Cite this: *J. Mater. Chem. C*, 2016, 4, 2252

Graphene enhances the magnetoresistance of FeNi₃ nanoparticles in hierarchical FeNi₃–graphene nanocomposites†

G. Abellán,^{‡ab} H. Prima-García^{‡a} and E. Coronado^{*a}

An increase in the giant magnetoresistance of FeNi₃ nanoparticles of 20 times has been observed in FeNi₃–graphene nanocomposites synthesized using NiFe-layered double hydroxide hybrids as precursors. The magnetic, transport and magneto-transport properties of these nanocomposites are studied and compared with those of the pure FeNi₃ nanoparticles. The hierarchical structure and hybrid composition of these magnetic nanocomposites lead to the observation of two unusual magneto-transport properties, namely (i) an enhancement in the low-field magnetoresistance effects, and (ii) a crossover from negative to positive MR upon cooling down the sample.

Received 30th December 2015,
Accepted 17th February 2016

DOI: 10.1039/c5tc04445f

www.rsc.org/MaterialsC

1. Introduction

Magnetoresistance (MR) is a phenomenon that reflects the resistance change of a material when an external magnetic field is applied to it, and can be categorized into five distinct types including ordinary magnetoresistance (OMR), anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), tunnelling magnetoresistance (TMR) and colossal magnetoresistance (CMR).¹ The discovery of GMR in magnetic multilayers² and subsequently in magnetic granular films^{3,4} opened a new perspective in the development of innovative materials for applications such as biological detection,⁵ magnetic recording and information storage.⁶

In particular, polymer nanocomposites with functional particles have created much interest due to their cost-effective processability and high flexibility rendering possible many applications such as microwave absorbers⁷ or smart stimuli-responsive materials.⁸ These polymer nanocomposites can be considered as granular systems, in which the GMR originates from the spin-dependent scattering of conduction electrons at the interface between the ferromagnetic particles and the nonmagnetic matrix, as well as within the ferromagnetic particles. Indeed, GMR has a close relationship with the local magnetization of ferromagnetic nanoparticles (NPs). However, the magnitude of MR depends on various factors, such as the magnetic to non-magnetic

constituent ratio, the chemical nature of the matrix, the size and shape of the particles and also the inter-particle (grain) distance.³ Therefore, the nature of the nonmagnetic matrix plays a crucial role in these sorts of nanocomposites. Compared to multilayers, the advantage of granular films is the ability to change the size of magnetic NPs and the microstructures, varying completely their magnetoresistance properties.⁹

Beyond traditional materials, graphene is being widely studied as a functional matrix due to its superior electronic properties. The direct exposure of the active-conducting area of graphene to the external world, and the expected long spin coherence lifetimes and lengths, makes this 2D material suitable for spintronics.¹⁰ Until recently, graphene has been considered a nonmagnetic material, but now numerous investigations are focused on studying its MR properties.^{11–13} In this sense, organic magnetoresistance (OMAR) has recently been found in graphene, few-layer graphene, nanotubes or carbon spheres among other carbon-based materials.^{14,15} Moreover, our group has recently described how the chemical doping of graphene with electronically active organic functionalities can modify its MR response.¹⁶

Herein we will study the chemically designed magnetic nanocomposites recently reported by our group, which are formed by magnetic FeNi₃ NPs embedded in a graphene matrix.^{17,18} We will incorporate graphene as a matrix in granular magnetic nanocomposites. In these hybrid materials, the close proximity between the two components may lead to strong synergistic interactions between electronic conductivity and magnetism, which may result in new MR effects. Thus, we will show that the presence of the graphene shell in these hierarchically structured materials provokes a large enhancement of the GMR compared to the pristine FeNi₃ ferromagnetic NPs, operating at low magnetic fields up to 500 G, and a crossover in the MR

^a Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Catedrático José Beltrán 2, 46890 Paterna, Spain. E-mail: eugenio.coronado@uv.es; Fax: +34 96 354 3273; Tel: +34 96 354 4419

^b Department of Chemistry and Pharmacy and Institute of Advanced Materials and Processes (ZMP), University Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen and Dr.-Mack Str. 81, 90762 Fürth, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5tc04445f

‡ These authors contributed equally to this work.

effects which change from negative to positive upon cooling down the sample.

2. Experimental section

Synthesis materials

All chemicals, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$ (sebacic acid), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80%), NaOH, KOH, benzyl alcohol and ethanol (Sigma-Aldrich and Fluka), were used as received without further purification. Ultrapure water was obtained from Millipore Milli-Q equipment.

