Supplementary Information

A new non-complex synthesis of NiO nanofoams for hydrogen storage application

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Small Angle X-Ray Scattering (SAXS) measurements

The Small Angle X-ray Scattering (SAXS) measurements were conducted in the Nano-inXider (Xenocs) equipment. Around 12 mg of the sample composed by the mixture of salt precursor, glucose, and phytantriol during the synthesis of the NiO nanofoam at room temperature was inserted in the sample holder sealed by a kapton tape. The SAXS patterns were acquired with a Cu K-α x-ray source, a semitransparent beamstop and a Dectris Pilatus 3 detector. The measurements were performed in the transmission mode with a 2θ range from 0.00º to 5.25º and 60 s exposure time for each scan. The final SAXS pattern was the result from an average of 60 scans. The conversion of symmetric 2D SAXS data to 1D data and average between multiple scans were made on FOXTROT software.21. Figure S1 shows the SAXS pattern measured for the sample.
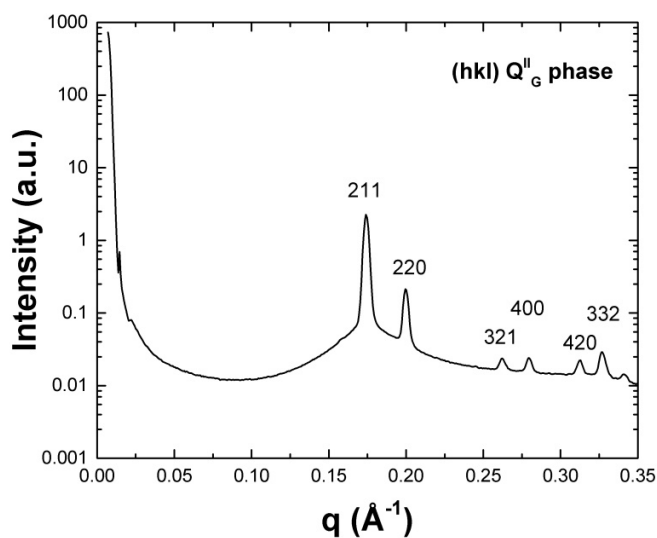

Figure S1 – SAXS pattern of the mixture between salt precursor, glucose and phytantriol during synthesis of the NiO nanofoams.

Thermogravimetric Analysis (TGA) measurements

     The TGA measurements were carried out using a SDT Q600 (TA Instruments) equipment. About 50 mg of phytantriol in the Q^G_{II} phase mixed with $NiCl_2.6H_2O$ and glucose were spread over an alumina crucible and heating to 600 °C with a heating rate of 10 °C/min and a flux of 100 mL/min of synthetic air. Figure S2 shows the TGA measurement indicating that the calcination at 500 °C ensures the removal of the organic components in the sample.
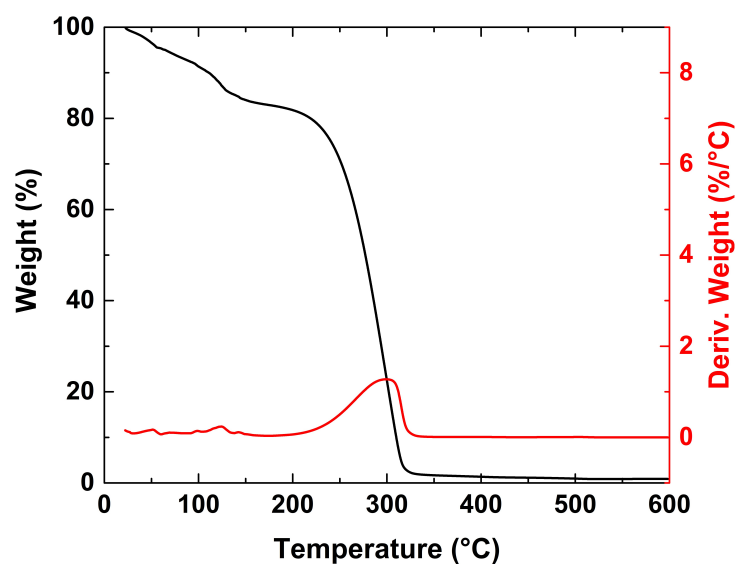

Figure S2 – TGA measurements of the mixture between salt precursor, glucose and phytantriol during synthesis of the NiO nanofoams.

Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) measurements

The TEM measurements were performed using a Tecnai G2-20 SuperTwin FEI 200 kV equipment. The STEM images were obtained using an XFEG Cs-corrected FEI Titan 80/300 microscope operated at 300 kV with a high-angle annular dark field (HAADF) detector. For both TEM and STEM measurements, the nanoparticles were dispersed in deionized water, stirred in ultrasound batch for 30 min, and then a drop of the solution was deposited on a C-coated Cu grid and dried.

X-ray Diffraction (XRD) measurements

The XRD measurements were performed in order to identify the crystalline phases present in the nanostructures and to obtain information about the crystallite size using the Rietveld analysis. An X-ray diffractometer (Rigaku Ultima IV) working at the Bragg-Brentano geometry at 40 kV and 25 mA with a Cu Kα radiation source (1.5405 Å) was used. The sample in the powder form was placed in the sample holder without sieving since the powder already presented sufficiently small grains. The measurements were performed in the 2θ range from 30° to 80° with a step size of 0.05° and an acquisition time of 3 s/point.

In order to determine quantitatively the percentages of metallic Ni and NiO phases that constitute the samples, the diffraction patterns were analysed with the Fullprof Suite software using the Rietveld refinement method. Aiming to obtain the domain crystallite size, the Thompson-Cox-Hastings pseudo-Voigt Axial divergence asymmetry profile

function was used. The cubic crystal structure of metallic Ni and NiO and the atomic positions of Ni and O atoms at the base vectors were used as input in the Fullprof software. Firstly, the diffraction pattern of a quartz standard sample was refined in order to obtain the equipment resolution file, which is necessary to determine the crystallite size of the nanofoams analysed. Then, the diffraction patterns were refined using the constrains:

- The V and W parameters of the Gaussian contribution of the profile function were determined by refining the quartz standard sample and fixed to 0 for the analysis of the diffraction patterns.
- The isotropic temperature parameter (B-factor) and the occupancy number values of each atomic species of each phase were fixed to the values obtained in the crystallographic information file (CIF) of metallic Ni[1] and NiO.[2]
- The overall B-factor was fixed to 0.

The χ^2, R_{wp} and R_{exp} values obtained were 1.21, 21.3 and 19.3, respectively, which demonstrates the good quality of the Rietveld refinement results.

X-ray Photoelectron Spectroscopy (XPS) measurements

The XPS measurements of the nanofoams synthesized were performed in order to investigate the chemical components present at the nanofoam surface. A NiO standard sample was also measured for comparison purposes. For the measurements, a thin layer of the nanofoams powder was dispersed on a copper tape, placed over a molybdenum sample holder, and exposed to the ultra-high vacuum (UHV) condition inside the analysis chamber. The base pressure during the measurements was around 10^{-9} mbar. The XPS measurements

were performed at room temperature utilizing an Al K_α X-ray source (1486.6 eV). The XPS measurements were performed at the Long Scan, Ni $2p_{3/2}$, O 1s, and C 1s electronic regions. The electron analyzer (Omicron Sphera) was set at a pass energy of 50 eV and 10 eV with energy step of 1.0 eV and 0.1 eV and acquisition time of 0.2 s/point and 2 s/point for the long scan and high resolution scans, respectively.

The Ni $2p_{3/2}$ XPS spectra were adjusted with the XPSPeak 4.1 software. A Shirley-type background[3] was used and symmetric Gaussian-Lorentzian sum functions with 18% Lorentzian contribution were included to adjust the spectra. The Lorentzian contribution was determined from the XPS spectrum at Au 4f region of a Au standard foil. The charging effects were corrected by the adventitious carbon component at 284.5 eV. The FWHM of the NiO component at Ni $2p_{3/2}$ electronic region was determined by fitting the XPS spectrum of the NiO standard. In addition, the relative intensity of the two NiO components present in the Ni $2p_{3/2}$ region was kept constant to the value obtained by fitting the Ni $2p_{3/2}$ XPS spectrum of the NiO standard.

