Supporting Information

Insights into the formation of metal carbon nanocomposites for energy storage using hybrid NiFe layered double hydroxides as precursors

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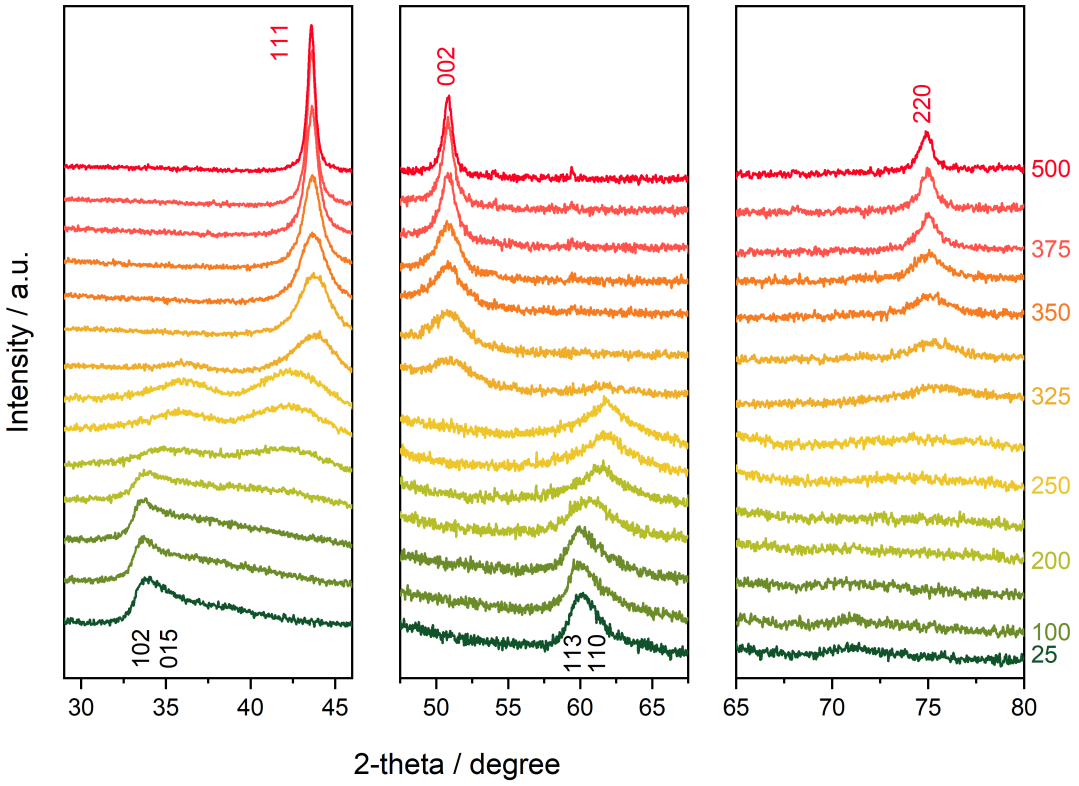

Fig. SI 1. In-situ X-Ray powder diffraction measurements in an inert heating chamber, showing the different peaks evolutions zones at different temperatures.

