Electronic Supplementary Information

Graphene as carbon source effects the nanometallurgy of nickel in Ni,Mn layered double hydroxide/graphene oxide composites

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SI 1. Experimental section

Synthesis of the materials

GO and NiMn-LDH were synthesized following the methods reported elsewhere [1-3]. NiMn-LDH was prepared with a $NiCl_2 \cdot 6H_2O$:$MnCl_2 \cdot 4H_2O$ molar ratio 3:1. This solution was added dropwise to another methanolic solution of sodium hydroxide. The mixture formed was magnetically stirred for 2 h for aging and then brought to neutral pH and centrifuged to remove undesirable solid particles that could have been formed by collapse of the LDH sheets. This material was suspended in Milli-Q water and ultrasonicated at 400 W for 2 h to get an exfoliated separated solution of 160 mg/l NiMn-LDH. The aqueous solution of GO prepared by Hummer's method was obtained by sonicating the oxidized graphite at 400 ºC for 2 h obtaining a final concentration of 150 mg/l. Good exfoliation for both samples was confirmed by observation of the Tyndall effect. The obtained suspensions were also very stable (no sedimentation occurred for a period longer than weeks) (see Figure SI 2 below).

The hybrid NiMn-LDH/GO was formed instantaneously upon mixing both aqueous solutions in the volume ratio 1:2, of GO and NiMn-LDH, respectively. Several experiments were carried out using different volumes of NiMn-LDH solutions in order to obtain a clear supernatant solution after precipitation of the hybrid NiMn-LDH/GO solid.

The precipitated hybrid NiMn-LDH/GO solid was centrifuged under 2000 rpm for 15 min followed by washing with Milli-Q water. After drying for two days at 100 ^{o}C, the solid was calcined at 450 or 800 ^{o}C for 24 h in Ar atmosphere, depending on the sample, yielding calcined sample.

The MnO_2/GO composite was prepared following a previously reported method [4]. The MnO_2:GO ratio used has an excess of C with respect to the stoichiometry necessary to achieve the completely reduction of the inorganic oxide according to the following reaction:

$MnO_2 + C \rightarrow Mn + CO_2$

Taking into account that the carbon content of the GO prepared here is 48%, the percentage of GO in the composite was 20% wt. This MnO_2/GO composite was pyrolyzed at 1000 ^{o}C under argon atmosphere for 24 h, to obtain a highly crystalline MnO powder.

Physical characterization

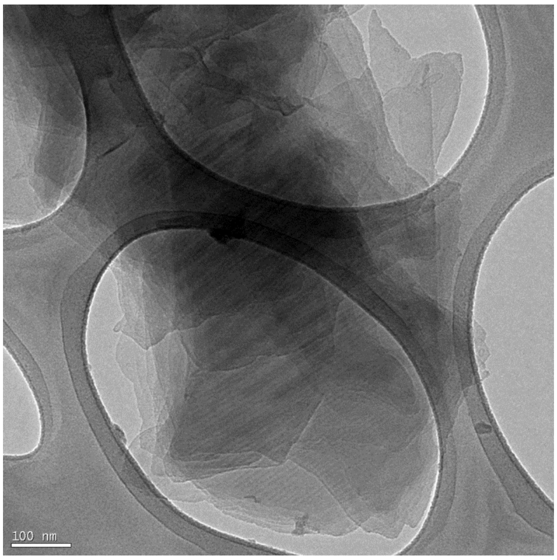
Atomic force microscopy (AFM) images of GO sheets were made with a Multimode Nanoscope 3A Bruker equipment. Typically, a fresh colloidal suspension of GO sheets was deposited onto a clean Si wafer by dip coating. The images were obtained using tapping-mode in air at room temperature. Transmission electron microscopy (TEM) images of the GO sheets were made with a Philips CM300 FEG microscope operating at 100 kV. High resolution TEM (HRTEM) studies of the materials were carried out on a Philips Tecnai F20 equipment operating at 200 kV. Samples were prepared by dipping a carbon-coated copper grid in a sonicated suspension of the sample in ethanol. The Raman measurements (Renishaw inVia Raman Microscope) were carried out at room temperature with the 514.5 nm line of an Ar ion laser as an excitation source. Field Emission Scanning Electron Microscopy (FESEM) studies were performed on a Hitachi S-4800 microscope operating at an accelerating voltage of 2 kV over metallized samples. XRD diffractions were obtained using a Philips X'Pert diffratometer using the Cu-Kα radiation (λ = 1.54178 Å). Magnetic measurements were carried out with a

Quantum Design (SQUID) Magnetometer MPMS-XL-5. The susceptibility data were corrected from the diamagnetic contributions of the atomic constituents of the samples as deduced from Pascal's constant tables and the sample holder. The dc data were collected under an external applied field of 100 or 1000 G in the 2–300 K temperature range. Magnetization studies were performed between −5 and +5 T at a constant temperature of 2 K.

