

## Supporting Information

### **An air-stable, reusable Ni@Ni(OH)<sub>2</sub> nanocatalyst for the hydrogenation of CO<sub>2</sub>/bicarbonates to formate**

Xin-Pu Fu<sup>a,‡</sup> Laurent Peres<sup>b,c,‡</sup> Catherine Amiens<sup>b,c</sup>, Jérôme Esvan<sup>d</sup>, Karine Philippot<sup>\*,b,c</sup>, Ning Yan<sup>\*,a</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore, 117585, Singapore.

<sup>b</sup> CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP44099, F-31077 Toulouse Cedex 4, France.

<sup>b</sup> Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France.

<sup>d</sup> CIRIMAT, CNRS-INP-UPS, INP-ENSIACET, 4 allée Emile Monso, BP 44362, F-31030, Toulouse Cedex 4, France

<sup>‡</sup> These authors contributed equally to this work.

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**Fig. S4.** Ni 2p XPS spectra of as-prepared Ni@Ni(OH)<sub>2</sub> foam (cyan, bottom line) and of Ni@Ni(OH)<sub>2</sub> foam after 21 weeks in air (black, top line). The reference peaks of the 2p<sub>3/2</sub> orbitals are for Ni metal (Ni(0)) : 852,6eV; for NiO (Ni(II)) : 853,7eV ; and for Ni(OH)<sub>2</sub> (Ni(I)) : 855,6eV.

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**Fig. S8.** XRD diffractogram of Ni@Ni(OH)<sub>2</sub> foam catalyst after NaHCO<sub>3</sub> hydrogenation reaction, showing the classical Ni fcc pattern (ICCD:96-901-2978). Crystallite size = 20.9 nm (Scherrer equation).

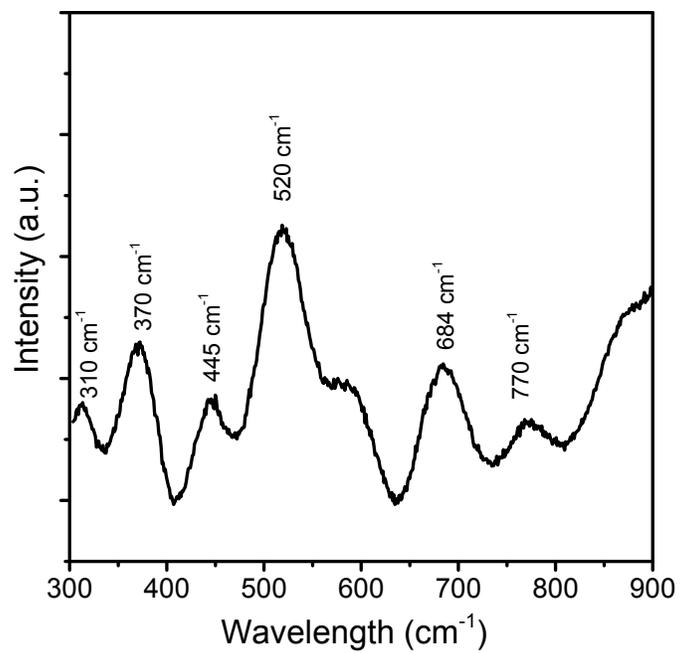
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**Fig. S10.** SEM micrographs of Ni@Ni(OH)<sub>2</sub> foam catalyst after NaHCO<sub>3</sub> hydrogenation reaction at different magnifications.

