Supplementary Information

Layered double hydroxide (LDH)–organic hybrids as precursors for low-temperature chemical synthesis of carbon nanoforms

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SI 1. Experimental details

All chemicals, Ni(NO₃)₂, ·6H₂O, Fe(NO₃)₃, ·9H₂O, HO₂C(CH₂)₈CO₂H (sebacic acid), NaOH, KOH and ethanol (Fluka) were used as received without further purification. The precursor LDH material NiFe-Sebacate (NiFe-Seb) was prepared following the general method described previously by our group [1], using sebacic acid/NaOH. In a typical synthesis, the salts of nickel and iron were dissolved in deionized water, keeping the stoichiometric coefficient \( x = \frac{M^{III}}{M^{II} + M^{III}} \) 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 a thick slurry with a 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 argon atmosphere to avoid incorporation of carbonate anions adsorbed from atmospheric CO₂ into the final precursor. Furthermore, the pH of the synthetic gel was controlled to avoid formation of solid phases different from LDH. The FeNi₃-C have been obtained by calcination under nitrogen atmosphere 6 hours at 400 °C in a programmable oven with a 1 °C min⁻¹ scan rate and nitrogen flow of 40 mL min⁻¹. The carbon nanoforms have been obtained by acid leaching of the as-synthesized composites with 2 M hydrochloric acid during 2 hours with magnetic stirring.
SI 2. Physical characterization

High resolution transmission electron microscopy (HRTEM) studies of the hybrid material were carried out on a JEM-2010 microscope (JEOL, Japan) operating at 200 kV. Samples were prepared by dipping a sonicated suspension of the sample in ethanol on a carbon-coated copper grid. The digital analysis of the HRTEM micrographs was done using DigitalMicrographTM 1.80.70 for GMS 1.8.0 by Gatan. Samples morphologies were studied with a Hitachi S-4100 scanning electron microscope at an accelerating voltage of 20 keV, over metalized samples with a mixture of gold and palladium during 30 s. Thermogravimetric analysis (TGA) of all compounds were carried out with a Mettler Toledo TGA/SDTA 851 apparatus in the 25 – 800 °C temperature range under a 10 °C min\(^{-1}\) scan rate and an air flow of 30 mL min\(^{-1}\). X-ray powder diffraction patterns were collected with a Siemens d-500 X-ray diffractometer (Cu-K\(\alpha\) radiation; \(\lambda = 1.5418\) Å) equipped with a rotating anode D-max Rigaku operating at 80 mA and 45 kV. Samples were mounted on a flat sample plate. Profiles were collected in the 2.5° < 2\(\theta\) < 100° range with a step size of 0.05°. Magnetic susceptibility measurements were performed on polycrystalline samples with a Quantum Design PPMS-9 model instrument. The susceptibility data were corrected by removing the diamagnetic contributions as deduced by using Pascal’s constant tables. The \(dc\) data were collected in the range 2 – 300 K upon decreasing temperatures with an applied field of 1000 G. The Raman measurements (Jobin-Yvon LabRam HR 800 Raman Microscope) were carried out at room temperature with the 532 nm line of an Ar ion laser as an excitation source. Metallic atomic composition of bulk samples was determined by means of electron probe microanalysis (EPMA) performed in a Philips
SEM-XL30 equipped with an EDAX microprobe. Carbon, nitrogen and hydrogen contents were determined by microanalytical procedures by using a LECO CHNS.
SI 3. Magnetic measurements

Temperature dependence of the magnetic susceptibility measured with an applied field of 1000 G for a pure NiFe-Seb phase (spheres, blue) and another batch contaminated with impurities of amorphous iron oxide (triangles, black). The intense magnetic response at room temperature clearly accounts for the presence of a XRD non-detectable non-LDH phase.
SI 4. PXRD of compound 1.

Main Peaks from the Powder X-Ray Diffraction Pattern of NiFe-Sebacate LDH compound (1).

<table>
<thead>
<tr>
<th></th>
<th>$2\Theta [^\circ]$ (hkl)</th>
<th>$[^a]$ Calc. Param. [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(003)</td>
<td>(006)</td>
</tr>
<tr>
<td>NiFe-Sebacate</td>
<td>5.75</td>
<td>11.55</td>
</tr>
</tbody>
</table>

$[^a] a = 2d_{110} ; c = d_{003} + 2d_{006} + 3d_{009} ; BS = c/3.$
SI 5. (a) TGA-SDTA of compounds 1 and (b) 2.

(a) The temperature dependence of the weight loss of 1 (NiFe-Seb LDH precursor) was studied in an inert atmosphere between 25 and 1100 °C.
(b) TGA-SDTA curves in air of FeNi$_3$-C nanocomposites. The sample exhibit gradual weight gain in the range 270-370 °C associated with an exothermic peak at 350 °C, implying that the FeNi$_3$ are slowly oxidize. It is also an indication that graphitically coated FeNi$_3$ nanoparticles are stable in air below _ca._ 270 °C [6].
SI 6. XPS study of compound 2 and carbon nanoforms.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Ni 2p$_{3/2}$ Binding energy (eV)</th>
<th>Fe 2p$_{3/2}$ Binding energy (eV)</th>
<th>Ni/Fe ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^0$</td>
<td>Ni$^{+2}$ (1)</td>
<td>Ni$^{+2}$ (2)</td>
<td>Ni satellite</td>
</tr>
<tr>
<td>FeNi$_3$-C</td>
<td>853.2</td>
<td>0</td>
<td>862.5</td>
</tr>
<tr>
<td>Carbon nanoparticles</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>711.2</td>
<td>1.71</td>
<td></td>
</tr>
</tbody>
</table>

The **figure 5** of the main text shows the Ni 2p and Fe 2p spectra measured by XPS in FeNi$_3$ nanoparticles and in their corresponding carbon nanoforms. Each one of the two spin-orbit components of the Ni 2p spectra shows three resolved features. However, only one asymmetric feature can be resolved for the spin-orbit doublet of the Fe 2p spectra. For the deconvolution and fitting of these spectra, a Shirley background [2] has been taken into account. Deconvolution of the Ni 2p spectra has been carried out by considering three Gaussian line-shape spin-orbit doublets (with a spin-orbit splitting of around 18 eV). The Fe 2p spectra has been reproduced by considering one spin-orbit doublet (with a spin-orbit splitting of 13.2 eV) whose components appear to be well described by Doniach-Súnjic line-shapes [3]. Regarding the three components detected for the Ni 2p$_{3/2}$ spectra, these located at 853.2 and 856.4 eV can be attributed to metallic and divalent Ni, respectively, whereas that located at 862.5 eV can be attributed to the so-called 6-eV Ni satellite [4,5]. Conversely, the only component detected for the Fe 2p$_{3/2}$ spectrum can be attributed to divalent Fe.
SI 7. References.


