

Supplementary Information

Hexagonal nanosheets from the exfoliation of Ni²⁺-Fe³⁺ LDHs:
a route towards layered multifunctional materials.

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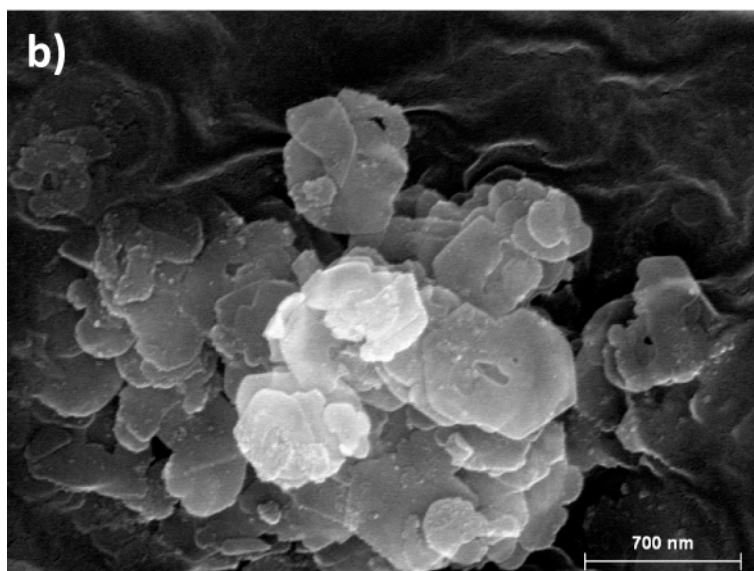
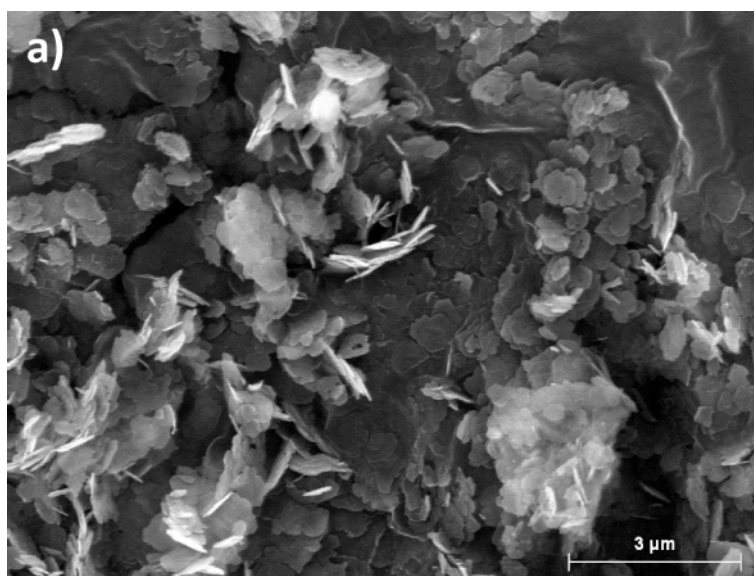
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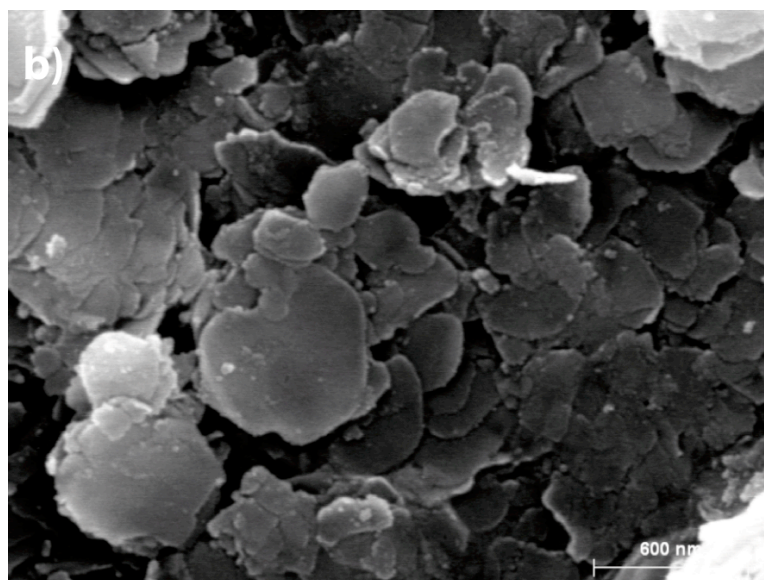
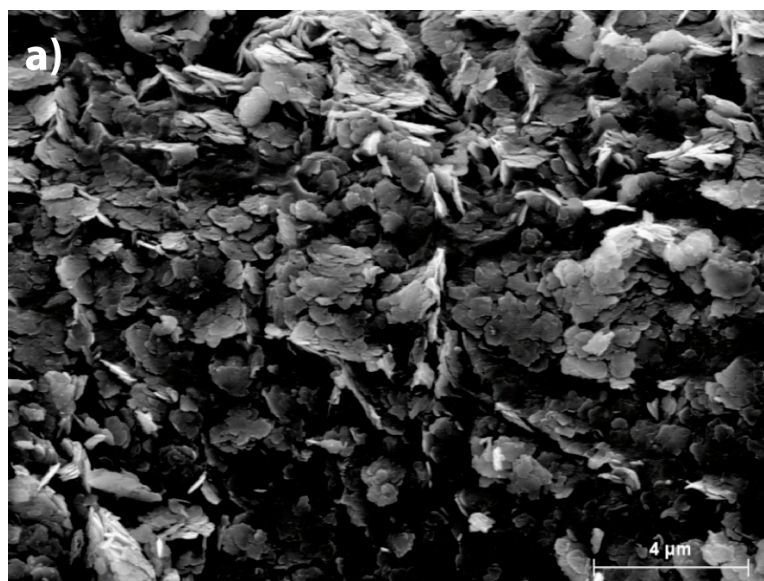
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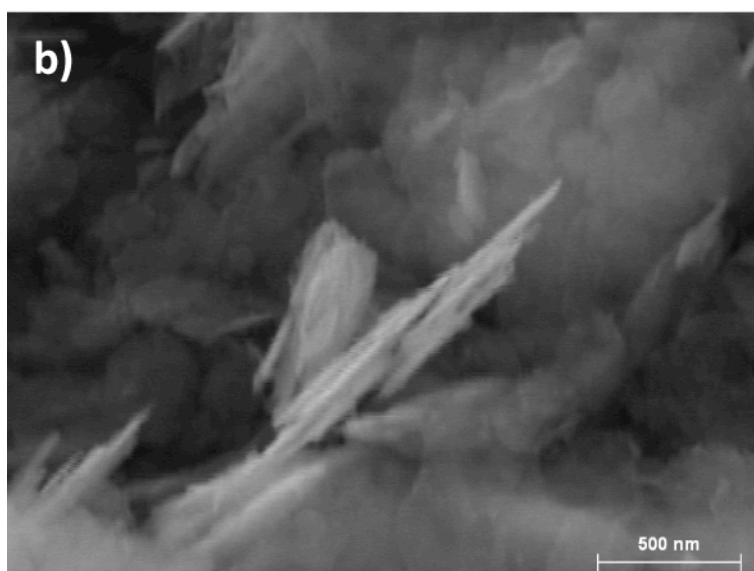
SI 1. (a) SEM images of **1**. (b) Zoom-in showing the hexagonal morphology of the particles.



