Supplementary Information (SI) for New Journal of Chemistry.

Supporting information

Effect of CoS components on electrochemical and physical-chemical properties of porous CoS-Co_3FeS_8 heterogeneous-sheet

Nuo Xu[a], Kun Song*[a], Guoli Chen[ab], Nan Zhao[ab], Jianjiao Xin[a], Yongzhi Liu[a], Guangming Yin[a]

[a] College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, Heilongjiang, P. R. China.

[b] China School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China.

* Corresponding author: Tel: +86 452 2738 750; Fax: +86 452 2738 750

E-mail: sky253838@163.com

Experimental Procedures

Materials and Characterization

Cobalt chloride, ferric chloride, mercaptoacetic acid, n-Butanol, thiourea, acetone and carbon cloth were purchased from Aladdin. All chemicals used in this study were of analytical grade.

The X-ray diffractometer is the Japanese science SmartLab, the X-ray source is Kα series, the copper target, the maximum test voltage is 45 kV, the maximum current is 150 A, the incident wavelength is lambda =0.1541 nm, the test range is 2θ Angle from 0 to 210, the scanning speed can be set, and the minimum step length of the goniometer is 1/10000 degree. High precision goniometer, goniometer with program variable slit, automatic identification of all optical components sample table, CBO cross light path, provide focused light path and high intensity high resolution parallel light path (with Mirror), multi-purpose film test kit. Powder sample, Measurement and analysis software is SmartLab Guidance, Little error.

The scanning electron microscope (SEM) is a Japanese electronic JSM-7200F, and the electronic optics system of JSM-7200F uses the Japanese electronic flagship. The immersive schottky gun technology of The JSM-7200F, and the standard TTLS (Through-The-Lens System), both under high/low acceleration voltage, the spatial resolution has been greatly improved over the traditional models. The maximum amplification factor of JSM-7200F is 1 million times, and it can obtain both secondary electron image and backscattered electron image. JSM-7200F has objective lens adopts hybrid lens. This hybrid lens is an electromagnetic field superposition objective lens combining magnetic lens and electrostatic lens, which is smaller than the traditional aberration and can obtain higher spatial resolution. Test conditions: Powder sample, the ambient temperature should be controlled at 22-25℃, the relative humidity should be less than 70%, to ensure the laboratory clean and tidy, to avoid loud noise and vibration of magnetic field interference.

The high resolution transmission electron microscope (HRTEM) is Hitachi H-9500 which can quickly conduct sample analysis, sample change in 1 minute. The atomic resolution of HRTEM by is 300 kV, rise to (300 kV) in 5 minutes. The point resolution is 0.18 nm, the lattice resolution is 0.1 nm and the amplification ratio is continuous amplification mode (1000~1500000), selection mode (4000~500000), and low power mode (200~500). The electron gun filament is LaB6 (lanthanum hexboride filament, dc heating), the lens is a four-stage lens, the concentrator aperture is 4-hole variable. Micron beam mode: 0.05-0.2 μm (level 4), nanometer beam mode: 1-10 nm (level 4), electron beam tilting ± 3°, image sway adjustment, positive focus compensation using astigmatism monitor. Image processing: digital CCD camera, effective pixel 1024×1024 pixels. EDS element range: B5~U92, EDS energy resolution: 138 eV. Test conditions: Powder sample, the ambient temperature should be controlled at 22-25℃, the relative humidity should be less than 70%, to ensure the laboratory clean and tidy, to avoid loud noise and vibration of magnetic field interference.

X-ray photoelectron spectroscopy (XPS): Thermo Fisher Scientific ESCALAB Xi X is an integrated test tool with a wide range of analytical techniques. The excitation source is monochromator ALK beam (h =1 486.6ev), power is 250 W, vacuum degree of the analysis room is 5×10^{-10} Mbar, full spectrum scanning range is 0~1350 eV, passing energy is 100 eV, step size is 1.00 eV. The imaging resolution of XPI is up to 1 μm, and the obtained data has no back-bottom feature of the detector and no back-bottom correction is needed to directly obtain the micron-scale resolution of the quantitative element distribution imaging results. During high-resolution fine scanning, the binding energy of samples with a pass energy of 20 eV and a step size of 0.10 eV is used to conduct charge correction on other test spectral peaks by using carbon pollution C1s (284.8 eV). The minimum energy resolution of the instrument is 0.48 eV (Ag 3d 5/2 peak) and avantage software is used for spectral peak fitting and quantification. Powder sample, Avantage analysis software, Little error.

