Co nanoparticles inserted into a porous carbon amorphous matrix: the role of cooling field and temperature on the exchange bias effect

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We report unusual cooling field dependence of the exchange bias in oxide-coated cobalt nanoparticles embedded within the nanopores of a carbon matrix. The size-distribution of the nanoparticles and the exchange bias coupling observed up to about 200 K between the antiferromagnetic Co-oxide shell (~3-4 nm) and the ferromagnetic Co-cores (~4-6 nm) are the key to understand the magnetic properties of this system. The estimated values of the effective anisotropy constant and saturation magnetization obtained from the fit of the zero-field cooling and field cooling magnetization vs. temperature curves agree quite well with those of the bulk fcc-Co.

Introduction

The fabrication and manipulation of monodispersed metallic and magnetic nanoparticles (NPs) has opened some of the current more promising applications in materials science or biosciences.¹⁻³ Magnetic NPs can be easily manipulated by external magnetic field gradients and thus, be used for separation of different catalytic solids, hyperthermia treatments or magnetic resonance imaging.⁴⁻⁶ In order to use innovative magnetic NPs for artificial engineering, a systematic characterization is needed to control not only the magnetic properties of an individual particle, but also the collective behavior of an ensemble of interacting magnetic NPs.⁷⁻⁹

From the fundamental point of view, magnetic NPs serve as model systems for investigating the Stoner-Wohlfarth, and the Néel-Brown models, to study finite-size effects or magnetic proximity effects.¹⁰⁻¹³ In particular, most of the core-shell systems for potential applications have been prepared from oxidation of transition metal NPs, leading to interface exchange interactions between the core (typically ferromagnetic, FM) and the shell (antiferromagnetic, AFM or ferrimagnetic FIM).^{14, 15} This core-shell morphology often gives rise to striking and independent mechanisms like the hysteresis-loop shift (the so called exchange bias, EB, effect) and the coercivity (H_c) enhancement.¹⁶⁻¹⁹ On the other side, both high magnetization and coercivity are desirable for applications of nanoscale systems in high-density magnetic storage, hard magnets or magnetoelectric devices.²⁰

In particular, EB effect has been intensively studied in Co nanostructured systems (core-shell NPs, nanowires and thin films) obtained through different synthesis routes, with the aim of understanding the origin of microscopic competing mechanisms at the Co/Co-oxide interface.^{10, 21-24} Recently, the observation of EB in Co/CuMn bilayer, with unusual features of a FM in contact with a spin glass (SG), has been reported,²⁵ showing an orientation reversal of the bias field in a small

temperature range just below the blocking temperature, T_B . However, less attention has been paid to the effect of the cooling field on the EB in nanostructured system of Co-nanostructured systems.

In this article, the magnetic properties of Co metal-core/Co-oxide-shell NPs inserted into a porous activated carbon amorphous matrix have been investigated. These nanomaterials were synthesized using a procedure similar to the one reported elsewhere.^{6, 7, 9, 12, 15}

Experimental

The synthesis procedure to fabricate these Co-NPs with a core/shell morphology is based on a pyrolysis process occurring at the restricted volume formed inside the pore intersections of an activated carbon (AC). It was employed a commercial amorphous porous AC supplied by Osaka Gas (Japan) with a large Brunauer-Emmett-Teller (BET) surface area of 2350 m²·g⁻¹ and a high pore volume of 1.47 cm³·g⁻¹. The resulting samples consist in solid powders of micrometer macroscopic sizes, and some grams of mass can be obtained at the same time. More details concerning the methodology for the preparation of these nanomaterials can be found elsewhere.^{4, 6, 9}

The NP size distribution was obtained after measuring the diameter of more than 1500 NPs from several Transmission Electron Microscopy (TEM) images recorded in a JEOL2000-EXII microscope. The samples were prepared by depositing a small amount of powder in ethanol and then, several drops of this solution were placed on carbon-film copper grids.

A room temperature x-ray powder diffraction (XRD) pattern was collected using a Seifert XRD3000 diffractometer, in order to identify the crystalline phases present in the sample. Mo K_α radiation was used instead of Cu K_α for avoiding problems related to the absorption and fluorescence of Co.