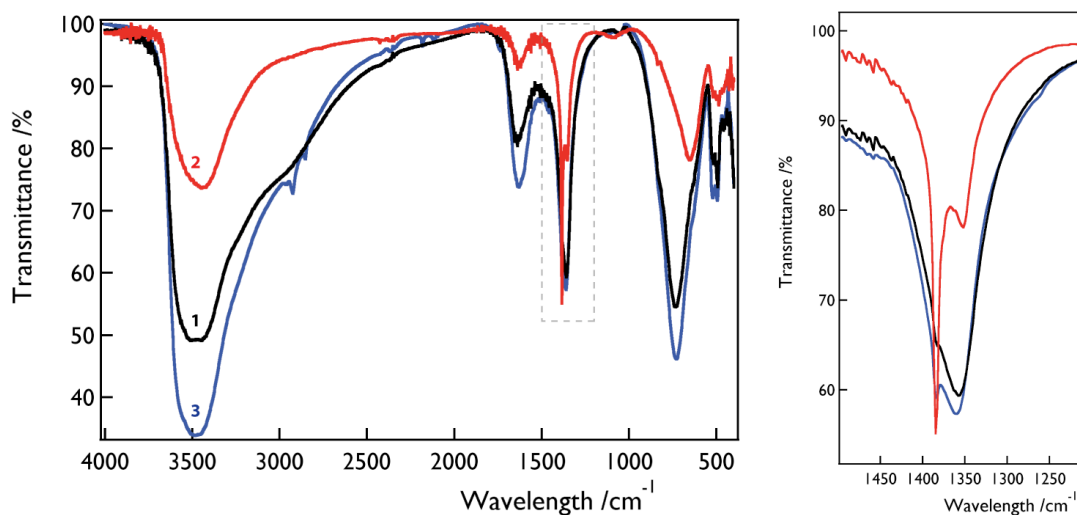
SI 2. SEM images of **2**.



