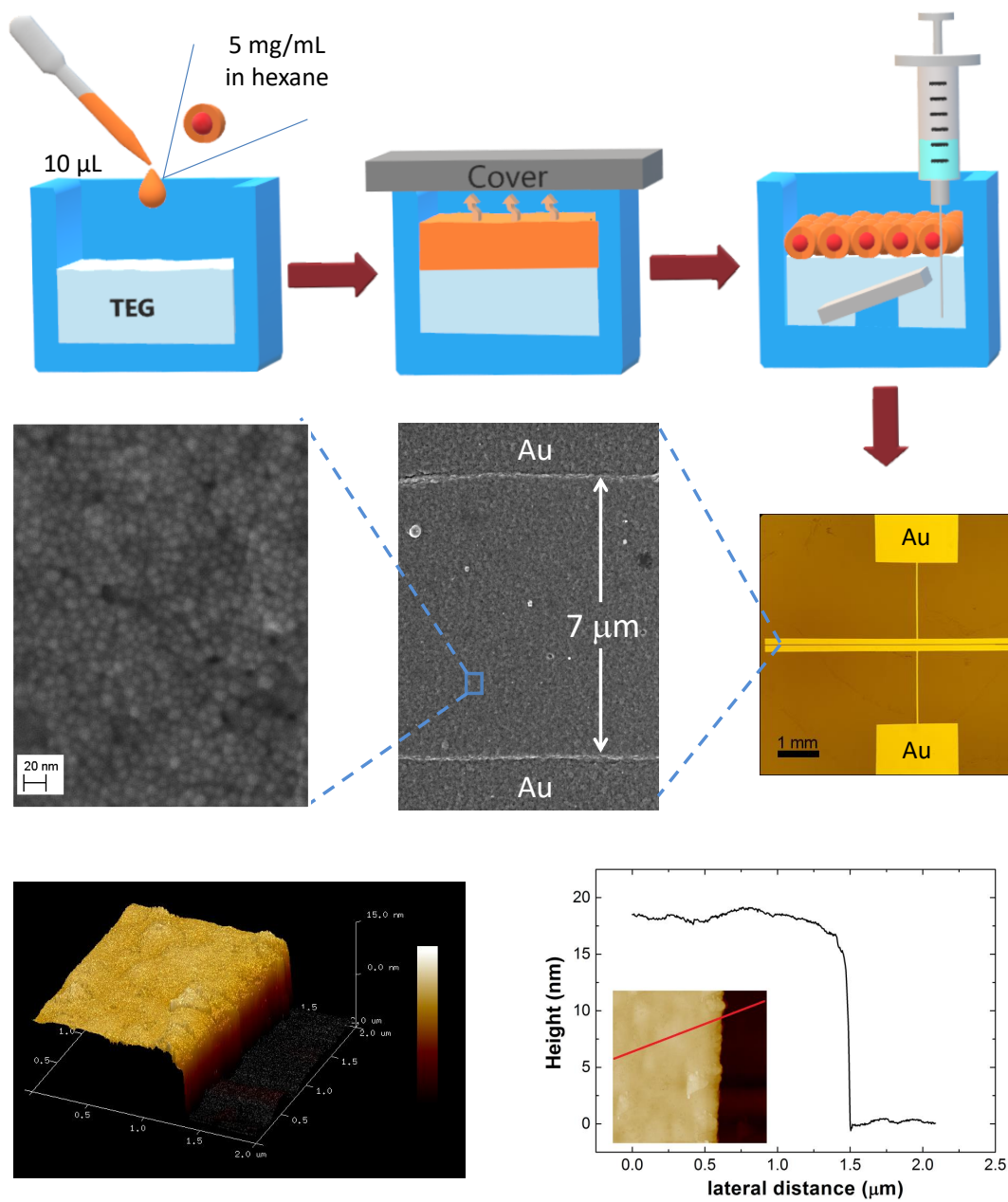


FIG. 1. Scheme of the process of self-assembly of the particles at liquid-air interface and the transfer of the assemblies on a substrate. The middle part of the figure shows an optical image (right), along with two SEM images of the glass substrate patterned with Au electrodes, separated by $7 \mu\text{m}$, with the self-assembled nanoparticles deposited on top. The bottom part of the figure shows the topography and height profile cross section of the annealed nanoparticles assemblies analyzed by atomic force microscopy (AFM). The height profile across the film edge shows a thickness of $\approx 20 \text{ nm}$, consistent with a two-layer assembly.

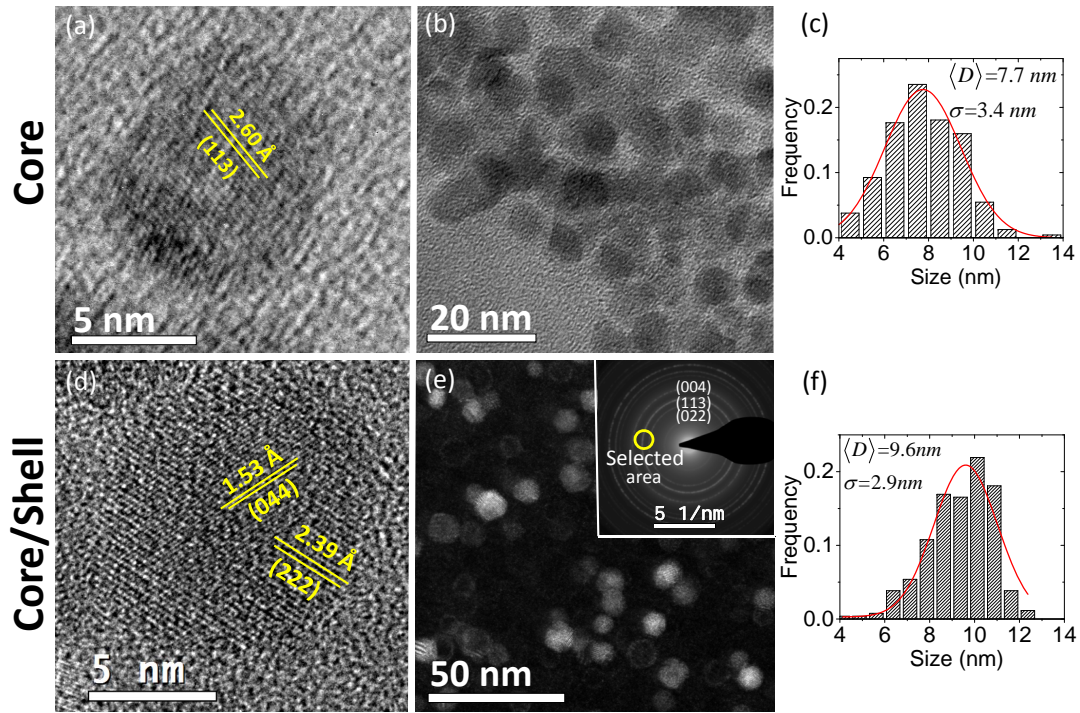


FIG. 2. Top panels: (a-b) TEM images of the Fe_3O_4 core nanoparticles annealed at 400° in vacuum atmosphere, HRTEM where the interplanar distance of (113) spinel phase are signaled, and (c) size histogram fitted with a Gaussian function. Bottom panels:(d) HRTEM image of $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ nanoparticles annealed at 400° in vacuum atmosphere, where different crystalline orientations (044) and (222) of spinel structure for core and shell are indicated. (e) Dark field TEM image reconstructed with a fraction of the (113) of the spinel diffraction ring and (f) size dispersion for the core/shell nanoparticles with the corresponding Gaussian fitting.

the HRTEM and dark field TEM images, and from the comparison with the core size, the thickness of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ shell was estimated as ~ 1 nm. The composition of the nanoparticles was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). From this analytical technique the concentration of the transition metal ions for all the samples were obtained and reported in Table I. From these data, and assuming a Fe_3O_4 core of 7.7 nm of diameter, we calculated the shell stoichiometry which shows a systematic evolution consistent with the nominal concentration.