Room temperature x-ray absorption spectroscopy (XAS) experiments collected around the Co K-edge (7.709 keV) and up to $k = 18 \text{ \AA}^{-1}$ were carried out at the XAFS beamline (BL 11.1) of the Elettra synchrotron laboratory (Trieste, Italy) in transmission mode.²⁶ Homogeneous layers of the powder sample were prepared for the XAS measurements by spreading the powder over an adhesive Kapton[®] tape. The thickness and homogeneity of the samples were selected to obtain an optimal signal-to-noise ratio. Ionization chambers filled with an optimized gas mixture were used for both incident (I_0) and transmitted (I_1) x-ray intensities. The absorption signal was calculated as $\mu_t = \ln I_1/I_0$. In addition, a reference sample (Co foil) was placed after the I_1 chamber and the transmitted intensity (I_2) was simultaneously measured with a third ionization chamber, in order to calibrate de

energy. The extended x-ray absorption fine structure (EXAFS) spectra were analyzed according to standard procedures and the spectra were normalized to the absorption coefficient averaged at high energy in order to eliminate the dependence of absorption with the sample thickness.

Two kind of magnetic measurements were performed combining SQUID and a Quantum Design PPMS magnetometer with the vibrating-sample (VSM) option: (i) after a zero field cooling (ZFC) from 300 K down to 10 K, it was measured the variation of the magnetization as a function of the temperature between 10 and 340 K, $M_{ZFC}(T)$, and after field cooling (FC), $M_{FC}(T)$. In both cases the applied magnetic field was fixed to $H = 10$ Oe. (ii) the hysteresis loops, $M(H)$, between ± 85 kOe were recorded at $T = 4$ K after cooling the sample from 300 K in zero field and under different values (positive and negative) of the applied magnetic field ranging from 100 Oe to 85 kOe. In addition, the hysteresis loops at several selected temperatures were measured after cooling from 300 K to 4 K under an applied magnetic field of $H = 20$ kOe.

Results and discussion

Morphology and Structural characterization

In Fig. 1a a typical TEM image is shown, where several NPs, with almost spherical shapes, can be visualized. The broad size distribution, ranging from 2 to 40 nm, observed in the histogram of Fig. 1 is quite well described by a log-normal function centered at $\langle \mu(\sigma) \rangle = 10(4)$ nm (Fig. 1b). Figures 1c and 1d show more detailed views of individual NPs with a Co-metal/Co-oxide core-shell morphology, the core being of ~ 4 -6 nm in diameter and a 3-4 nm thick shell.

In Fig. 2 we show the room temperature XRD pattern of the Co-NPs embedded in the AC matrix, where poorly defined crystalline diffraction peaks superimposed to large haloes coming from the predominant (90 %) amorphous carbon matrix are seen. This feature was previously found in other magnetic AC composites.^{9, 15} All the observed peaks can be indexed as the Bragg reflections of metallic cobalt with face centered cubic (fcc) crystal structure ($Fm\bar{3}m$) and a lattice parameter of $a = 3.56(1)$ Å. The rest of the peaks correspond to the reflections of Co_3O_4 oxide with a fcc spinel crystal structure ($Fd\bar{3}m$) and a lattice parameter of $a = 8.12(2)$ Å. The large contribution of the carbon matrix and the low intensity ratio between the diffraction peaks and the background, makes the Rietveld analysis of the XRD pattern very difficult (see Fig. 2), hence, a precise estimation of the mean particle size of the NPs is not possible although the large broadening of the diffraction peaks suggest average particle sizes in the nanometer length scale.²⁷

Fig.1 a) TEM image of the Co-NPs embedded in the porous carbon amorphous matrix. b) Histogram of the diameters of the Co-NPs. c) and d) Details of some NPs with well defined Co-metal-core (4-6 nm)/Co-oxide-shell (3-4 nm) morphologies.

Fig.2 Room temperature powder x-ray diffraction pattern of the Co-NPs embedded in the AC matrix using Mo K_α radiation ($\lambda=0.7107$ Å). Observed (points), calculated (solid line) and difference (bottom) profiles are plotted on the same scale. Bragg peaks are indicated by tick marks. The first row corresponds to fcc-Co, while the second one is associated with Co_3O_4 . No traces of CoO can be resolved.