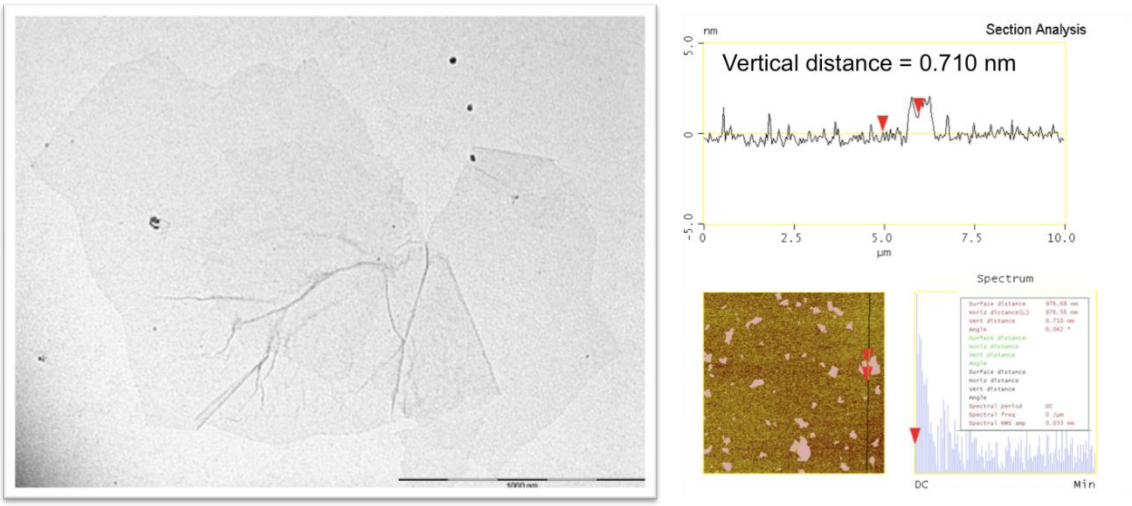
Electrochemical measurements

Electrochemical tests for the material obtained after pyrolysis of MnO_2/GO composite were carried out at room temperature in a home-made Swagelok type cell using Li foil as the counter electrode. A glass microfiber Whatman film was used as separator. A 1M solution of LiPF6 in a 1:1 (volume ratio) mixture of diethyl carbonate and ethylene carbonate was used as the electrolyte. The working electrode was prepared from a ball milling paste of 70 wt% of the active material (MnO), 15 wt% of carbon black (Alfa Aesar) and 15 wt% of polyvinylidene difluoride (PVDF) binder in N-methyl-2-pyrrolidone solvent. The paste was coated onto a copper foil and then dried at 120 ºC before electrochemical tests. The cell was assembled in a glove box filled with pure Ar. The cell was galvanostatically cycled in the potential range of 3-0.01 V (vs Li^+/Li) at a current density of 100 mA g^{-1} using an Ametek Versastat 3 potentiostat/galvanostat.

SI 2. NiMn-LDH and GO sheets characterization



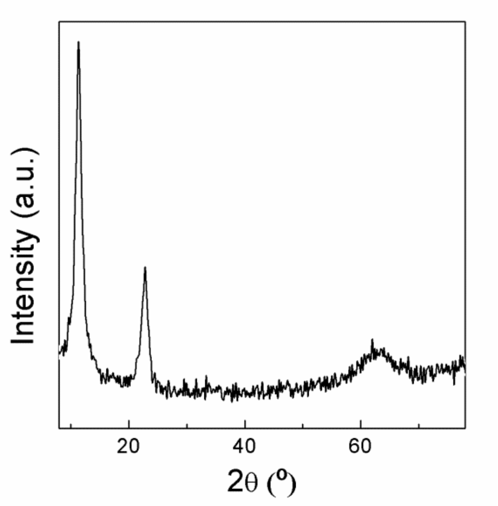
HRTEM image of the centrifugated NiMn-LDH nanosheets showing the 2D morphology. Scale bar represents 100 nm.



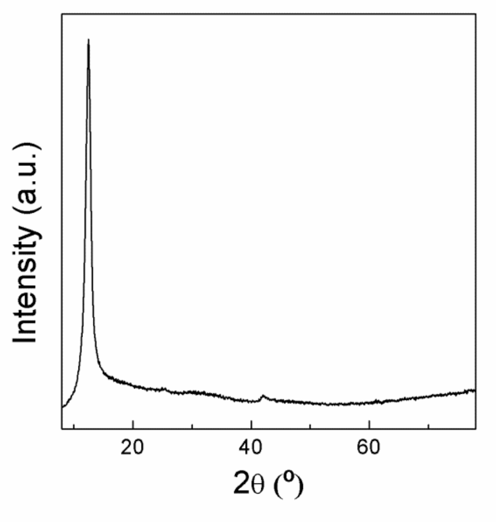
Transmission electron microscopy (TEM) image of GO reveals the bidimensional morphology of the GO sheets of several micrometers in length. Scale bar represents 1 micrometer. Tapping-mode AFM topography image (10 x 10 µm) of the GO sheets deposited on a silicon wafer substrate reveals a height profile according with that expected for a single GO layer.