TABLE I. Total concentration of transition metal ions in core/shell nanoparticles measured from inductively coupled plasma mass spectrometry (ICP-OES). The last column presents the calculated shell stoichiometry considering the mean nanoparticles size obtained by TEM and a Fe_3O_4 core of 7.7 nm of diameter.

Samples	Total concentration			Calculated shell stoichiometry
	%Co	%Zn	%Fe	
$x = 0.00$	9.40	0.00	90.60	$\text{Co}_{0.61}\text{Fe}_{2.39}\text{O}_4$
$x = 0.25$	7.71	2.36	89.93	$\text{Co}_{0.45}\text{Zn}_{0.15}\text{Fe}_{2.40}\text{O}_4$
$x = 0.50$	6.01	4.80	89.19	$\text{Co}_{0.39}\text{Zn}_{0.35}\text{Fe}_{2.26}\text{O}_4$
$x = 0.75$	2.68	5.78	91.54	$\text{Co}_{0.18}\text{Zn}_{0.44}\text{Fe}_{2.38}\text{O}_4$
$x = 1.00$	0.00	9.94	90.06	$\text{Zn}_{0.80}\text{Fe}_{2.20}\text{O}_4$

TABLE II. Nanoparticles size distribution parameters of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ obtained from the TEM images, where $\langle D \rangle$ is the mean particle size, and σ is the standard deviation. The last columns present the mean blocking temperature $\langle T_B \rangle$ and the effective magnetic anisotropy constant K_{eff} calculated from the ZFC-FC magnetization curves.

Sample	$\langle D \rangle$	σ	$\langle T_B \rangle$	K_{eff}
	nm	nm	K	10^6erg/cm^3
Fe_3O_4	6.9	2.6	17	0.32
$x = 0.00$	9.6	2.9	191	1.54
$x = 0.25$	9.9	3.8	171	1.25
$x = 0.50$	9.5	2.9	135	1.12
$x = 0.75$	9.4	2.7	115	0.99
$x = 1.00$	9.2	3.3	8	0.07

The self assemblies of Fe_3O_4 -core/ $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ -shell nanoparticles were obtained by the liquid-air interface process [20–22] as explained in the Experimental Procedure Section. In order to perform the different measurements, the self-assembly and the subsequent thermal treatment was reproduced using a commercial silicon nitride support grid for TEM characterization, and a glass substrate patterned with two Au electrodes separated by $\sim 7 \mu\text{m}$ (as shown in the SEM image of Figure 1) for the magnetotransport studies. The topog-

raphy of the annealed assemblies was analyzed by atomic force microscopy. Images acquired at different regions of the films reveal a large homogeneity with uniform and smooth surface, as observed in the bottom panel of Figure 1. From the AFM height profile cross section at the film boundary, an average film thickness of 20 nm was measured, which corresponds to two layers of nanoparticles.

Homogeneity and narrow size distribution are essential conditions to reach large area of self-organization; for core/shell nanoparticles, as observed from Figure 3 and Figure S1(a) (see Supplemental Material [43]), assemblies of several microns are obtained. From Figure S1(f) it is also noticed that the self-organized nanoparticles are separated by a gap of ~ 1 nm. As the thermogravimetric analysis indicates that approximately 7% of residual mass remains in the systems after the thermal treatment at 400 °C in vacuum atmosphere, and infrared spectroscopy measurements do not detect organic molecules (see Figure S3 in Supplemental Material [43]), we conclude that the gap between the nanoparticles is formed by amorphous carbon. The nanoparticles size distributions measured from the TEM micrographs, are shown in the middle panels of Figure 3. From the fitting of the histograms with a Gaussian function, the mean nanoparticles size $\langle D \rangle$ was calculated and summarized in Table II, which vary between 9.2-9.9 nm for all the systems. We also notice that the nanoparticle size and also the superstructure of the self-assembly is preserved at higher annealing temperature, however at 600 °C the nanoparticles start to coalesce (see Figure S2 Supplemental Material [43]). From the HRTEM images (shown in Figure 2 for $x = 0$ and in Figure 3 for $x = 0.75$ and $x = 1$) it is observed that the core/shell microstructure is preserved after the annealing at 400 °C, where different interplanar distances and crystallographic planes orientation for the inner and outer part of the particle can be measured. As mentioned before, this morphology is confirmed by dark field images, as shown in Figure 3 for $x = 0.00, 0.25$ and 0.50 . Although the core/shell microstructure is preserved, we can not discard some degree of interdiffusion at the interface as reported for similar nanoparticles systems [44, 45]; however, as we are going to discuss later, the magnetoresistance measurements confirms the half-metallic nature of the Fe_3O_4 core.

Figure 4(a) and Figure S4 (see Supplemental Material [43]) show the magnetization hysteresis loops of the annealed self-assembled nanoparticles, measured with the magnetic field applied in the plane of the substrate. The hysteresis loops show a single magnetization reversal for all compositions, with the coercive field (H_C) decreasing approximately linearly