SI 3. SEM images of **3**.



SI 4. (a) FT-IR of NiFe-CO₃ (**1**, black), NiFe-NO₃ (**2**, red) and restacked NiFe-CO₃ (**3**, blue) LDHs. (b) Zoom-in highlighting the carbonate and nitrate anions stretching area. The table below summarizes the assignment of the IR main vibration modes of **1-3**.



| Vibration modes [cm ⁻¹] | 1 | 2 | 3 |
|-------------------------------------|----------|----------|----------|
| ν [O-H] | 3446 | 3448 | 3485 |
| ν [H-O-H] | 1637 | 1637 | 1637 |
| ν [N-O] | - | 1385 | 1385 |
| ν [C-O] _s | 1358 | 1352 | 1360 |
| ν [M-O] | 735 | 654 | 727 |
| δ [O-M-O] | 492 | 486 | 521, 494 |

FT-IR has been extensively employed in the characterization of LDH materials, focusing on the study of the nature of the intercalated anionic moieties and their relative orientation with respect to the host brucite-like lamellae. All compounds show a strong absorption with a broad profile in the 3490-3440 cm⁻¹ interval, associated to the presence of H-bonding interactions between the interlamellar water molecules and the OH groups belonging to the hydroxide-based layers.¹ The presence of water in these materials is additionally supported by the sharp medium-intensity absorption band at 1637 cm⁻¹, related to the H₂O vibrational bending mode. Absorption at lower wavenumbers, between 740 and 485 cm⁻¹, must be attributed to vibrational modes associated to the [M^{II,III}(OH)₆]^{-4,-3} complexes distributed along the LDH layers.²

More specifically, we have employed this technique to identify the presence of carbonate anions in the pristine/reconstituted NiFe LDHs (**1**, **3**) and confirm the

¹ (a) Ulibarri, M. A.; Hernandez, M. J.; Cornejo, J. *J. Mater. Sci.* **1991**, *26*, 1512-1516. (b) Grey, I. E.; Ragozzini, R. *J. Solid State Chem.* **1991**, *94*, 244-253.

