

Electronic Supplementary Information

High conductive NiCo₂S₄ urchin-like nanostructures for high-rate pseudocapacitors

Haichao Chen, Jianjun Jiang,* Li Zhang, Houzhao Wan, Tong Qi and Dandan Xia

School of Optical and Electronic Information, Huazhong University of Science and Technology (HUST), Wuhan 430074, China.

* E-mail: jiangjj@mail.hust.edu.cn (Prof. Jianjun Jiang)

Experimental details

Synthesis of the Ni, Co-based precursor: In a typical procedure, NiCl₂·6H₂O (4mmol), CoCl₂·6H₂O (8mmol), and urea (36mmol) were added to deionized water (60 ml) under vigorous stirring until a homogeneous apparent solution was obtained. The pink solution was then transferred into a Teflon-lined stainless-steel autoclave, sealed and subsequently heated to 120 °C for 6 h in an oven. After cooling down to room temperature, the precipitate was collected, washed by deionized water and ethanol, and dried in an oven at 60 °C for 12 h.

Synthesis of the NiCo₂S₄: The urchin-like Ni, Co-based precursor was converted into NiCo₂S₄ while totally maintaining the morphology of the precursor by a simple hydrothermal treatment. 0.25 g of above synthesized precursor was dispersed in deionized water (60 ml) by ultrasonic treatment. Then, 0.75 g of Na₂S·9H₂O was added under stirring. After completely mixed, the mixture was transformed into a Teflon-lined stainless-steel autoclave and heated to 160°C for 6 h. After cooling down naturally to the room temperature, the black product was collected and washed with deionized water and ethanol for several times by centrifugation, then dried at 60°C for 12 h.

Synthesis of the Co_9S_8 , NiS : The Co_9S_8 and NiS samples in the comparative experiments are prepared in the absence of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by the same experimental procedures as that of NiCo_2S_4 .

Synthesis of the NiCo_2O_4 : The NiCo_2O_4 sample used in the *I-V*, UV-vis measurements and in the capacitive performance tests was prepared by heating the Ni, Co-based precursor in an air atmosphere at 300 °C for 3 h.

Materials characterization: The crystalline structure of the Ni, Co-based precursor and NiCo_2S_4 sample were evaluated by XRD (Philips X'Pert Pro; Cu $K\alpha$, $\lambda=0.1542$ nm). The morphology and structure of the products were characterized by SEM (FEI Quanta 200 and Sirion 200) and HRTEM (JEOL JEM-2100F). The elemental composition of NiCo_2S_4 was determined by the XRF (EDAX Inc. Eagle III). Energy dispersive X-ray spectroscopy (EDS) microanalysis of the NiCo_2S_4 was performed during HRTEM measurements. The near-surface elemental composition and the chemical state of the NiCo_2S_4 product were measured by XPS (VG Multilab 2000). UV-visible absorption spectra were recorded by a spectrophotometer (PerkinElmer Lambda 35).

Electrochemical tests: Electrochemical measurements were conducted in a solution of 6 M KOH aqueous electrolyte in a three-electrode glass cell. Platinum foil and Hg/HgO electrodes were used as counter and reference electrodes, respectively. The working electrode is consisted of active material, acetylene black and poly(tetrafluoroethylene) in a mass ratio of 80:10:10. For the electrochemical measurements, the slurry was drop-dried to a circular nickel foam ($d=1.2$ cm) and pressed at 10 MPa. The mass of active material in each electrode is about 2–3 mg. The electrodes were first activated by several CV cycles until the CV curves remained stable. All of the electrochemical measurements were performed by a CHI 660D electrochemical workstation.

I-V measurements: The electrode was prepared by first pressing the sample into a wafer ($d=1.2$ cm) at 15 MPa. Then the sample was sandwiched between two big stainless steel discs and firmly pressed together with a clip. The current-voltage curves were tested by a linear sweep voltammetry using a CHI 660D electrochemical workstation.