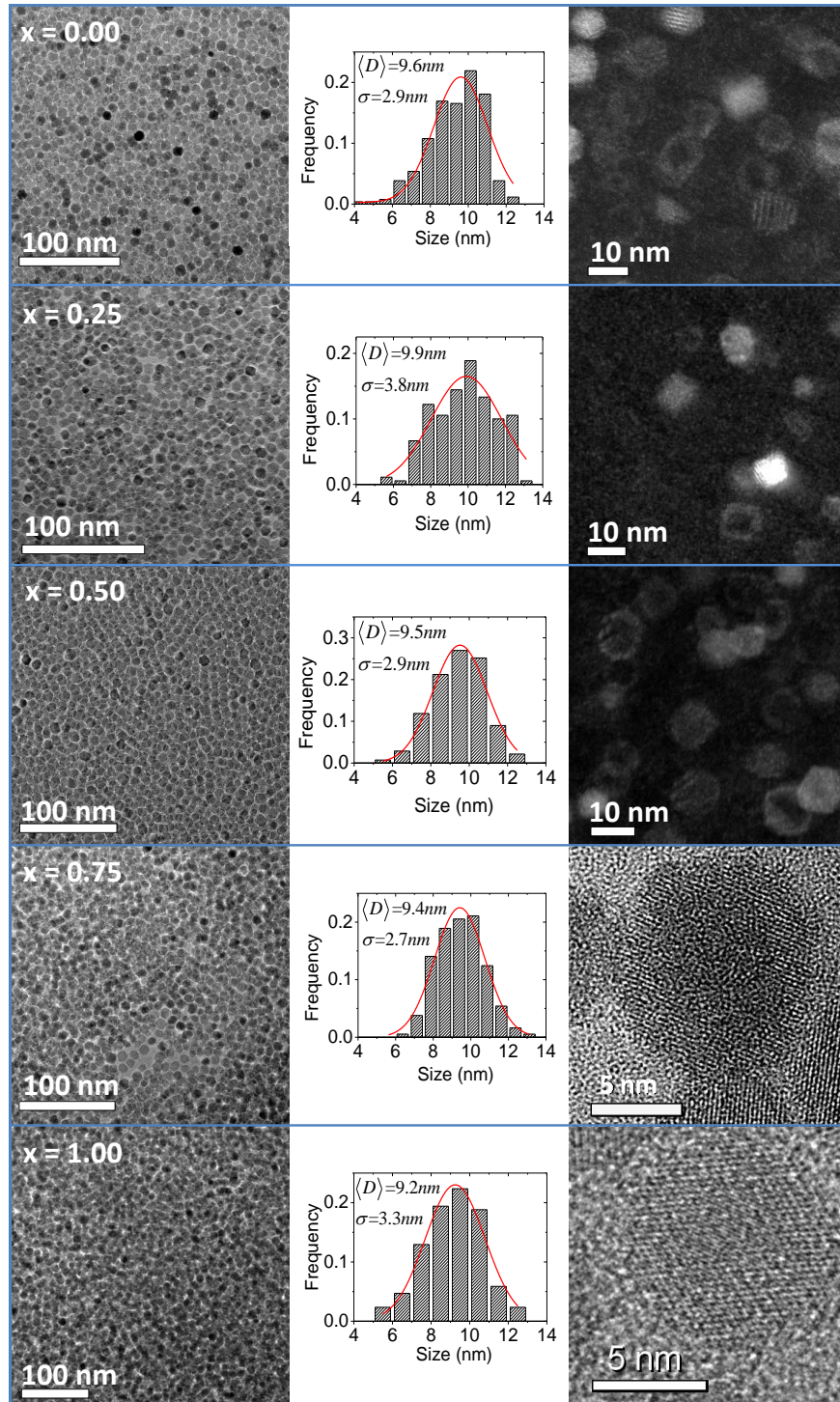


FIG. 3. TEM images of the self-assembled $\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ core/shell nanoparticles for the different compositions from $x = 0$ to $x = 1$, along with the corresponding size distribution histograms. The right panel show representative images where the core/shell structure can be appreciated from dark field images for $x = 0, 0.25$ and 0.50 and from high resolution TEM for $x = 0.75$ and 1 . The bright contrast in the dark field images corresponds to the spinel grains with the particular crystallographic orientation selected by positioning the small objective TEM aperture on the brighter (113) electron diffraction ring of the spinel phase.

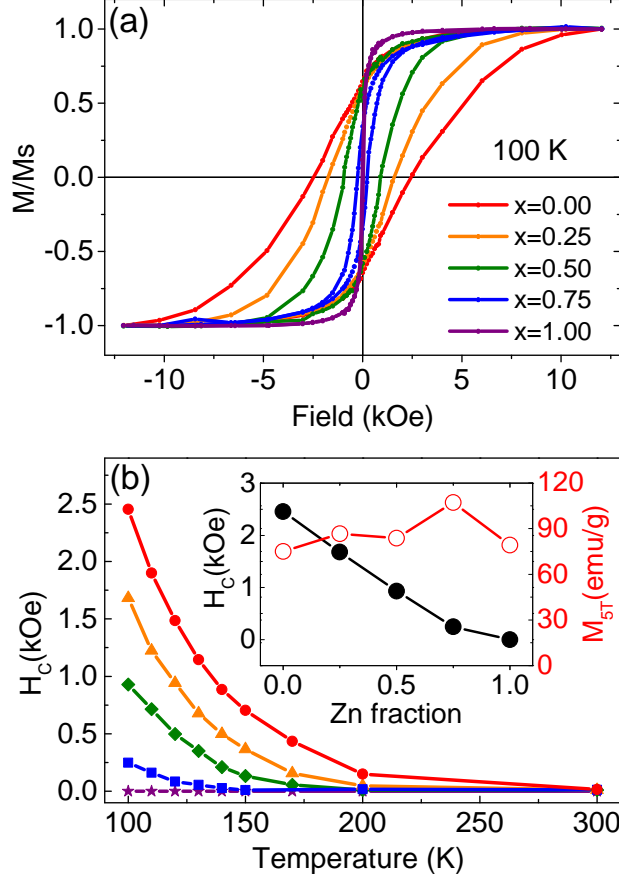


FIG. 4. (a) Hysteresis loops measured at 100 K, and (b) coercive field as a function of the temperature for the annealed $\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ core/shell nanoparticles assemblies. The inset shows the H_C for the annealed self-assembled particles as a function of x , and also the magnetization measured at 5 T (M_{5T}) for powder sample annealed under the same conditions as the self-assemblies. Both measurements were acquired at 100 K.

with the Zn concentration x , as shown in Figure 4(b). Notice that the magnetization hysteresis loop reported for binary nanocrystal superlattice $\text{CoFe}_2\text{O}_4-\text{Fe}_3\text{O}_4$ results from the superposition of the individual component and an annealing treatment is an essential step to obtain an exchange interaction between the half-metallic Fe_3O_4 and the magnetic insulator CoFe_2O_4 [20]. On the contrary, in the core/shell morphology, both phases are strongly coupled at the interface and homogeneous loop is obtained even in the as-synthesized system as shown in Figure S5. The magnetization inversion process of $\text{Fe}_3\text{O}_4/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ core/shell nanoparticles can be analyzed from the theoretical approach developed for bimagnetic soft/hard exchange coupled nanostructures.[46–50] From these studies a critical size for

the soft magnetic component, δ_{crit} , was found below which both phases are rigidly coupled by interface exchange interaction and reverse their magnetization in a coherent mode at the nucleation field, H_N . This critical size is approximately twice the magnetic Bloch wall width of the hard phase $\delta_w = \pi\sqrt{A/K}$, where A is the exchange stiffness. In this regime, a single square hysteresis loop is obtained, with $H_C = H_N = 2(K_c f_c + K_{sh} f_{sh}) / (M_c f_c + M_{sh} f_{sh})$; where M , f and K are the magnetization, film thickness (or volume fraction), and magnetic anisotropy of the core (c) and shell (sh), respectively.[28, 51, 52] Instead, if the size of the soft magnetic phase is larger than δ_{crit} exchange spring behavior is found, the magnetization reversal is nonuniform and lower coercivities are obtained. [48, 49, 51] For CoFe_2O_4 the values reported for δ_w span in the range of 13-20 nm,[28, 53] larger than the diameter of the Fe_3O_4 soft core used in this work. Therefore, rigid exchange coupling of the magnetizations of the core/shell phases is expected. This conclusion is supported by the study of $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ soft/hard bilayers, where a critical thickness of 8 nm was found for the crossover from rigid coupling to exchange spring behavior as a function of the Fe_3O_4 thickness[54]. Therefore, the decrease of H_C with x can be accounted by the diminution of the magnetic anisotropy of the shell from $\sim 4 \cdot 10^6 \text{erg/cm}^3$ for $x = 0$, to $\sim 2 \cdot 10^5 \text{erg/cm}^3$ for $x = 1$ [55] in agreement with the expression for H_C in the rigid exchange coupled regime.