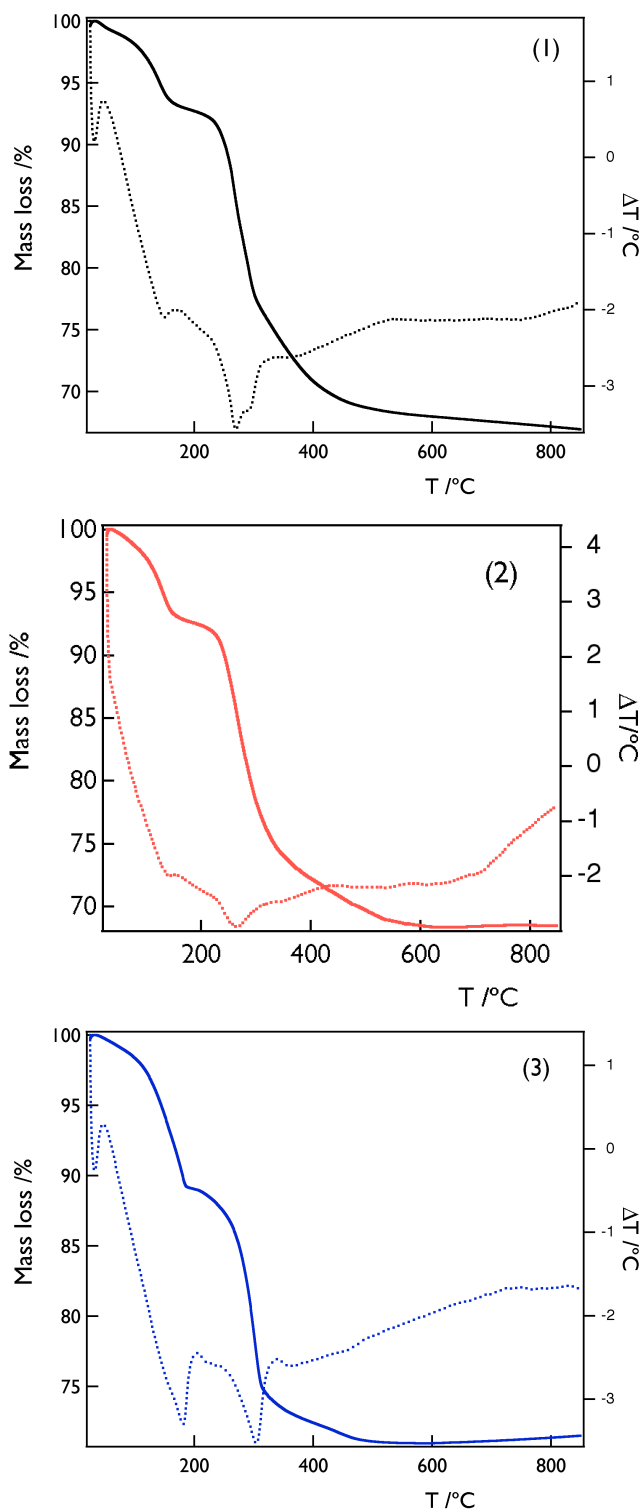
² Busca, G.; Trifiro, F.; Vaccari, A. *Langmuir* **1990**, *6*, 1440-1447.

success of the anionic exchange step in **2**. To provide the reader with a clear signature of the presence of both anionic species, we have extracted a zoom-in (*vide supra*) from the general FT-IR spectra. The CO₃-intercalated LDHs (**1**, **3**) show a strong-intensity band at *ca.* 1360 cm⁻¹, as typically observed for the carbonate anion's ν_3 stretching mode.³ The NO₃-exchanged LDH (**2**) shows a more complex doublet in the same region composed of: a) A sharp stronger band at 1385 cm⁻¹, associated to the nitrate anion's ν_3 stretching mode⁴ and b) A much weaker band centred at 1352 cm⁻¹, which is probably related to the presence of a residual amount of non-exchanged intercalated carbonate. This fact is probably responsible of the smaller interlayer distance observed for **2**, estimated from powder X-ray diffraction data, when compared with the values typically reported for other NO₃-intercalated LDH materials.

³ Hernandez-Moreno, M. J.; Ulibarri, M. A.; Rendon, J. L.; Serna, C. J. *Phys. Chem. Miner.* **1985**, *12*, 34-38.

⁴ Kruissink, E. C. ; Vanreijen, L. L.; Ross, J. R. H. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 649-663.

SI 5. (a) TG (solid lines) and DTA (dashed lines) analysis of NiFe-CO₃ (**1**), NiFe-NO₃ (**2**) and restacked NiFe-CO₃ (**3**) LDHs.



The temperature dependence of the weight loss of **1-3** was studied in an oxygen atmosphere between 25 and 800 °C. Analogous TG and DTA curves (solid and dashed lines, respectively) were obtained in each case. As expected for LDH

materials, the weight loss undergoes through a two-step process:⁵ a) The first low-temperature weight loss, in the 25-220 °C range, can be decomposed in two sub-processes associated to the removal of hydration and more strongly attached interlaminar water molecules b) The higher temperature weight loss process, from 220 to 800 °C, is promoted by the loss of carbonate anions and further dehydroxylation of the brucite-like layers.

DTA profiles recorded for compounds **1-3** (dashed lines) show two well defined strong intensity endothermic peaks between 25 and 200 °C, associated to the two-step loss of water molecules. The peaks' maxima below 200 °C define the temperature employed to estimate the mass loss and calculate the number of water molecules per unit formula in each particular case (see **table 2** in text). Finally, broader endothermic peaks can be observed above 220 °C. These signals must be attributed to the higher temperature mass loss processes.

⁵ (a) Cavani, F.; Trifirò, F.; Vaccari, A. *Catalysis Today* **1991**, *11*, 173-301. (b) Mascolo, G.; Marino, O. *Mineralogical Magazine* **1980**, *43*, 619-621.