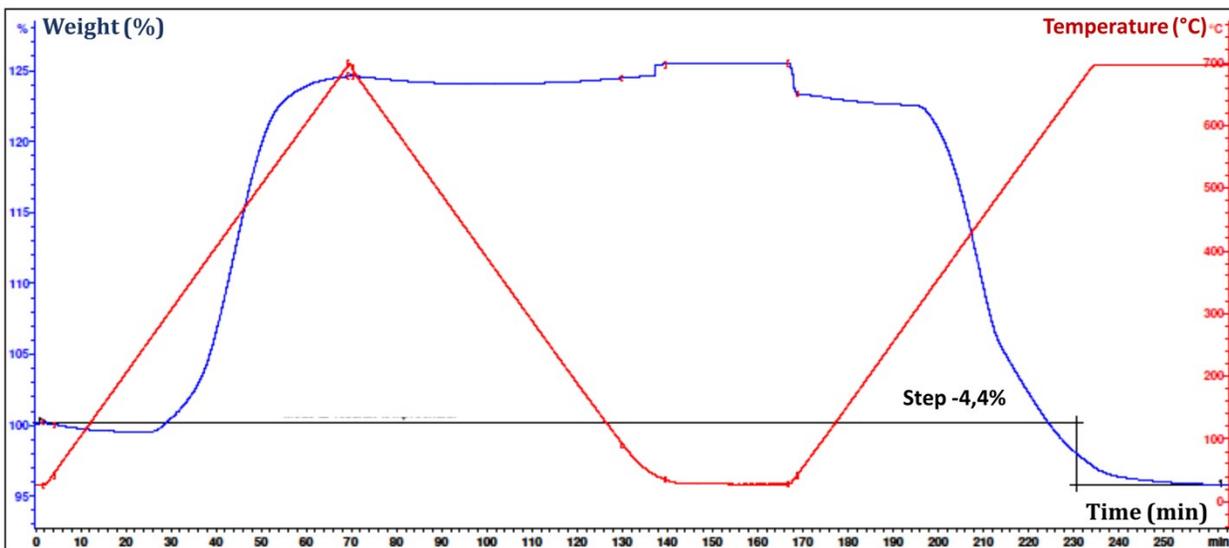
**Fig. S11.** *In-situ* DRIFTS spectra collected at 100°C from as-prepared Ni@Ni(OH)<sub>2</sub> foam under gas flow (switching from N<sub>2</sub> to CO<sub>2</sub> to H<sub>2</sub>). IR range for adsorbed (a) CO<sub>2</sub> and (b) HCO<sub>3</sub> species.

**Fig. S12.** (a) TEM micrograph and (b-d) SEM micrographs of Ni@Ni(OH)<sub>2</sub> foam prepared in 100%EtOH.

**Fig. S13:** (a) Ni 2p XPS spectra of Ni@Ni(OH)<sub>2</sub> foam prepared in THF/EtOH (90/10%v/v) (black, top line) and Ni@Ni(OH)<sub>2</sub> foam prepared in 100% EtOH (magenta, bottom line). The reference peaks of the 2p<sub>3/2</sub> orbitals are for Ni metal (Ni(0)) : 852.6eV; for NiO (Ni(II)) : 853.7eV ; and for Ni(OH)<sub>2</sub> (Ni(I)) : 855,6eV. (b) O 1s XPS spectrum of Ni@Ni(OH)<sub>2</sub> foam prepared in 100% EtOH and (c) XRD diffractogram of Ni@Ni(OH)<sub>2</sub> foam prepared in 100% EtOH, showing the classical Ni cfc pattern (ICCD:96-901-2978). Crystallite size = 6 nm (Scherrer equation).