Flame Atomic Absorption Spectrometry (FAAS) measurements

About 50 mg of NiO nanofoams supported on activated carbon was used for the FAAS measurements and weighted directly into Xpress model PTFE vials (CEM). After, 3 mL of aqua regia and 2 mL of ultra-purified water were added to the sample. After 10 min, each vial containing sample was properly sealed and inserted into the Mars6 microwave system (CEM). The sample was heated to 120 °C during 10 min and maintained at this temperature for 30 min. After this, the sample was cooled to room temperature during 1 h

and transferred to graduated polypropylene tubes containing 5 mL of ultrapurified water, then filling 30 mL of the tube. The final solution showed residual material. Therefore, in order to enable analysis by FAAS, the solution was centrifuged at 3000 rpm for 10 min. The measurements were performed in a Perkin-Elmer - AAnalyst 200 equipment, using hollow cathode lamps (LUMINATM Hollow Cathode Lamp - Perkin-Elmer), in air-acetylene flame mode at flow rates of 10 and 2.75 L/min. The measurements were performed with a photon wavelength of 341.48 nm without using a background corrector (AA mode).

Hydrogen Adsorption measurements

The hydrogen adsorption measurements were conducted using activated carbon charcoal SX Ultra from Norit, presenting a surface area of (1042 ± 15) m^2/g, as a support. A sample of pure activated carbon was also measured for comparison purposes. A multipurpose equipment coupled to a thermal conductivity (TCD) detector was used. The equipment consists of a U-shaped quartz tube connected to two mass flow controllers of N_2 and H_2. N_2 was used as a reference and carrier gas. Before the measurements, the sample was exposed to 30 mL/min of 100% N_2 and heated to 110 °C (10 °C/min heating rate). At this temperature, the sample was kept during 30 min in order to remove humidity and to clean the nanofoams surface. At the end, the sample was cooled to room temperature. The adsorption measurements were performed at room temperature with the sample exposed to 30 mL/min of 5% H_2 + 95% N_2 at 1 bar. The result shown by the equipment consists of the

difference between the thermal conductivities of the gas mixture and the pure N_2 gas used as reference as a function of time.

In order to quantitatively determine the amount of hydrogen adsorbed, the difference in the areas (ΔA) of the curves corresponding to the signal of the adsorption measurement described above and the theoretical signal of the completely saturated sample was used (Figure S3). The ΔA quantity is related to the amount of hydrogen adsorbed by the sample. The time required for the sample to adsorb hydrogen and to saturate (t_{sat}) can be determined by equation 1.

$$t_{sat} = \frac{\Delta A}{H_{sat}} \qquad (1)$$

where H_{sat} is the thermal intensity after sample saturation. The volume of hydrogen adsorbed by the sample can be calculated by multiplying t_{sat} by the H_2 flux used during the measurement (Q_{H2}), as shown in equation 2.

$$V_{H2}^{ad} = t_{sat} \, Q_{H2} \qquad (2)$$

The gravimetric density can be obtained with the V_{H2}^{ad} value using the ideal gas state equation, by considering the temperature and pressure conditions in which the hydrogen adsorption measurements were performed.
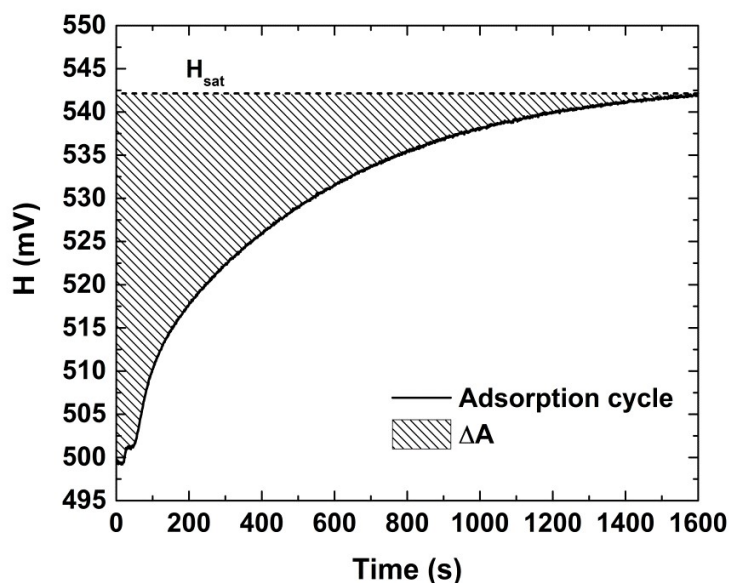
Figure S3 – Adsorption measurement. The ΔA area is indicated by the hatched region. The H value after sample saturation (H_{sat}) is indicated as well.

