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Supporting Information

Solvothermal synthesis of hierarchical flower-like β-NiS with excellent electrochemical performance for supercapacitors

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Detailed Experiments

Synthesis:

All the chemicals were of analytical grade and used without further purification. The detailed process for the synthesis was as follows: 1 mmol $NiCl_2$•$6H_2O$ was dissolved in a mixture solvent (the volume ratio of diethanol amine to water is 1:1), following by the addition of 4 mmol thiourea. The mixture kept on stirring for several minutes and then transferred to a teflon lined steel autoclave with a capacity of 30 mL, maintained at 180 °C for 12 h. After the reaction was completed, the autoclave cooled to room temperature naturally. Precipitates were centrifuged, sequentially washed with water and ethanol for several times to remove the ions possibly remaining in the products, and finally dried at 80 °C for 12 h in a vacuum. The contrast experiment were carried out through adjusting the experiment condition.

Characterization:

The crystalline structures of the as-prepared samples were characterized by X-ray diffraction (XRD) spectra (Rigaku D/Max-2500, Cu Kα radiation, λ=0.1518 nm). The morphologies were detected by scanning electron microscopy (SEM) on a JEOL JSM-6700F (Field Emission) scanning electron microscope, transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) on a Tecnai G2 F20 TEM. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Micromeritics Tristar-3000 surface area and porosity analyzer).

Electrochemical measurements:

The as-prepared flower-like NiS was used as electrode material for supercapacitors. The working electrodes were fabricated by mixing the active material (flower-like NiS or NiS nanoparticle), acetylene black and binder (PVDF) in a weight ratio of 80:10:10. The formed paste was pressed at 20 MPa to a piece of nickel foam (1.0 cm×1.0 cm), and dried under vacuum at 60 °C for 10 h. Electrochemical measurements were conducted in a three-electrode arrangement in 2 M KOH electrolyte. A bright Pt plate and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) was conducted with a Zahner IM6e electrochemical workstation with voltage scan rates of 5, 10, 20 and 50 mV s^{-1}. The galvanostatic charge-discharge tests were conducted on a LAND battery system at the current densities of 0.5, 1, 2, 5 and 10 A g^{-1}. The specific capacitance is calculated according to the following equation:

$$C=\frac{I\Delta t}{m\Delta V} \qquad (1)$$

where C (F g^{-1}) is the specific capacitance, I (A) represents the discharge current, and m (g), ΔV (V) and Δt (s) designate mass of active materials, potential drop during discharge and total discharge time, respectively.

Table S1 Summary of different solvent volume of DEA and water and their corresponding morphologies of NiS obtained at 180 °C for 12 h.

V_{H2O}/mL	V_{DEA}/mL	Morphology
24	0	irregular particles
20	4	aggregation of nanoparticles
16	8	aggregation of nanoparticles
14	10	ill-defined flower-like architecture
8	16	defined flower-like architecture

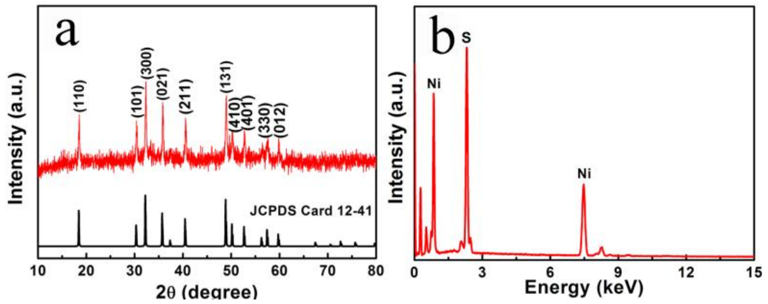

Fig. S1 (a) XRD pattern and (b) EDS pattern of as-prepared flower-like β-NiS.