SI 3. XRD patterns of NiMn-LDH and GO

A

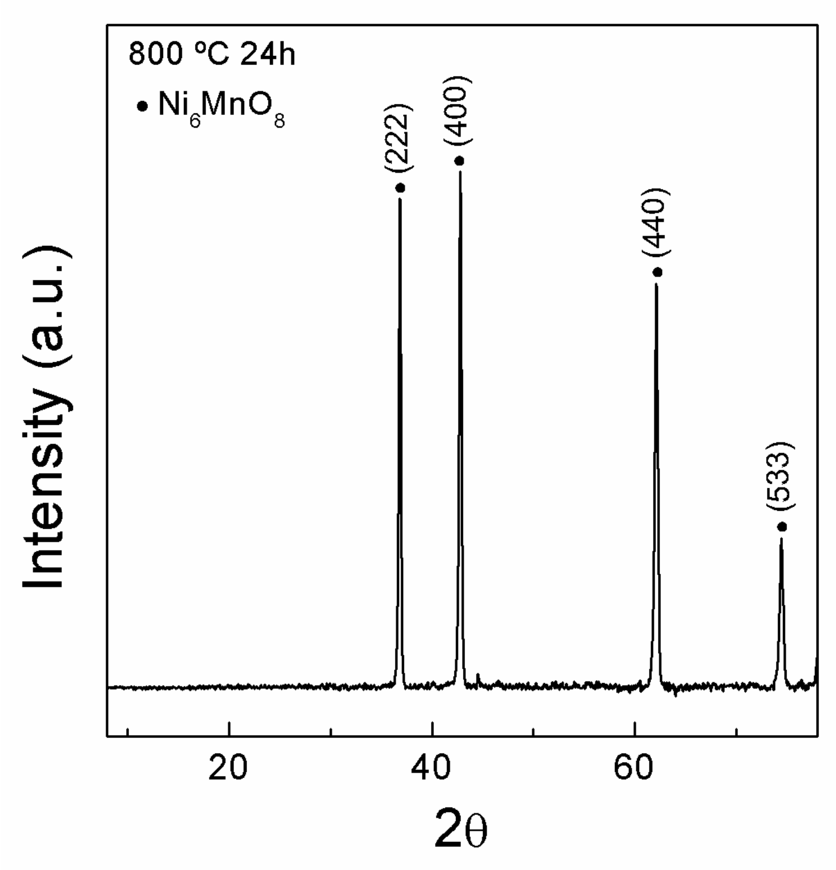


B



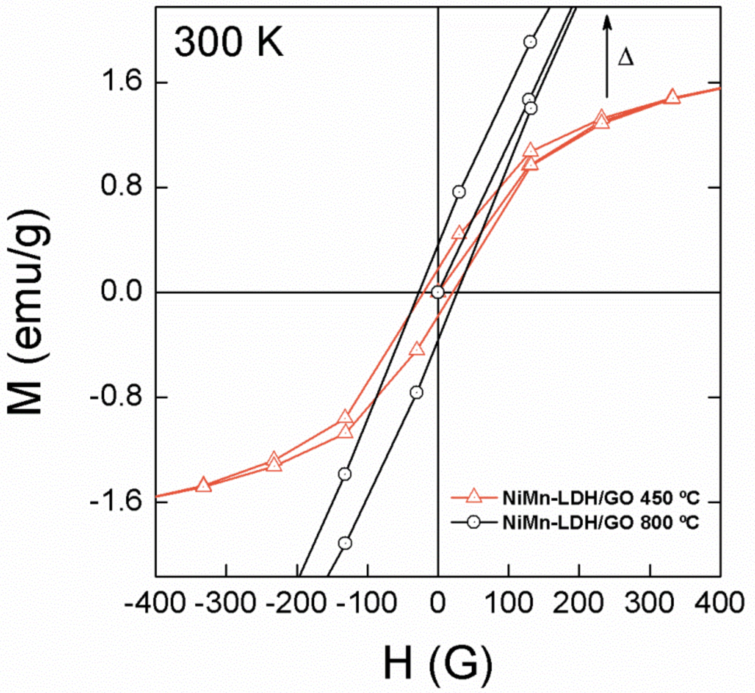
XRD patterns recorded at ambient temperature using the Cu–Kα radiation of (A) the precursor NiMn–LDH, (B) the GO precursor.

SI 4. XRD pattern of calcined NiMn-LDH (800 ºC 24 h)

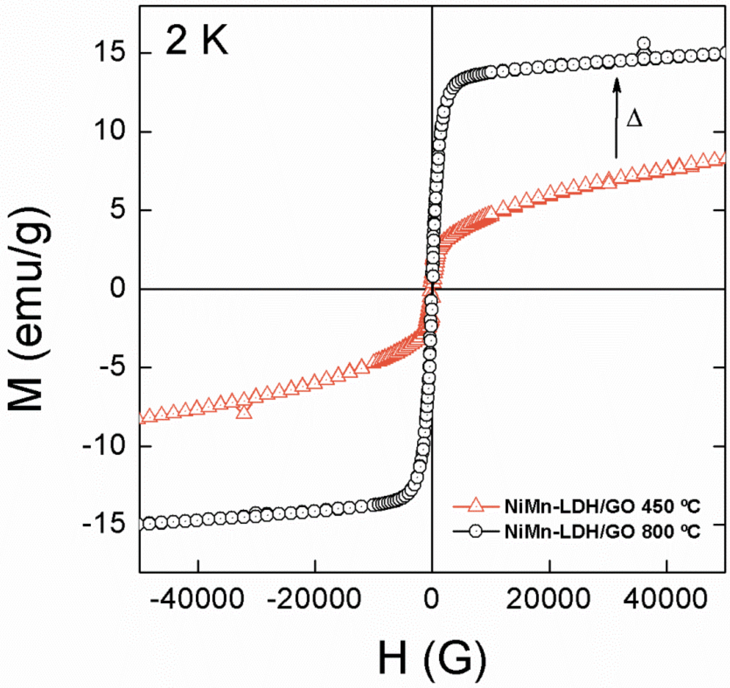


XRD pattern recorded at ambient temperature using the Cu–Kα radiation of the NiMn–LDH precursor after calcination under inert atmosphere at 800 ºC during 24 h. As it can be observed, a highly cristalline Ni_6MnO_8 mixed oxide is obtained, showing that the calcination of this NiMn-LDH precursor is a straightforward procedure for the synthesis of this interesting mixed oxide.