The systematic dependence of the magnetic anisotropy with the shell composition is also reflected in the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves shown in Figure S6 of Supplemental Material [43]. The temperature where the change from blocked to the superparamagnetic regime is observed decreases progressively with increasing x . From the maximum of the energy barrier distribution calculated as $f(T_B) = (1/T)(d(M_{ZFC} - M_{FC})/dT)$ the mean blocking temperature, $\langle T_B \rangle$, and the effective magnetic anisotropy constant, $K_{eff} = 27 k_B T_B / v$, can be obtained for particles of total volume v , as reported in Table II.[56] For comparison, Table S1 (see Supplemental Material [43]) reports the parameters that characterize the magnetic properties of dispersed nanoparticles before the annealing process. Both systems, the dispersed nanoparticles and the annealed assemblies, present qualitative and quantitative similar behavior, with an enhancement of the effective magnetic anisotropy when the concentration of Co in the shell increases, which points out that the magnetic behavior is governed by the hard/soft rigid coupling magnetization inversion process, as analyzed previously. However, the annealed assemblies present an approximately 20% larger $\langle T_B \rangle$, H_C and K_{eff} , probably due to an increase of the dipolar

interaction and the improvement of the crystallinity in the annealed assemblies.

The magnetic measurements demonstrate that the effective magnetic anisotropy of the system can be controlled by adjusting the shell composition, without appreciably modifying the morphology and the overall magnetic saturation, as observed from the inset of Figure 4(b). Given that the anisotropy of the system is to a great extent responsible of the switching field of the TMR, devices made of self-assembled core/shell nanoparticles provide an ideal system for studying spin-dependent transport between magnetic nanoparticles. Although both materials at the core/shell structure are strongly exchange coupled and behave as a unique magnetic entity with an average magnetic anisotropy, the conductivity of each phase is different. While the Fe_3O_4 core is half-metallic, the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ shell is a semiconductor. Therefore, in order to observe TMR properties it is crucial to have Fe_3O_4 phase to provide the spin polarized transport, whereas the role of the shell is to modulate the switching field by tuning the magnetic anisotropy, while acting as a tunnel barrier.

The electronic transport in the annealed self-assembled devices was studied from the current-voltage ($I - V$) measurements and from the temperature dependence of the resistivity ρ , as reported in Figure 5. From this figure it can be affirmed that the electron conduction in the devices is given by two independent mechanisms: thermally activated hopping, which is revealed from the temperature dependence of ρ ; and the tunneling conduction manifested by the non-Ohmic behavior in the I-V curve with the characteristic V^3 dependence at low temperature, as discussed next. From the Simmons's model, which considers inelastic tunneling across an insulating barrier, the $I - V$ curves can be quantitatively linked to the physical parameters of the system, *i.e.* the tunnel barrier height (h) and width (w), the effective contact area, etc. [57]. This model also considers linear dependence approximation of the barrier potential profile with V and w . For voltage smaller than the potential barrier, the Simmons's model can be approximated with the well known polynomial relationship:[58]

$$\frac{I}{V} \approx G_0 (1 + FV^2) \quad (1)$$

where G_0 is the equilibrium conductance and $F \propto \xi^2$, where $\xi = w/h$ is the shape factor of the barrier.[59] From the plot shown in the inset of Figure 5(a), the shape factor of the barrier is clearly increasing with x . Given that the barrier width is approximately constant for all samples, this reflects a progressive decrease of the tunneling barrier height as the Zn content increases. Considering the geometry of the assemblies devices, *i.e.* the area

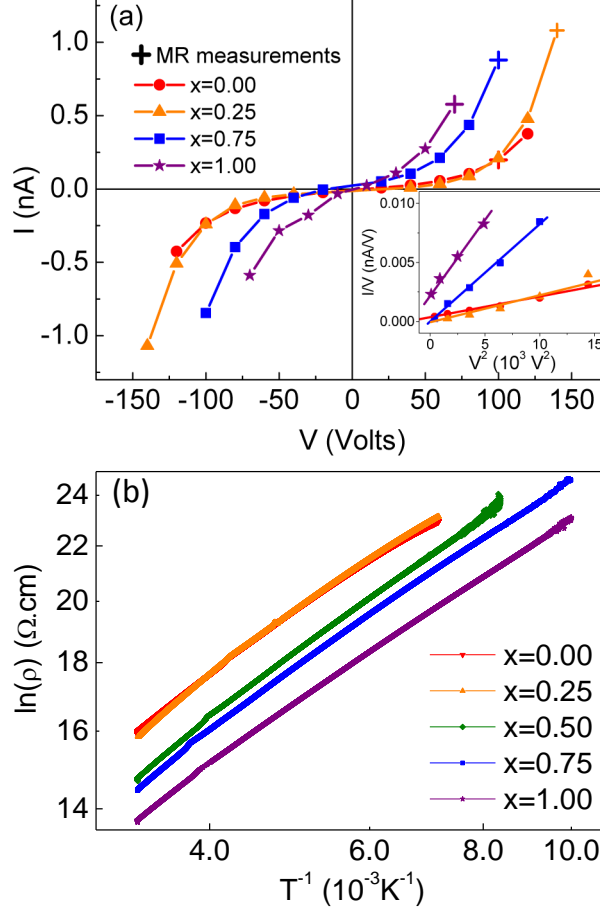


FIG. 5. (a) Current-voltage characteristics measured at 100 K for all the $Fe_3O_4/Co_{1-x}Zn_xFe_2O_4$ annealed devices. The inset shows I/V versus V^2 . (b) Logarithm of the electrical resistivity as a function of $1/T$, both in logarithmic scale.

measured by SEM and the film thickness obtained by AFM microscopy, we have plotted $\rho(T)$ in Figure 5(b), which suggests that a thermally activated transport mechanism is also involved in the conduction of the devices. The temperature dependence follows the relation $\ln(\rho) \propto T^{-1/\alpha}$, where $\alpha = 0.4(1)$ was found as the best fitted parameter for all the systems. This value is close to the dependence found in the Efros's variable range hopping model $\ln(\rho) \propto T^{-1/2}$, [60] and it is consistent with the behavior measured in other nanoparticles arrays. [14, 17, 21, 24, 61]. Moreover, $\rho(T)$ in the core/shell assemblies is, at least, two orders of magnitude smaller than the reported for pellets of $Co_{1-x}Zn_xFe_2O_4$ powder ferrite (for example at room temperature $\rho(CoFe_2O_4) \sim 1.10^7 \Omega.cm$ and $\rho(Co_{0.4}Zn_{0.6}Fe_2O_4) \sim 1.10^8 \Omega.cm$ [62–64]). This result shows that the tunnel conduction strongly increases the conductivity of the core/shell assemblies compared to the values measured in the semiconductor shell

