

Supporting Information

High-Performance Asymmetric Supercapacitor Designed with Three-Dimensional Interconnected Porous Carbon Framework and Sphere-like Nickel Nitride Nanosheets

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S1. Material characterization

X-ray diffraction (XRD) of materials were performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu K α radiation ($k = 1.5418 \text{ \AA}$). The morphologies and structures of the as-prepared materials were examined with field emission scanning electron microscopy (FE-SEM, Carl Zeiss-Ultra Plus, Germany) and transmission electron microscopy (TEM, FEI Tecnai G² F20, USA). The Brunauer-Emmett-Teller (BET) surface area of the samples was analyzed by nitrogen adsorption-desorption in a surface area and porosimetry analyzer (ASAP 2020, Micromeritics, U.S.A.). Raman spectras were performed on an inVia Raman spectrometer (Rainie Salt Public Co. Ltd., Britain) with a laser wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 210 system (Germany) with Al K α radiation source.

S2. Three-and two-electrode fabrications

In this section, both the three-electrode and two-electrode configurations were used to study the electrochemical properties of the samples on a CHI660D electrochemical workstation (Shanghai Chenhua Instruments Co., China). The test was carried out in 2 M KOH solution at room temperature. The preparation of the electrodes used in the three-electrode setup following conventional optimization methods. The carbon material sample, acetylene black and polyvinylidene fluoride (PVDF) were mixed in a weight ratio of 80:10:10 using N-methyl-2-pyrrolidone (NMP) as a solvent to form slurry (before the electrode materials were mixed, PVDF was added to the NMP solution to form a homogeneous PVDF/NMP solution at 0.02 g/mL). After the mixture was stirred for 12 h, the resulting composite was pressed onto a nickel foil with a size of 1 cm \times 1 cm, then the nickel foil was transferred into a vacuum oven and dried overnight at 60 °C to remove the NMP. The

mass loading of the active materials in each working electrode was approximately 3 mg/cm².

The capacitive performance of asymmetric supercapacitors was investigated using a two-electrode testing cell. The working electrode was prepared by mixing the electroactive material with PVDF and commercial carbon black (80:10:10, mass ratio) in NMP until homogeneous slurry. The slurry was coated on nickel foam with a working area about 2.0 cm² and the electrodes were dried at 60°C for 12 h and then weighted and pressed into sheets under 15 MPa. To construct an ASC, the charge balance for a supercapacitor should be follow the relationship: $q^+ = q^-$, where the charge stored by each electrode depends on the specific capacitance (C), the potential range for the charge/discharge process (ΔV), and the mass of the electrode (m) following equation: $q = C \times \Delta V \times m$. Therefore, the mass balancing will follow the equation: $m^+ / m^- = (C^- \times \Delta V^-) / (C^+ \times \Delta V^+)$. Thus, the loading mass ratio of active materials (Ni₃N/PRPC-1K) was estimated to be 0.51 from the specific capacitance calculated from galvanostatic charge/discharge curves (at current density of 1 A g⁻¹). For this article, the loading mass of active materials is 3.0 mg for Ni₃N and 5.88 mg for PRPC-1K. The Ni₃N positive electrode and PRPC-1K negative electrode fitted with the separator (thin polypropylene film) and 2 M KOH electrolyte solution were pressed together into sandwich-type cells construction (electrode/separator/electrode).

S3. Electrochemical measurements

The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements in three-electrode cell and two-electrode configuration using a CHI660D electrochemical workstation (Chenghua, Shanghai China). The cycle-life stability was performed using computer controlled cycling equipment (LAND CT2001A, Wuhan China).

Electrochemical impedance spectroscopy (EIS) measurements were performed at the frequency ranging from 0.1 Hz to 100k Hz and an impedance amplitude of ± 5 mV at open circuit potential.

The gravimetric capacitance from galvanostatic charge/discharge was calculated by using the formula of $C_s = 4I\Delta t / (m\Delta V)$ for the two-electrode cells, while, $C_s^* = I\Delta t / (m\Delta V)$ for the three electrode system, where I is the constant current (A) and m is the mass (g) of electrode material (For the two-electrode cells, m is the total mass of positive and negative electrodes), Δt the discharge time and ΔV the voltage change during the discharge process.

The specific energy density (E , Wh kg^{-1}) and power density (P , W kg^{-1}) for a supercapacitor cell can be calculated using the following equations: $E = 1/2CV^2$ and $P = E/t$, where C is the specific capacitance of supercapacitor cell, V is voltage change during the discharge process after IR drop in V-t curve, and t is the discharge time.