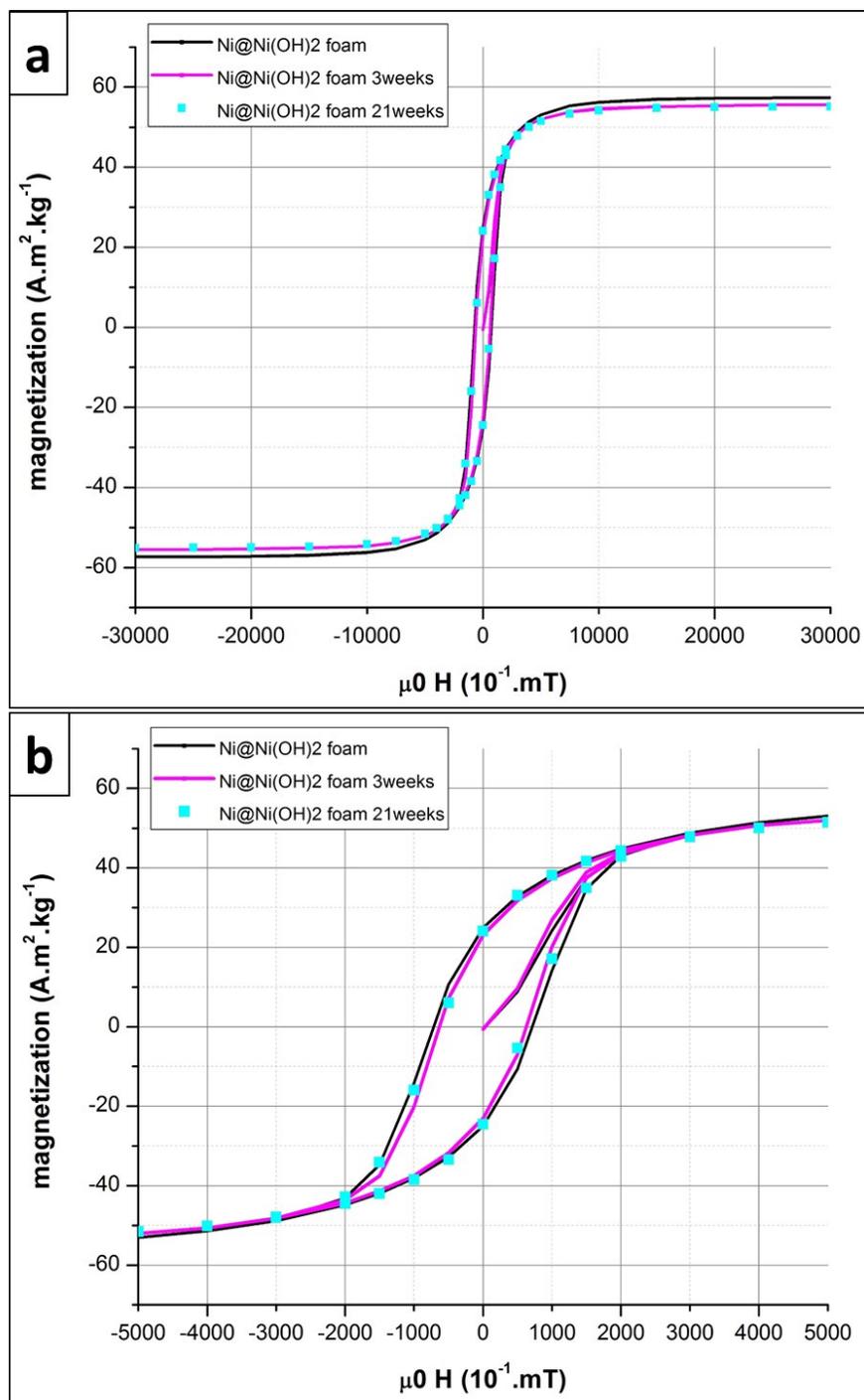


**Fig. S1.** Raman spectrum of as-prepared Ni@Ni(OH)<sub>2</sub> foam.



**Fig. S2.** TGA of as-prepared Ni@Ni(OH)<sub>2</sub> foam under oxidative/reductive atmosphere. Red line: temperature variation as a function of time; blue line: mass variation as a function of time.

The TGA sequence under oxidative/reductive conditions was performed in order to determine the nickel content in the as-prepared Ni@Ni(OH)<sub>2</sub> foam. First, the sample was heated under air to 700 °C (from 0 to 70min). This treatment led to organics removal while nickel was oxidized into NiO. After cooling down to 25°C, (from 70min to 140min) the sample was put under an H<sub>2</sub>/Ar (2% H<sub>2</sub>) atmosphere and then heated again to 700°C (from 170min to 260min). The final mass measured corresponds thus to the reduced Ni content in the Ni@Ni(OH)<sub>2</sub> foam (95%).



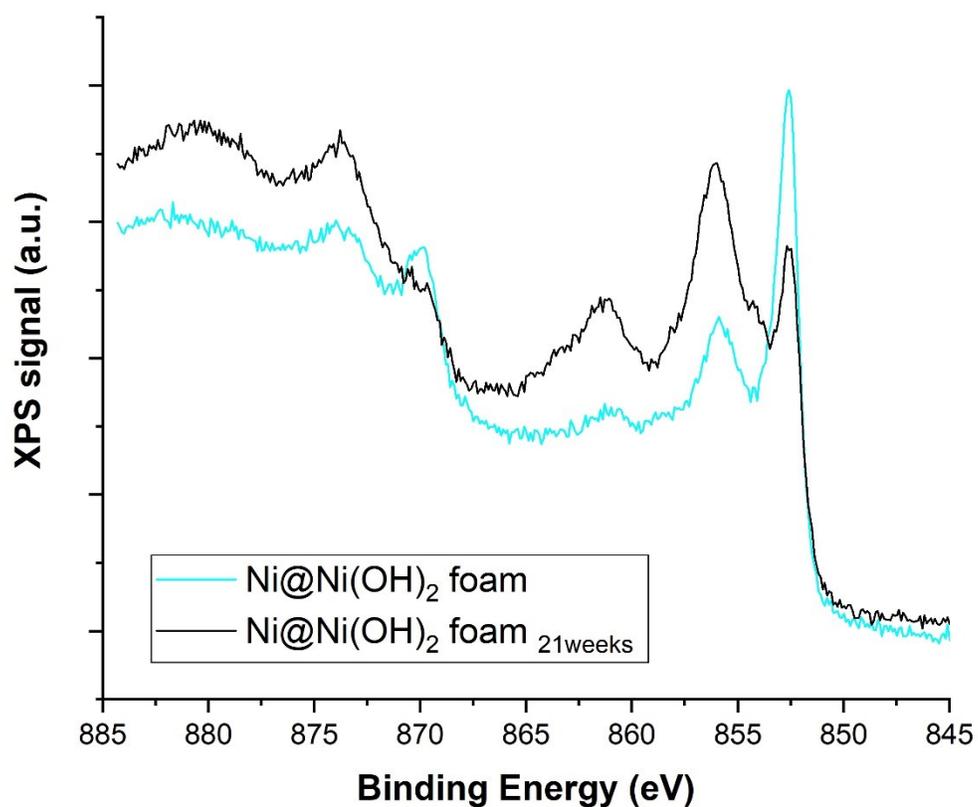
**Fig. S3.** Hysteresis cycles recorded at 5 K of: in black: as-prepared Ni@Ni(OH)<sub>2</sub> foam (ZFC process); in magenta: Ni@Ni(OH)<sub>2</sub> foam<sub>3weeks</sub> (FC process under 5T) and in cyan : Ni@Ni(OH)<sub>2</sub> foam<sub>21weeks</sub> (FC process under 5T).