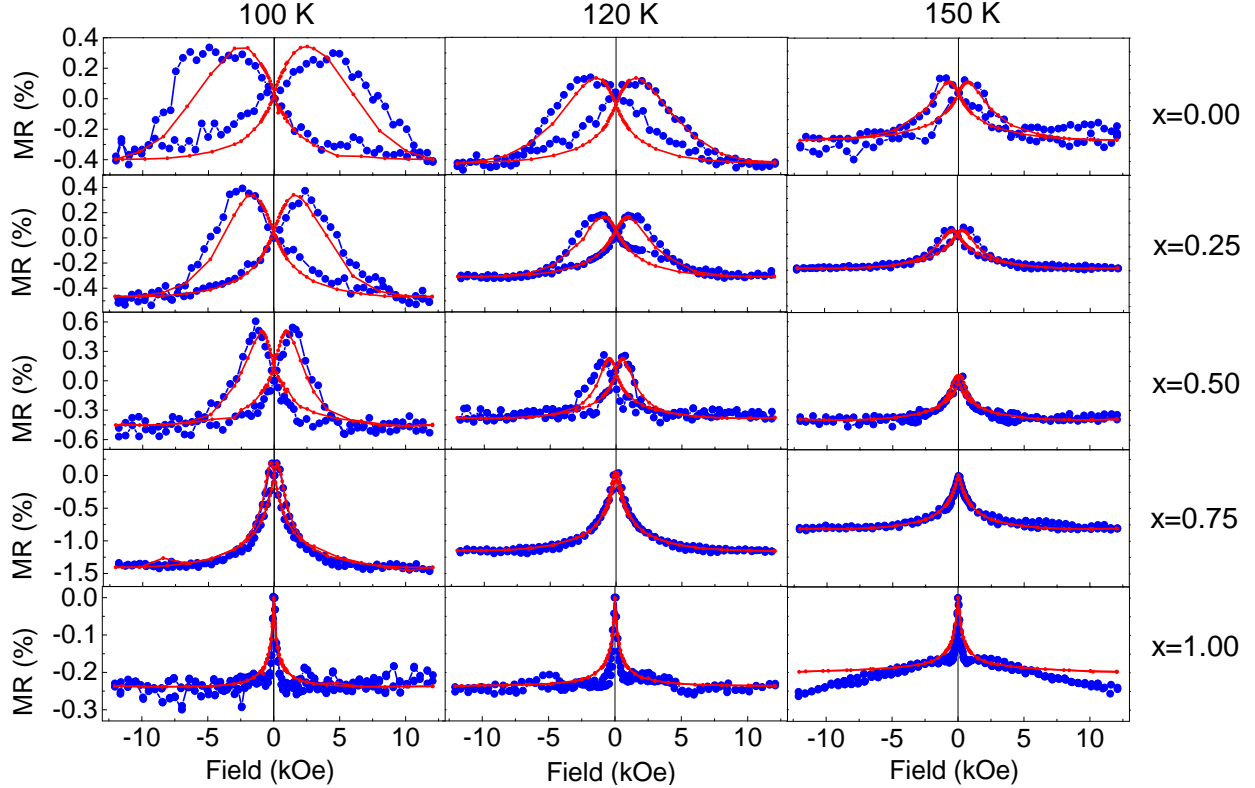


FIG. 6. TMR of the devices studied in this work at different temperatures. The magnetoresistance is defined as $MR = 100 \times [R(H) - R(0)]/R(0)$, and it was measured with H in the plane of the self-assembled films. The red line represents the fitting to equation 2 using the experimental $M(H)$ curves shown in Figure 4, measured for each self-assembly of magnetic nanoparticles.

material. Notice that the larger the tunneling current, the lower the resistivity of the devices. Therefore, the material that has the lower tunneling barrier will be the one that is most influenced by this contribution. Consistently, from Figure 5 we have measured that the assemblies of nanoparticles with a ZnFe_2O_4 shell present the lowest energy barrier, and a systematic increase with decreasing x is observed.

The main findings of this work are summarized in Figure 6 and 7. Magnetoresistance curves measured at different temperatures for the five devices studied in this work are shown in Figure 6 and Figure S7 of Supplemental Material [43]. At a given temperature, the switching field of the magnetoresistance curve monotonously decreases when the Zn concentration of the shell increases. Moreover, as shown in Figure 7, each sample shows a smooth decrease of the switching field with temperature, consistently with the temperature evolution of the coercive field. Also, a saturation behavior of TMR at high magnetic field is

observed when x decreases, in good correspondence with the $M(H)$ curves, see Figure 4.

For spin-polarized intergrain tunneling the TMR is related to the macroscopic magnetization.[9, 10, 25] For a ferromagnetic-insulator granular system, the electron tunneling across the insulating barrier was calculated including an additional exchange energy arising from the interaction between the tunneling electron spin and the non-parallel magnetic moment of the neighboring grains. [25, 65]. Assuming that the exchange energy can be expressed in terms of the spin correlation function of two ferromagnetic neighboring grain, the magnetoresistance can be expressed as:

$$TMR = -\frac{JP}{4k_B T}[m^2(H, T) - m^2(0, T)] \quad (2)$$

where J accounts for the magnetic correlations when the electron tunnels through the insulating barrier and $m = M/M_S$. Notice that within this model the magnetoresistance does not depend on the total resistivity of the sample. The fittings to this equation using $C = JP/4k_B T$ as the single adjusted parameter for each temperature, are shown in Figure 6. The good agreement between both measurements from equation 2 confirms the spin polarized tunnel transport in the present devices, where the C parameter gives the proportionality between two independent experiments, $M(H)$ and $\rho(H)$. Moreover, in agreement with equation 2, the fittings show that C varies approximately linearly with $1/T$ over the measured temperature range (see Figure 7(b)). However, although equation 2 adjusts the field and temperature dependence of TMR with the magnetization, due to the complex nature of the present system, it is hard to determine the dependence between the C parameter and the shell stoichiometry. Even though all the systems have the same Fe_3O_4 core, the $Co_{1-x}Zn_xFe_2O_4$ shell was synthesized in a second step which lead to a shell thickness dispersion along the Zn composition, moreover from the synthesis and later thermal treatment the nanostructures could also present dispersion in the nanoparticle coating. These experimental factors could affect the magnetic correlations when the electron tunnels through the insulating magnetic barrier and also the surface Fe_3O_4 spin polarization. Nevertheless, although it is hard to estimate the evolution of the magnetic correlation with the shell stoichiometry, the magnitude of the interaction can be estimated. Assuming the spin polarization of magnetite, ($P \approx 39\%$) [27] a coupling constant of $J \approx 1.0(0.4)$ meV (≈ 10 K) is obtained, comparable to the calculations for the intergrain tunneling transport of manganese perovskites [66].