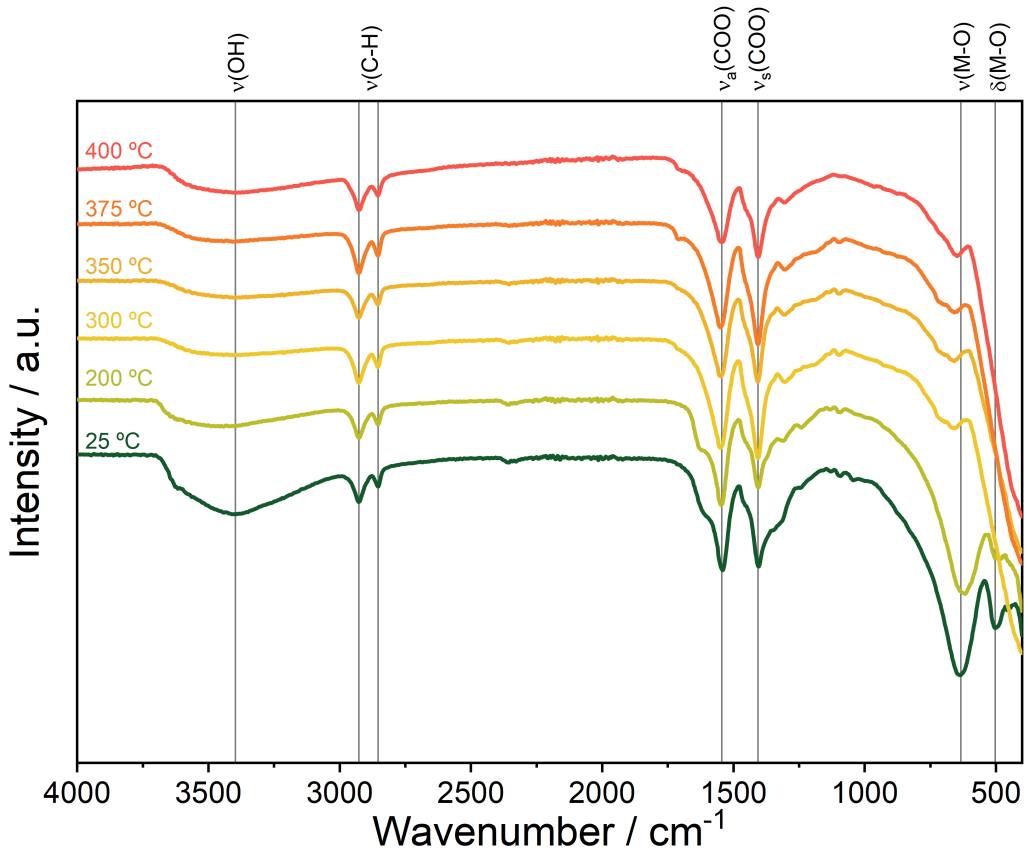

Fig. SI 2. Infra-Red spectra of the pristine material and the *ex situ* calcinations at different temperatures.

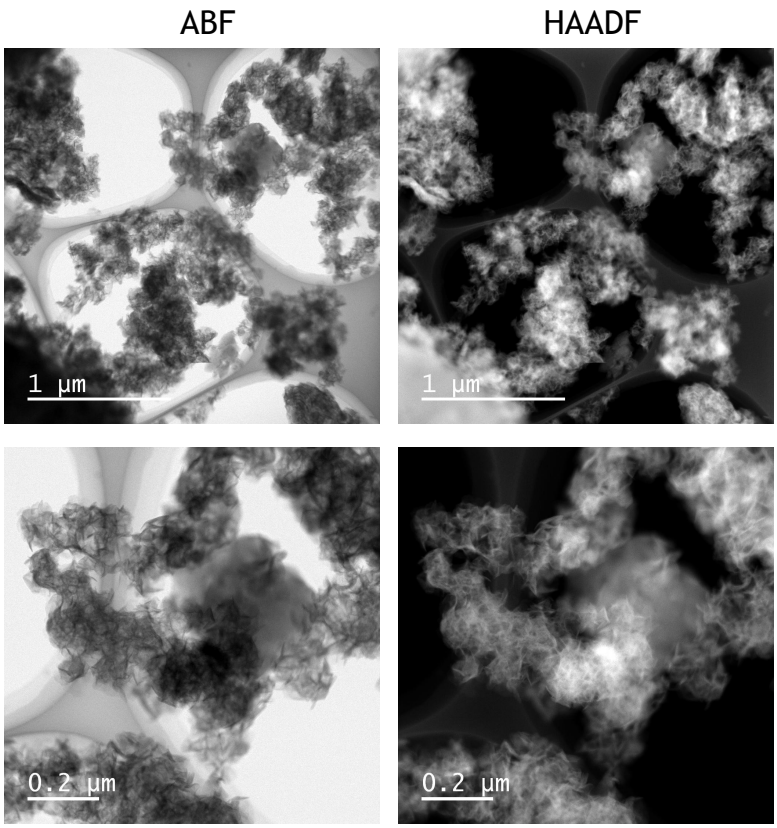

Fig. SI 3. Low magnification, simultaneously acquired annular bright field (ABF) and high angle annular dark field (HAADF) images of the pristine NiFe-LDH-Seb at low magnifications.