Nickel is known for its resistance to oxidation when a passivation layer covers the metallic surface. The as-prepared Ni@Ni(OH)<sub>2</sub> foam displays a layer of nickel hydroxide covering the nickel cores which

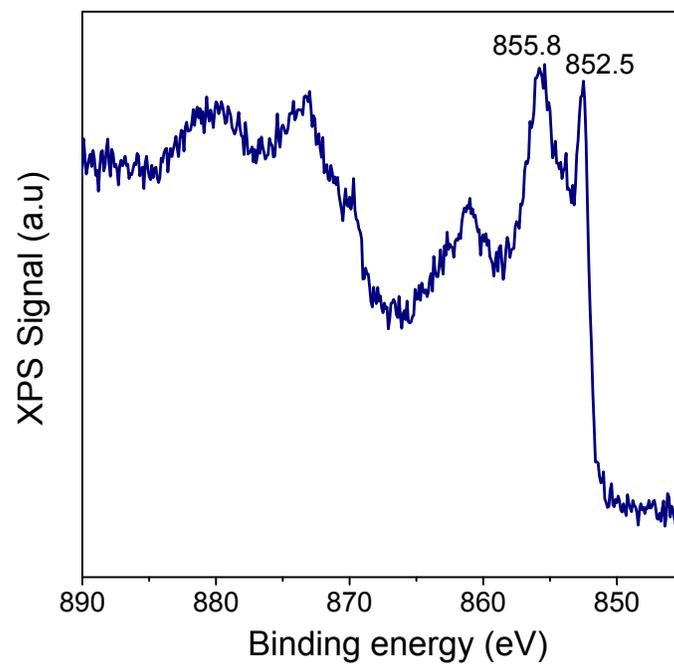
could provide protection against complete oxidation. To evaluate this protection, the as-prepared and argon-stored Ni@Ni(OH)<sub>2</sub> foam was exposed to ambient air for 1, 3, 6 and 21 weeks. The sample after 1 week of air exposure is named Ni foam<sub>1week</sub>, that after 3 weeks of air exposure Ni@Ni(OH)<sub>2</sub> foam<sub>3weeks</sub>, that after 6 weeks Ni foam<sub>6weeks</sub> and the last one, after 21 weeks of air exposure, Ni@Ni(OH)<sub>2</sub> foam<sub>21weeks</sub>.

After 3 weeks and then 21 weeks of air exposure, a SQUID analysis was performed (saturation magnetization is given per kg of material). Also, on the 21 weeks sample, a XPS analysis was performed. The magnetic properties of the Ni@Ni(OH)<sub>2</sub> foam<sub>3weeks</sub> and Ni foam<sub>21weeks</sub> were very close to those of the as-prepared Ni@Ni(OH)<sub>2</sub> foam (Fig. S3). The saturation magnetization decreased by less than 5% over 21 weeks: from 57.4 A·m<sup>2</sup>·kg<sup>-1</sup> (Ni@Ni(OH)<sub>2</sub> foam, corresponding to 97.4% of Ni(0)) to 55.7 A·m<sup>2</sup>·kg<sup>-1</sup> after 3 weeks of air exposure (Ni@Ni(OH)<sub>2</sub> foam<sub>3weeks</sub>, corresponding to 94.5% of Ni(0)) and to 55.0 A·m<sup>2</sup>·kg<sup>-1</sup> after 21 weeks of air exposure (Ni@Ni(OH)<sub>2</sub> foam<sub>21weeks</sub>, corresponding to 93.4% of Ni(0)). The coercive field was unchanged after 3 weeks (140 mT) and only slightly decreased after 21 weeks (125 mT). The magnetic measurement performed on Ni@Ni(OH)<sub>2</sub> foam<sub>3weeks</sub> and Ni@Ni(OH)<sub>2</sub> foam<sub>21weeks</sub> samples followed a field cooling sequence from 300 K to 5 K under 5T. Contrarily to what is usually observed in crystalline Ni-Ni(OH)<sub>2</sub> structures, the corresponding hysteresis cycles did not show any exchange bias, in agreement with the amorphous character of the Ni(OH)<sub>2</sub> surface layer.