We show in Fig. 3 the room temperature experimental XANES spectra of the Co-NPs sample and that of the Co foil together with those corresponding to CoO and Co_3O_4 oxides. In order to reproduce the shape, energy position and relative energy separation of the Co-NPs sample spectrum, a weighted sum of 10% of metallic Co + 10% of CoO + 80% of Co_3O_4 , is needed.

Fig. 3 Co K-edge XANES spectra (open circles) together with the simulation (solid red line) calculated considering a mixture of fcc-Co (10%), CoO (10%) and Co₃O₄ (80%). The spectra of the fcc-Co, CoO and Co₃O₄ are also shown for clarity. The difference between the experimental and simulated spectrum is displayed at the bottom of the figure.

Therefore, it can not be discarded the existence of a very thin CoO layer (< 1 nm) in between the metallic core and the thicker (3-4 nm) Co₃O₄ shell, even though it is not possible to find any evidence of its presence from XRD measurements. However, the formation of this thin CoO layer can be explained as a disordered Co₃O₄ spinel-type structure due to a different degree of oxidation between the core/shell interlayer and the oxide shell. Moreover, and as it will be discussed below, the existence of a CoO AFM layer is the key to understand the magnetic behaviour of the system.

Besides that, if we focus our attention to the k^3 -weighted ($k^3\chi$) EXAFS data (see Fig. 4a), we can visualize a completely different sequence of oscillations when comparing both Co foil and Co-NPs sample data. The latter being almost identical to that of Co₃O₄.²⁸ The Fourier transforms (FT) of the k^3 -weighted experimental data corresponding to Co foil and Co-NPs sample are depicted in Fig. 4b. It can be easily observed the completely different radial structure functions. While that of Co foil shows the well-defined peaks corresponding to the first four Co-Co neighbour distances, the FT of the Co-NPs sample resembles that of Co₃O₄ oxide,^{28, 29} with peaks around 1.6, 2.5 and 3 Å, associated with the six Co-O bonds, the four Co-Co bonds (edge-shared CoO₆ octahedra) and the 8 Co-Co bonds (corner-shared CoO₆ octahedra), respectively. However, the contribution of both metallic Co-cores and the CoO thin shell can only be appreciated as slight broadening of the FT peaks and/or shoulder-like features.

Fig.4 Room temperature k^3 -weighted experimental EXAFS data (a) and their Fourier transform plots (b) of Co foil (thin blue line) and Co-NPs (thick red line) measured at Co K-edge.

Magnetic properties

The ZFC and FC temperature dependencies of the magnetization, $M_{ZFC}(T)$ and $M_{FC}(T)$ curves, are depicted in Fig. 5. The $M_{ZFC}(T)$ curve displays two different regimes. Below 150 K an almost flat trend is observed, while the magnetization rapidly augments above this temperature. However, the FC magnetization slightly increases on cooling from 340 K and exhibits a broad maximum at around 220 K. The observed experimental $M_{ZFC}(T)$ and $M_{FC}(T)$ dependencies can be accounted for by using a simple Stoner-Wohlfarth model considering Co-NPs with an almost spherical shape (see Fig. 1a, 1c and 1d). From the fits we obtain: i) an effective anisotropy constant, K_{eff} , value about 2.5×10^6 erg/cm³, close to that of bulk β -Co (fcc) and similar to those previously reported for fcc-Co NPs^{10, 14}; ii) an average diameter for the Co-core around 5 nm in good agreement with that of 4-6 nm estimated from TEM images and, iii) a saturation magnetization (M_s) of 156 emu/g almost equal to that measured at room temperature (see inset of Fig. 5). Contrary to other reported values³⁰ on Co-based nanostructured systems, in which a large discrepancy for M_s respect to the bulk-Co value was attributed to size effects and enhanced surface-to-volume ratio, the proper quantification of Co-metal combining XANES spectroscopy (see Fig. 3) together with the 11 wt.% of Co-metal obtained by TGA, reveals that the magnetization of the Co NP-core is almost the same as that of Co bulk (166 emu/g). The main features shown in Fig. 5 (the quick increase of the ZFC magnetization between 150 and 300K and the slight maximum observed in the FC one at around 220 K) can be

explained by the fact that according to the size-distribution of NPs, most of them are unblocked in the temperature range 150-300 K. However this blocked into superparamagnetic (SPM) mechanism can not describe all the magnetic behaviour of the system because an EB effect is observed below 200 K in the $M(H)$ loops (see below) and, therefore other mechanisms need to be involved. These features have been previously observed in other Co-based nanostructured systems^{14, 31-33} and several explanations have been proposed.

