

## Electronic Supplementary Information

### Highly Exposed Metal Sulfide-rGO Nanoporous Structures: An Advanced Energy Storage Electrode Material

K.P. Annamalai,\*<sup>a</sup> Lile Liu,<sup>a</sup> and Yousheng Tao\*<sup>a,b</sup>

<sup>a</sup>CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Haixi Institutes, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

<sup>b</sup>R & D Center of Saline Lake and Epithermal Deposits, Chinese Academy of Geological Sciences, Beijing 100037, China

Email: [taoys@tom.com](mailto:taoys@tom.com); [kpannamalai@outlook.com](mailto:kpannamalai@outlook.com)

## Experimental section

### Chemicals and reagents

HNO<sub>3</sub> (68% aq. solution) was purchased from Sinopharm Chemicals and Reagents Co Ltd. Single wall carbon nanohorns (SWCNHs) were purchased from XFNANO Materials Nanjing, China. Graphite, Diisopropylamine (DIPA, 98%), sodium carbonate (99%) and N-methyl 2-pyrrolidone (NMP, 99%) were purchased from Adamas, China. Ni (acetate)<sub>2</sub>·4H<sub>2</sub>O (98%), Co (acetate)<sub>2</sub>·4H<sub>2</sub>O (99.5%), Na<sub>2</sub>S·9H<sub>2</sub>O (98%) poly vinylidene fluoride (PVDF, 98%) were purchased from Aladdin China.

### Preparation of G-SWCNHs negative electrode

50 mg SWCNHs were dispersed in 50 ml of Con. HNO<sub>3</sub> (15.9 M) and heated to 60 °C for 12 h under constant stirring. Acid treated SWNHs (O-SWCNHs) were washed with distilled water, centrifuged at 5000 rpm for 10 min and dried at 70 °C overnight. Graphene oxide (GO) dispersed in distilled water under sonication. 5:1 ratio concentration of GO to O-SWCNHs dispersion was mixed together and sonicated for 3 h. GO and O-SWCNHs mixture was vigorously stirred to obtain a uniform colloidal dispersion. This colloidal suspension was transferred to Teflon lined autoclave and heated to 180 °C for 18 h. After cooled to room temperature, the products was

transferred into distilled water and then separated and dried at room temperature. The samples were obtained after annealing at 800 °C for 2 h under N<sub>2</sub> flow.

### **Characterization methods**

Morphologies of the samples were characterized with Field emission scanning electron microscopy (FE-SEM) using JEOL-6700 operated at 5 kV. The nanostructures and chemical composition of the samples were studied by transmission electron microscopy (TEM) with a transmission electron microscope (Tecnai F20, Philips) equipped with EDX spectrometer, operated at 100 kV. N<sub>2</sub> adsorption-desorption was carried out with ASAP2020 (Micromeritics). Samples were degassed at 150 °C for 2 h prior to the measurements. X-ray photo electron spectroscopy (XPS) measurements were carried out with ESCALAB 250Xi (Thermo Fisher Scientific) using Al K $\alpha$  monochromatic X-ray source. Spectrum was fitted based on Gaussian fitting method. The Powder X-ray diffraction (XRD) results were obtained with RigakuDmax 2500 using Cu K $\alpha$  ( $\lambda=1.5406$  Å) operated at 10 kV and 50 mA at a scan speed of 0.2  $\theta$ /min. Electrochemical measurements were carried out with CHI 660E (CH Instruments, Shanghai) electrochemical workstation.

### **Electrode fabrications**

Active materials were mixed with PVDF in the ratio of 95:5 to make slurry using NMP. Uniform slurry was coated on 1 cm  $\times$  1 cm Ni foam current collector, dried in vacuum oven at 70 °C overnight and pressed under 10 MPa pressure. Weight of the active materials on Ni foam was 2.0 mg/cm<sup>2</sup>. Capacitance were determined based on conventional three electrode measurements in 1.0 M KOH electrolyte. Active materials were applied as working electrode, while Hg/HgO and platinum foil electrode acted as reference and counter electrode, respectively. Capacitance were calculated from CV curves using equation 1.

$$C = \frac{Q}{2(m \times v \times \Delta V)} \dots\dots\dots (1)$$

Where C was specific capacitance; Q was integral area of CV curve; m was mass of electrode; v was scan rate;  $\Delta V$  was voltage range.