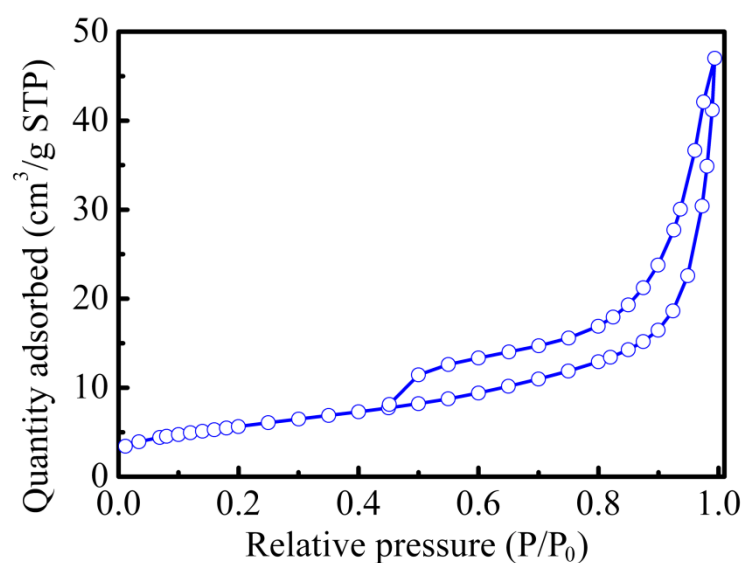


Fig. S1 Nitrogen adsorption-desorption isotherm of the NiCo_2S_4 sample.

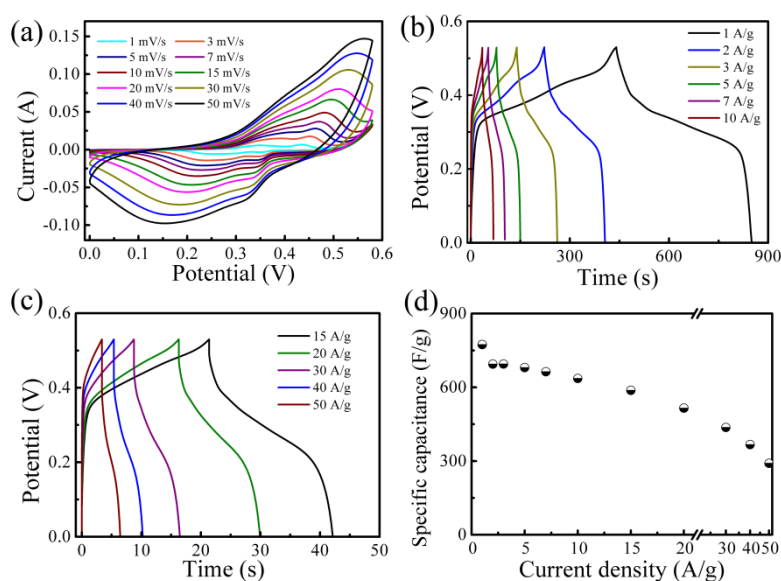


Fig. S2 Electrochemical characterizations of the NiCo_2O_4 hybrid electrode: (a) CV curves at different scan rates ranging from 1 to 50 mV s^{-1} ; (b, c) charge and discharge curves at various current densities ranging from 1 to 50 A g^{-1} ; (d) the capacitance versus current density curve.