Preparation of FeNi_3 -carbon nanocomposites ($\text{FeNi}_3\text{-G}$)

The precursor LDH material NiFe-sebacate (NiFe-Seb) was prepared following the general method described previously by our group, using sebacic acid/NaOH.¹⁹ In a typical synthesis, the salts of nickel and iron were dissolved in deionized water, keeping the stoichiometric coefficient $x = \text{M}^{\text{III}}/(\text{M}^{\text{II}} + \text{M}^{\text{III}})$ at the value of $x = 0.33$ and the total metal concentration constant at 1 M. A second solution of NaOH and sebacic acid was also prepared using deionized water. Both solutions were mixed together by dropwise addition to form thick slurry with a fixed pH of 7. Subsequently, the slurry was heated up to 80 °C under constant stirring, and kept at this temperature for 4 days at atmospheric pressure. The solid was then filtered, abundantly washed with water and ethanol, and dried at room temperature under vacuum. All procedures were carried out under an argon atmosphere to avoid incorporation of carbonate anions adsorbed from atmospheric CO_2 into the final precursor. Furthermore, the pH of the synthetic gel was controlled to avoid formation of solid phases different from LDH. The $\text{FeNi}_3\text{-G}$ nanocomposites were obtained by calcination under a nitrogen atmosphere for 6 hours at 900 °C in a programmable oven with a 1 °C min^{-1} scan rate and a nitrogen flow of 80 mL min^{-1} . The carbon matrixes of the as-synthesized nanocomposites were obtained by sonication and acid leaching of the same with 2 M hydrochloric acid for 48 hours with magnetic stirring.

Preparation of FeNi_3 nanoparticles ($\text{FeNi}_3\text{-NP}$)

The synthesis of $\text{FeNi}_3\text{-NP}$ was achieved following the method recently described by our group.²⁰ In a typical procedure, 7.5 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 22.5 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL of benzyl alcohol. After that, the mixture was heated up to 80 °C in a thermostatic bath for *ca.* 30 min. Afterwards, a 5 M NaOH solution was drop-wise added to the mixture until it reached a pH of *ca.* 11. Then, 13 mL of hydrazine hydrate was added, followed by gas evolution, as well as the precipitation of small black particles. This reduction procedure was set for 30 min. Finally, the particles were collected using a magnet and washed with Milli-Q water and EtOH several times, and then dried in an oven at 60 °C for 5 h. EDAX microanalysis gave a Ni : Fe ratio of 2.82(± 0.06).

Physical characterization

HRTEM studies of the hybrid material were carried out on a JEM-2010 microscope (JEOL, Japan) operating at 200 kV.

Samples were prepared by dropping a sonicated suspension of the sample in ethanol on a carbon-coated copper grid. The digital analysis of the HRTEM micrographs was done using Digital Micrograph TM 1.80.70 for GMS 1.8.0 by Gatan. The magnetic properties of the nanocomposites at different temperatures were measured using a physical properties measurement system (PPMS-9) by Quantum Design. The susceptibility data were corrected by removing the diamagnetic contributions as deduced by using Pascal's constant tables. X-ray photoelectron spectroscopy measurements were performed in an ultra-high vacuum system ESCALAB210 (base pressure 1.0×10^{-10} mbar) from Thermo VG Scientific. Photoelectrons were excited by using the Mg-K α line (1253.6 eV). All spectra were referred to the Fermi level. Temperature dependent conductivity (σ) and magnetoresistance (MR) were measured using a standard four-probe method with Pt wire as leads in PPMS-9 equipment, in the temperature range between 2 K and 300 K using Keithley devices, a current source (model 2400) and an electrometer (model 6154). Electrical contacts were made with highly conducting silver paints. Sample sizes were approximately 3 mm^2 . The powders of nanocomposites were pressed into pellets for resistivity and MR measurements.