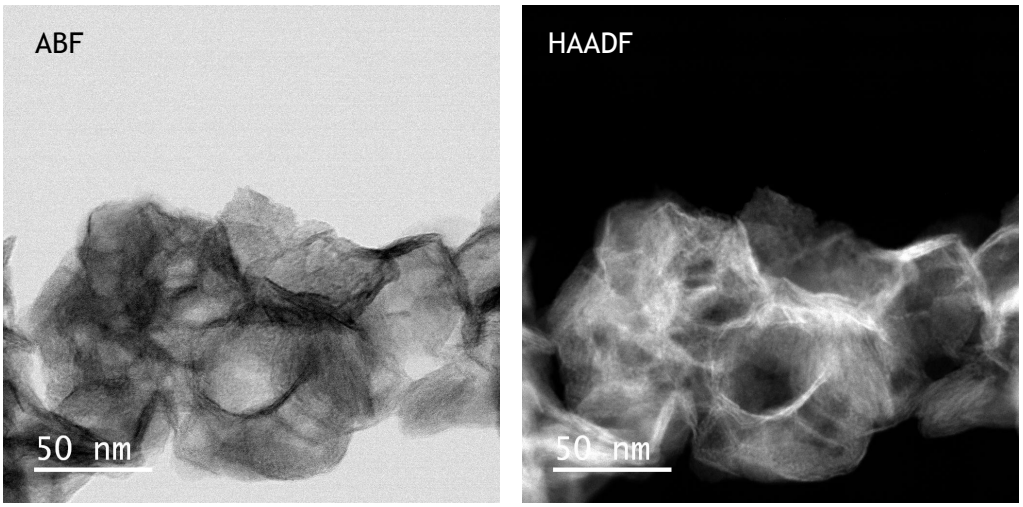

Fig. SI 4. ABF and HAADF images of the pristine NiFe-LDH-Seb at intermediate magnifications.

