Electronic Supplementary Information

**Cobalt-doping in Hierarchical Ni$_3$S$_2$ Nanorod Arrays Enables High Areal Capacitance**

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**Calculations:**

**1. Co-Ni$_3$S$_2$ Electrode:**

The areal capacitances of electrodes were measured by galvanostatic charge/discharge method according to the following equation:

$$C_a = \frac{I \times \Delta t}{\Delta V \cdot S}$$

(1)
where $C_a$ (F cm$^{-2}$) is the areal capacitance, $I$ (A) is the constant discharging current, $\Delta t$ is the discharging time, $\Delta V$ (V) is the potential window, and $S$ (cm$^2$) is the surface area.

2. Co-Ni$_3$S$_2$/FeOOH HSCs:

The areal capacitance ($C_S$) of the Co-Ni$_3$S$_2$/FeOOH HSCs was calculated from the slope of the discharge curve using the following equations:

$$C_S = \frac{I \times \Delta t}{S \times \Delta V}$$  \hspace{1cm} (2)

where $C_S$ (F cm$^{-2}$) is the areal capacitance, $I$ (A) is the applied current, $S$ (cm$^2$) is the volume of the whole device (The area and thickness of the Co-Ni$_3$S$_2$/FeOOH HSCs device are about 0.5 cm$^2$ and 0.1 cm, respectively), $\Delta t$ (s) is the discharging time, $\Delta V$ (V) is the voltage window. It is worth mentioning that the volumetric capacitances were calculated based on the volume of the whole device. This includes the volume of electrode and the separator with electrolyte.

The time constant was calculated from the following equation:

$$\tau_0 = \frac{1}{f_0}$$  \hspace{1cm} (3)

where $\tau_0$ (s) is the time constant, $f_0$ (Hz) is the characteristic frequency at the phase angle of -45°.

Areal energy density, equivalent series resistance and power density of the devices
were obtained from the following equations:

\[ E = \frac{1}{3600 \times 2} C_S \times \Delta V^2 \]  

(4)

\[ P = \frac{3600E}{\Delta t} \]  

(5)

where \( E \) (Wh cm\(^{-2}\)) is the energy density, \( C_S \) is the volumetric capacitance obtained from Equation (2) and \( \Delta V \) (V) is the voltage window. \( P \) (W cm\(^{-2}\)) is the power density.

3. Balance the charge of electrodes in HSCs device:

As for a SC, the charge balance will follow the relationship \( q^+ = q^- \). The charge stored by each electrode depends on the capacitance (\( C_s \)), the potential range for the charge/discharge process (\( \Delta E \)) and the area of the electrode (\( A \)). It follows the Equation (6):

\[ q = C_s \times \Delta E \times m \]  

(6)

In order to get \( q^+ = q^- \) at 100 mV s\(^{-1}\), the area balancing between Co-Ni\(_3\)S\(_2\) and FeOOH electrode will be calculated as follow (7):

\[ \frac{A_{Co-Ni3S2}}{A_{FeOOH}} = \frac{C_{A(FeOOH)} \times \Delta E_{(FeOOH)}}{C_{A(Co-Ni3S2)}} \approx \frac{1.2}{1} \]  

(7)

The calculated \( C_{A(FeOOH)} \) is 0.58 F cm\(^{-2}\), \( \Delta E_{(FeOOH)} \) is 1.2 V, \( C_{A(Co-Ni3S2)} \) is 0.57 F cm\(^{-2}\).

Therefore, the calculated areal ratio between the Co-Ni\(_3\)S\(_2\) electrode and FeOOH electrode is about 1.2 : 1.
The electrochemical active surface area (ECSA) measurement: The capacitive current was used to determine the ECSA of the as-prepared Ni$_3$S$_2$ and Co-Ni$_3$S$_2$ with a scan window of 0.4 to 0.5 V vs. SCE. The current density differences at 0.45 V against the scan rate (4 to 16 mV s$^{-1}$) were fitted to obtain the double-layer capacitance ($C_{dl}$) and ECSA.

