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Role of conducting polyaniline interphase on the low field magnetoresistance for LSMO-PANI nanocomposites

Mariano Romero[a,*], Ricardo Faccio[a,*], Benjamín Montenegro[a], Milton A. Tumelero[b], Cristiani Campos Plá Cid[c,d], André A. Pasa[c,d], Alvaro W. Mombrú[a,*]

[a] Centro NanoMat/CryssMat & Física, DETEMA, Facultad de Química, Universidad de la República (UdelaR), Montevideo C.P. 11800, Uruguay
[b] Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre C.P. 91501-970, Brazil
[c] Laboratório de Filmes Finos e Superfícies, Departamento de Física, Universidade Federal de Santa Catarina (UFSC), Florianópolis C.P. 88040-900, Brazil
[d] Laboratório Central de Microscopia Electrónica, Universidade Federal de Santa Catarina (UFSC), Florianópolis C.P. 88040-900, Brazil

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ABSTRACT

The aim of the present report is to show the synergistic effect of conducting polyaniline and manganite nanoparticles on the low field magnetoresistance response. We specially focused on the role of the conducting polyaniline interphase in a broad range of temperatures and low applied magnetic fields. Our results showed an increment on the electrical conductivity and enhancement on the magnetoresistance for lower amounts of conducting polyaniline additions with respect to the manganite unloaded samples. We also found that close to room temperature, the changes in magnetoresistance are mostly due to an increment of the spin polarization and spin disorder due to the presence of polyaniline interphase. However, at intermediate temperatures the polyaniline interphase intrinsic magnetoresistance showed an additional contribution to the total negative magnetoresistance response. These results, suggest that conducting polymer interphase shows both passive and active roles in the enhancement of the low field magnetoresistance of inorganic-organic nanocomposites.

1. Introduction

Since the first evidence of large low field magnetoresistance (LFMR) at room temperature for $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) with artificial grain boundaries [1], extensive work regarding the electric and magnetic properties of inorganic ferromagnetic nanomaterials has been performed. This LFMR response arises from the spin polarized transport across magnetic domains boundaries, as it was also earlier observed by Hwang et al. for $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) polycrystalline samples at lower temperatures [2]. The enhancement of this LFMR response is promoted by the presence of grain boundaries disorder, which produces higher spin disorientations in the absence of magnetic fields. This effect leads to an enhancement of the magnetoresistance when a low magnetic field is applied [1,2]. There are several reports studying the consequence of the addition of a secondary phase -typically polymers-, in order to control the microstructure and grain boundary disorder and thus to achieve an enhancement in the low field magnetoresistance [3–10]. In fact, such reports triggered an increasing interest in interphase phenomena in hybrid organic-inorganic nanomaterials due to the potential applications in optical, magnetic and electronic devices. A variety of polymers, mainly of insulator nature have been already used for this purpose showing the required enhancement in the LFMR response [3–10]. However, there are very few studies about the addition of a conducting polymer with an intrinsic organic magnetoresistance (OMAR) response [11–15]. In a previous manuscript, we focused in the study of the magnetoresistance synergistic effect between one of the most studied conducting polymers, polyaniline, due to its organic magnetoresistance response and one of the most common inorganic ferromagnetic manganite, with colossal magnetoresistance response [14]. In that case, we studied the temperature dependence of the LFMR in the diluted manganite nanoparticle regime, focusing mainly in the enhancement of the OMAR response, for which the major response was observed at low temperatures ($T < 100$ K) [14]. In a first approach to the study in a concentrated manganite nanoparticle regime, we have recently reported a direct correlation between the dipole-dipole interactions and the low field magnetoresistance response at room temperature [15]. However, limited attention was paid to the polyaniline interphase contribution to the total magnetoresistance response as a function of the applied magnetic field in a broader range of temperature. In the present report, we aim to show the synergistic effect on these nanocomposites, focusing in the contribution of the polyaniline thin interphase between the manganite nanoparticles and its

* Corresponding authors.
E-mail addresses: mromero@fq.edu.uy (M. Romero), rfaccio@fq.edu.uy (R. Faccio), amombru@fq.edu.uy (A.W. Mombrú).

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consequences on the electric and magneto-electric transport.

2. Materials and methods

LSMO-PANI nanocomposites were prepared using $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) nanoparticles synthesized by the polymer precursor method and sulfonate doped-polyaniline emeraldine salt (PANI) as previously reported [15]. Briefly, LSMO nanoparticles and PANI were mixed, grinded and pelletized at a pressure of 60 kN during 10 min using 0, 10 and 20% weight fractions of PANI. The pellets were then annealed at T = 473 K during 30 min under a 20 mL/min nitrogen flow to promote a low temperature sintering and avoid PANI partial decomposition at the nanocomposite interphase. TEM images were taken at 200 kV using a JEOL JEM 2010 after previous dispersion of the powders in isopropyl alcohol, sonication in aqueous bath for 10 min and deposition onto a carbon holey film. FT-IR spectra were obtained using a Shimadzu Prestige 21 FT-IR spectrometer using KBr pellets in the range of 400–4000 cm^{-1} by averaging 30 scans with a 4 cm^{-1} for each spectrum. Infrared spectra simulation was performed using density functional theory (DFT) [16,17] selecting the hybrid exchange correlation potential B3LYP [18–21] for a 6–31 + + G(d,p) basis set, as implemented in Gaussian 09 [22]. For the purpose of this work, we calculate infrared spectra for a two-monomer polyaniline oligomer in its emeraldine salt conformation, after a full structural optimization. DC resistivity measurements were obtained in the T = 20–300 K temperature range using the four-probe technique. Magnetoresistance (MR) was calculated following $MR(\%) = 100.(\rho_H - \rho_0)/\rho_0$, with ρ_H as the DC resistivity with ($0 < H < 5$ kOe) and ρ_0 as the resistivity without applied magnetic field (H = 0) in the T = 20–300 K temperature range.