Capacitance were also calculated from GCD curves using equation 2.

$$C = \frac{I}{-\left(\frac{\Delta V}{\Delta t}\right)_m} = \frac{I}{(-slope \times m)} \dots\dots\dots (2)$$

Where  $I$  represented the applied current,  $\Delta V/\Delta t$  was the slope of discharge curves after IR drop at the beginning of discharge curves.

Time constant of the material was calculated from the equation (3), based on capacitor to discharge the energy (V) to  $1/e=36.8\%$

$$Time\ constant = Discharge\ time\ (t) * \frac{63.2}{100} \dots\dots\dots (3)$$

### Asymmetric supercapacitor cell fabrication

NiCo<sub>2</sub>S<sub>4</sub>@rGO and G-SWCNHs were coated on Ni foam current collectors, respectively. 1 M KOH electrolyte dropped into Whatman filter paper, which was placed between the positive and negative electrodes. Whole setup was bind together and covered with glass plate for the electrochemical experiments. Mass optimization was calculated based on the capacitance value of positive and negative electrode in 1A/g, using the following equations.

$$q_+ = q_- \dots\dots\dots (4)$$

Where

$$q = C_{sp} \times \Delta V \times m \dots\dots\dots (5)$$

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \dots\dots\dots (6)$$

Energy density and power density were calculated by equations (7) and (8)

$$E = C_{cell} \times \frac{\Delta V^2}{7.2} \dots\dots\dots (7)$$

$$P = E \times \frac{3600}{\Delta t} \dots\dots\dots (8)$$

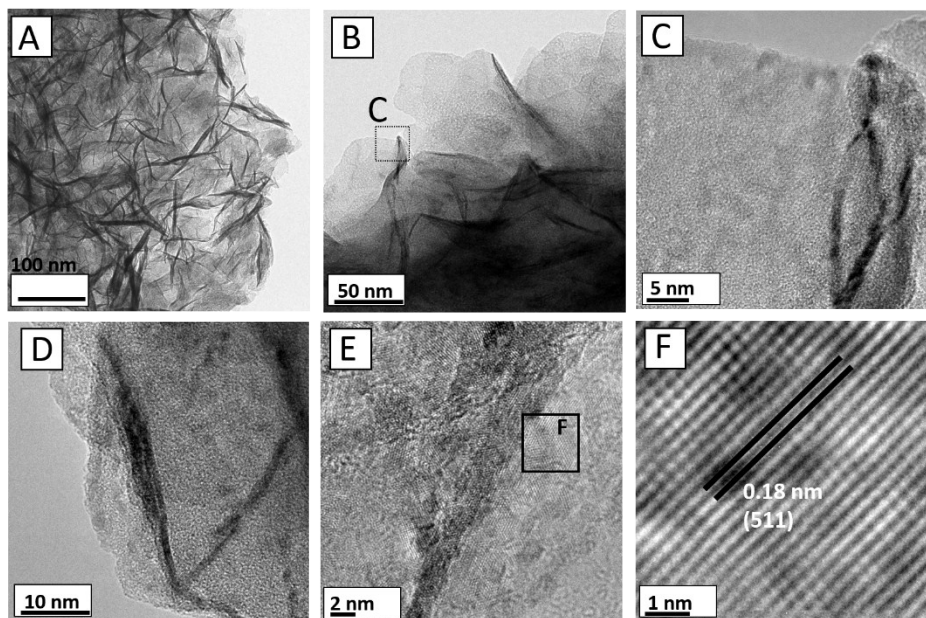


Fig. S1. (A, B) TEM images of NiCo<sub>2</sub>S<sub>4</sub>@rGO (C-E) HR-TEM images of NiCo<sub>2</sub>S<sub>4</sub>@rGO (F) Fast Fourier Transformation image shows the clear crystal lattice.