In Fig. S1a, all the observed diffraction peaks can be perfectly indexed to the rhombohedral structure of β-NiS with lattice constants a = 9.62 Å, c = 3.149 Å (JCPDS Card. 12-41, space group: R3m (no. 160)). To further validate the chemical composition, energy dispersive X-ray spectroscopy (EDS) was carried out and the pattern was shown in Fig. S1b. Both the peaks of the elements Ni and S are detected and the atomic ratio are 51.66% and 48.34%, respectively, which is about 1:1.

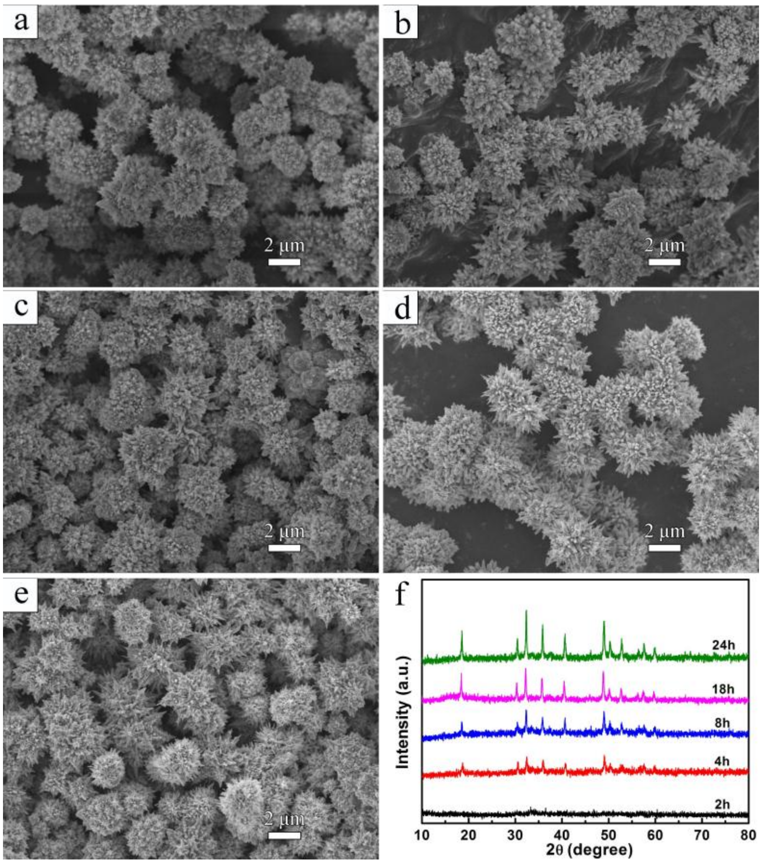

Fig.S2 The XRD patterns and SEM images of the products collected at different time intervals: a) 2 h, b) 4 h, c) 8 h, d) 10 h, e) 24 h, f) XRD patterns.