The existence of a certain amount of CoO on the XANES analysis (see Fig. 3) may be responsible for a coupling between the FM Co-core and the AFM CoO (or SPM due to the small size of the CoO grains) interface/shell^{33, 34}. According to recent studies³⁵ the Néel temperature of CoO can be reduced down to 235 K (or lower) from the value of their bulk counterpart [T_N (CoO) $\sim$ 290 K]. However, the maximum observed in the $M_{FC}(T)$ curve can not be due to the AFM CoO because the magnetic signal coming from the FM Co-core (with the same number of Co atoms according to the XANES, see Fig. 3) would completely mask this AFM signal. Other possibility is that the presence of AFM small grains with uncompensated spins and disorder generated by grain boundaries are likely at a very thin (< 1 nm) CoO layer, due to the roughness and intermixing at the interface.^{36, 37} Therefore, the maximum seen in the FC and the EB effect could be associated with the transition into a frozen state of the spin-glass (SG) Co-oxide shell.³⁸

Furthermore, the temperature derivative of the difference between the FC and ZFC magnetizations [see the $d(M_{FC}-M_{ZFC})/dT$ vs temperature curve in the inset of Fig. 5] supports this feature. For temperatures below 150 K the curve is flat with nearly constant values for the $M_{FC}-M_{ZFC}$ difference, indicating a completely frozen magnetic state for the system. In contrast, at higher temperatures, the curve exhibits a broad maximum centered at 220 K, which could be a signature of a progressive unfrozen process of the magnetic moments in the oxide SG shell.³⁹

The fact that the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves do not overlap in the whole temperature range of the measurements, together with the existence of hysteresis in the $M(H)$, curves at 340 K, imply that the system has not reached the fully SPM regime. The latter could be explained considering that the existence of NPs with Co-metal-core diameters larger than 8 nm with the magnetic anisotropy estimated from the fitting (see above) have not unblocked their magnetic moments yet ($T_B > 300$ K). Also the possible magnetic coupling and interactions between the NPs could be responsible for such variation of the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves.^{33, 34}

Fig.5 ZFC-FC magnetization vs temperature curves measured under an applied magnetic field of $H = 10$ Oe. Solid lines correspond to the simulations using a Stoner-Wohlfarth model (see text). Inset: $d(M_{FC}-M_{ZFC})/dT$ vs temperature curve. The arrow is pointing the freezing temperature ~ 220 K (see text).

On the other hand, the $M(H)$ curve measured between ± 85 kOe and at $T = 4$ K, exhibits hysteresis and is symmetric respect to $H = 0$ when the sample is cooled down from 300 K in the absence of any applied magnetic field (ZFC, black solid line in Fig. 6). However, if the sample is cooled down to 4 K under an applied magnetic field, $H_{cool} > 0$, a considerable EB effect is observed and, the $M(H)$ curve shifts horizontally a value (H_{EB}) to the left ($H < 0$), thus indicating the presence of a unidirectional anisotropy. This EB effect, originated from the core-shell interface coupling, decreases its value with increasing temperature, but exist up to $T_{EB} \approx 200$ K, nearby the temperature where the peak in $d(M_{FC}-M_{ZFC})/dT$ vs temperature curve is observed (see inset of Fig. 5). For $T < T_{EB}$ the exchange interaction energy governs the reversal of the Co core magnetic moments.³³ For $T > T_{EB}$ the magnetic moment of the Co atoms both in the core and shell are free to reverse with the applied magnetic field and the $M(H)$ curves do not exhibit any shift from the origin.