3. Results and discussion

Structural characterization

Our synthetic approach involves the facile thermal decomposition of hybrid sebacate-intercalated catalytic $\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}$ layered double hydroxides (LDH) at 400 °C leading to a hybrid consisting of $\text{FeNi}_3\text{-NP}$ embedded in a carbon nanoform matrix.^{17,19,21} Interestingly, if the calcination step is increased to 900 °C, a graphene matrix instead of the as-reported carbon nanoforms is formed.^{18,22,23} The nanocomposite consists of well dispersed highly crystalline FeNi_3 nanoparticles of small dimension (average size *ca.* 20–50 nm) embedded in a graphene matrix, which facilitates the imaging of lattice fringes and “graphitic” coatings (Fig. 1 and Fig. S1, ESI†). A detailed observation of the nanocomposite reveals that the NPs are heterogeneously distributed on the graphene, forming a series of aggregates. The distance between these aggregates can be of several nanometres on the basis of HRTEM observations. The measured *ca.* 0.34 nm spacing for the carbon coating is consistent with literature values for the interlayer spacing of graphene.^{18,24} As evidenced by HRTEM, highly corrugated graphene sheets surrounding the metal NPs can be observed (Fig. 1B–D). The intricate structure of the graphene matrix is related to the evolution of the previous carbon nanoions (CNO) obtained at 400 °C.^{18,19} Clear evidence of this assumption could be obtained from HRTEM images of the hybrids depicted in Fig. 1E, in which a deployed graphene monolayer from a CNO can be clearly seen. Highly corrugated single- to few-layer graphene sheets surrounding $\text{FeNi}_3\text{-NP}$ can be observed in several areas, having good flexibility; moreover, this morphology reveals how close the particles are, showing a minimum carbon coating of *ca.* 2 nm. Thereby, this chemical approach provides a model system to study the new MR effects

Fig. 1 (A) XRD pattern of the **FeNi₃-G** nanocomposite synthesized at 900 °C. (B and C) High-resolution TEM micrographs of the **FeNi₃-G** nanocomposite synthesized at 900 °C showing the carbon shell, the NPs and the carbon nanoforms. (D) HRTEM image highlighting the morphology of the graphene surrounding the metal NPs. (E) HRTEM image showing the deployment of a graphene monolayer from a carbon nano-onion. (F) Hysteresis loops of the nanocomposite at different temperatures ranging from 2 to 350 K. The inset shows the low-field area.

arising when magnetic NPs and corrugated graphene are placed in close proximity. For comparative purposes we have synthesized highly crystalline and monodisperse **FeNi₃-NP** following a sol-gel methodology recently described by our group (see Fig. S2, ESI†).²⁰ These NPs show a size of *ca.* 80 nm, which is around two times the size estimated in the **FeNi₃-G** nanocomposites (in the range 20–50 nm), and interparticle distances of less than 1 nm in those which are connected.

In order to get some insights into the surface of the materials, X-ray photoelectron spectroscopy (XPS) was used, confirming the presence of Fe and Ni in both **FeNi₃-NP** and **FeNi₃-G** nanocomposites (Fig. S3, ESI†). Each of the two spin-orbit components of the Ni 2p spectra shows three resolved features; those located at 853.2 and 856.4 eV can be attributed to metallic and divalent Ni (mainly NiO and Ni(OH)₂), respectively, whereas the one located at 862.5 eV can be attributed to the so-called 6 eV Ni satellite.^{25,26} The Fe 2p survey revealed photoelectron peaks at around 707.7, 711 and 725 eV, confirming the presence of zero-valent iron (Fe 2p_{3/2}) and oxidized Fe(II) and/or Fe(III). In order to account for the differences between the samples, we analysed the O 1s level, revealing that the oxygen content of FeNi₃ nanoparticles coated with graphene

decreases sharply in comparison with the pristine **FeNi₃-NP**, indicating a less oxidized surface (Fig. S4, ESI†). It is worth saying that graphene has been previously reported as an effective protective shell for Ni electrodes.²⁷ All of the XPS spectra have been corrected to the position of the C1s peak at 284.60 eV.¹⁹

Magnetic measurements

As depicted in Fig. 1F, we performed magnetic measurements of the **FeNi₃-G** nanocomposite at temperatures ranging from 350 K to 2 K. A ferromagnetic behaviour is observed in the isothermal magnetization *vs.* *H* curves with no significant differences as a function of temperature.²⁸ The magnetization curves saturate at fields higher than 1.5 T reaching a saturation value of 122 emu g⁻¹, in excellent agreement with the values reported for bulk permalloy.²⁹ The coercive force is *ca.* 20 G, being characteristic of soft ferromagnets.³⁰

