
Electronic Supplementary Information

Novel solid metal-organic self-propagation combustion for controllable synthesis of hierarchically porous metal monoliths

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Experimental Section

Materials Synthesis: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent, AR) was employed as oxidizer, glycine (AR) as fuel. In a typical case, 50mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (N) and 75mM glycine (G) with $G/N=1.5$ were first dissolved in 30ml deionized water to form a uniform solution. The solution was then heated at 100°C for 30min to vaporize water and obtain viscous transparent gel. Afterwards, the gel was dried at different T_s (70°C , 100°C , 160°C and 200°C) for 12h in a vacuum oven and solidified into an irregular foam. After being ground into powders in Ar-filled glove box, precursor powders were compacted into pellets with desired shape and size under pressure of 10MPa. Finally, the precursor pellets were fixed between quartz plates before locally ignited at room temperature (RT) under air atmosphere by a Ni-Cr resistance wire with a current of 700mA. The high gas pressure combustion experiments of precursors pellets ($T_s=160^\circ\text{C}$) have been conducted at RT in a 10L stainless steel reactor filled with N_2 pressure ranging from 1atm up to 7MPa.

Hierarchically porous (HP) Ni monoliths ($T_s=200^\circ\text{C}$, ignited at RT under air atmosphere) with a weight of 85 mg and a diameter of 16mm were used as current collectors for supercapacitor electrodes. NiCo_2O_4 were loaded on HP Ni monoliths according to reference.^[1] For comparison, commercial Ni foams with comparable weight and size were also used as current collectors. The mass of active material synthesized under the same condition was estimated to be 13.4 mg and 3.4mg for NiCo_2O_4 on HP Ni monolith and commercial Ni foam, respectively.

Process Monitor. Maximum temperature (T_{max}) of combustion wave was carefully measured by a 0.1 mm K-type thermal couple. Data were collected by Agilent 34980A with 34921A module and BenchLink Data Logger Pro software at a frequency of 250 Hz. The combustion processes in air were recorded by a digital camera (Panasonic DMC-LX5GK), based on which the propagating velocities were estimated.

Materials Characterization. The pyrolysis behaviour of gel precursors was analyzed by thermal gravimetric–differential scanning calorimetry (TG–DSC, Netzsch STA449C Jupiter) in air at a heating rate of $10^\circ\text{C}/\text{min}$. The structural information of precursors and products was characterized with X-ray powder diffractometer (Rigaku D/max-2550, Cu K α radiation, $\lambda=1.5406 \text{ \AA}$). The bonding states of solidified precursors were characterized using Fourier Transformation Infrared Spectroscopy (Thermo Scientific Nicolet 6700) in the range of 4000–400 cm^{-1} with KBr discs. SEM micrographs and X-ray energy dispersive spectra (EDX) were acquired on a FEI Qanta FEG 250 microscope operated at 10 kV. The specific surface area and pore size distribution were characterized by mercury intrusion porosimetry (Micromeritics AutoPore IV 9500) and Brunauer-Emmett-Teller method of nitrogen adsorption at low temperature (Quanta Quadrasorb SI-3MP).

Electrochemical performance. The as-prepared electrodes were tested with a three-electrode cell configuration, consisted of a Pt counter electrode and Hg/HgO as the reference electrode.

A 3M KOH aqueous solution was used as the electrolyte. The electrodes were electrochemically activated on an Arbin battery testing system by cyclic voltammetry(CV) method between 0 to 0.6V v.s. Hg/HgO at a scanning rate of 20 mV/s for 1000 cycles. Afterwards, cyclic voltammograms were collected at a scanning rate of 5mV/s and the galvanostatic charge–discharge tests were conducted between 0 to 0.55V v.s. Hg/HgO at a current density of 10mA/cm².