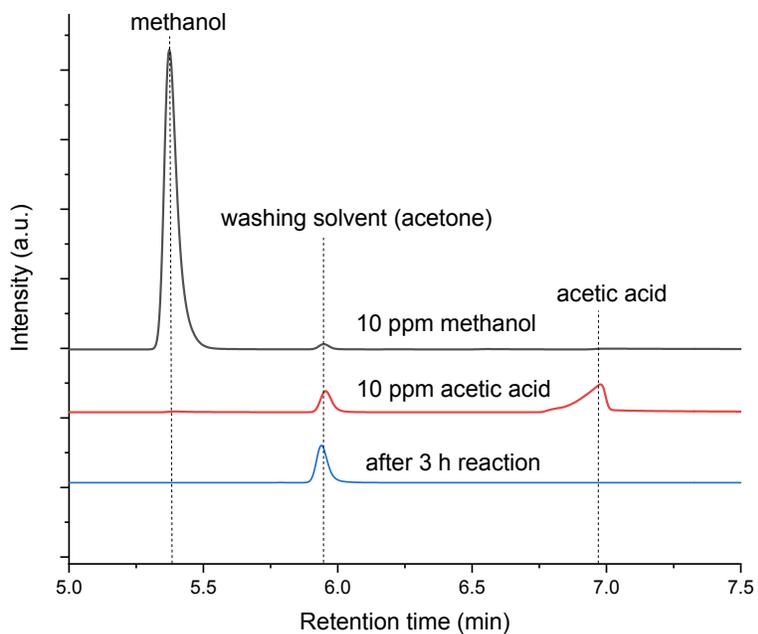
The XPS spectra of the as-prepared Ni foam (Ni@Ni(OH)<sub>2</sub> foam, blue) and the 21 weeks air exposed Ni foam (Ni@Ni(OH)<sub>2</sub> foam<sub>21weeks</sub>, orange) are presented in the Fig. S4. A clear increase of the Ni(OH)<sub>2</sub> contribution and decrease of the Ni metal one were observed after 21 weeks, indicating that the outside Ni hydroxide layer thickened with time under air. We also observed a small contribution of NiO (peak at 853.7 eV) thus indicating a progressive apparition of the oxide after a very long period of air exposure. Based on the results obtained after air exposure, we can conclude that the Ni foam oxidation process is quite slow, and that its core-shell Ni@Ni(OH)<sub>2</sub> structure is maintained in the oxidation conditions applied.