On the other hand, **FeNi₃-NP** exhibit a similar saturation magnetization value (115 emu g⁻¹) with a coercive field of *ca.* 90 G, which is four times larger than that for **FeNi₃-G** (Fig. S5, ESI†). This is probably due to the oxide shell formed around the metallic NPs, which is thinner for the **FeNi₃-G** nanocomposite, as demonstrated by the XPS analysis (Fig. S4, ESI†). The hysteresis

loop measured upon field cooling to 2 K from 300 K shows a shift in the coercive field, indicative of an exchange bias effect (H_{ex}). The presence of exchange bias in these samples may arise from the interactions between the surface antiferromagnetic spins and the ferromagnetic FeNi_3 core spins.³⁰ Since this exchange bias depends on the thickness of the AF oxide layer, the smaller coercive field encountered in the FeNi_3 -G nanocomposite simply reflects the lower thickness of the oxide layer in this system.³¹

Electrical transport measurements

The electrical conductivity of the nanocomposite was measured by a standard four-probe method in compressed pellets. One can observe that the conductivity decreases by two orders of magnitude upon cooling the sample from 300 K (σ of 3.09 S cm^{-1}) to 2 K (0.078 S cm^{-1}) (Fig. 2A), the decrease becoming much sharper below 20 K. In addition, temperature dependent I - V measurements also show strong temperature dependence (Fig. 2B) with a thermal transition from metallic to semiconducting behaviour at *ca.* 20 K.³²

This behaviour is probably due to the specific hierarchical structure of the nanocomposite. At this point, it is important to separately study the two components of the nanocomposite (*i.e.*, the FeNi_3 -NP and the carbon matrix) in order to elucidate the conduction mechanisms.

In a first step, we have characterized the pristine monodisperse FeNi_3 -NP (see Fig. S2, ESI†).²⁰

The electrical transport on pressed pellets demonstrates the metallic character of the NPs above 20 K, with a conductivity at

room temperature of 2.300 S cm^{-1} . Below 20 K a small curvature of the straight line has been observed, which is possibly induced by the amorphous oxide shell that covers the metallic NP (see Fig. S6, ESI†).³³ Notice that the conductivity values in the FeNi_3 -NP are one order of magnitude smaller than those found for the bulk.³⁴ This difference indicates that the electron scattering (or tunnelling) at the interface of the NPs produces higher barriers than the grain boundary in the bulk material. In addition, the conductivity of the FeNi_3 -NP is three orders of magnitude larger than that encountered in the FeNi_3 -G nanocomposites, indicating that the graphene layer significantly blocks the electrons and increases the interface barrier.

The observation of nonlinear symmetric I - V curves at temperatures lower than 20 K for FeNi_3 -G also confirms the existence of a tunnelling barrier for the FeNi_3 -G nanocomposite as shown in Fig. 2B.

In a second step and for comparative purposes, we tried to isolate the carbon matrix *via* acid leaching of the nanocomposite. The as-obtained product consists of a highly defective non-magnetic corrugated graphene matrix, exhibiting a typical semiconducting behaviour. The electrical conductivity of this blank is sharply reduced to $1.3 \times 10^{-6} \text{ S cm}^{-1}$ at 300 K and to *ca.* $9 \times 10^{-13} \text{ S cm}^{-1}$ at 2 K, indicative of the damage induced by the acid leaching procedure (Fig. S7, ESI†). These control experiments show that the graphene matrix surrounding the metallic NPs plays a crucial role in the electrical behaviour of the FeNi_3 -G hybrid nanocomposites. In fact, the deviation from the metallic behaviour observed at low temperatures in the I - V curves is probably related to the semiconducting character of the graphene matrix, although we expect that the pristine matrix is much less defective than the isolated one.

Conduction mechanisms

A good understanding of the conduction mechanisms is of utmost importance in order to elucidate the magneto-transport behaviour. All the measurements support the presence of two different conduction mechanisms, which are strongly influenced by temperature: (a) Ohmic region, where $I(V)$ is linear with the voltage, for temperatures ranging from 300 K to *ca.* 20 K. In this region metallic conductance is observed. (b) Non-ohmic region, where the $I(V)$ curves show a non-linear behaviour, and the I - V curves show zero conductance in the low voltage area, indicating the appearance of a gap.