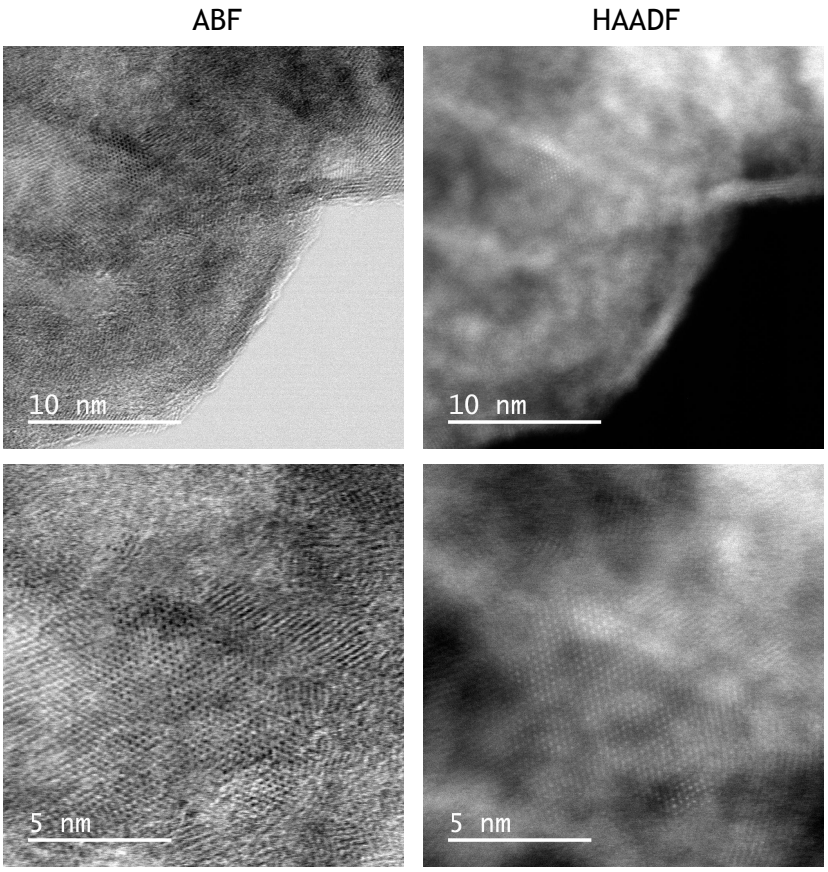

Fig. SI 5. Atomic resolution ABF and HAADF images of the pristine NiFe-LDH-Seb.

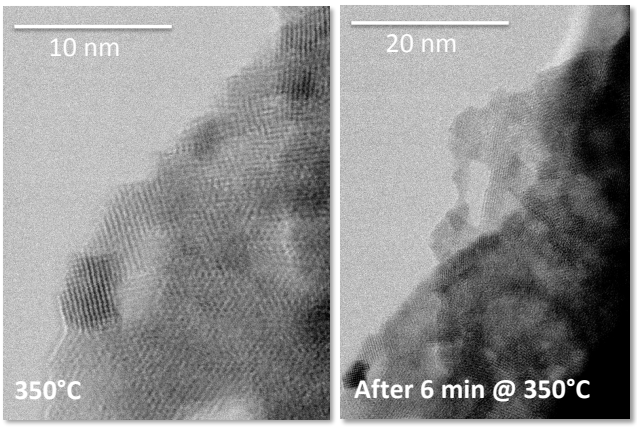

Fig. SI 6 Atomic resolution ABF images showing the slow evolution of the dynamic behavior of the material after holding the temperature at 350 °C for 6 minutes.

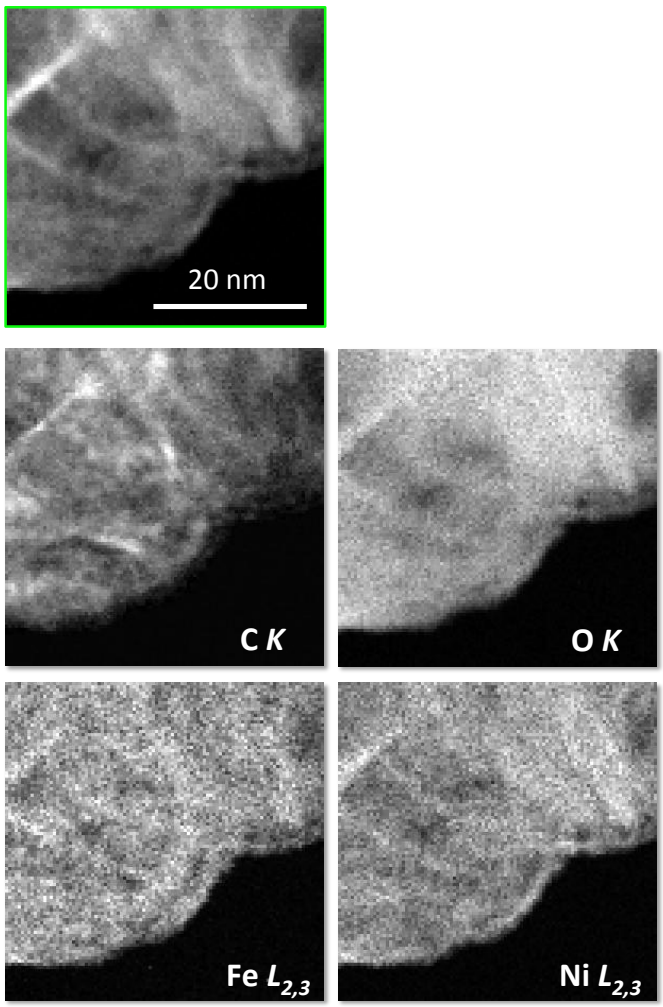

Fig. SI 7 Electron energy-loss (EELS) compositional maps of the pristine NiFe-LDH-Seb at RT.