The TMR amplitude, which is in the 0.3 – 1.5% range depending on the composition,

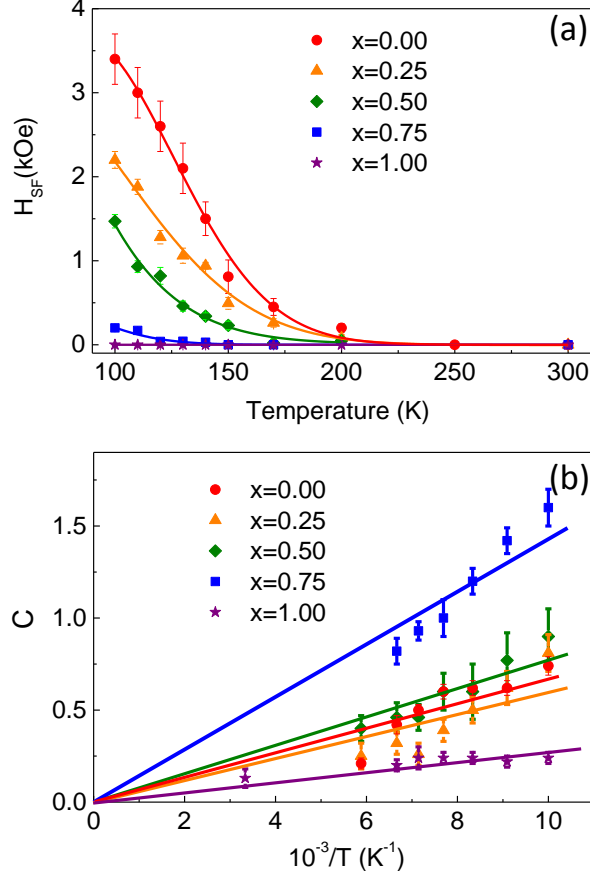


FIG. 7. (a) Switching field (H_{SF}) as a function of the temperature for $Fe_3O_4/Co_{1-x}Zn_xFe_2O_4$ nanoparticles and (b) $C = JP/4k_B T$ obtained as the adjusted parameter from equation 2 as a function of the inverse of the temperature.

is similar to other reported values for self assembled nanoparticles, [16, 21, 24] however, it is much smaller than the calculated from the Julliere's model: $TMR = \frac{2P^2}{(1-P^2)}$ on the basis of the spin polarization values of magnetite. This reduction may be due to the fact that the tunneling probability decreases exponentially with the barrier width. According to Refs. [67, 68] for TMR multilayers, the optimal barrier thickness is in the 1 – 1.5 nm range; however, the tunnel current between Fe_3O_4 cores in the self-assembled structure must pass through the insulator barrier of ~ 3 nm width, which is composed by the cobalt ferrite shell and the amorphous carbon nanoparticles coating. On the other hand, although it is known that the TMR diminishes with increasing bias voltage,[53] the high resistance of the magnetic nanoparticles devices determines the experimental parameters, and high voltage bias ~ 100 V had to be applied to perform the transport measurements at low temperature. These

factors make evident the importance of optimizing the different stages of the fabrication process in order to increase the conductivity to produce large amplitude and low switching field TMR devices based on core/shell magnetic nanoparticles. However, irrespective of the absolute value of TMR, this study demonstrates that the switching field of TMR can be tailored at will in self-assemblies of exchange coupled core-shell nanoparticles, synthesized by an affordable chemical route.

IV. CONCLUSION

In summary, we have fabricated self-assemblies of core/shell nanoparticles with controlled TMR. Particularly, we have shown that the magnetic properties can be finely tuned by changing the shell composition which provides a tool to adjust the TMR switching field. We show whereas that the Fe_3O_4 core provides the spin polarized transport, the shell acts as tunnel barrier in the self assembly and also modulates the switching field by tuning the magnetic anisotropy through the interface exchange coupling. This approach shows the feasibility to use assemblies of exchange coupled magnetic nanoparticles in TMR devices, where different combinations of soft/hard and hard/soft core/shell configurations can be envisaged. In this way, combinations of materials can be carefully designed to move across the rigid coupling to exchange bias regime, to design devices with tailored magnetotransport response, which gives a promising base for the design of core/shell nanoparticles based devices for fundamental studies or for spintronic applications.

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- [1] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, “Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices,” *Phys. Rev. Lett.* **61**, 2472–2475 (1988).
- [2] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, “Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange,” *Phys. Rev. B* **39**, 4828–4830 (1989).
- [3] I. Zutic, F. Jaroslav, and S. Das Sarma, “Spintronics: Fundamentals and applications,” *Rev. Mod. Phys.* **76**, 323–410 (2004).
- [4] S.D. Bader and S.S.P. Parkin, “Spintronics,” *Annual Review of Condensed Matter Physics* **1**, 71–88 (2010).
- [5] M. Julliere, “Tunneling between ferromagnetic films,” *Physics Letters A* **54**, 225 – 226 (1975).
- [6] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, “Large magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions,” *Phys. Rev. Lett.* **74**, 3273–3276 (1995).
- [7] S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, “Giant room-temperature magnetoresistance in single-crystal Fe/MgO/Fe magnetic tunnel junctions,” *Nature Materials* **3**, 868 (2004).
- [8] D. D. Djayaprawira, K. Tsunekawa, M. Nagai, H. Maehara, S. Yamagata, N. Watanabe, S. Yuasa, Y. Suzuki, and K. Ando, “230% room-temperature magnetoresistance in CoFeB/MgO/CoFeB magnetic tunnel junctions,” *Applied Physics Letters* **86**, 092502 (2005).
- [9] M. A. López-Quintela, L. E. Hueso, J. Rivas, and F. Rivadulla, “Intergranular magnetoresistance in nanomanganites,” *Nanotechnology* **14**, 212 (2003).
- [10] H. Y. Hwang, S-W. Cheong, N. P. Ong, and B. Batlogg, “Spin-polarized intergrain tunneling in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$,” *Physical Review Letters* **77**, 2041 (1996).
- [11] C.B. Murray, C.R. Kagan, and M.G. Bawendi, “Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies,” *Annual Review of Materials Science* **30**, 545–610 (2000).

- [12] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, “Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices,” *Science* **287**, 1989–92 (2000).
- [13] H. Zeng, C. T. Black, R. L. Sandstrom, P. M. Rice, C. B. Murray, and Shouheng Sun, “Magnetotransport of magnetite nanoparticle arrays,” *Phys. Rev. B* **73**, 020402 (2006).
- [14] C. T. Black, C. B. Murray, R. L. Sandstrom, and S. Sun, “Spin-dependent tunneling in self-assembled cobalt-nanocrystal superlattices,” **290**, 1131–1134 (2000).
- [15] S. Wang, F. J. Yue, D. Wua, F. M. Zhang, W. Zhong, and Y. W. Du, “Enhanced magnetoresistance in self-assembled monolayer of oleic acid molecules on Fe₃O₄ nanoparticles,” *Applied Physics Letters* **94**, 012507 (2009).
- [16] J. Dugay, R. P. Tan, A. Meffre, T. Blon, L. M. Lacroix, J. Carrey, P. F. Fazzini, S. Lachaize, B. Chaudret, and M. Respaud, “Room-temperature tunnel magnetoresistance in self-assembled chemically synthesized metallic iron nanoparticles,” *Nano Letters* **11**, 5128–5134 (2011).
- [17] K. Mohan Kant, K. Sethupathi, and M. S. Ramachandra Rao, “Role of oxide barrier in intergranular tunnel junctions: An enhanced magnetoresistance in SiO₂ and ZnO coated Fe₃O₄ nanoparticle compacts,” *Journal of Applied Physics* **103**, 07F318 (2008).
- [18] N. Taub, A. Tsukernik, and G. Markovich, “Interparticle spin-polarized tunneling in arrays of magnetite nanocrystals,” *Journal of Magnetism and Magnetic Materials* **321**, 1933 (2009).
- [19] T. B. Tran, I. S. Beloborodov, Jingshi Hu, X. M. Lin, T. F. Rosenbaum, and H. M. Jaeger, “Sequential tunneling and inelastic cotunneling in nanoparticle arrays,” *Phys. Rev. B* **78**, 075437 (2008).
- [20] J. Chen, X. Ye, J. O. Soong, J. M. Kikkawa, C. R. Kagan, and C. B. Murray, “Bistable Magnetoresistance Switching Binary Nanocrystal Superlattices by Self-Assembly and Thermal Annealing,” *ACS Nano* **7**, 1478–1486 (2013).
- [21] A. Dong, J. Chen, J. M. Vora, P. M. and Kikkawa, and C.B. Murray, “Binary Nanocrystal Superlattice Membranes Self-Assembled at the Liquid-Air Interface,” *Nature* **466**, 474–477 (2010).
- [22] C. Jiang, C. W. Leung, and P. W.T. Pong, “Self-assembled thin films of Fe₃O₄-Ag composite nanoparticles for spintronic applications,” *Applied Surface Science* **419**, 692 – 696 (2017).
- [23] P. A. Kumar, S. Ray, S. Chakraverty, and D. D. Sarma, “Engineered spin-valve type magnetoresistance in Fe₃O₄-CoFe₂O₄ core–shell nanoparticles,” *Appl. Phys. Lett.* **103**, 102406