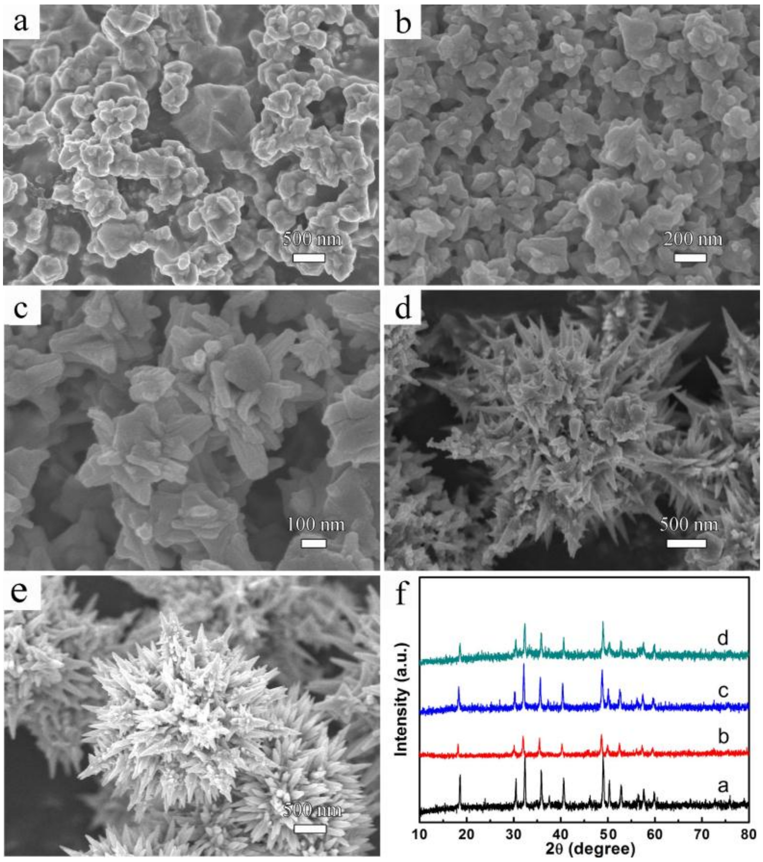

Fig.S3 The XRD patterns and SEM images of the as-prepared products with different additional amount of DEA: a) 0 mL; b) 4 mL; c) 8 mL; d) 10 mL; e) 16 mL; f) XRD patterns. The XRD patterns are all well indexed to β-NiS, in accordance with the XRD pattern of the product obtained with 12 mL DEA.

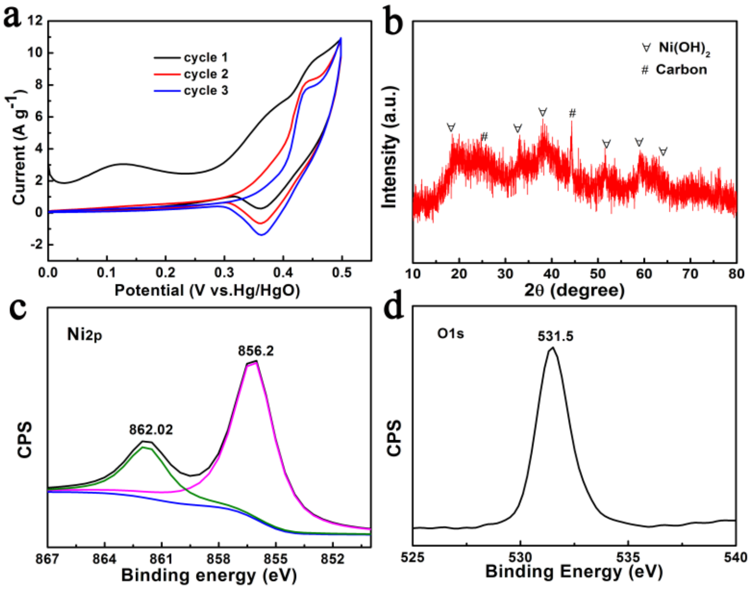

Fig.S4 (a) the typical initial three CV curves of S2 at the scan rate of 5 mV s^{-1}; the XRD pattern (b) and XPS spectra of (c) Ni2p, (d) O1s for the S2 electrode after 300 cycles of CV.