The nitrogen desorption apparatus is Quadrasorb SI of kantar USA, an automatic specific surface area analyzer. It uses the gas adsorption principle (typically nitrogen) to determine the adsorption desorption isotherm. The BET specific surface area of single point and multi-point can be determined by Langmuir method, and the particle size estimation and true density test porosity and porosity analysis can be performed. The BJH method can also be used for the analysis of mesoporous and macroporous, as well as the determination of the surface area. The micropore area and pore size distribution are analyzed by MP method. It can also be used to analyze the microporous DR theory HK slit hole theory SF cylindrical hole theory, and can be upgraded to calculate the DFT density function theory. Test conditions: before degassing, the sample is degassed at 100 °C for 6 h after degassing. The sample is cooled slowly by liquid nitrogen, and the adsorption and desorption experiment is carried out. Powder sample, Microactive Interactive Data analysis software. ST2253 digital four-probe resistivity tester and high-wear-resisting tungsten carbide probe are used to test the resistivity/square resistance of hard materials such as silicon semiconductor metal conductive plastics.

Syntheses of electrodes

Preparation of carbon cloth: A piece of 2×2 cm² carbon cloth was immersed in acetone solution and subjected to ultrasonic treatment for 30 minutes, followed by drying and sealed storage. Subsequently, 0.08 mL of thioglycolic acid (TGA) was ultrasonically dissolved in 15 mL of deionized water, and the pretreated carbon cloth was immersed in the resulting TGA solution for 5 minutes.

Synthesis of CoS-Co_3FeS_8/CC: 1.70 mmol of $CoCl_2$, 4.26 mmol of $FeCl_3$ and 2.63 mmol of CH_4N_2S were added to 15 ml of n-butanol and stirred magnetic ally for 15 min. Then, the pre-treated carbon cloth (2 × 2 cm²) was immersed in the above solution and stirred together for 10 min. After stirring, the mixed solution and carbon cloth were transferred to a 50 mL polytetrafluoroethylene-li ned autoclave and kept at 200 °C for 12 h. After cooling to room temperature, the carbon cloth was taken out, rinsed with pure water three times, and finally dried at 60°C to obtain the carbon cloth electrode material with CoS-Co_3FeS_8 nanosheets grown on it. By changing the hydrothermal synthesis temperature (3 h, 4 h, 5 h, 6 h, 9 h, 35 h, 45 h), CoS-Co_3FeS_8/CC-3h, CoS-Co_3FeS_8/CC-6h, CoS-Co_3FeS_8/CC-9h, CoS-Co_3FeS_8/CC-12h and CoS-Co_3FeS_8/CC-15h were prepa red as controls.

Electrochemical Measurement

The CoS-Co_3FeS_8/CC is tailored and applied to working electrodes (1 cm× 1.5 cm, effective worked area of 1 cm × 1 cm). A platinum foil (10 mm × 10 mm) is employed as the counter electrode and SCE electrode as reference electrode, which apply to a three-electrode system in 3 M KOH solution. The CHI 660D electrochemistry workstation is used to the electrochemical measurements. Cyclic voltammetry (CV) tests are conducted in a potential range of 0-2 V (versus SCE) at scan rates of 10-100 $mV \cdot s^{-1}$. The cycling behavior is particular up to 4000 cycles, and galvanostatic charge–discharge (GCD) tests are carried out at various current densities with a potential range of 0-0.5 V (versus SCE).

The symmetrical supercapacitors are assembled with CoS-Co_3FeS_8/CC-12 h as positive electrode and negative electrode. To preparing electrode CoS-Co_3FeS_8/CC-12 h is about 10 mg. The two electrodes of the hybrid flexible supercapacitor are separated by a separator (NKK, MPF30AC-100), and 1 M KOH is used as the electrolyte.

In the three-electrode system, saturated standard calomel electrode (SCE) and a piece of Pt foil (1 × 1 cm^2) were used as the reference electrode and counter electrode, respectively. An aqueous solution of KOH (1 mol L^{-1}) was used as the electrolyte in the three electrode. The mass specific capacity (Cm, F g^{-1} or Csp, C g^{-1}) of a single electrode is following the equation:

$$Cm = \frac{I \times \Delta t}{m \times \Delta V} \qquad \text{(F1)}$$

$$Csp = \frac{I \times \Delta t}{m} \qquad \text{(F2)}$$

Where Δt is discharge time, I is the discharge current and m is the active mass of the electrode, ΔV is the potential range of the electrode.

The mass specific capacity (C_{ASC}, F g^{-1}) of the hybrid supercapacitor is following the equation:

$$C_{ASC} = \frac{I \times \Delta t}{2 \times M \times \Delta V} \qquad \text{(F3)}$$

Where M is the total mass of the positive and negative electrode active materials, I is the discharge current, Δt is the discharge time, ΔV is the potential range of the electrode of the ASC.