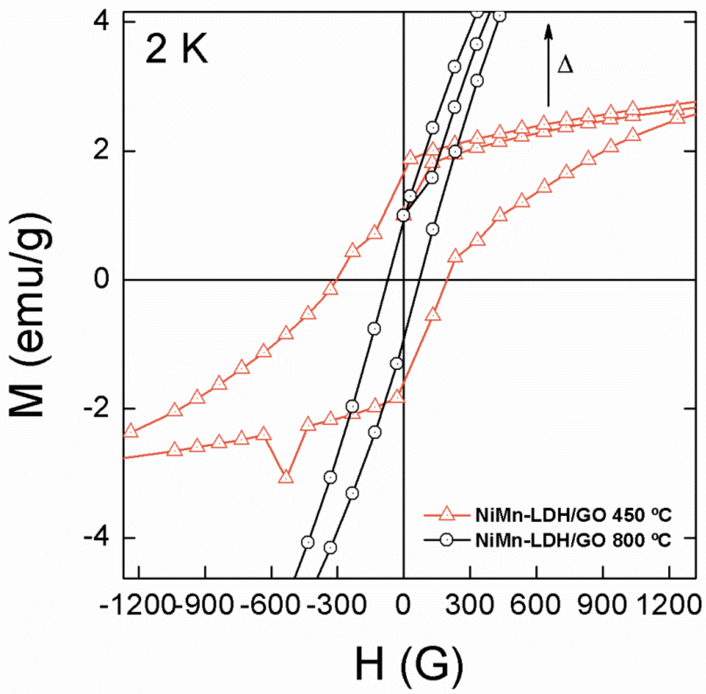
SI 5. M-H curves of the hybrid materials at 300 K and 2 K



Low field region of the magnetization curves measured at 300 K. As it can be observed in the plot, the sample resulting after calcination of NiMn–LDH/GO at 450 ºC exhibits a slightly paramagnetic slope. For 300 K, the field-dependent magnetization shows small coercivity values (20-25 G). The remnant magnetization for samples NiMn–LDH/GO at 450 ºC and NiMn–LDH/GO at 800 ºC are 0.2 and 0.4 emug^{-1}, respectively.

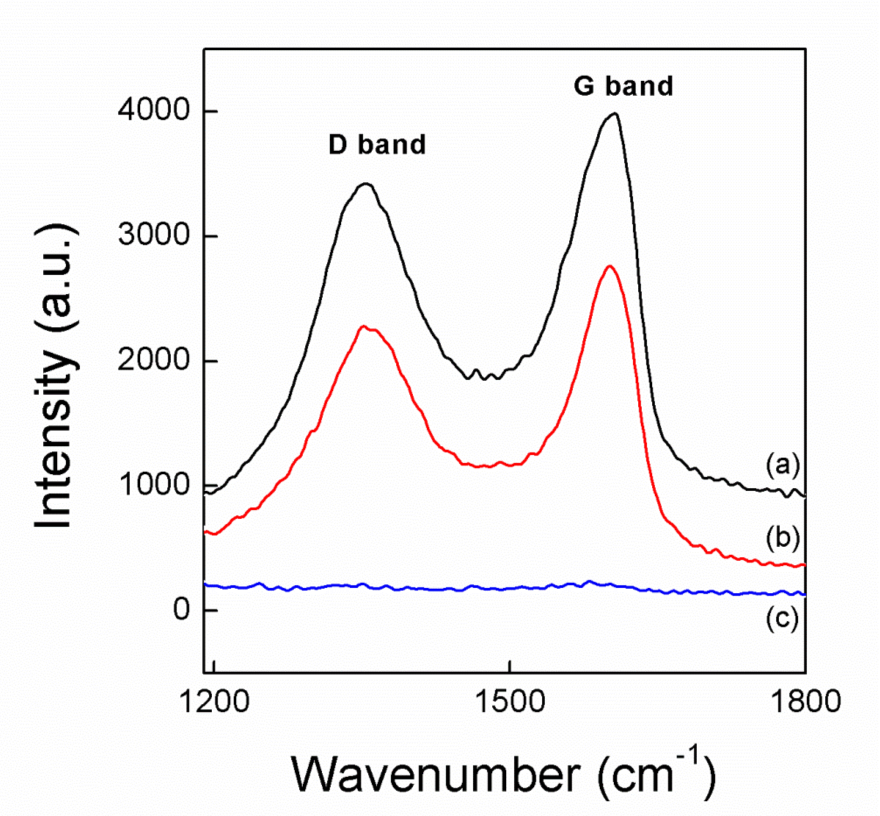


M–H curve of calcined NiMn-LDH/GO hybrid material under a magnetic field of up to 50 kG at 2 K. A dramatic increase in the magnetization can be monitored at 300 K when the calcination temperature is increased. Moreover, no significant differences between low and high temperatures are observed in the sample NiMn–LDH/GO at 800 ºC. In contrast, in the sample NiMn–LDH/GO at 450 ºC, a remarked difference between low and high temperature is observed, indicating superparamagnetic character.