Results section

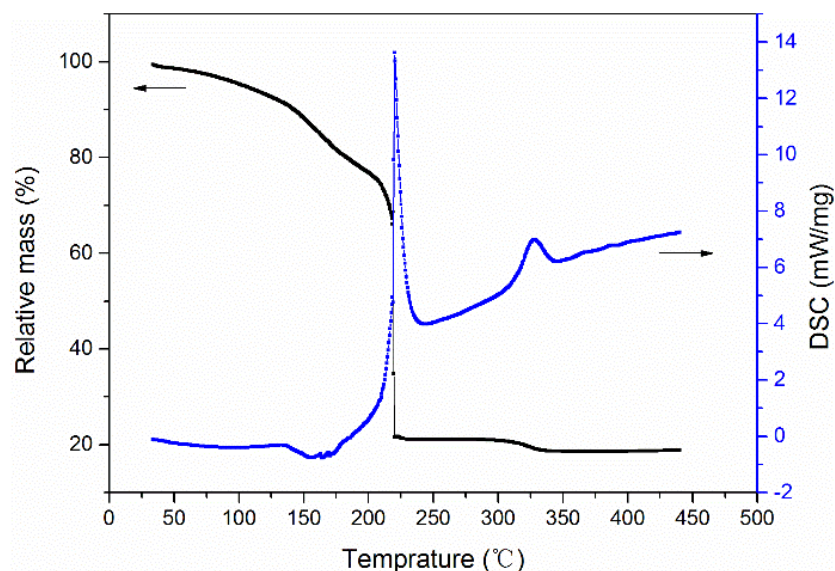


Fig. S 1 Thermal gravimetric–differential scanning calorimetry (TG–DSC) of gel precursors with G/N=1.5.