Temperatura-programmed Desorption (TDS) measurements

Temperature-programmed desorption of hydrogen (TPD-H_2) was performed in a dynamic mode apparatus, equipped with a mass spectrometer QMG-220 (Pfeiffer). The sample (typically 0.1 g) was treated with Ar up to 110 °C (10 °C min^{-1}) for 30 min, and then cooled to room temperature. The H_2 adsorption was carried out at room temperature with a mixture of 2 % H_2/Ar (30 mL min^{-1}) for 1 h, followed by purging with Ar for 1 h. The desorption of chemisorbed H_2 was performed by heating up to 1000 °C (20 °C min^{-1}) under Ar flow (30 mL min^{-1}). The ratio m/z = 2 was used to determine the amount of desorbed H_2. Figure S4 shows the TPD-H_2 measurement result.
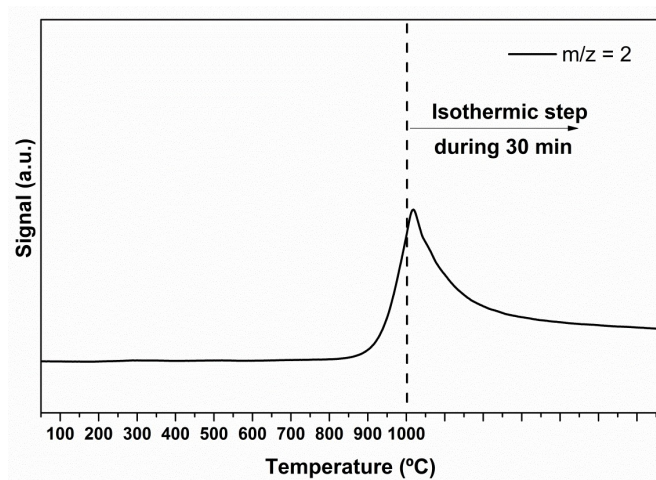
Fig. S4 – TPD-H_2 measurement of the NiO nanofoams showing the H_2 signal (m/z = 2) detected during the thermal treatment.

DFT calculations

The spin-polarized DFT calculations were performed using the Quantum-ESPRESSO 5.4.0 package. An ultrasoft pseudopotential was employed using the projector-augmented wave (PAW) method to describe the effect of the core electrons on the valence electrons of Ni, O and H atoms. For the exchange correlation functional, the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) was used. In order to consider the effects of Van der Waals interactions, a semiempirical model of dispersive forces was used. A plane wave kinetic energy cut-off of 62 Ry and a charge density kinetic energy cut-off of 240 Ry were used. Gaussian smearing was used with a 5×10^{-3} Ry width aiming to describe the electronic occupations. For the relaxation procedure, the convergence threshold on the total energy and convergence threshold on

forces for ionic minimization were chosen as 10^{-4} and 10^{-3} Ry, respectively. The convergence threshold for self-consistency calculations was chosen as 10^{-6} Ry.

The atomic positions of Ni_{13} and Ni_4O_4 clusters were first relaxed and then the total energy of the ground state was determined through a selfconsistency calculation. This energy was determined for the case of 0, 1, 2, and 3 H_2 molecules around the cluster. In all cases, the H_2 molecule was initially placed 2.5 Å away from a Ni atom present at the cluster surface so that each H atom was at the same distance of this atom. Moreover, it was used a cubic unit cell of 20 Å size in order to minimize the interactions due to the unit cell's periodicity. The difference on the total energy is smaller than 5×10^{-6} Ry whether changing 5 Å in the cubic unit cell size.

For the Ni(111) and NiO(100) slabs, the calculations were performed using 4 atomic layers of the cubic crystal structure of Ni, oriented in the (111) direction, and NiO, oriented in the (100) direction. A vacuum layer of 15 Å was set between the slabs to minimize their interaction. The atomic positions of the two bottom layers were fixed while those of the two top layers were relaxed.

In order to determine the binding energy and the adsorption regime (physisorption, chemisorption or quasi-molecular bonding) of the H_2 molecules in the clusters, the adsorption energy per H_2 (E_{ads}) and the variation in the sequential H_2 adsorption energies (ΔE_x) were calculated using:

$$E_{ads} = \frac{E[xH_2/M_n] - E[M_n] - xE[H_2]}{x} \tag{3}$$

$$\Delta E_x = E[xH_2/M_n] - E[(x-1)H_2/M_n] - E[H_2] \tag{4}$$

where x is the number of H_2 molecules, E is the total energy of the ground state and M_n refers to the cluster with n atoms.

References

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