Hierarchical Ultrathin Rolled-up Co(OH) (CO$_3$)$_{0.5}$ Films
Assembled on Ni$_{0.25}$Co$_{0.75}$S$_x$ Nanosheets for Enhanced
Supercapacitive Performance

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Characterization: The samples were examined by employing field-emission scanning electron microscopy (FESEM & Element mapping; Hitachi, S5500, SEM&EDS; Merlin), transmission electron microscopy (TEM; FEI, Tecnai G²20 and JEOL 2011), X-ray photospectroscopy (XPS, Escalab 250, Al Kα), and X-ray powder diffractometer (XRD) with Cu -Kα irradiation (λ= 1.5418 Å). The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.). Fresh film on the metal substrate (1 cm × 1 cm) was used as the working electrodes. A platinum electrode and a saturated calomel electrode were used as counter and reference electrodes, respectively. Freshly prepared 2 mol/L KOH aqueous solution was used as the electrolyte.

**Mass of active material calculation:**

The H-NSAs of specific mass-loading ‘m₁’ were calculated according to article reported by Sun and his coworker¹ from the Δ mass using Equation 1, where ‘Δ m’ was the mass difference between the Ni foam before and after hydrothermal process (step 1), ‘M Ni₀.2₅Co₀.₇₅(OH)₂’ was the molar mass of Ni₀.₂₅Co₀.₇₅(OH)₂, M Ni₀.₂₅Co₀.₇₅(OH)₂ – M Ni₀.₂₅ instead the molar mass of Co₀.₇₅(OH)₂.

\[
m₁ = \frac{Δm \times M_{Ni0.25Co0.75(OH)2}}{M_{Ni0.25Co0.75(OH)2} - M_{Ni0.25}}
\]

(Equation 1)

The specific mass ‘mNi₀.₂₅’ of Ni reacted from Ni substrate were calculated using Equation 2. Subtract the mass ‘mNi₀.₂₅’ from the initial mass of Ni foam and the mass of inactive material Ni ‘m’ can be obtained.

\[
m_{Ni0.25} = \frac{Δm \times MNi0.25}{M_{Ni0.25Co0.75(OH)2} - M_{Ni0.25}}
\]

(Equation 2)

The mass of electroactive materials in S-NSAs (m₂) and in UNTFSAs (m₃) were calculated according to the difference between the mass ‘m’ and the mass of S-NSAs and UNTFSAs after reaction.

The specific capacitances C were calculated from the galvanostatic discharge curves using Equation 3, where ‘I’ was the current applied, ‘ΔV/Δt’ was the slope of the discharge curve, and ‘m’ was the mass of the sample on one electrode. If the ‘m’ was replaced by the unit area, the derived equation could be used to calculate the areal capacitance.

\[
C = \frac{IΔt}{mΔV}
\]

(Equation 3)

**Capacitance calculation:**

**Theoretical capacitance calculation:** Theoretical specific capacitance is calculated as equation 4:

\[
C_{theor} = \frac{Q}{U}
\]

(Equation 4)

Where U is the voltage window, Q is electrical energy per gram of active material.
For $\text{Co(OH)}(\text{CO}_3)_{0.5}$, theoretical specific capacitance can be calculated as follow:

\[
C_{\text{theor}}/\text{Co(OH)}(\text{CO}_3)_{0.5} = \frac{\Delta Q}{\Delta U} = \frac{2Na \times e}{U \times M} = \frac{2 \times 96320}{0.5 \times 105.93} = 3637 \text{ F/g}
\]

Where Na is Avogadro constant which is $6.02 \times 10^{23}$, $e$ is $1.6 \times 10^{-19}$. $M$ (molar mass) is 105.93 g/mol. When $U$ is 0.5 V, the theoretical pseudocapacitance is 3637 F/g.

For $\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x$, the theoretical pseudocapacitance is calculated according to following equation.

\[
C_{\text{theor}}/\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x = \frac{\Delta Q}{\Delta U} = \frac{(0.25 + 2 \times 0.75) \times 96320}{0.5 \times M}
\]

When $x$ is 1, the molar mass ($M$) of $\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x$ is 90.92, thus its theoretical pseudocapacitance calculated is 3708 F/g. When $x$ is more than 1, the theoretical pseudocapacitance is less than 3708 F/g.

In our work, the theoretical specific pseudocapacitance for the hierarchical nanoarray should be between $C_{\text{theor}}/\text{Co(OH)}(\text{CO}_3)_{0.5}$ and $C_{\text{theor}}/\text{Ni}_{0.25}\text{Co}_{0.75}\text{S}_x$.

![SEM image of H-NSAs](image1)

**Figure S1.** SEM image of H-NSAs.

![EDS analysis results](image2)

**Table:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td>Co K</td>
<td>73.14</td>
<td>75.07</td>
</tr>
<tr>
<td>Ni K</td>
<td>24.99</td>
<td>24.93</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Figure S2.** The ratio of the Nickel atoms and Cobalt atoms obtained by EDS in the corresponding boxed area of the SEM images, A) a small area and B) a big area. (The powder scratched from Ni foam substrate).
Figure S3. Elemental mappings of Co, Ni, S, and O acquired from a typical S-NSAs nanosheet by employing SEM (Hitachi S 5500).

Figure S4. XPS spectra of A) Co 2p, B) Ni 2p, and C) S 2p with the UTNFSAs. The Co 2p XPS spectra of the composite exhibit two peaks at 781.2 and 797.0 eV, corresponding to the Co 2p$_{1/2}$ and Co 2p$_{3/2}$, indicating the existence of Co$^{2+}$ and the Ni 2p spectra show two obvious peaks at 855.7 and 873.5 eV which correspond to Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$. The main Ni 2p$_{3/2}$ peaks is close to 854.9 eV for Ni$^{2+}$ but much lower than 857.1 eV for Ni$^{3+}$, suggesting that it was in the divalent state. In the S 2p spectrum, the appearance of the peak at 163.4 eV and 168.6 eV proves there is sulfur element in UTNFSAs.

Figure S5. XRD patterns of the deposition in the procedure of step 3.
Figure S6. The galvanostatic charge/discharge curves of A) H-NSAs and B) S-NSAs at different current densities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>Maximum areal capacitance (F cm(^{-2}))</th>
<th>Maximum specific capacitance (F g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-NSAs</td>
<td>3.58</td>
<td>0.45</td>
<td>125.59</td>
</tr>
<tr>
<td>S-NSAs</td>
<td>3.77</td>
<td>1.41</td>
<td>372.94</td>
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<tr>
<td>UTNFSAs</td>
<td>3.45</td>
<td>5.9</td>
<td>1710.41</td>
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