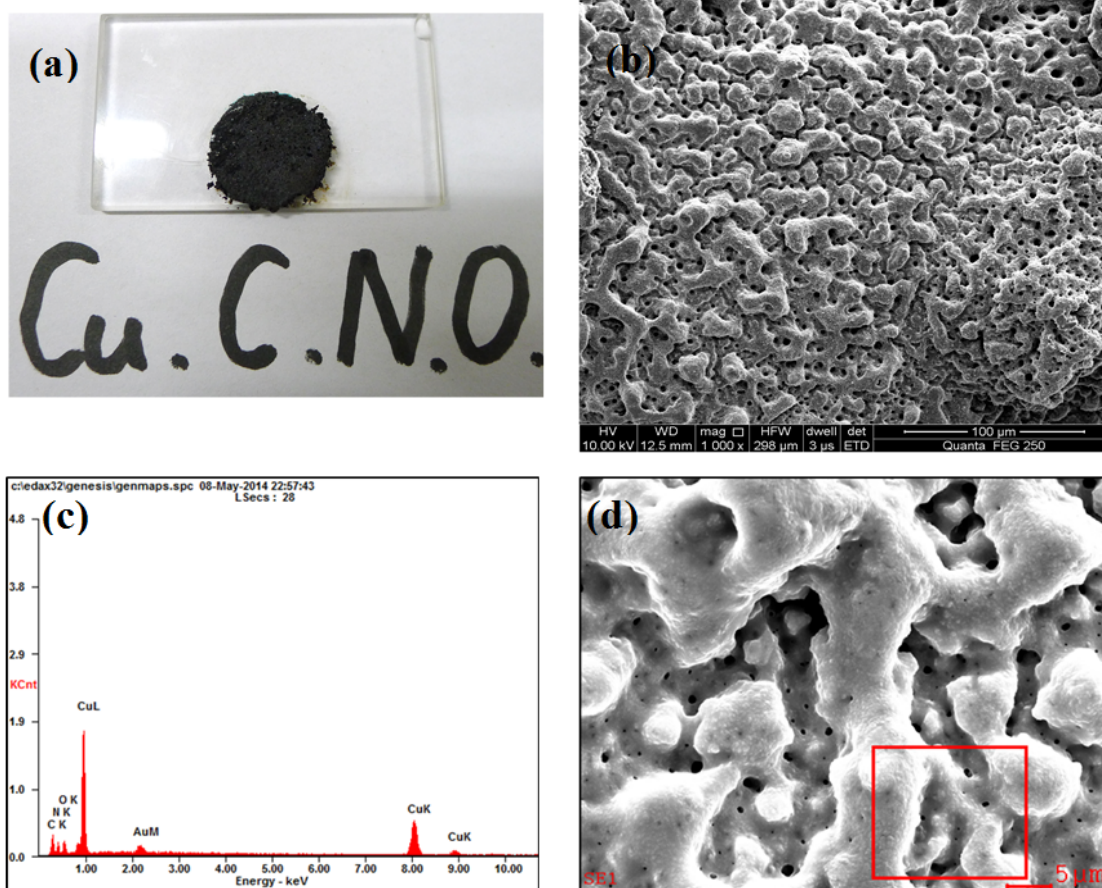


Fig. S 2 (a) Optical picture (b) SEM micrograph (c) and (d) energy dispersive spectroscopy of copper monoliths synthesized by the solid metal-organic self-propagation combustion method (with G/Cu ratio =2.5, precursors dried at $T_s=120^{\circ}\text{C}$ and ignited at RT under air atmosphere).