Evolution of the oxidation states: EELS analysis of the fine structure of the *3d* metal $L_{2,3}$ edges

The analysis of the fine structure of the *3d* metal $L_{2,3}$ edges allows a qualitative analysis of the evolution of oxidation states in the different samples upon thermal treatment. In particular, the L_3 to L_2 intensity ratio (L_{23} ratio from now on) typically increases for *3d* metals such as Fe as they become more oxidized [1-3]. Here we have analyzed the L_{23} intensity ratio of the NiFe-LDH-Seb pristine, the NiFe-LDH-Seb after being annealed at 400 °C in-situ and the pristine NiFe-carbon nanocomposite sample, which are summarized in Fig. SI8 (panels a, b and c, respectively). The pristine NiFe nanoparticles (Fig. SI8a) exhibit a relatively homogeneous oxidation state for both Ni and Fe consistent with an over all metallic state (see the flat behavior and histograms for the L_{23} ratio maps obtained from the Fe and Ni $L_{2,3}$ edges). A minor proportion of oxidized Fe is detected, as hinted by the delayed tail of the right side of the Fe histogram. These pixels correspond to the areas with brighter contrast observed in the Fe L_{23} ratio maps, localized on the particle surface. The pristine NiFe-LDH-Seb sample shows fairly homogenous oxidation states for both Ni and Fe as well, with slightly higher values due to the fact that the metallic species in this sample are more oxidized than the metallic state (Ni^{2+} and Fe^{3+}, Fig. SI8b). Meanwhile, the NiFe-LDH-Seb sample annealed in-situ at 400 °C exhibits the most inhomogeneous behavior. While Ni stays mostly in the metallic state (most of the Ni is in the form of segregated Ni nanoclusters and particles), the Fe L_{23} intensity ratio maps exhibit the most disperse distribution, with a wide histogram compatible with some metallic Fe being present but also a wide amount of oxidized Fe (Fig. SI8c).