Accordingly, in this graphitic matrix the NPs are well described by arrays of localized electrons interacting through long-range Coulomb forces.³⁵ In the frame of this model, the transition to nonlinear I - V curves at low temperature is expected to appear when the thermal energy is lower than the Coulomb interaction energy, a phenomenon known as Coulomb blockade (Fig. S9, ESI†).^{35,36} Similar transitions have been observed in nanocomposites and nanowires embedded in a carbon matrix^{33–37} and in granular materials.³² In order to show the transition and Coulomb gap much more clearly, a plot of the calculated dI/dV differential conductance curves vs. V at different temperatures is represented in Fig. S9B (ESI†). The dI/dV curves have a pronounced minimum at low temperatures, with the suppression of conductance

Fig. 2 (A) Temperature dependence of the conductivity for the FeNi_3 -G nanocomposite. (B) I - V curves for the FeNi_3 -G nanocomposite.

around zero bias, which indicates the gradual opening of a Coulomb gap. Above 10 K the Coulomb gap becomes filled by thermal excitations and almost vanishes at 20 K.

From a macroscopic point of view, the different conducting regions can be described by two different conduction mechanisms: in the first region ($20 < T < 300$ K) the conductivity follows a thermal activation mechanism given by the Arrhenius formula $\sigma_1 = \sigma_{01} \exp(-\Delta E/kT)$, (300 to 20 K), where σ_{01} is a constant and ΔE is the activation energy. The best fit of the data gives $\sigma_{01} = 3.33 \text{ S cm}^{-1}$ and $\Delta E = 1.83 \text{ meV}$ (Fig. S8A, ESI†). Interestingly, the value of ΔE is comparatively lower than that reported for MWCNT composites (in the range from 14 to 30 meV).³⁸ This lower activation energy may be due to the close contacts existing between these conductive NPs, which facilitate electron hopping across the NPs.

In the second region ($2 < T < 20$ K) the conductivity shows a sharp decrease and the electronic transport is dominated by strong Coulomb interactions. In this region the conductivity follows the Efros-Shklovskii variable range hopping mechanism (ES-VRH) depicted by $\sigma_2 = \sigma_{02} \exp - (T_0/T)^{1/2}$, with $\sigma_{02} = 5.4 \text{ S cm}^{-1}$ and $T_0 = 39 \text{ K}$, where T_0 is the characteristic temperature that determines the thermally activated hopping among localized states that occurs at low temperatures (Fig. S8B, ESI†).^{35,39}

This parameter is considered as a measure of the disorder and gives an idea about the crossover temperature where the metallic to semiconductor transition occurs. These values are similar to those reported in nanocomposites formed by iron doped amorphous carbon.⁴⁰

Magnetotransport measurements

These measurements were performed in the 2–300 K temperature range from pressed pellets. The data were recorded several times in different samples showing a good reproducibility. Fig. 3A and B shows the MR of the **FeNi₃-G** nanocomposites calculated from the expression $\text{MR} (\%) = (R(H) - R(0))/R(0) \times 100$, where $R(0)$ and $R(H)$ are the resistance at zero and at an applied field H , respectively.

From these measurements there are two remarkable features that are worth mentioning: (i) the enhancement of the MR when the magnetic NPs are embedded in a graphene matrix and (ii) a thermal crossover in the MR, which changes from negative at high temperatures ($\sim 3\%$ at 300 K at an applied magnetic field of 40 kG) to positive when the temperature decreases below 20 K (Fig. 3C) until reaching a maximum value of $\sim 6\%$ at 2 K and low field (500 G) with a bias of 0.5 V.

The enhancement of the MR can be clearly seen by comparing the MR of the **FeNi₃-NP** with that of the **FeNi₃-G** nanocomposite. In these samples a low field MR (LFMR) effect is observed, which reaches its maximum value at 2 K. Thus, in the nanocomposite, the MR vs. H curve at 2 K exhibits a sharp peak centred at zero field, which increases in MR from 0 to 6% upon application of a magnetic field as small as 500 G. In the **FeNi₃-NP** a positive MR with a LFMR effect is also observed. Still, this low-field MR effect is significantly lower (less than 0.6% at 2 K) and occurs in a much more limited temperature range (below 2 K) than for the **FeNi₃-G** nanocomposite.

Fig. 3 (A) Magnetoresistance of **FeNi₃-G** nanocomposites versus applied magnetic field, H , measured at 2 and 300 K, with an applied voltage of 0.5 V. (B) Zoom-in view of the low-field MR. (C) Temperature dependence of the resistivity at zero magnetic field and at a magnetic field of 0.1 T.