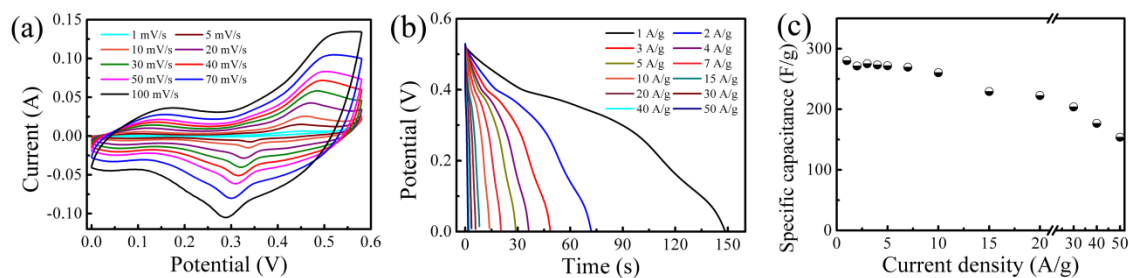


Fig. S3 Electrochemical evaluations of the Co₉S₈ electrode: (a) CV curves at various scan rates ranging from 1 to 70 mV s⁻¹; (b) galvanostatic discharge curves measured with different current densities of 1-50 A g⁻¹; (c) the capacitance as a function of current density.

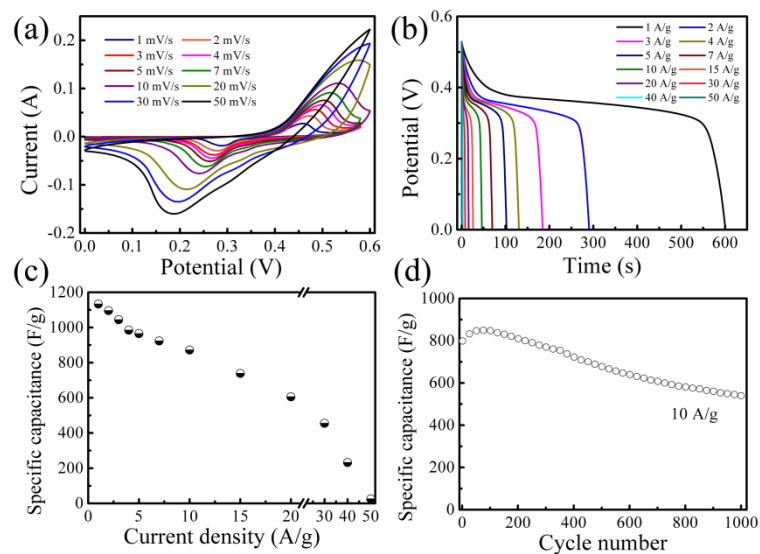


Fig. S4 Electrochemical evaluations of the NiS electrode: (a) CV curves measured with different scan rates ranging from 1 to 50 mV s⁻¹; (b) galvanostatic discharge curves at different current densities of 1-50 A g⁻¹; (c) the capacitance as a function of current density; (d) specific capacitance versus cycle number at a current density of 10 A g⁻¹.

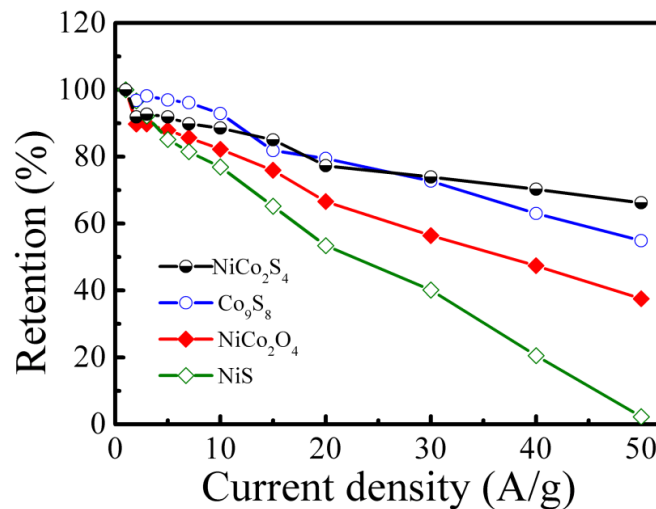


Fig. S5 Comparison of capacitance retention of the NiCo₂S₄, NiCo₂O₄, Co₉S₈ and NiS samples.