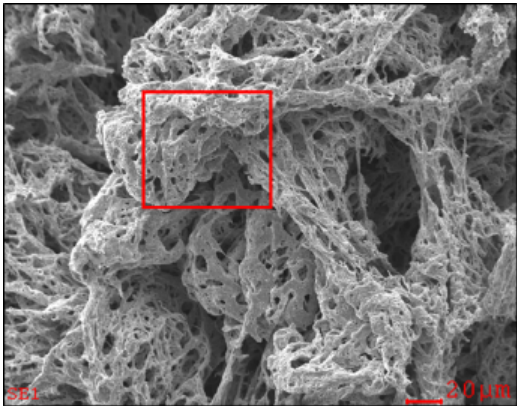
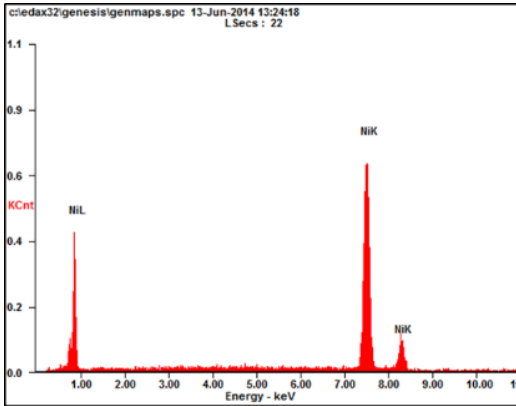
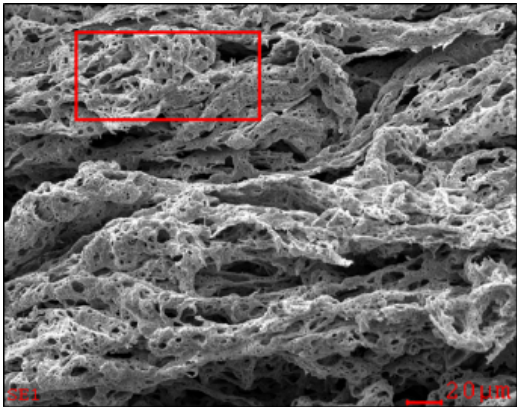
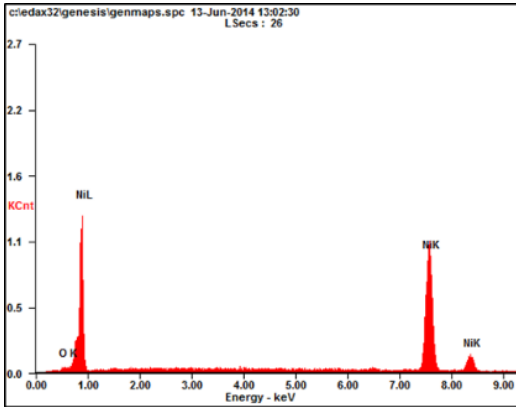
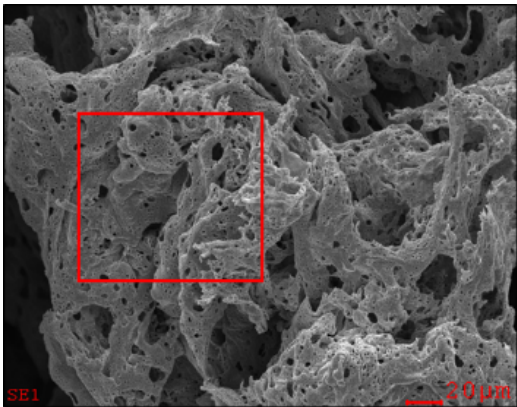
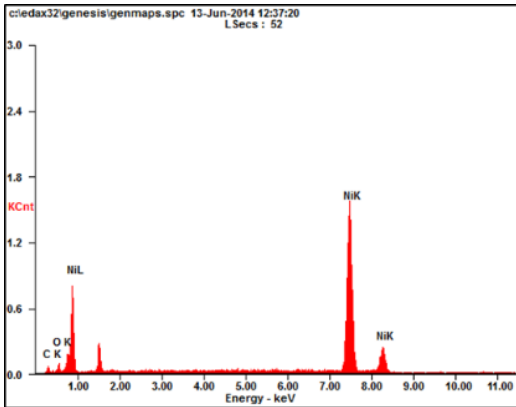
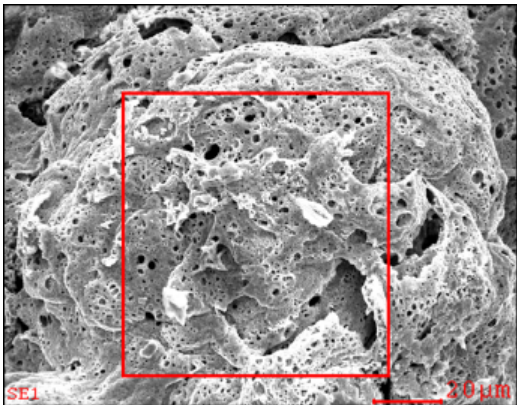
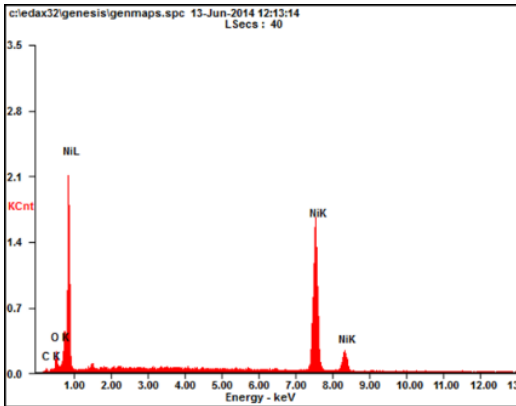