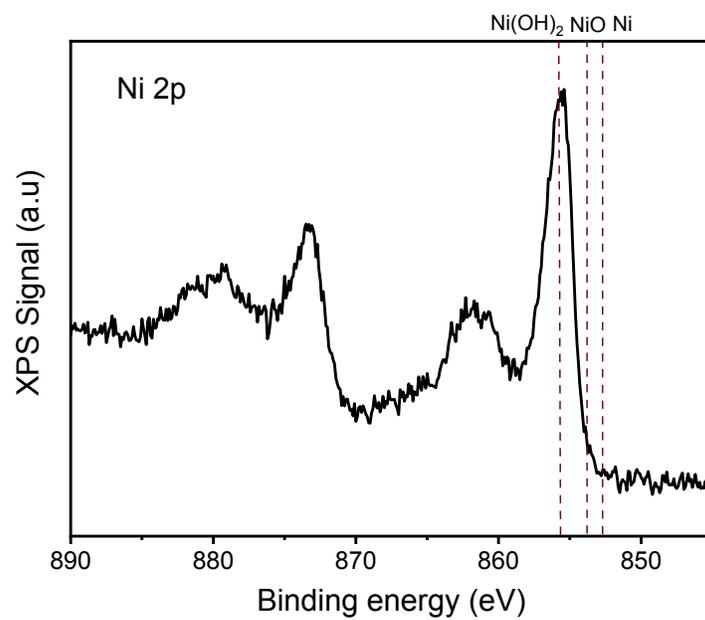
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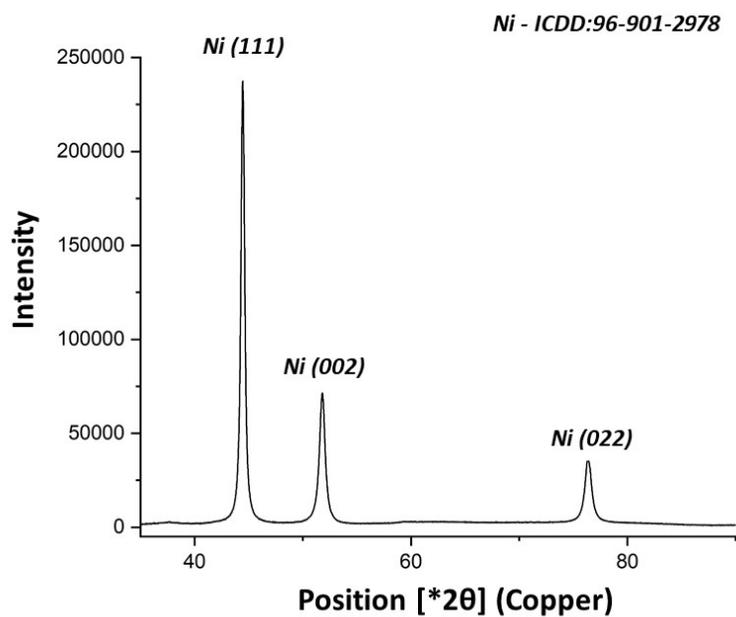
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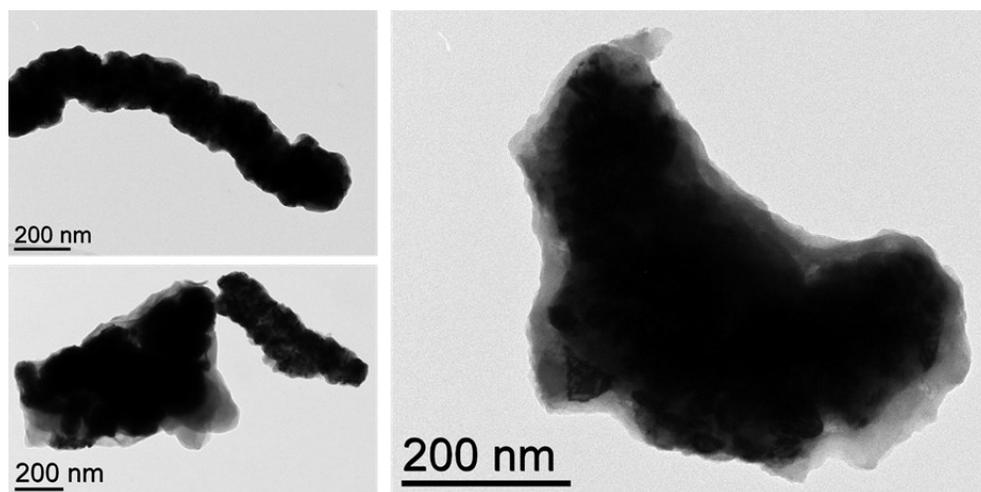