The specific energy density E and power density P are following the equation:

$$E = \frac{0.5 \times C_{ASC} \times \Delta V}{3.6} \qquad \text{(F4)}$$

$$P = \frac{E \times 3600}{\Delta t} \qquad \text{(F5)}$$

Where C_{ACS} is mass specific capacity of the asymmetric supercapacitor, Δt is the discharge time, ΔV is the potential of the ASC.

Results and Discussion

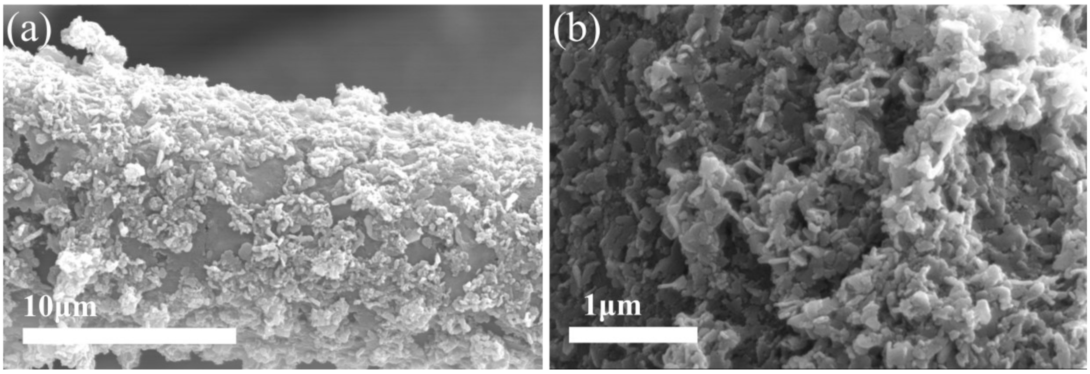

Figure S1. SEM image of CoS-Co_3FeS_8/CC-12h (a) before the 10,000 cycle process, (b) after the 10,000 cycle process.

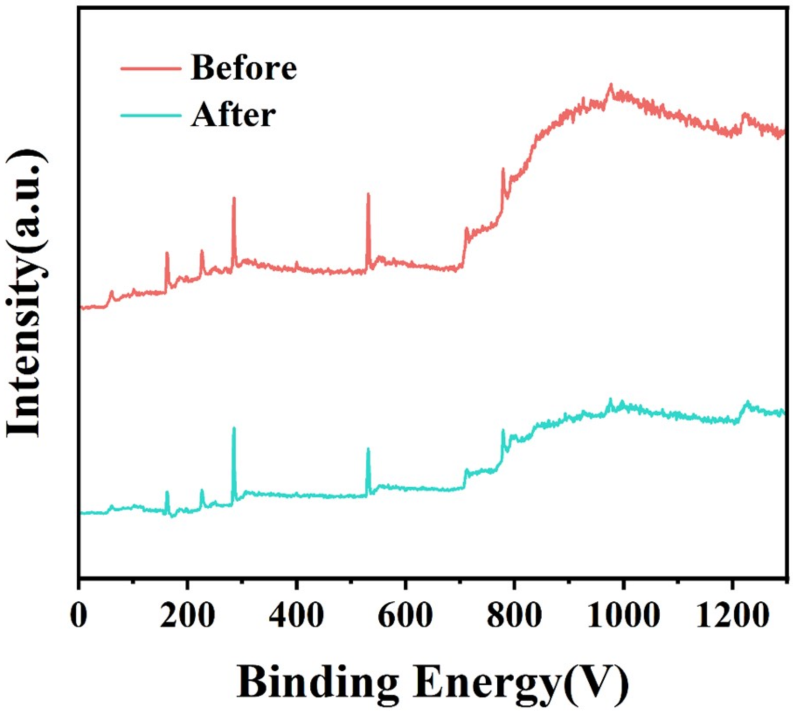

Figure S2. The XPS full spectra of CoS-Co_3FeS_8/CC-12h before and after 10,000 cycles.