Fig. S 3 Energy dispersive spectroscopy of as-synthesized porous Ni monoliths with precursors dried at different T_s : 70 °C, 100 °C, 160 °C and 200 °C (from top to bottom, all ignited at RT under air atmosphere).

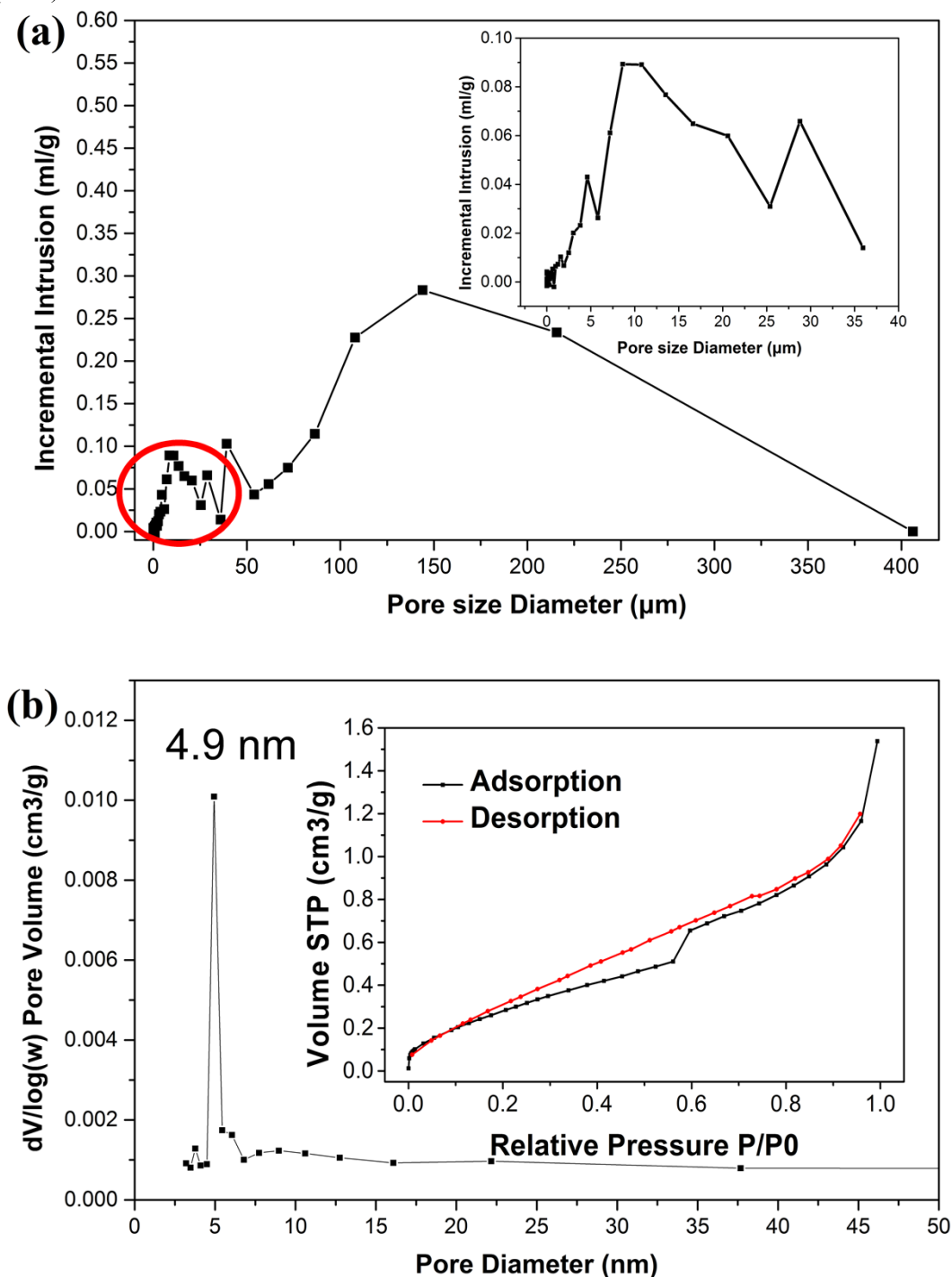


Fig. S 4 Pore size distribution of Ni monoliths (with precursors dried at $T_s=200^{\circ}\text{C}$, ignited at RT under air atmosphere) by (a) mercury intrusion porosimeter (the inset is the enlarged view of the red-circled part) and (b) low temperature N₂ adsorption-desorption (the inset is the adsorption-desorption isotherms) calculated by the BJH method from the adsorption branch.