![Co 2p XPS spectrum of the Co-Ni$_3$S$_2$.](image1)

**Fig. S1** Co 2p XPS spectrum of the Co-Ni$_3$S$_2$.

![CV curves of the (a) Ni$_3$S$_2$ and (b) Co-Ni$_3$S$_2$ at different scan rate.](image2)

**Fig. S2** CV curves of the (a) Ni$_3$S$_2$ and (b) Co-Ni$_3$S$_2$ at different scan rate.
Fig. S3 GCD curves of the Ni$_3$S$_2$ nanosheets at different current densities.
Table S1. Comparison of the capacitance of Co-Ni$_3$S$_2$ nanorods with recently reported state-of-the-art supercapacitor electrode materials.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Morphology</th>
<th>Current density $\left(\text{mAcm}^{-2}\right)$</th>
<th>CP areal capacitance $\left(\text{Fcm}^{-2}\right)$</th>
<th>Scan rate $\left(\text{mVs}^{-1}\right)$</th>
<th>CV areal capacitance $\left(\text{Fcm}^{-2}\right)$</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Ni$_3$S$_2^{a)}$</td>
<td>nanorods</td>
<td>8</td>
<td>3.46</td>
<td>10</td>
<td>1.81</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>This work</td>
</tr>
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<td>Ni$_3$S$_2^{a)}$</td>
<td>nanosheets</td>
<td>8</td>
<td>1.07</td>
<td>10</td>
<td>0.74</td>
<td>NF</td>
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<td>This work</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@CdS$^{a)}$</td>
<td>nanorods</td>
<td>8</td>
<td>2.92</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>3.0 M KOH</td>
<td>S1$^1$</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$@MnO$_2^{a)}$</td>
<td>nanowires</td>
<td>8</td>
<td>1.91</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>1.0 M NaOH</td>
<td>S2$^2$</td>
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<tr>
<td>Ni$_3$S$_2$@β-NiS$^{c)}$</td>
<td>nanosheets</td>
<td>8</td>
<td>2.48</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>6.0 M KOH</td>
<td>S3$^3$</td>
</tr>
<tr>
<td>Activated NF$^{a)}$</td>
<td>thin film</td>
<td>8</td>
<td>2.04</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>6.0 M KOH</td>
<td>S4$^4$</td>
</tr>
<tr>
<td>Co$_3$O$_4$@C@Ni$_3$S$_2$</td>
<td>nanoneedle</td>
<td>10</td>
<td>2.25</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>3.0 M KOH</td>
<td>S5$^5$</td>
</tr>
<tr>
<td>NF@NiO$^{a)}$</td>
<td>nanosheets</td>
<td>8</td>
<td>2.01</td>
<td>10</td>
<td>1.3</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>S6$^6$</td>
</tr>
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<td>NiCo-O$^{a)}$</td>
<td>nanowires</td>
<td>5</td>
<td>2.20</td>
<td>N.A.</td>
<td>N.A.</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>S7$^7$</td>
</tr>
<tr>
<td>Ni-Co-S$^{b)}$</td>
<td>nanosheets</td>
<td>8</td>
<td>1.08</td>
<td>N.A.</td>
<td>N.A.</td>
<td>CC</td>
<td>1.0 M KOH</td>
<td>S8$^8$</td>
</tr>
</tbody>
</table>

$^{a)}$ vs SCE; $^{b)}$ vs Ag/AgCl; $^{c)}$ vs Hg/Hg
Fig. S4 Nyquist plots of Ni$_3$S$_2$ and Co-Ni$_3$S$_2$.

Fig. S5 CV curves in the double layer region at scan rate of 4, 6, 8, 10, 12, 14, 16 mV s$^{-1}$ of (a) Ni$_3$S$_2$ and (b) Co-Ni$_3$S$_2$.