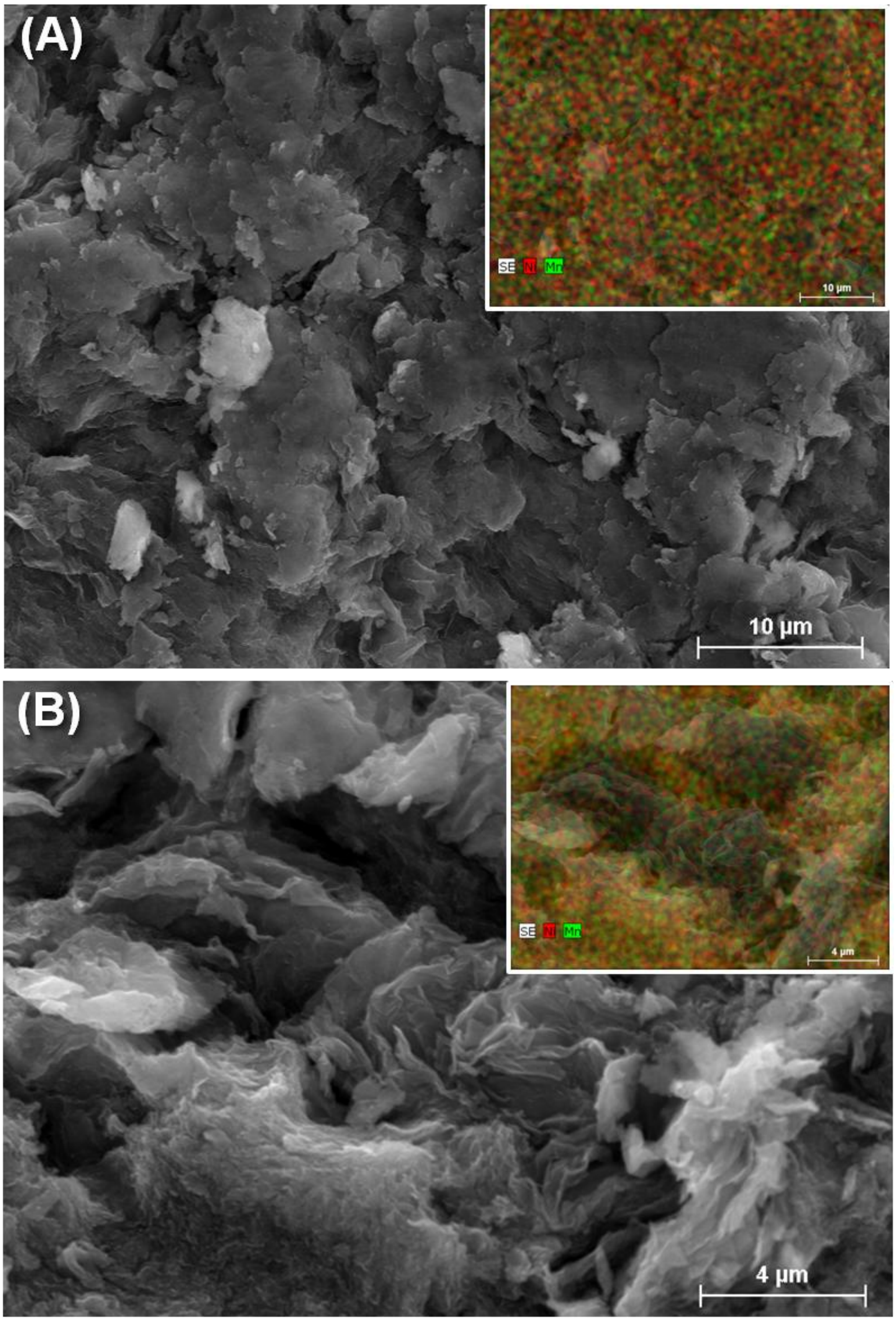
Low field region of the magnetization curves measured at 2 K. As can be observed in the plot, the sample NiMn–LDH/GO at 800 ºC exhibits a significantly different behavior, with the presence of a relatively high coercive field of *ca*. 300 G, and exchange bias probably due to the interface exchange coupling between the Ni_6MnO_8 and the Ni nanoparticles. [5]

SI 6. Raman spectra of NiMn-LDH/GO, NiMn-LDH/GO (450 ºC 24h), and NiMn-LDH/GO (800 ºC 24h)



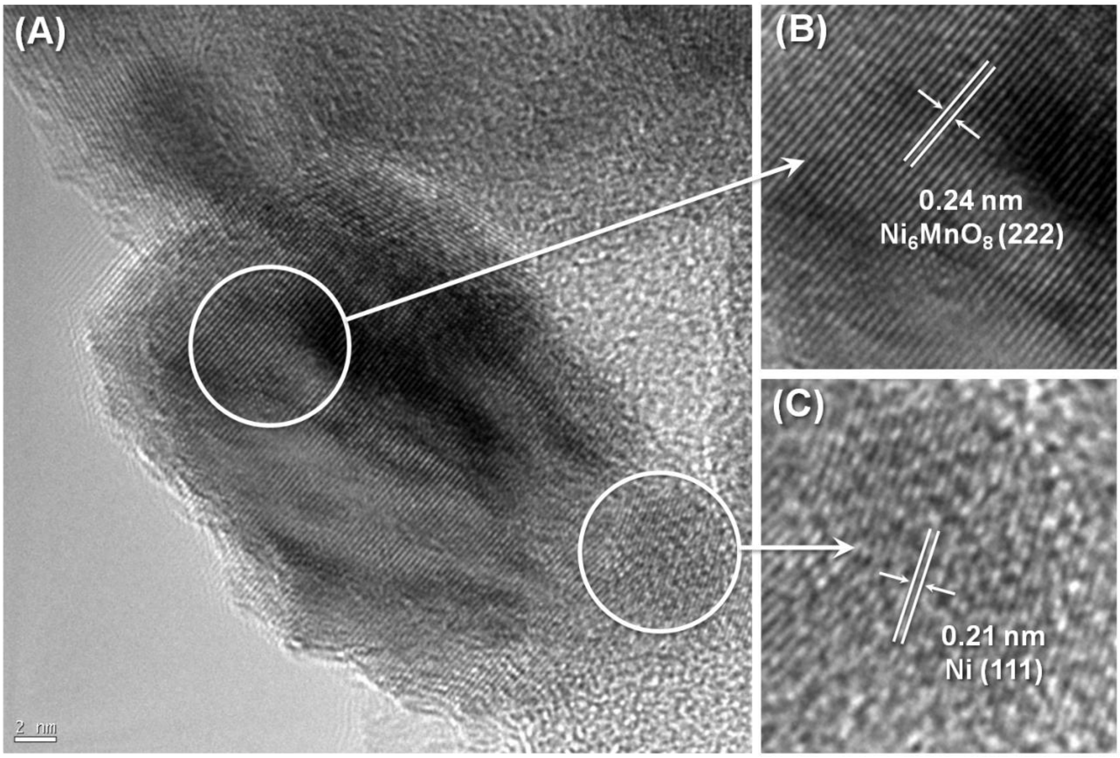
Raman spectra of (a) NiMn-LDH/GO, (b) NiMn-LDH/GO calcined at 450 ºC 24h, and (c) NiMn-LDH/GO calcined at 800 ºC 24h recorded at room temperature with the 514.5 nm line of an Ar ion laser as an excitation source.