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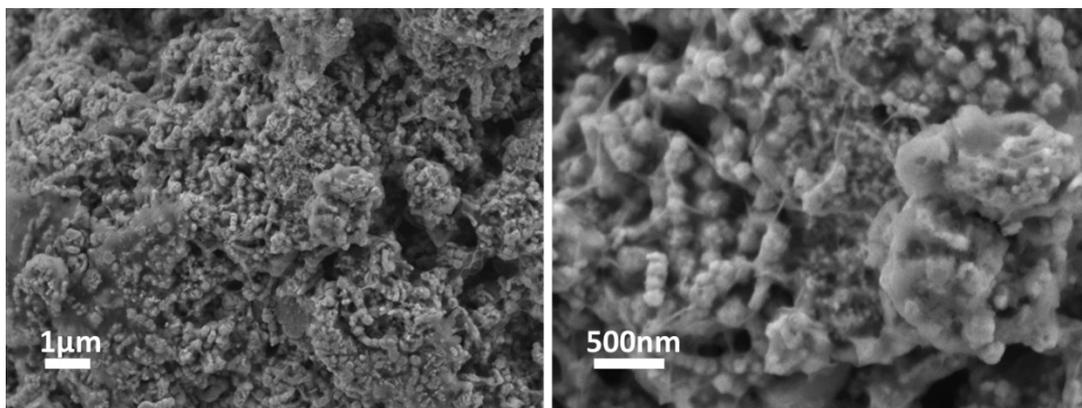
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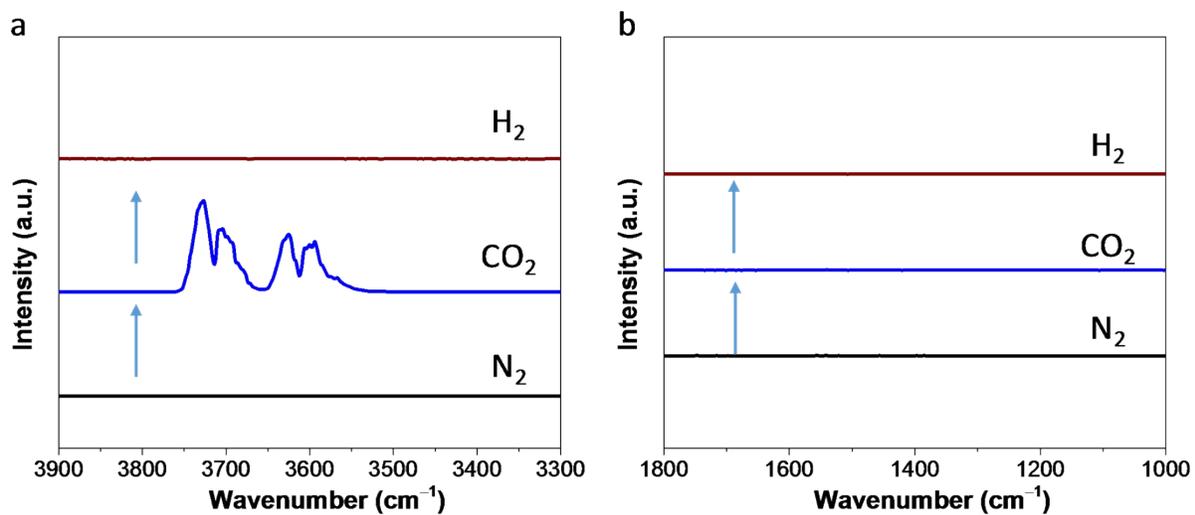