Fig. S6 Current density as a function of scan rate for Ni$_3$S$_2$ and Co-Ni$_3$S$_2$. 

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**Fig. S7** SEM images of Ni$_3$S$_2$ electrode after 10 000 cycles in three-electrode system.

![SEM images of Ni$_3$S$_2$ electrode after 10 000 cycles in three-electrode system.](image)

**Fig. S8** XRD pattern of the Ni$_3$S$_2$ electrode before and after 10 000 cycles in three-electrode system.

![XRD pattern of the Ni$_3$S$_2$ electrode before and after 10 000 cycles in three-electrode system.](image)

**Fig. S9** SEM images of Co-Ni$_3$S$_2$ electrode after 10 000 cycles in three-electrode system.

![SEM images of Co-Ni$_3$S$_2$ electrode after 10 000 cycles in three-electrode system.](image)
**Fig. S10** XRD pattern of Co-Ni$_3$S$_2$ electrode before and after 10 000 cycles in three-electrode system.

**Fig. S11** SEM images of Co-Ni$_3$S$_2$ with different cobalt nitrate feeding amounts. (a-c) Co-Ni$_3$S$_2$-L; (d-f) Co-Ni$_3$S$_2$-H.
Fig. S12 XRD pattern of the Co-Ni$_3$S$_2$ with different cobalt nitrate feeding amounts.

Fig. S13 CV curves of the Co-Ni$_3$S$_2$ with different cobalt nitrate feeding amount at a scan rate of 100 mV s$^{-1}$.

Fig. S14 SEM images of FeOOH nanoparticles at different magnification.
Fig. S15 Electrochemical performances of the FeOOH electrode. (a) CV curves collected at various scan rates, and (b) GCD curves collected at different current densities.

Fig. S16 CV curves of FeOOH and Co-Ni$_3$S$_2$ electrodes collected at 100 mV s$^{-1}$. 
**Table S2.** Comparison of the electrochemical performances of Co-Ni$_3$S$_2$//FeOOH HSCs with recently reported state-of-the-art supercapacitors.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Morphology</th>
<th>Current density</th>
<th>CP areal capacitance</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Ni$_3$S$_2$//FeOOH</td>
<td>nanorods</td>
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<td>1.61</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>This work</td>
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<td>Ni$_3$S$_2$@CdS//C</td>
<td>nanorods</td>
<td>8</td>
<td>0.60</td>
<td>NF</td>
<td>3.0 M KOH</td>
<td>S1$^1$</td>
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<tr>
<td>Ni$_3$S$_2$@β-NiS//AC$^c$</td>
<td>nanosheet</td>
<td>4</td>
<td>0.08</td>
<td>NF</td>
<td>6.0 M KOH</td>
<td>S3$^3$</td>
</tr>
<tr>
<td>Co$_3$O$_4$@C@Ni$_3$S$_2$//AC</td>
<td>nanoneedle</td>
<td>20</td>
<td>0.327</td>
<td>NF</td>
<td>3.0 M KOH</td>
<td>S5$^5$</td>
</tr>
<tr>
<td>NF@NiO//FeOOH</td>
<td>nanosheet</td>
<td>8</td>
<td>0.527</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>S6$^6$</td>
</tr>
<tr>
<td>Ni-Co-O//AC</td>
<td>nanosheet</td>
<td>15</td>
<td>0.517</td>
<td>NF</td>
<td>3.0 M KOH</td>
<td>S7$^7$</td>
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<tr>
<td>Ni-Co-S//graphene</td>
<td>nanosheet</td>
<td>1.6</td>
<td>0.263</td>
<td>NF</td>
<td>1.0 M KOH</td>
<td>S8$^8$</td>
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</tbody>
</table>
**Fig. S17** XRD patterns of the Co-Ni$_3$S$_2$ electrode before and after 5 000 cycles in Co-Ni$_3$S$_2$//FeOOH HCSs.

**Reference**