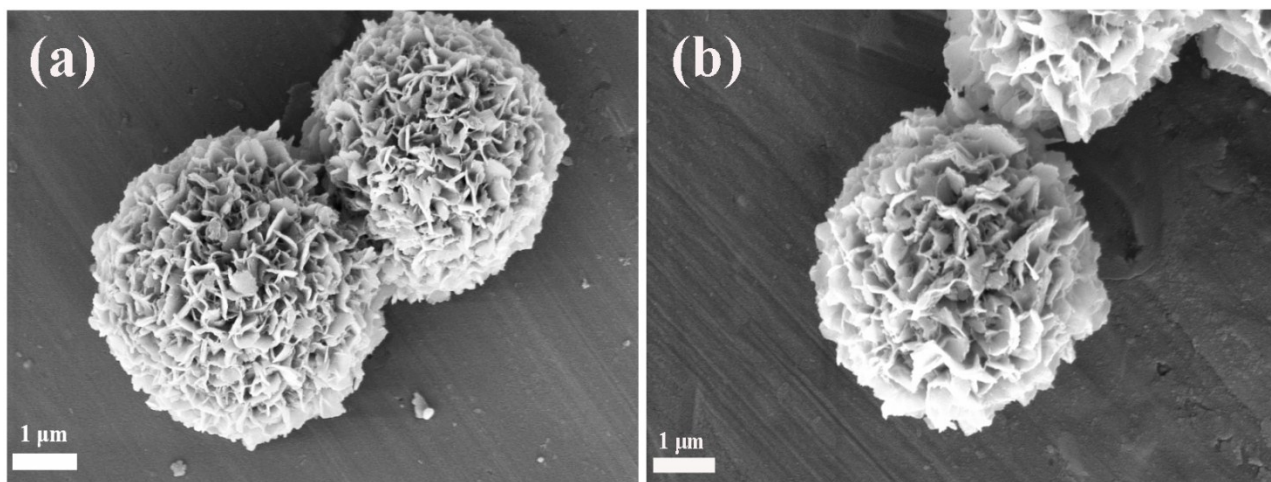


Fig. S1 (a) SEM image of Ni precursor ($\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$); (b) SEM image of NiO.

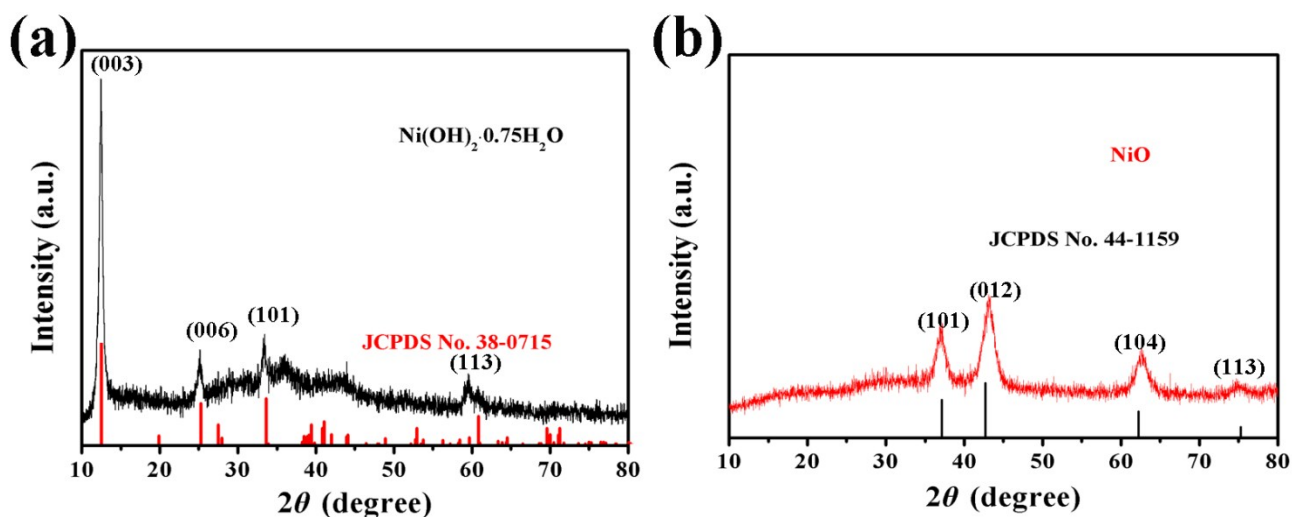


Fig. S2 (a) XRD pattern of Ni precursor nanosheets; (b) XRD pattern of NiO nanosheets.