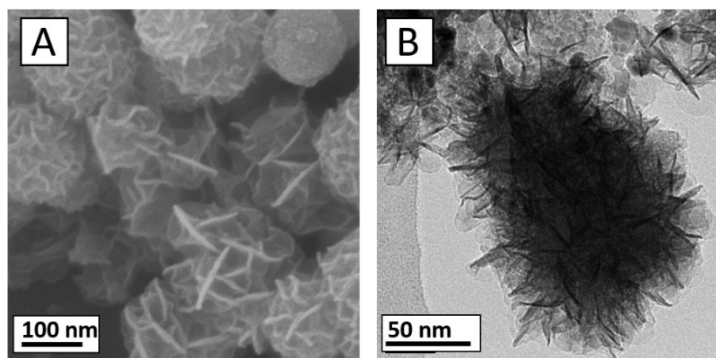


Fig. S2. (A) SEM and (B) TEM images of NiCo<sub>2</sub>S<sub>4</sub> (without GO).

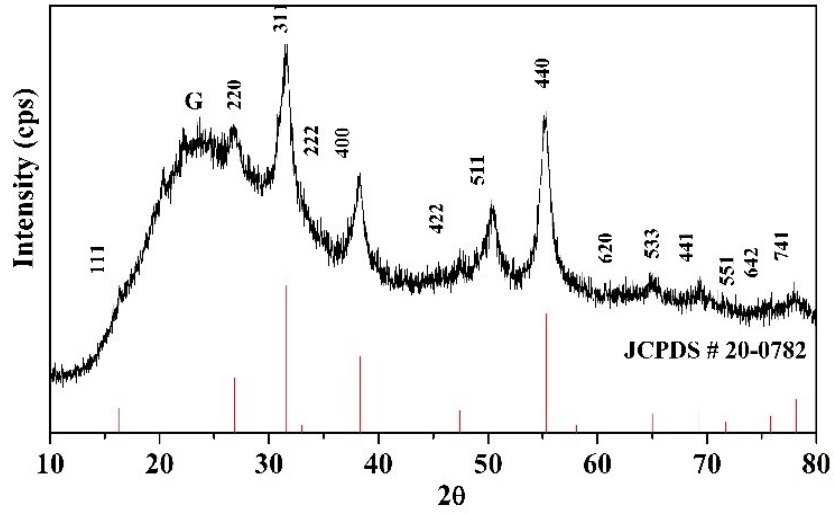


Fig. S3. XRD pattern of NiCo<sub>2</sub>S<sub>4</sub>@rGO nanocomposite.

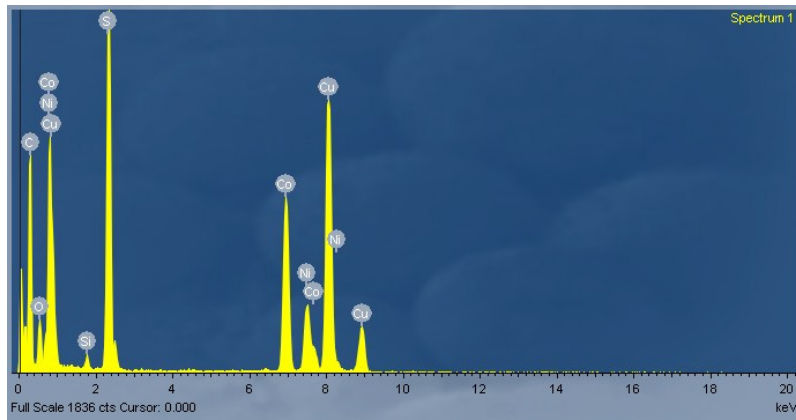


Fig. S4. Energy dispersive (EDX) analysis on NiCo<sub>2</sub>S<sub>4</sub>@rGO.