3. Results and discussion

Fig. 1a presents a scheme of PANI interphase covering the LSMO nanoparticles. Transmission electron microscopy (TEM) images for LSMO-PANI-X nanocomposites are shown in Fig. 1b. The presence of nanoparticles with a quasi-spherical shape sized between D = 30–50 nm is observed and the formation of clusters is also evidenced. TEM bright field (TEM-BF) mode images show the presence of the polymer interphase in these nanocomposites with a ~2 nm thickness, as shown in Fig. 1c. The selected area electron diffraction (SAED) pattern for LSMO nanoparticles is also shown in Fig. 1d, revealing the presence of spots with distance to center expected for *(h k l)* reflections belonging to orthorhombic symmetry with *Pbnm* space group in agreement with X-ray diffraction analysis already reported for these nanocomposites [15]. The microstructure of these samples was rigorously studied in our previous report by means of small angle X-ray scattering revealing a mean nanoparticle size of D ~ 40 nm and mean separation distances of d = 1–2 nm for all nanocomposites [15]. The non-zero but slight separation between LSMO nanoparticles (d ~ 1 nm) in the absence of polymer additions (X = 0), could be related to a remaining degree of porosity due to the low temperature of sintering.

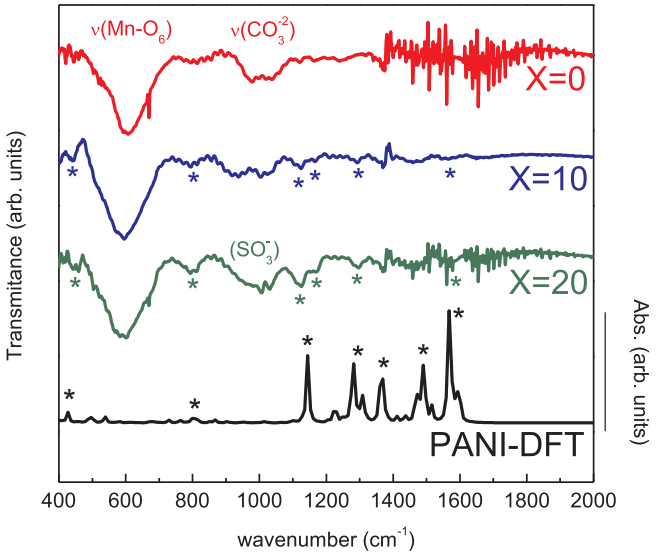

Fig. 2. FT-IR spectra for LSMO-PANI-X nanocomposites with X = 0, 10 and 20. The vibrational modes ascribed to PANI are marked with asterisks. The DFT simulated infrared spectra for a PANI oligomer in the emeraldine salt conformation is shown for comparison.

FT-IR spectra for LSMO-PANI-X nanocomposites are shown in Fig. 2. FT-IR spectra of pure LSMO sample showed a typical broad peak at

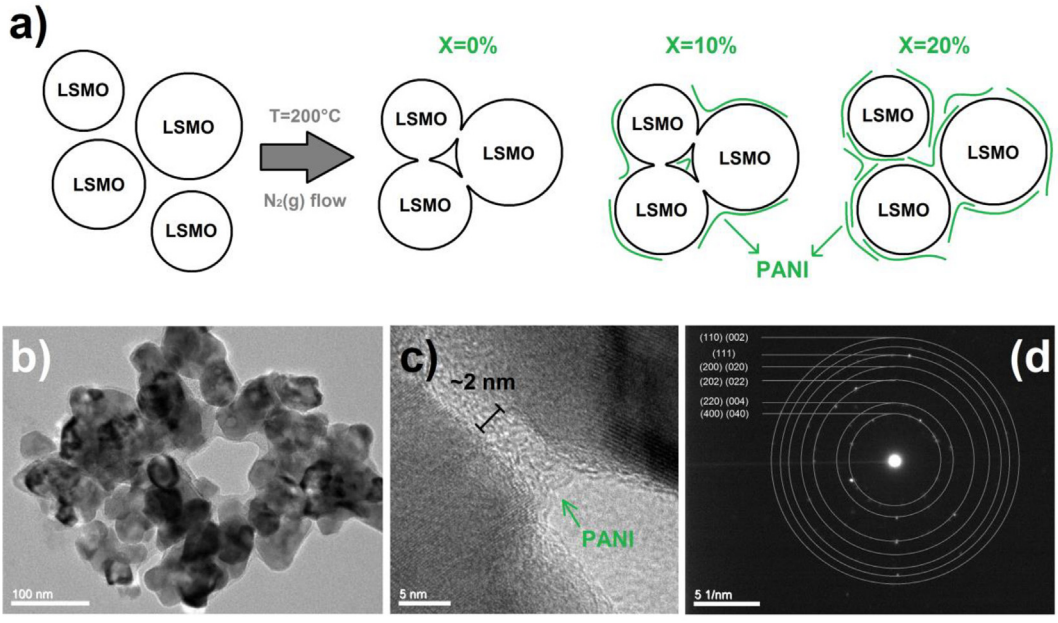

Fig. 1. (a) Scheme of the preparation procedure of LSMO-PANI-X nanocomposites with X = 0, 10 and 20. (b,c) TEM-BF images and (d) selected area electron diffraction (SAED) pattern showing most relevant *hkl* reflections for LSMO-PANI-X = 10 nanocomposite.