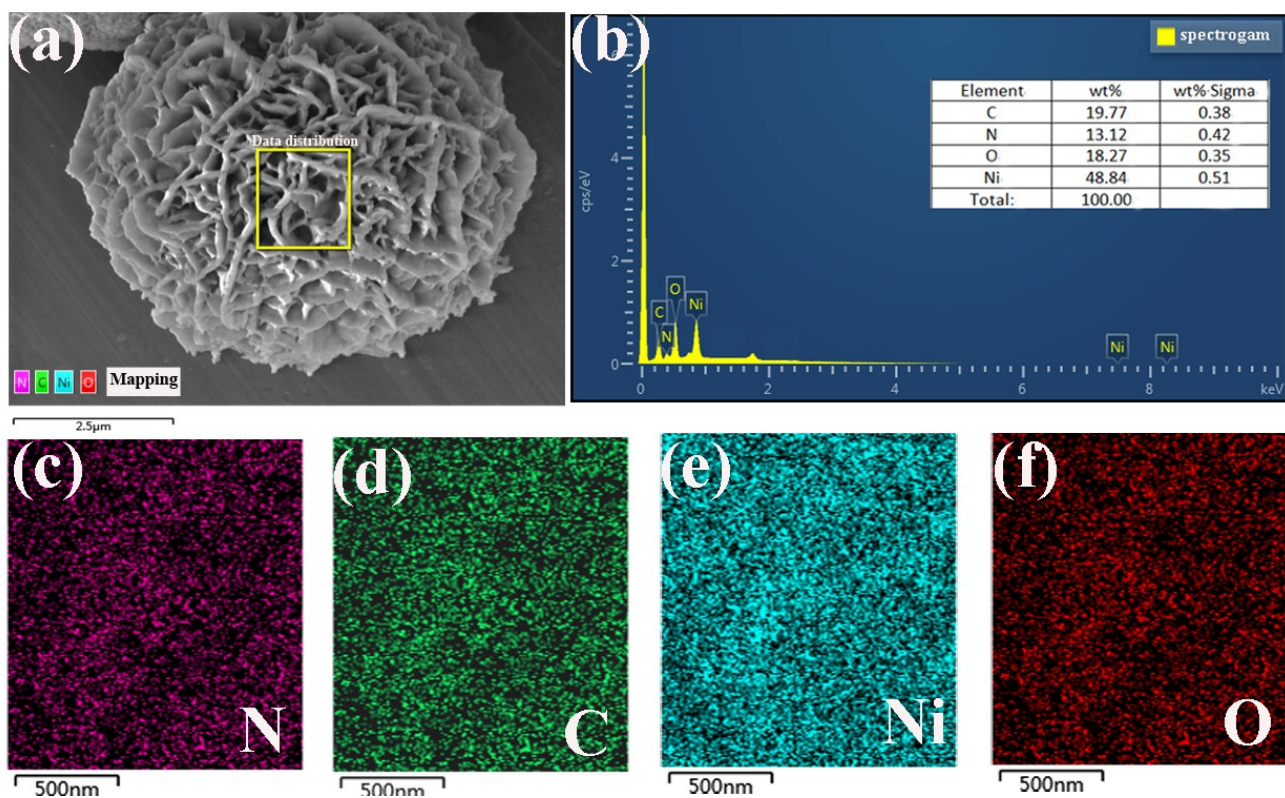


Fig. S3 (a) Element mapping images of the Ni_3N ; (b) EDS spectrum of the Ni_3N ; (c-f) Element signal images of the N, C, Ni, O element.