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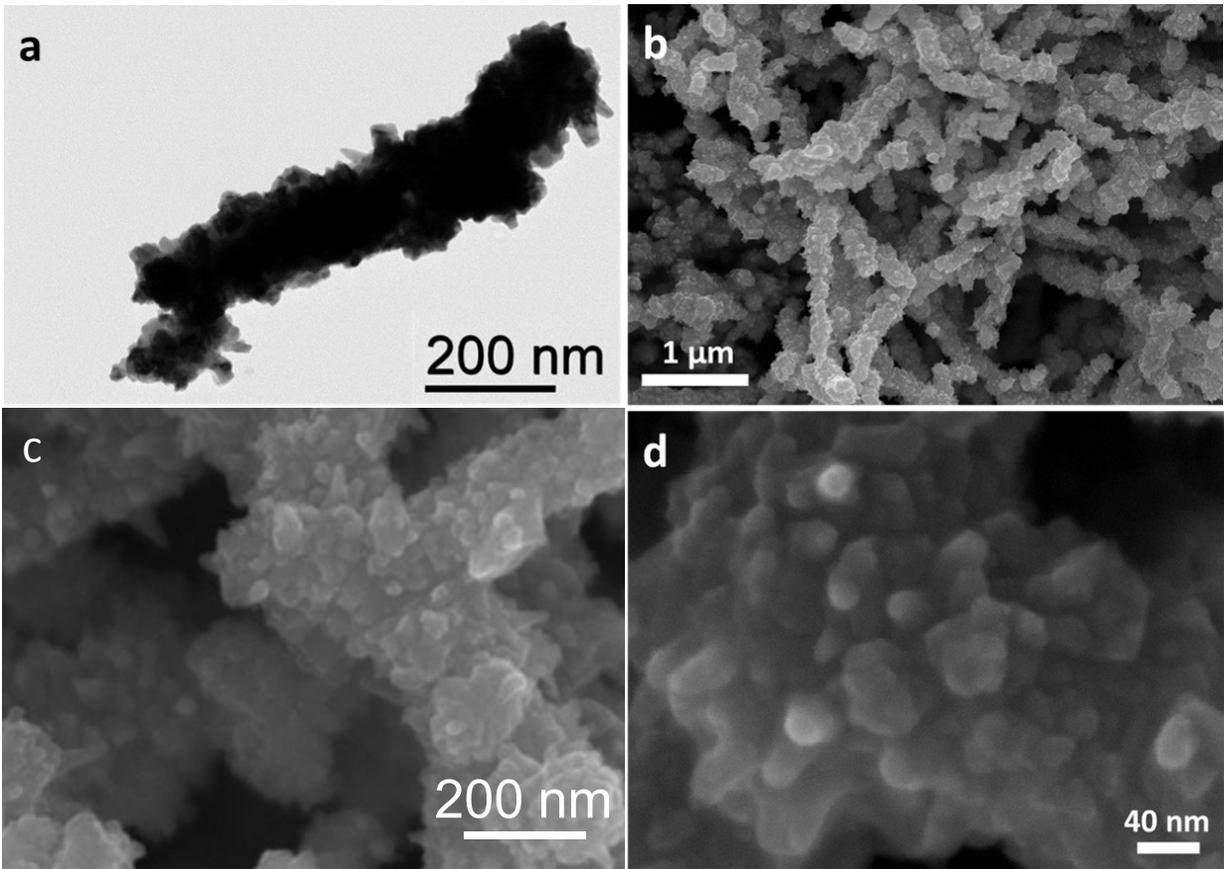
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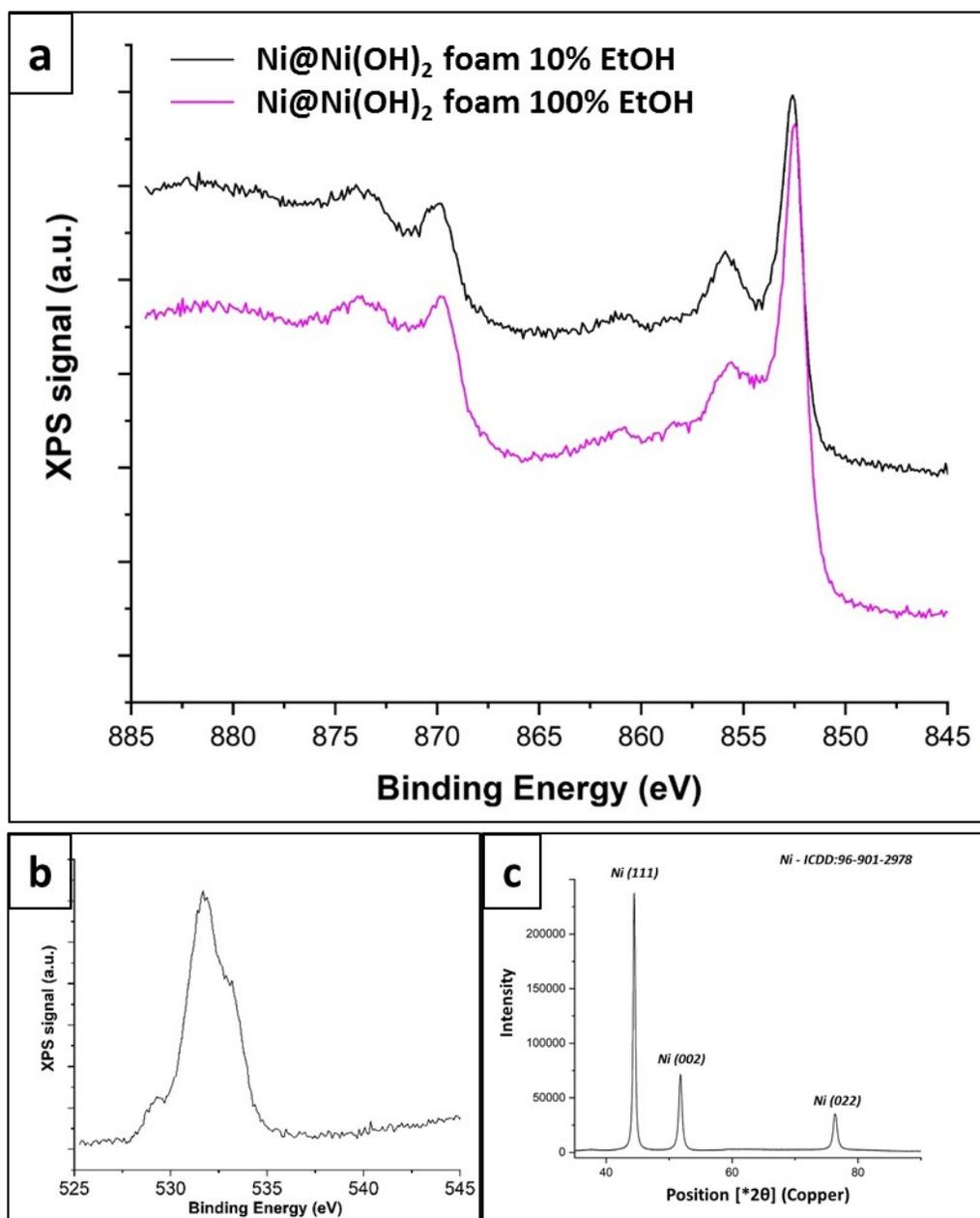
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