SI 7. FESEM-EDS study of NiMn-LDH/GO and NiMn-LDH/GO (450 ºC 24 h)

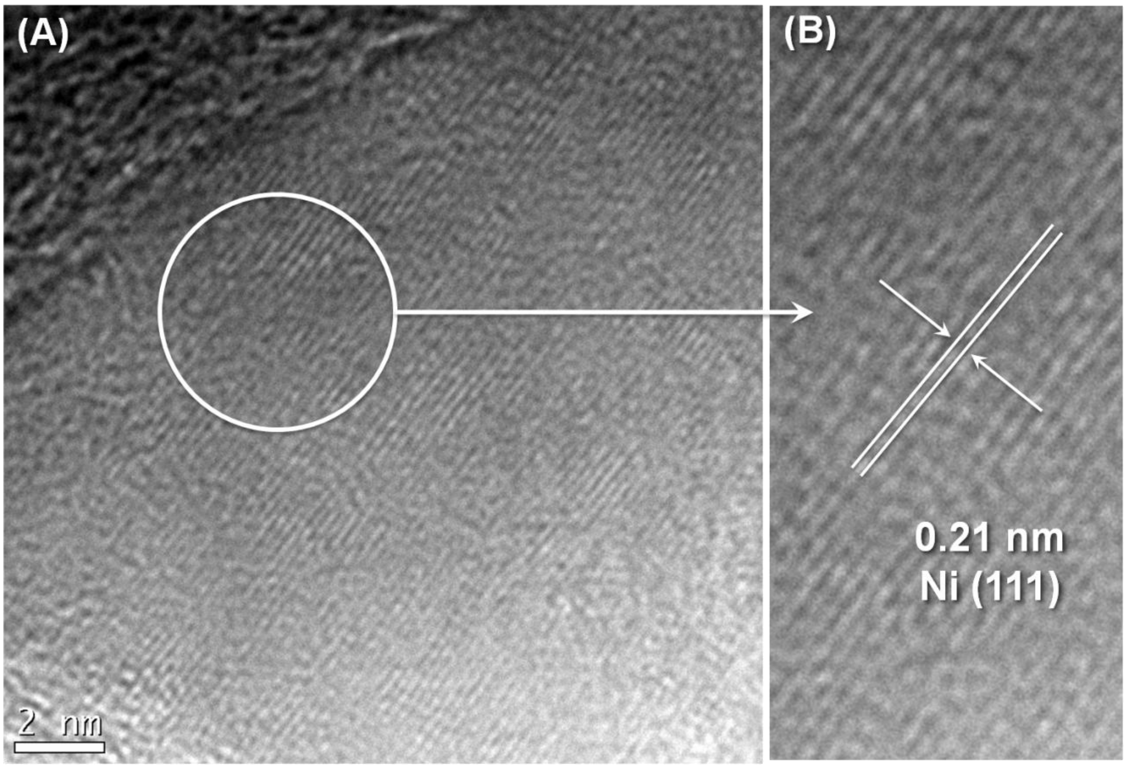


FESEM-EDS elemental mapping of (A) NiMn-LDH/GO and (B) NiMn-LDH/GO calcined at 450 ºC.