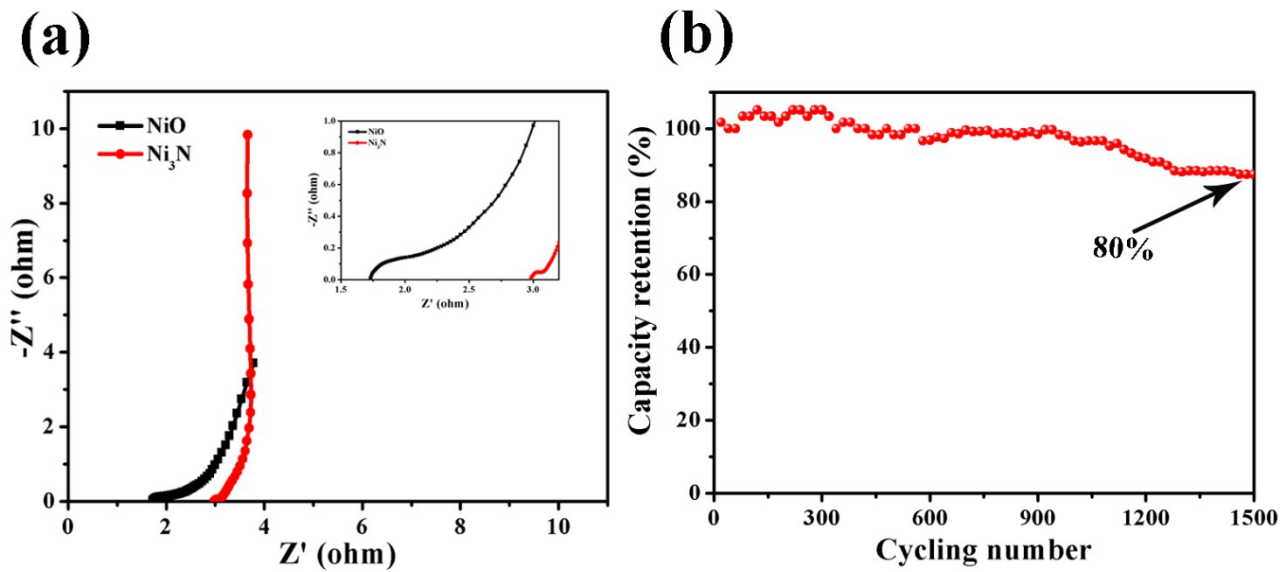


Fig. S4 (a) Nyquist plots of the Ni₃N and NiO; (b) cyclic stability at 3 A g⁻¹ for 1500 cycles of Ni₃N.

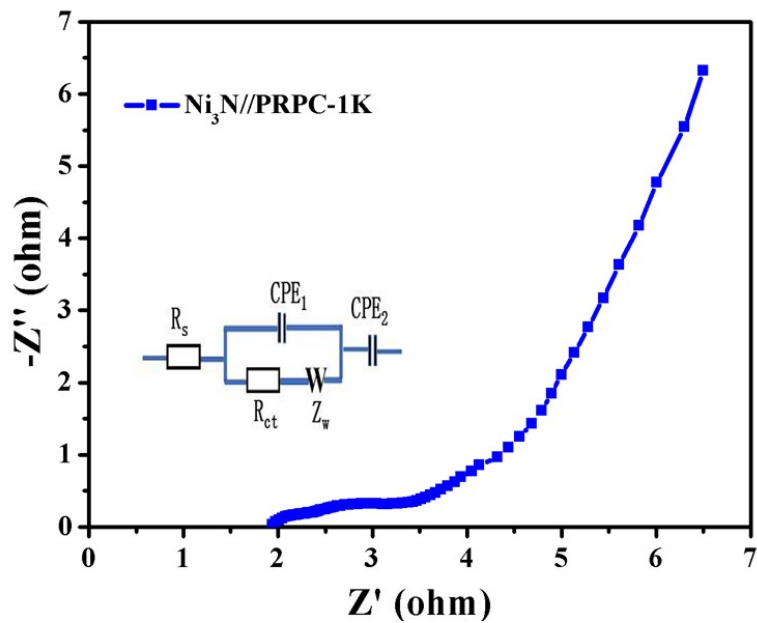


Fig. S5 Nyquist plots of the Ni₃N//PRPC-1K ASC.

Table S1. BET surface area and pore structure parameters of the as-prepared samples

Samples	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{mes}}^{\text{b}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{d}}$ ($\text{cm}^3 \text{g}^{-1}$)
PRPC	17.8	0.25	0.07
PRPC-1K	710.7	470.9	0.42
PRPC-2K	268.7	102.1	0.16

^aSpecific surface area determined according to the BET (Brunauer-Emmett-Teller) method.

^bMesoporous surface area from the t-plot method.

^cAdsorption average pore diameter.

^dTotal pore volume.

Table S2. Comparison of other ASC full cells

ASC	Electrolyte	Operating voltage (V)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Ref.
PCNS@VNNP//NiO	2 M KOH	1.6	16	800	S1
Ni(OH) ₂ //N-CNS/VNNPs	2 M KOH	1.6	29.5	385	S2
Ni/VN//Ni _{1-x} V _x O ₂	2 M KOH	1.6	23.3	176.7	S3
Co(OH) ₂ //VN	2 M KOH	1.6	22	160	S4
Ni-Co oxide//AC	1 M KOH	1.2	12	95.2	S5
Ni ₃ N//PRPC-1K	2 M KOH	1.65	30.9	412.1	Our work

References

- [S1] Y. Liu, L. Liu, L. Kong, L. Kang and F. Ran, *Electrochim. Acta*, 2016, **211**, 469-477.
- [S2] Y. Tan, Y. Liu, Z. Tang, Z. Wang, L. Kong and L. Kang, et al., *Sci Rep*, 2018, **8**, 2915.
- [S3] C. Ji, J. Bi, S. Wang, X. Zhang and S. Yang, *J. Mater. Chem. A*, 2016, **4**, 2158-2168.
- [S4] R. Wang, X. Yan, J. Lang, Z. Zheng and P. Zhang, *J. Mater. Chem. A*, 2014, **2**, 12724-12732.
- [S5] C. Tang, Z. Tang and H. Gong, *J. Electrochem. Soc.*, 2012, **159**, A651-A662.