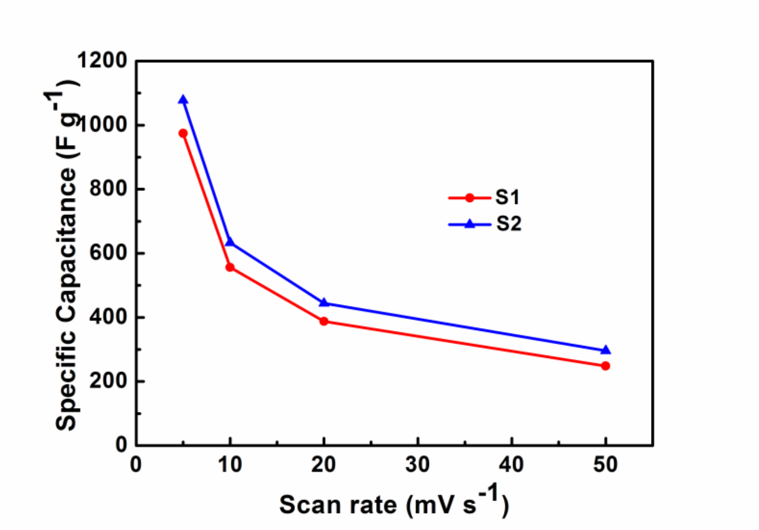

Fig.S5 The calculated average specific capacitance of S1 and S2 at scan rates of 5, 10, 20 and 50 mV s^{-1}. Notably, the calculated specific capacitances of S2 are 592.8 F g^{-1}, 519.2 F g^{-1}, 472.9 F g^{-1} and 380.3 F g^{-1} at the scan rates of 5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1} and 50 mV s^{-1}, respectively, which are higher than S1. The specific capacitance (*C*sp) from the voltammetric response was calculated according to the following equation,

$$C_{sp} = \frac{1}{m\, v\, (V_f - V_i)} \int_{V_i}^{V_f} I(V)\,dV \qquad (6)$$

where m is the mass of the active electrode material (g), v is the scan rate (V s^{-1}), V_f and V_i are the integration potential limits of the voltammetric curve (V), and $I(V)$ is the voltammetric current (A).

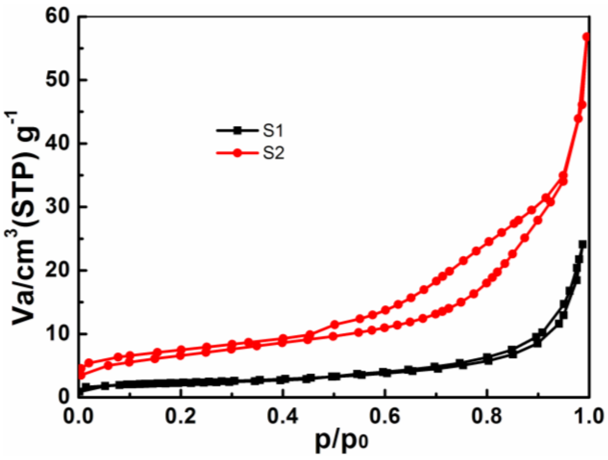

Fig.S6 Nitrogen adsorption-desorption isotherms of as-prepared S1 and S2, respectively.

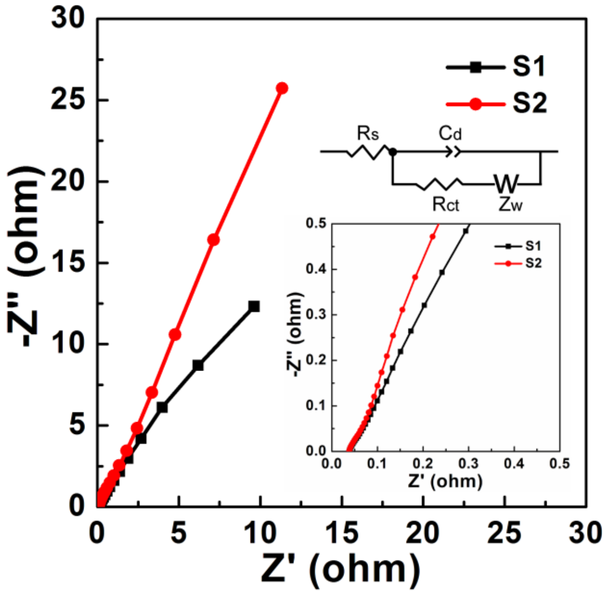

Fig.S7 Impedance Nyquist plots of S1 and S2 at open circuit potential. The equivalent circuit contains Rs (the intrinsic resistance of substrate, contact of material with substrate, electrolyte resistance), Rct (the resistance of Faradic reaction), Cd (the electric double layer capacitance) and Z_W (the Warburg impedance), (The insert is the portion of magnification pattern and the equivalent circuit).

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