The low-field effects are usually associated with the presence of magnetic NPs and arise from the spin-polarized tunnelling occurring between neighbouring NPs. Such a process depends on the distance between the NPs and the nature of the surrounding matrix⁴¹ since it may determine the interparticle tunnelling. These effects have been observed for example in core-shell structured $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ NPs, revealing a -20% LFMR effect at 5 K, which has been attributed to the presence of non-crystalline insulating layers.⁴²

In the nanocomposite material, the interparticle tunnelling is governed by the AF metal-oxide shell surrounding the **FeNi₃-NP** and the graphene matrix, which behaves as an insulating thin layer at low temperatures. The **FeNi₃-G** shows a MR ratio of 6% in an applied field of 1000 G while the MR ratio for pure **FeNi₃-NP** at the same magnetic field (Fig. 4) is only 0.3% (*i.e.*, lower by a factor of 20). In the **FeNi₃-NP** system the spin-polarized tunnelling occurs solely through a metal-oxide shell,

Fig. 4 (A) Magnetoresistance vs. applied magnetic field curves of the $\text{FeNi}_3\text{-NP}$ measured at low temperatures. (B) Zoom-in view of the LFMR for the magnetoresistance curves at 2 K.

which is thicker than that encountered in $\text{FeNi}_3\text{-G}$, while in the last system the graphene is also surrounding the neighbouring NPs. This illustrates the significant role exerted by the graphene shell in the enhancement of the MR effect, improving the interface between the ferromagnetic NPs and showing it to be a more effective interface than the metal-oxide layer in transmitting the spin information. The observed improvement of the MR properties demonstrates that graphene may be a promising candidate for applications in spintronics.

As far as the crossover in the MR is concerned, its mechanism can be summarized as follows:

(i) Negative MR. For the high temperature range (from 300 K to 20 K) the resistance decreases when a magnetic field is applied (Fig. 3A). Hopping between the localized states of the $\text{FeNi}_3\text{-NP}$ and hopping between different graphene sheets mainly govern the transport mechanism for this range. The MR measurement indicates that the surface spins of the $\text{FeNi}_3\text{-NP}$ can be aligned by an external applied magnetic field, resulting in a significant reduction of the resistance. In contrast to bare polycrystalline systems (e.g. $\text{Ni}_{80}\text{Fe}_{20}$, Fe_3O_4 , CrO_2 or Prussian Blue analogues, among others), the incorporation of graphene appears to exert a crucial role, reducing the magnetic fields required to saturate the MR.^{43,44} Similar GMR effects have been reported by Guo *et al.* in magnetic nanocomposites formed by core-shell magnetic NPs disposed on the surface of graphene sheets.⁴⁵

(ii) Positive MR. For the low temperature range (from 20 K to 2 K) the resistance increases when a magnetic field is applied (Fig. 3B). In this regime, the ES-VRH process due to the

enhanced Coulomb interactions between charge carriers dominates the electronic transport of the $\text{FeNi}_3\text{-G}$ nanocomposite at low temperatures. Consequently, the presence of a magnetic field results in a decrease in the hopping probability of the carrier transport, causing an increase in the resistance and finally leading to positive MR.³⁵ An optimal fit of the MR curves of both the pristine $\text{FeNi}_3\text{-NP}$ and $\text{FeNi}_3\text{-G}$ samples has been obtained using the ordinary magnetoresistance (OMR) (Fig. S12, ESI†). This demonstrates that the positive MR in the samples depends, at low temperature, on the Lorentz force on the mobile charges.

Examples describing crossover phenomena from positive to negative MR are very scarce and include spinels with magnetic phase transitions⁴⁶ and graphene monolayers with controlled induced disorder.⁴⁷ As far as we know, this is the first example of a graphene-based nanocomposite showing this striking and unusual effect.

Conclusions

All of our data indicate that we have ferromagnetic NPs embedded in a graphene matrix forming a granular nanocomposite whose matrix conductivity can be tuned with temperature (conductive at high temperatures and insulating below 20 K), thus offering the possibility of modulating the MR behaviour.⁴⁸

This unprecedented hierarchical structure herein obtained by a cost-effective chemical methodology exhibits an enhancement of the GMR with temperature-dependent crossover and low-field MR. These hybrid nanocomposites show a 20 times higher MR ratio than the pristine NPs, demonstrating experimentally the important role exerted by graphene in the improvement of the spin injection. Moreover, as these magnetic nanocomposites have also exhibited promising performances as electrochemical capacitors,^{17,18} a magnetic control over the charge or discharge process can be envisioned, aiming at improving the properties of the resulting magneto-supercapacitive devices.