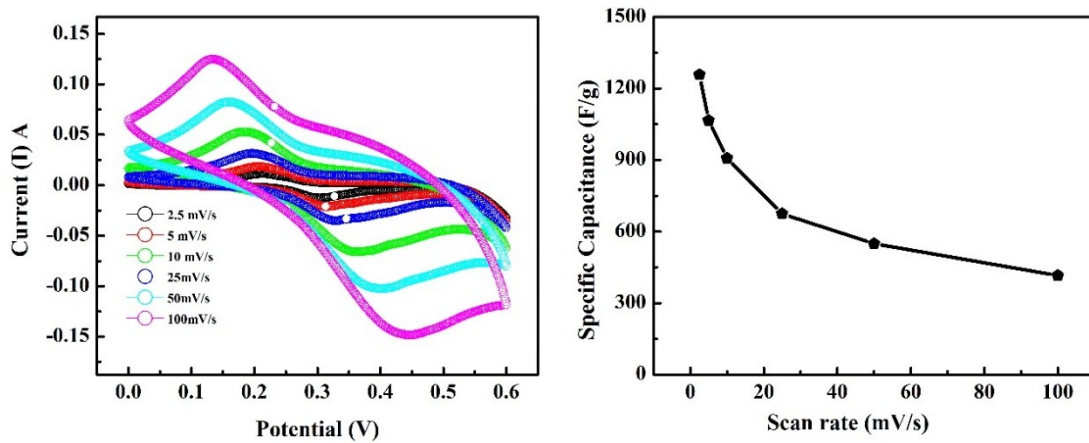


Fig. S5. Cyclic voltammetry curves of NiCo<sub>2</sub>S<sub>4</sub> (right) and the capacitance values (left).

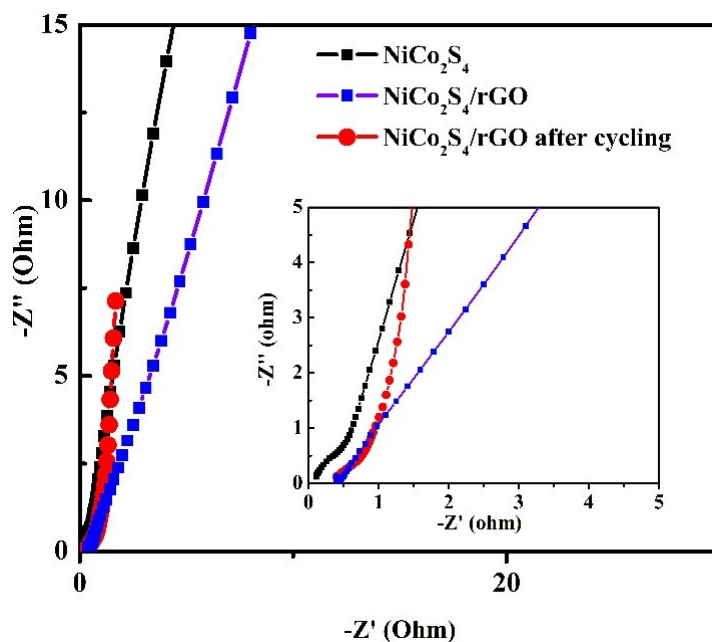


Fig. S6. EIS spectra of  $\text{NiCo}_2\text{S}_4$  and  $\text{NiCo}_2\text{S}_4/\text{rGO}$  before and after cycling.