Fig. 6 Enlarged views cycles around $H = 0$ of hysteresis loops measured at $T = 4$ K after ZFC (black solid line) and after FC from 300 K ($H_{cool} = +85$ kOe, red open squares and $H_{cool} = -85$ kOe blue full triangles). Note that the $M(H)$ shifts are symmetric (see text). The solid lines are guides to the eye. Inset: $M(H)$ cycles at 300 K.

It is worth noting that on cooling under $H_{cool} = 85$ kOe the negative shift of the $M(H)$ curve (open squares in Fig. 6) is almost equal in magnitude to the positive shift observed when the sample is cooled under $H_{cool} = -85$ kOe (full triangles in Fig. 6). This invariance symmetry (H_{EB} is an odd function of H_{cool}) is due to the fact that the cooling field is applied at 300 K, in the paramagnetic phase of the Co-oxide shell, where there is neither coercivity (H_c) nor remanence (M_r) coming from the shell. Note that H_c is enhanced from ~ 600 Oe in ZFC to ~ 800 Oe for $H_{cool} = \pm 85$ kOe.

In Fig. 7 the H_{EB} dependence on the absolute value of the cooling field ($|H_{cool}|$) at low temperature ($T = 4$ K) is shown. The value of H_{EB} exhibits a fast initial augment with increasing $|H_{cool}|$ up to a maximum value $H_{EB} \approx 0.55$ kOe for $|H_{cool}| = 5$ kOe, and remains almost constant up to the largest cooling fields of $H_{cool} \pm 85$ kOe. When the sample is cooled down to low temperatures under H_{cool} , the offset of the loop is ascribed to the pinned magnetic moments at the FM/SG interface. For $|H_{cool}| < 5$ kOe, H_{EB} increases abruptly because the FM moments can rotate toward the direction of H_{cool} as the cooling field is not strong enough to pin the FM magnetic moments.

In this way, when all the interface magnetic moments are aligned, the increase of H_{cool} has no effect on H_{EB} for becoming greater, reaching a limit. Contrary to other Fe- or Ni- based NP systems where larger H_{cool} could modify the magnetic state of the shell leading to a notorious decrease of H_{EB} , in this Co-based NPs, the effect of a cooling field as large as ± 85 kOe does not strongly influence H_{EB} . The reason of this particular situation could be attributed to the fact that magnetocrystalline anisotropy in Co-based systems is much larger (one order of magnitude or more) than that of Ni or Fe.^{40, 41}

Fig. 7 Cooling field dependence of the exchange bias field, H_{EB} (dotted line is a guide to the eye). Inset: temperature dependence of H_{EB} , measured under a cooling field, $H_{cool} = 20$ kOe. The solid line is a linear fit (see text).

The temperature dependence of H_{EB} , under a cooling field of 20 kOe, is shown in the inset of Fig. 7. It is observed an almost linear decrease, which can be fitted to a $1 - T/T_{crit}$ dependence, according to the predictions of the random-field model of exchange anisotropy.⁴² The obtained critical temperature $T_{crit} \approx 200$ K, corresponds to that at which the H_{EB} vanishes, being lower than 220 K where the maximum of $d(M_{FC} - M_{ZFC})/dT$ vs temperature curve is observed in ZFC-FC measurements.^{21, 43}

Conclusions

In conclusion, we have shown that the effect of the cooling field on the exchange bias, in Co-nanoparticles embedded into a porous carbon amorphous matrix presents remarkable differences at high cooling fields with regard to the behavior found in Fe- or Ni- based systems, because of the larger magnetocrystalline anisotropy of Co. At low temperature the role of Co-oxide in the magnetic behaviour of the system was mainly to induce a coercivity enhancement without a global loss of saturation magnetization of the metallic Co-core respect to the bulk value and to create a moderate EB effect which persists even for $H_{cool} = \pm 85$ kOe. Therefore, our results show that the strong spin disorder at the thick Co-oxide shells does not deteriorate the strong ferromagnetic order of the Co-cores even spin-randomness at the core/shell interface is incorporated. These findings offer new possibilities for studying and manipulating exchange bias effect on the widely studied Co/Co-oxide nanostructured systems.

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Notes and references

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