Acknowledgements

Financial support from the EU (ERC Advanced Grant SPINMOL), the Spanish MINECO (MAT2014-56143-R co-financed by FEDER and Excellence Unit “María de Maeztu” MDM-2015-0538), and the Generalitat Valenciana (Prometeo Program and ISIC-Nano) is gratefully acknowledged. We thank the Universidad de Valencia for support from the VLC/CAMPUS and INNOCIDE program. G. A. thanks the EU for a Marie Curie Fellowship (FP7/2013-IEF-627386). We also acknowledge Prof. J. Yakhmi for helpful scientific discussions, as well as J. M. Martínez and G. Agustí for magnetic measurements and J. V. Usagre for his chemical help.

Notes and references

- 1 B. Hu and Y. Wu, *Nat. Mater.*, 2007, **6**, 985–991.
- 2 M. N. Baibich, J. M. Broto, a. Fert, F. N. Van Dau, F. Petroff, P. Eitenne, G. Creuzet, a. Friederich and J. Chazelas, *Phys. Rev. Lett.*, 1988, **61**, 2472–2475.

- 3 J. Q. Xiao, J. Samuel Jiang and C. L. Chien, *Phys. Rev. Lett.*, 1992, **68**, 3749–3752.
- 4 a. Berkowitz, J. Mitchell, M. Carey, a. Young, S. Zhang, F. Spada, F. Parker, a. Hutten and G. Thomas, *Phys. Rev. Lett.*, 1992, **68**, 3745–3748.
- 5 G. Li, S. Sun, R. J. Wilson, R. L. White, N. Pourmand and S. X. Wang, *Sens. Actuators, A*, 2006, **126**, 98–106.
- 6 J. M. Daughton, *Thin Solid Films*, 1992, **216**, 162–168.
- 7 B. Sareni, L. Krahenbuhl, A. Beroual and C. Brosseau, *J. Appl. Phys.*, 1996, **80**, 4560.
- 8 H. Koerner, G. Price, N. A. Pearce, M. Alexander and R. A. Vaia, *Nat. Mater.*, 2004, **3**, 115–120.
- 9 H. Sang, N. Xu, J. Du, G. Ni, S. Zhang and Y. Du, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **53**, 15023–15026.
- 10 A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer and M. Affronte, *Nano Lett.*, 2011, **11**, 2634–2639.
- 11 F. Muñoz-Rojas, J. Fernández-Rossier and J. J. Palacios, *Phys. Rev. Lett.*, 2009, **102**, 136810.
- 12 Z.-M. Liao, H.-C. Wu, S. Kumar, G. S. Duesberg, Y.-B. Zhou, G. L. W. Cross, I. V. Shvets and D.-P. Yu, *Adv. Mater.*, 2012, **24**, 1862–1866.
- 13 J. Jobst, D. Waldmann, I. V. Gornyi, A. D. Mirlin and H. B. Weber, *Phys. Rev. Lett.*, 2012, **108**, 106601.
- 14 H. Gu, X. Zhang, H. Wei, Y. Huang, S. Wei and Z. Guo, *Chem. Soc. Rev.*, 2013, **42**, 5907–5943.
- 15 J. A. Carrasco, H. Prima-Garcia, J. Romero, J. Hernandez-Saz, S. Molina, G. Abellán and E. Coronado, *J. Mater. Chem. C*, 2016, **4**, 440–448.
- 16 C. Bosch-Navarro, F. Busolo, E. Coronado, Y. Duan, C. Martí-Gastaldo and H. Prima-Garcia, *J. Mater. Chem. C*, 2013, **1**, 4590.
- 17 G. Abellán, E. Coronado, WO2013-124503-A1, 2013.
- 18 G. Abellán, E. Coronado, C. Martí-Gastaldo, A. Ribera and T. F. Otero, *Part. Part. Syst. Charact.*, 2013, **30**, 853–863.
- 19 G. Abellán, E. Coronado, C. Martí-Gastaldo, A. Ribera and J. F. Sánchez-Royo, *Chem. Sci.*, 2012, **3**, 1481.
- 20 G. Abellán, J. a. Carrasco, E. Coronado and H. Prima-García, *J. Sol-Gel Sci. Technol.*, 2014, **70**, 292–299.