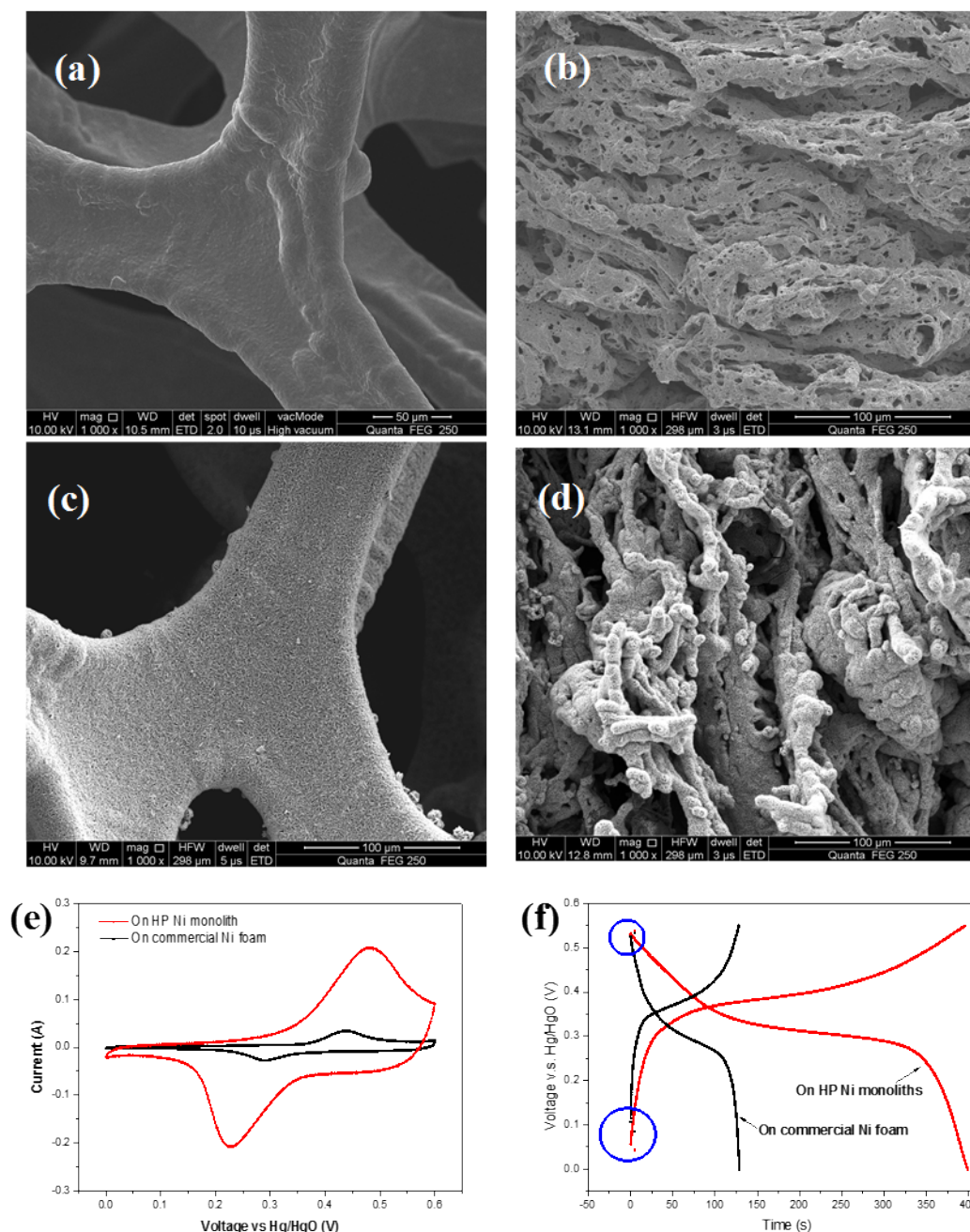


Fig. S 5 SEM micrographs of (a) (c) commercial Ni foams and (b) (d) as prepared HP Ni monoliths ($T_s=200\text{ }^{\circ}\text{C}$, ignited at RT under air atmosphere) before (a) (b) and after (c) (d) electrochemically active materials loading; (e) cyclic voltammograms of both electrodes at a scanning rate of 5 mV/s ; (f) galvanostatic charge-discharge of both electrodes at a current density of 10 mA/cm^2

The mass loading of electrochemically active materials on the HP Ni monoliths (13.4 mg) is much higher than that on commercial Ni foams (3.4 mg) under the same synthesis condition, suggesting that the HP Ni monoliths possess higher specific surface area (also see Fig. S 5 (a~d)). The CV and galvanostatic charge-discharge results confirm that higher specific capacitance was achieved in the HP Ni monolith electrodes at the same testing conditions

(Fig. S 5 (e) and (f)). Also, the voltage drifts are comparative for both electrodes when current is reversed (see the blue circles in (Fig. S 5 (f)), indicative of small internal resistance of the HP Ni monolith electrodes. This reveals higher capacitance and good rate performance for HP Ni monoliths as the current collectors for supercapacitors.