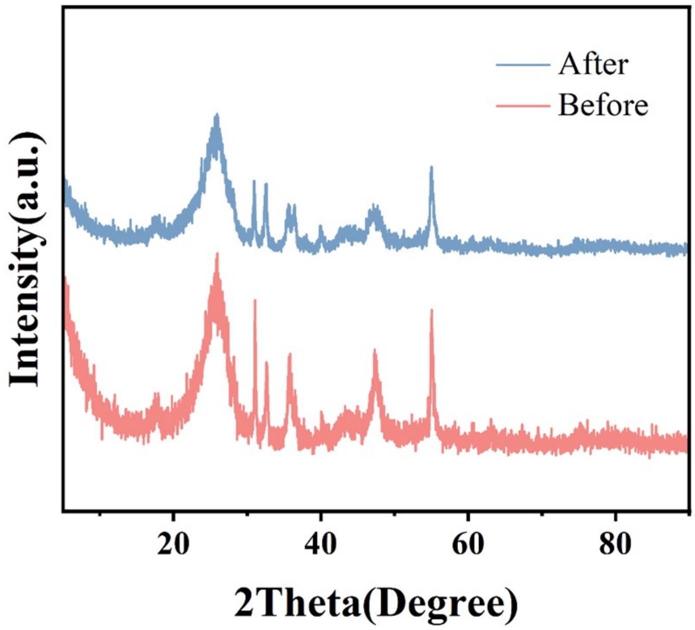

Figure S3. XRD patterns of CoS-Co_3FeS_8/CC-12h before and after 10,000 cycles.

Table S1. The content of iron and CoS in the CoS-Co_3FeS_8 reaction at different reaction times, as well as the discharge time and specific capacitance.

Reaction Time	EDS Fe%	CoS%	discharge time(s)	Specific capacitance
1h	11.4%	0%	102.4 s	170.7 F g^{-1}
3h	10.0%	12.6%	130.7 s	217.8 F g^{-1}
6h	9.6%	16.1%	301.9 s	498.1 F g^{-1}
9h	8.0%	30.1%	294.9 s	496.7 F g^{-1}
12h	6.8%	40.6%	409.1 s	682.3 F g^{-1}
15h	4.1%	64.2%	340.0 s	566.7 F g^{-1}
20h	2.7%	76.4%	321.3 s	535.5 F g^{-1}
30h	1.1%	90.40%	301.6 s	502.7 F g^{-1}
45h	0.2%	98.3%	289.7 s	482.8 F g^{-1}

Table S2. The discharge time, specific capacitance, energy density and power density of CoS-Co_3FeS_8/CC under different current densities in symmetrical electrodes.

Current Density	Discharge time	Specific capacitance	Energy density	Power density
1 A g^{-1}	345 s	123.2 F g^{-1}	120.7 Wh kg^{-1}	1259.5 W kg^{-1}
2 A g^{-1}	143 s	102.2 F g^{-1}	100.2 Wh kg^{-1}	2522.5 W kg^{-1}
4 A g^{-1}	62.6 s	89.5 F g^{-1}	87.7 Wh kg^{-1}	5043.5 W kg^{-1}
6 A g^{-1}	31.4 s	67.3 F g^{-1}	65.9 Wh kg^{-1}	7555.4 W kg^{-1}
8 A g^{-1}	18.6 s	66.5 F g^{-1}	65.2 Wh kg^{-1}	12619.4 W kg^{-1}
10 A g^{-1}	8.5 s	30.4 F g^{-1}	29.8 Wh kg^{-1}	12621.2 W kg^{-1}

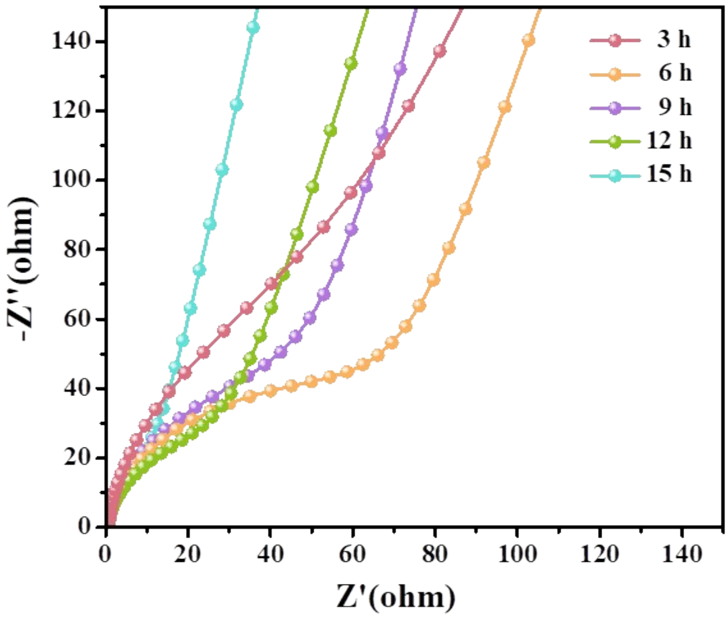

Figure S4. EIS diagrams of CoS-Co_3FeS_8/CC with different reaction times