- 21 G. Abellán, J. a. Carrasco, E. Coronado, J. P. Prieto-Ruiz and H. Prima-García, *Adv. Mater. Interfaces*, 2014, **1**, 1400184.
- 22 G. Abellán, J. G. Martínez, T. F. Otero, A. Ribera and E. Coronado, *Electrochem. Commun.*, 2014, **39**, 15–18.
- 23 G. Abellán, C. Martí-Gastaldo, A. Ribera and E. Coronado, *Acc. Chem. Res.*, 2015, **48**, 1601–1611.
- 24 B. K. Teo, X. H. Sun, C. P. Li, N. B. Wong and S. T. Lee, *Chem. Mater.*, 2010, **22**, 1297–1308.
- 25 O. Karis, S. Svensson, J. Ruzs, P. M. Oppeneer, M. Gorgoi, F. Schäfers, W. Braun, W. Eberhardt and N. Mårtensson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 233105.
- 26 P. Prieto, V. Nistor, K. Nouneh, M. Oyama, M. Abd-Lefdil and R. Díaz, *Appl. Surf. Sci.*, 2012, **258**, 8807–8813.
- 27 B. Dlubak, M. B. Martin, R. S. Weatherup, H. Yang, C. Deranlot, R. Blume, R. Schloegl, A. Fert, A. Anane, S. Hofmann, P. Seneor and J. Robertson, *ACS Nano*, 2012, **6**, 10930–10934.
- 28 A.-H. Lu, E. L. Salabas and F. Schüth, *Angew. Chem., Int. Ed.*, 2007, **46**, 1222–1244.
- 29 X. Zhou and X. Wei, *Cryst. Growth Des.*, 2010, **9**, 7–12.
- 30 J. Nogués, J. Sort, V. Langlais, V. Skumryev, S. Suriñach, J. S. Muñoz and M. D. Baró, *Phys. Rep.*, 2005, **422**, 65–117.
- 31 C. Baker, S. Ismat Shah and S. Hasanain, *J. Magn. Magn. Mater.*, 2004, **280**, 412–418.
- 32 P. Love, *J. Phys. C: Solid State Phys.*, 1983, **16**, 5985.
- 33 E. Liu, H. Yuan, Z. Kou, X. Wu, Q. Xu, Y. Zhai, Y. Sui, B. You, J. Du and H. Zhai, *Sci. Rep.*, 2015, **5**, 11164.
- 34 G. Counil, T. Devolder, J. V. Kim, P. Crozat, C. Chappert, S. Zoll and R. Fournel, *IEEE Trans. Magn.*, 2006, **42**, 3323–3325.
- 35 B. I. Shklovskii and A. L. Efros, *Electronic properties of doped semiconductors*, Springer-Verlag, 1984.
- 36 A. A. Middleton and N. S. Wingreen, *Phys. Rev. Lett.*, 1993, **71**, 3198–3201.
- 37 P. Beecher, A. J. Quinn, E. V. Shevchenko, H. Weller and G. Redmond, *Nano Lett.*, 2004, **4**, 1289–1293.
- 38 G. Chakraborty, K. Gupta, A. K. Meikap, R. Babu and W. J. Blau, *Solid State Commun.*, 2012, **152**, 13–18.
- 39 J. Zhang and B. Shklovskii, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 115317.
- 40 R. Bott, *J. Phys.: Condens. Matter*, 1995, **7**, 6297.
- 41 L. E. Hueso, J. Rivas and F. Rivadulla, *J. Appl. Phys.*, 2013, **3881**, 3–7.
- 42 Y. Wang and H. J. Fan, *Small*, 2012, **8**, 1060–1065.
- 43 E. Coronado, J. P. Prieto-Ruiz and H. Prima-Garcia, *Chem. Commun.*, 2013, **49**, 10145–10147.
- 44 A. O. Adeyeye, G. Lauhoff, J. A. C. Bland, C. Daboo, D. G. Hasko and H. Ahmed, *Appl. Phys. Lett.*, 1997, **70**, 1046.
- 45 J. Zhu, Z. Luo, S. Wu, N. Haldolaarachchige, D. P. Young, S. Wei and Z. Guo, *J. Mater. Chem.*, 2012, **22**, 835.
- 46 D. R. Parker, M. A. Green, S. T. Bramwell, A. S. Wills, J. S. Gardner and D. A. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 2710–2711.
- 47 O. Chauvet, J. M. Benoit and B. Corraze, *Carbon*, 2004, **42**, 949–952.
- 48 I. Bakonyi and L. Péter, *Prog. Mater. Sci.*, 2010, **55**, 107–245.