- (2013).
- [24] Y. Zhang, H. Xing, N. Poudyal, V. Nandwana, C. B. Rong, S. S. Yan, H. Zeng, and J. P. Liu, “Inversed tunneling magnetoresistance in hybrid FePt/Fe₃O₄ core/shell nanoparticles systems,” *Journal of Applied Physics* **108**, 103905 (2010).
- [25] J. S. Helman and B. Abeles, “Tunneling of spin-polarized electrons and magnetoresistance in granular ni films,” *Phys. Rev. Lett.* **37**, 1429–1432 (1976).
- [26] M. El-Hilo, R. W. Chantrell, and K. O’Grady, “A model of interaction effects in granular magnetic solids,” *Journal of Applied Physics* **84**, 5114–5122 (1998).
- [27] G. Hu and Y. Suzuki, “Negative spin polarization of fe₃o₄ in magnetite/manganite–based junctions,” *Phys. Rev. Lett.* **89**, 276601 (2002).
- [28] Alberto López Ortega, Marta Estrader, German Salazar Alvarez, Alejandro G. Roca, and Josep Nogués, “Applications of exchange coupled bi–magnetic hard/soft and soft/hard magnetic core/shell nanoparticles,” *Phys. Rep.* **553**, 1–32 (2015).
- [29] G. C. Lavorato, E. Lima, H. E. Troiani, R. D. Zysler, and E. L. Winkler, “Tuning the coercivity and exchange bias by controlling the interface coupling in bimagnetic core/shell nanoparticles,” *Nanoscale* **9**, 10240–10247 (2017).
- [30] G. Salazar-Alvarez, J. Sort, S. Suriñach, M. D. Baró, and J. Nogués, “Synthesis and Size-Dependent Exchange Bias in Inverted Core/Shell MnO/Mn₃O₄ Nanoparticles,” *J. Am. Chem. Soc.* **129**, 9102–9108 (2007).
- [31] V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, and J. Nogués, “Beating the superparamagnetic limit with exchange bias,” *Nature* **423**, 850–853 (2003).
- [32] A. Sarkar, N. Behera, R. Adhikari, and A. K. Das, “Studies on nonlinear electrical transport and magnetoresistance in co/coo core-shell nanostructure,” *AIP Conference Proceedings* **1447**, 937–938 (2012).
- [33] E. L. Winkler, E. Lima Jr., D. Tobia, M. E. Saleta, H. E. Troiani, E. Agostinelli, D. Fiorani, and R. Zysler, “Origin of magnetic anisotropy in ZnO/CoFe₂O₄ and CoO/CoFe₂O₄ core/shell nanoparticle systems,” *Appl. Phys. Lett.* **101**, 252405 (2012).
- [34] G. Lavorato, E. Winkler, A. Ghirri, D. Lima Jr, E. and Peddis, H. E Troiani, D. Fiorani, E. Agostinelli, D. Rinaldi, and R. D. Zysler, “Exchange bias and surface effects in bimagnetic CoO-Core/Co_{0.5}Ni_{0.5}Fe₂O₄-Shell nanoparticles,” *Physical Review B* **94**, 054432 (2016).

- [35] X. Liu, B. P. Pichon, C. Ulhaq, C. Lefèvre, J. M. Grenèche, D. Bégin, and S. Bégin-Colin, “Systematic Study of Exchange Coupling in Core-Shell Fe_{3- δ} O₄/CoO Nanoparticles,” *Chemistry of Materials* **27**, 4073–4081 (2015), <https://doi.org/10.1021/acs.chemmater.5b01103>.
- [36] Lottini, E. and López-Ortega, A. and Bertoni, G. and Turner, S. and Meledina, M. and Tendeloo, G. Van and de Julián Fernández, C. and Sangregorio, C., “Strongly Exchange Coupled Core/Shell Nanoparticles with High Magnetic Anisotropy: A Strategy Toward Rare-Earth-Free Permanent Magnets,” *Chemistry of Materials* **28**, 4214–4222 (2016).
- [37] Gabriel C Lavorato, Enio Lima Jr, Dina Tobia, Dino Fiorani, Horacio E Troiani, Roberto D Zysler, and Elin L. Winkler, “Size Effects in Bimagnetic CoO/CoFe₂O₄ Core/Shell Nanoparticles.” *Nanotechnology* **25**, 355704 (2014).
- [38] M. Sytnyk, R. Kirchschlager, M. I. Bodnarchuk, D. Primetzhofer, D. Kriegner, H. Enser, J. Stangl, P. Bauer, M. Voith, A. W. Hassel, F. Krumeich, F. Ludwig, A. Meingast, G. Kothleitner, M. Kovalenko, and W. Heiss, “Tuning the magnetic properties of metal oxide nanocrystal heterostructures by cation exchange,” *Nano Letters* **13**, 586–593 (2013), PMID: 23362940.
- [39] F. Fabris, E. Lima Jr., E. De Biasi, H. E. Troiani, M. Vasquez Mansilla, T. E. Torres, R. Fernández-Pacheco, M. R. Ibarra, G. F. Goya, Zysler R., and E. Winkler, “Controlling the dominant magnetic relaxation mechanisms for magnetic hyperthermia in bimagnetic core-shell nanoparticles,” *Nanoscale* **11**, 3164–3172 (2019).
- [40] G.C. Lavorato, E. Lima, H.E. Troiani, R.D. Zysler, and E.L. Winkler, “Exchange-coupling in thermal annealed bimagnetic core/shell nanoparticles,” *Journal of Alloys and Compounds* **633**, 333 – 337 (2015).
- [41] S. Sun and H. Zeng, “Size-controlled synthesis of magnetite nanoparticles,” *Journal of the American Chemical Society* **124**, 8204–8205 (2002), PMID: 12105897.
- [42] S. H Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, and G. X. Li, “Monodisperse MFe₂O₄ (M = Fe, Co, Mn) nanoparticles,” *Journal of the American Chemical Society* **126**, 273–279 (2004).
- [43] “See Supplemental Material at URL for additional microstructural information of the core/shell nanoparticles assemblies annealed at different temperature, obtained by TEM and HRTEM microscopy. Further characterization of the as-synthesized and annealed