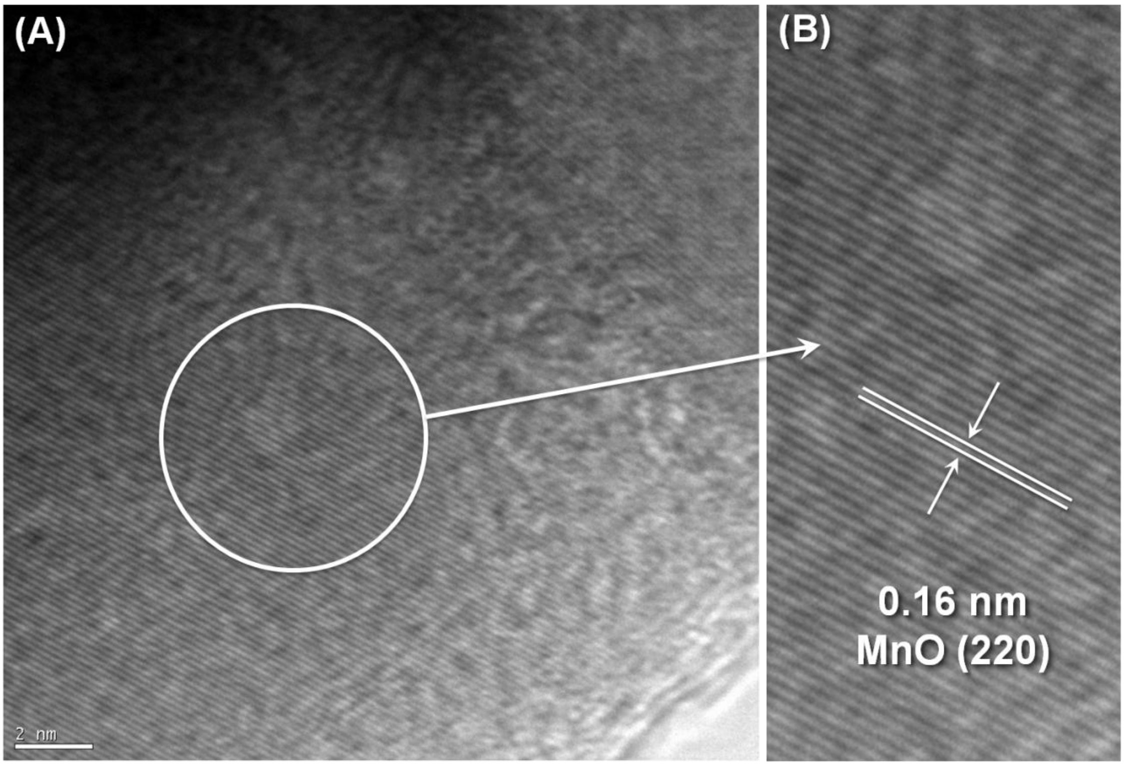
SI 8. HRTEM study of NiMn-LDH/GO (450 ºC 24 h) and NiMn-LDH/GO (800 ºC 24 h) x



HRTEM image of the NiMn-LDH/GO calcined at 450 ºC. (Scale bar represents 2 nm).

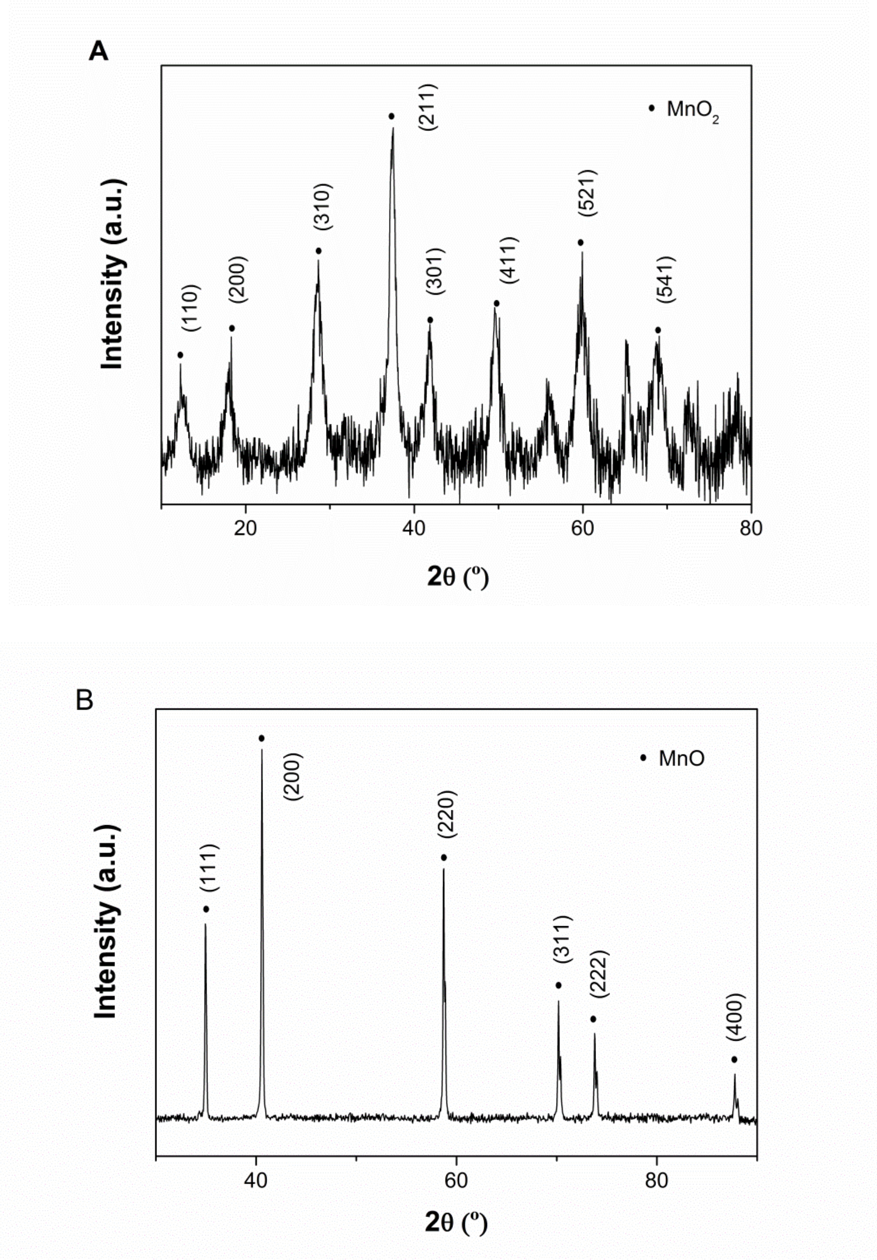


HRTEM image of the NiMn-LDH/GO calcined at 800 ºC. (Scale bar represents 2 nm).