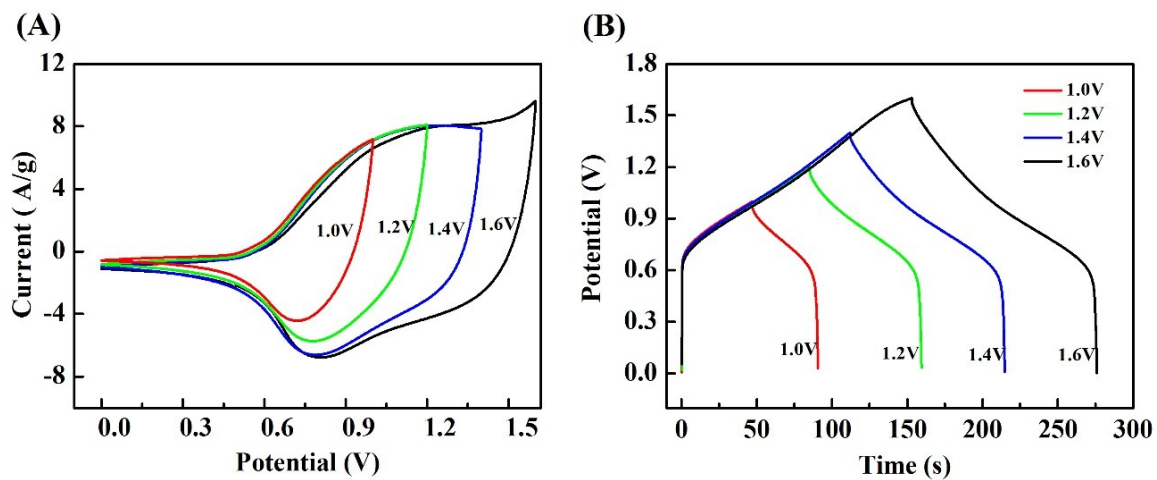


Fig. S7. Working potential optimization of  $\text{NiCo}_2\text{S}_4/\text{rGO}/\text{G-SWCNHs}$  ASC full cell. (A) CV curves at 25 mV/s and (B) GCD curves measured at 2.2 A/g current density.

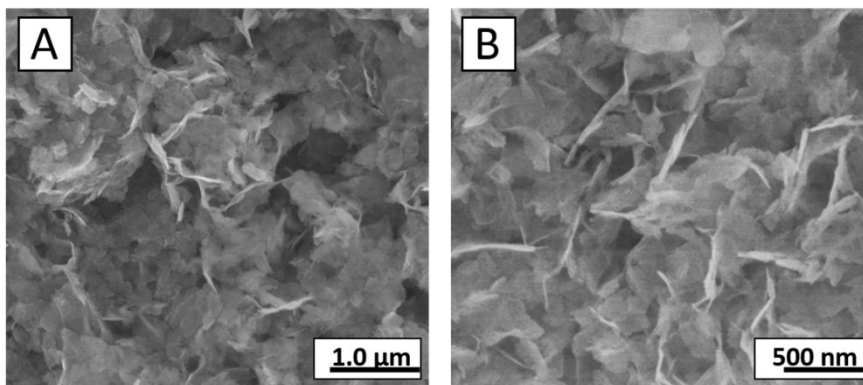


Fig. S8. SEM images of NiCo<sub>2</sub>S<sub>4</sub>@rGO after cycle stability test.

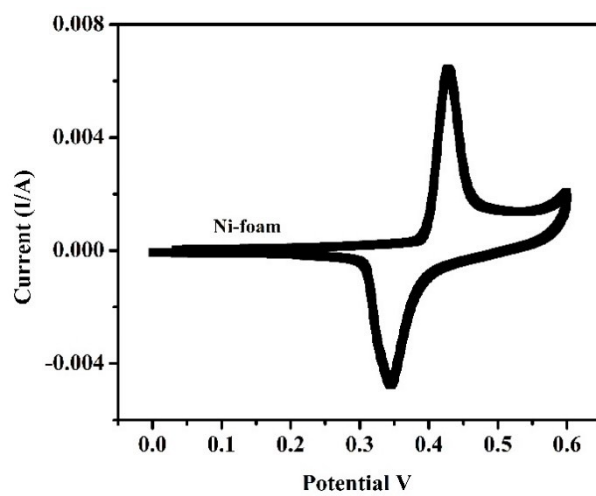


Fig. S9. Pseudo-capacitance behavior of Ni-foam in 1.0 M KOH.

Table S1. XPS deconvolution peak parameters

| S.No | Elements | Binding Energy (eV) |       |
|------|----------|---------------------|-------|
|      |          | 2p3                 | 2p1   |
| 1    | Co 2p    | 778.08              | 792.9 |
| 2    | Ni 2p    | 852.8               | 870.2 |
| 3    | S 2p     | 162.1               | 163.3 |

Table S2. Time constant based on the discharge time of NiCo<sub>2</sub>S<sub>4</sub>@rGO

| Current density (A/g) | Discharge time (s) | Time constant (s) |
|-----------------------|--------------------|-------------------|
| 1                     | 747.4              | 472.3             |
| 2                     | 361.7              | 228.6             |
| 3                     | 235.7              | 148.9             |
| 4                     | 174.0              | 109.9             |
| 5                     | 135.7              | 85.7              |
| 10                    | 62.33              | 39.4              |
| 20                    | 30.60              | 19.3              |
| 30                    | 19.07              | 12                |
| 40                    | 13.52              | 8.5               |