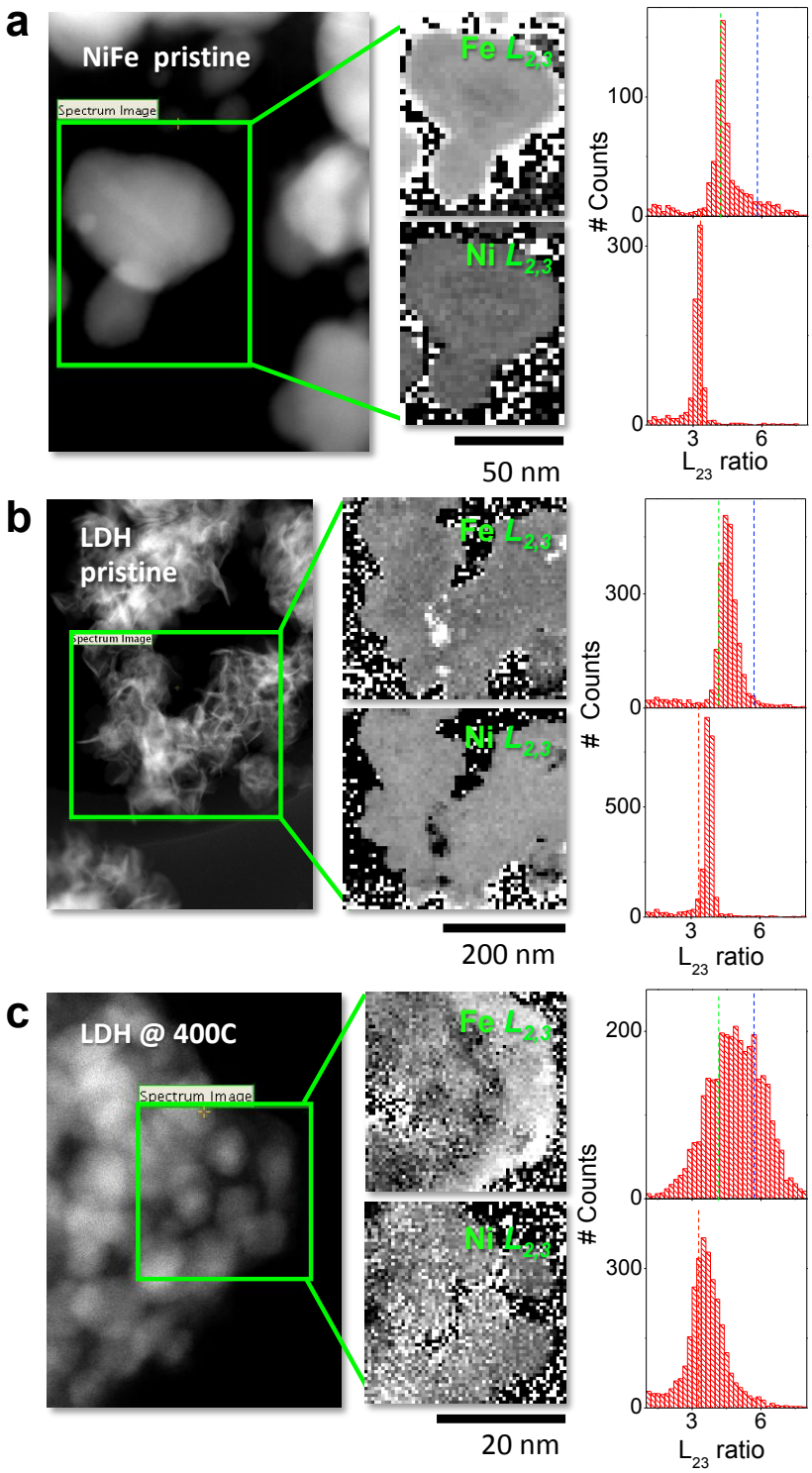

Fig. SI 8. L_{23} intensity ratio analysis for the pristine NiFe-carbon nanocomposite (a), the pristine NiFe-LDH-Seb compound (b) and the NiFe-LDH-Seb compound after an in-situ annealing at 400 °C (c). For L_{23} ratio calculations the second derivative method was used after applying principal component analysis to remove random noise to raw EEL spectrum images. The panels on the left exhibit the ADF images of the representative regions analyzed. A green rectangle marks the area where EEL spectrum images were acquired. The middle panels exhibit the L_{23} ratio values calculated within those regions. The grey scale for the Fe (Ni) L_{23} ratio maps goes as following: numeric values of 2 (2) correspond to white, all the way to values of 7 (5) for black. Vertical dashed lines are a guide to the eye to mark the tentative position of the L_{23} ratio value for metallic Ni (red) and Fe (green), and oxidized Fe (blue).

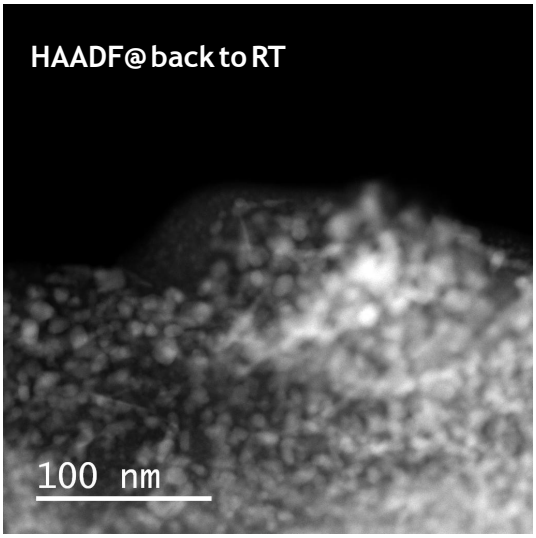

Fig. SI 9. HAADF image obtained at room temperature after heat treatment.

References:

[1] R. D. Leapman and L. A. Grunes, Phys. Rev. Lett. 45, 497 (1980).
[2] R. D. Leapman, L. Grunes, P. J. Fejes PL, Phys. Rev. B, 26, 614 (1982).
[3] C. Colliex, T. Manoubi, C. Ortiz. Phys. Rev. B 44, 11402 (1991).