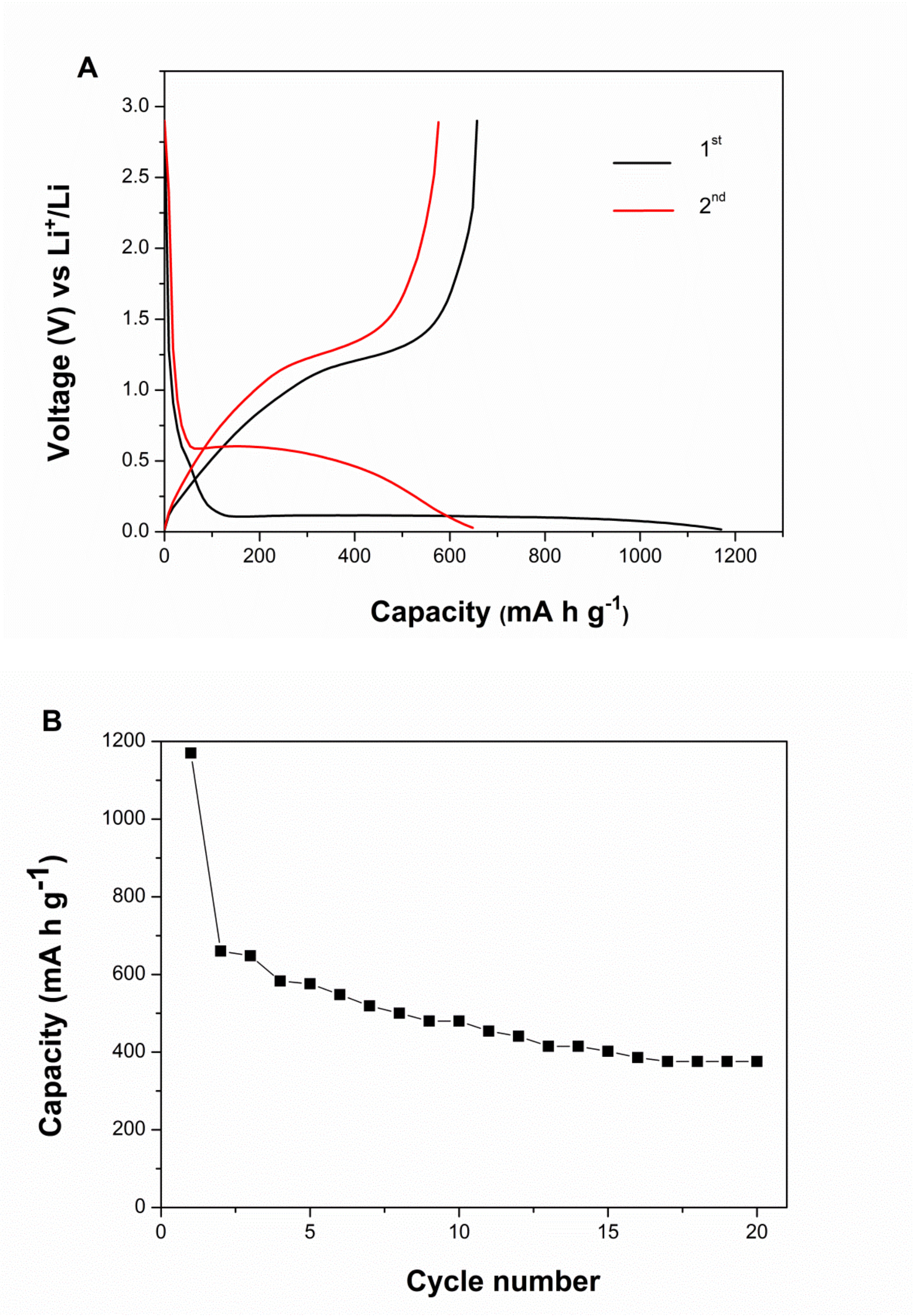
HRTEM image of the NiMn-LDH/GO calcined at 800 ºC. (Scale bar represents 2 nm).

SI 9. XRD patterns of the MnO_2/GO composite before and after calcination (1000 ºC for 24 h)



XRD patterns recorded at ambient temperature using the Cu–Kα radiation of (A) the MnO_2/GO composite before and (B) after pyrolysis at 1000ºC under argon atmosphere for 24 h.

SI 10. Electrochemical characterization of calcined MnO_2/GO



(A) Galvanostatic discharge-charge curve for the first two cycles and (B) cycling performance for the MnO_2/GO composite pyrolyzed at 1000ºC for 24 h under argon atmosphere.

Figure SI 10-A shows the discharge/charge profile of the MnO_2/GO composite pyrolyzed at 1000 ºC for the first two cycles, tested as anode material in a Li-ion battery at a 100 mA g^{-1} rate. These profiles are in agreement with those previously reported in the literature for other MnO particles prepared in a different way [6]. The high first discharge capacity (1170 mA h g^{-1}) can be attributed to the formation of the solid-electrolyte interface film associated to the electrolyte decomposition.

The cycling performance of the material for the first 20 charge-discharge cycles is shown in Figure SI 10-B. Although capacity retention is the major limitation for transition metal oxides when they are used as anode material in Li-ion batteries [7], a relatively high value of almost 400 mA h g^{-1} is obtained after 20 cycles at a rate of 100 mA g^{-1} for the MnO powder obtained after pyrolysis of MnO_2/GO.

SI 11. References

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