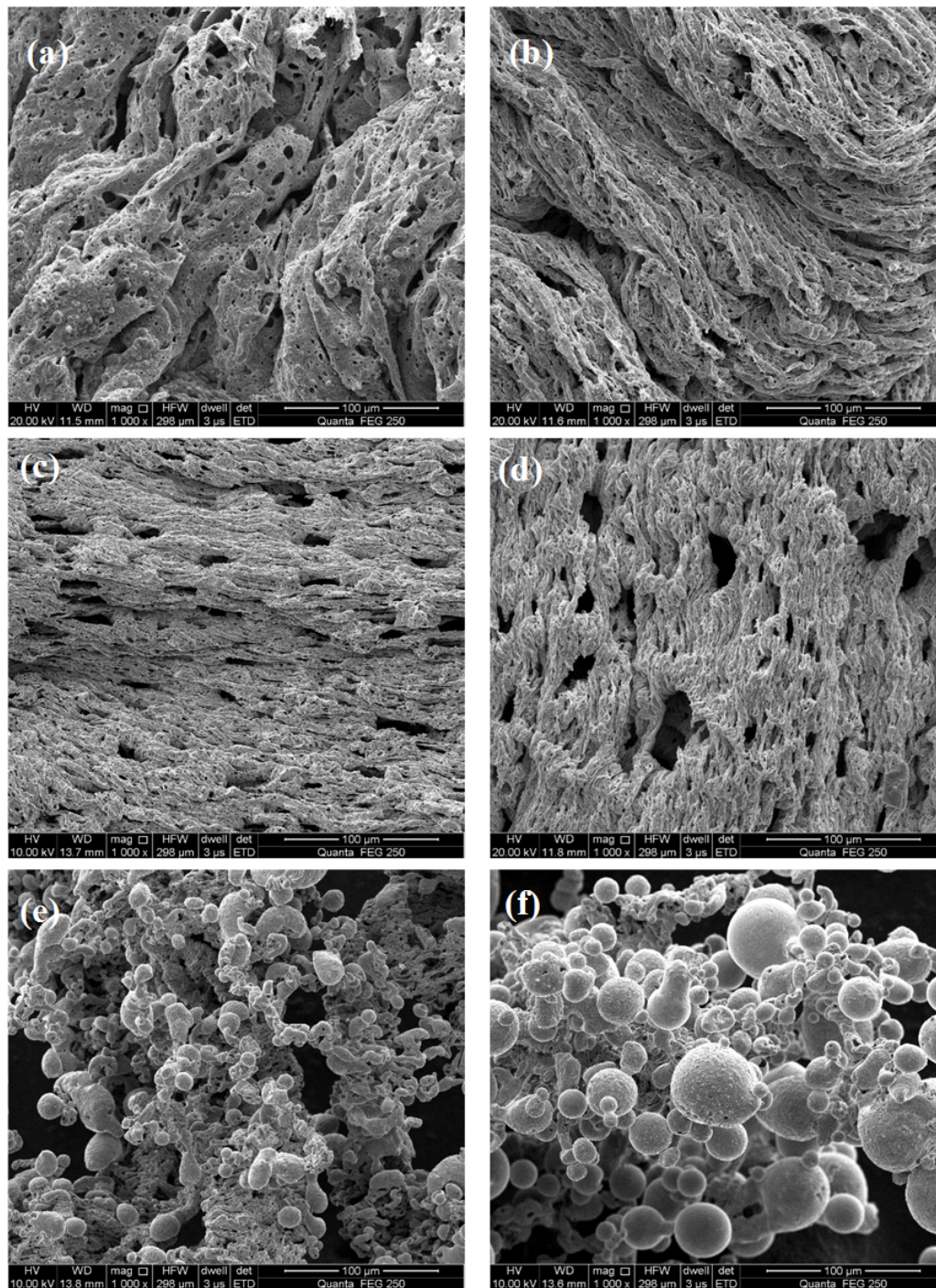


Fig. S 6 SEM micrographs of Ni monoliths (with precursors dried at $T_s=160^\circ\text{C}$) synthesized at RT but under different N₂ pressure (a) 1 atm (b) 1 MPa (c) 2 MPa (d) 3 MPa (e) 4 MPa (f) 7 MPa (scale bar 100 μm)

Reference

- [1] CHEN Y, QU B, HU L, et al. High-performance supercapacitor and lithium-ion battery based on 3D hierarchical NH₄F-induced nickel cobaltate nanosheet-nanowire cluster arrays as self-supported electrodes [J]. *Nanoscale*, 2013, 5(20): 9812-20.