- Fe₃O₄/CoFe₂O₄ core/shell nanoparticles by thermogravimetric (TGA) and infrared (FT-IR) measurements, and additional magnetic characterization, as the hysteresis cycles as a function of the temperature and ZFC and FC magnetization curves of the annealed nanoparticles, it is also included. See also details of the magnetoresistance temperature evolution of the self-assemblies.” .
- [44] A. López-Ortega, M. Estrader, G. Salazar-Alvarez, S. Estradé, I. V. Golosovsky, R. K. Dumas, D. J. Keavney, M. Vasilakaki, K. N. Trohidou, J. Sort, F. Peiró, S. Suriñach, M. D. Baró, and J. Nogués, “Strongly exchange coupled inverse ferrimagnetic soft/hard Mn_xFe_{3-x}O₄/Fe_xMn_{3-x}O₄ core/shell heterostructured nanoparticles,” *Nanoscale* **4**, 5138–5147 (2012).
- [45] K. L. Krycka, J. A. Borchers, G. Salazar-Alvarez, A. López-Ortega, M. Estrader, S. Estradé, E. Winkler, R. D. Zysler, J. Sort, F. Peiró, M. D. Baró, C.C. Kao, and J. Nogués, “Resolving material-specific structures within Fe₃O₄/γ-Mn₂O₃ core/shell nanoparticles using anomalous small-angle x-ray scattering,” *ACS Nano* **7**, 921–931 (2013), PMID: 23320459.
- [46] R. Skomski and J. M. D. Coey, “Giant energy product in nanostructured two-phase magnets,” *Phys. Rev. B* **48**, 15812–15816 (1993).
- [47] E. F. Kneller and R. Hawig, “The Exchange-Spring Magnet: A New Material Principle for Permanent Magnets,” *IEEE Trans. Magn.* **27**, 3588–3600 (1991).
- [48] G. P. Zhao and X. L. Wang, “Nucleation, pinning, and coercivity in magnetic nanosystems: An analytical micromagnetic approach,” *Phys. Rev. B* **74**, 012409 (2006).
- [49] G. P. Zhao, M. G. Zhao, H. S. Lim, Y. P. Feng, and C. K. Ong, “From nucleation to coercivity,” *Applied Physics Letters* **87**, 162513 (2005).
- [50] T. Leineweber and H. Kronmüller, “Micromagnetic examination of exchange coupled ferromagnetic nanolayers,” *Journal of Magnetism and Magnetic Materials* **176**, 145 – 154 (1997).
- [51] Eric E. Fullerton, J. S. Jiang, and S. D. Bader, “Hard/Soft Magnetic Heterostructures: Model Exchange-Spring Magnets,” *J. Magn. Magn. Mater.* **200**, 392–404 (1999).
- [52] G. P. Zhao, X. L. Wang, Y. P. Feng, and C. W. Huang, “Coherent rotation and effective anisotropy,” *IEEE Transactions on Magnetics* **43**, 2908–2910 (2007).
- [53] J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, 2010).
- [54] G. Lavorato, E. Winkler, B. Rivas-Murias, and F. Rivadulla, “Thickness dependence of exchange coupling in epitaxial Fe₃O₄/CoFe₂O₄ soft/hard magnetic bilayers,” *Phys. Rev. B*

- 94**, 054405 (2016).
- [55] S. Bullita, A. Casu, M. F. Casula, G. Concas, F. Congiu, A. Corrias, A. Falqui, D. Loche, and C. Marras, “ZnFe₂O₄ nanoparticles dispersed in a highly porous silica aerogel matrix: A magnetic study.” *Phys. Chem. Chem. Phys.* **16**, 4843–52 (2014).
- [56] J. Dormann, F. D’Orazio, F. Lucari, E. Tronc, P. Prené, J. Jolivet, D. Fiorani, R. Cherkaoui, and M. Noguès, “Thermal Variation of the Relaxation Time of the Magnetic Moment of γ -Fe₂O₃ Nanoparticles with Interparticle Interactions of Various Strengths,” *Phys. Rev. B* **53**, 14291–14297 (1996).
- [57] J. G. Simmons, “Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film,” *Journal of Applied Physics* **34**, 1793 (1963).
- [58] J. G. Simmons, “Low-voltage current-voltage relationship of tunnel junctions,” *Journal of Applied Physics* **34**, 238 (1963).
- [59] A. Vilan, “Analyzing molecular current-voltage characteristics with the simmons tunneling model: Scaling and linearization,” *J. Phys. Chem. C* **111**, 4431–4444 (2007).
- [60] A.L. Efros and B.I. Shklovskii, “Coulomb gap and low temperature conductivity of disordered systems,” *J. Phys. C: Solid State Phys.* **8**, L49 (1975).
- [61] N.N. Song, H. T. Yang, F. Y. Li, Z.A. Li, W. Han, X. Ren, Y. Luo, X.C. Wang, C. Q. Jin, X.Q. Zhang, and Z.H. Cheng, “Interspace dependence of spin-dependent variable range hopping for cold-pressed Fe₃O₄ nanoparticles,” *Journal of Applied Physics* **113**, 184309 (2013).
- [62] R. Rani, G. Kumar, K. M. Batoo, and M. Singh, “Electric and dielectric study of zinc substituted cobalt nanoferrites prepared by solution combustion method,” *American Journal of Nanomaterials* **1**, 9–12 (2013).
- [63] I.H. Gul, A.Z. Abbasi, F. Amin, M. Anis ur Rehman, and A. Maqsood, “Structural, magnetic and electrical properties of Co_{1-x}Zn_xFe₂O₄ synthesized by co-precipitation method,” *Journal of Magnetism and Magnetic Materials* **311**, 494 – 499 (2007).
- [64] A.V. Ramana Reddy, G Ranga Mohan, B.S Boyanov, and D Ravinder, “Electrical transport properties of zinc-substituted cobalt ferrites,” *Materials Letters* **39**, 153 – 165 (1999).
- [65] S. Barzilai, Y. Goldstein, I. Balberg, and J. S. Helman, “Magnetic and transport properties of granular cobalt films,” *Physical Review B* **23**, 1809 (1981).
- [66] L. L. Balcells, J. Fontcuberta, B. Martinez, and X. Obradors, “Magnetic surface effects and low-temperature magnetoresistance in manganese perovskites,” *Journal of Physics: Condensed*

Matter **10**, 1883 (1998).

- [67] J. S. Moodera, E. F. Gallagher, K. Robinson, and J. Nowak, “Optimum tunnel barrier in ferromagnetic-insulator-ferromagnetic tunneling structures,” *Applied Physics Letters* **70**, 3050–3052 (1997).
- [68] S. Joo, K. Y. Jung, K. I. Jun, D. S. Kim, K. H. Shin, J. K. Hong, B. C. Lee, and K. Rhee, “Spin-filtering affect of thin Al_2O_3 barrier on tunneling magnetoresistance,” *Applied Physics Letters* **104**, 152407 (2014).