Flexible yolk-shelled NiCo$_2$S$_4$ hollow spheres/RGO film electrodes for efficient supercapacitive energy storage

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**Formation of ball-in-ball hollow spheres.**

As shown in Fig. S1., we develop a hydrothermal method to prepare uniform nickel cobalt glycerate (NiCo-glycerate) spheres as the precursor. A solution sulfidation process under solvothermal condition is then utilized to convert the NiCo-glycerate solid precursors into yolk-shelled NiCo$_2$S$_4$ hollow spheres. The whole formation process can be generally divided into two stages as schematically. At stage I, sulfide (S$^{2-}$) ions released from the decomposition of TAA at high temperature react with metal ions on the surface of NiCo-glycerate and produce NiCo-glycerate@NiCo$_2$S$_4$ core-shell structure. This sulfidation process can be described as an anion exchange reaction of the NiCo-glycerate. Further reaction between the inward diffused S$^{2-}$ ions and faster outward diffused metal cations supplies the growth of the NiCo$_2$S$_4$ shell and leads to a well-defined gap between the shell and the NiCo-glycerate core. When the reaction proceeds to certain degree, it will be more difficult for the metal cations to diffuse to the outer shell through the enlarged empty gap. Thus, a secondary NiCo$_2$S$_4$ shell would be formed on the remaining core as shown at stage II. On the completion of the anion exchange reaction, unique yolk-shelled NiCo$_2$S$_4$ hollow spheres are obtained at the end.

![Diagram](image)

**Fig. S1.** schematic illustration of the formation process of yolk-shelled NiCo$_2$S$_4$ hollow spheres
Fig. S2. Nitrogen adsorption and desorption isotherm of the NiCo$_2$S$_4$/2RGO composite (a), the pore size distribution curve (b).

Fig. S3. CV curves of AC at 2 mV/s (a); GCD of AC at 1 Ag$^{-1}$ (b).
Fig. S4. CV curves of as-prepared Ni foam sample at the scan rates of 2 mV/s.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$^\text{a}C_{\text{max}}$</th>
<th>$^\text{b}T$</th>
<th>$^\text{c}C_{\text{m}}%_T$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo$_2$S$_4$ nanoboxes</td>
<td>777.0 F g$^{-1}$ (4 A g$^{-1}$)</td>
<td>5000</td>
<td>75.0%</td>
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<td>NiCo$_2$S$_4$ nanplates</td>
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<td>NiCo$_2$S$_4$@rGO@CNT</td>
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<td>2000</td>
<td>53.9%</td>
<td>[48]</td>
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<tr>
<td>NiCo$_2$S$_4$/2RGO films</td>
<td>1000.5 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>5000</td>
<td>80.5%</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^\text{a}$C$_{\text{max}}$, maximum specific capacitance,

$^\text{b}T$, cycles of cycle life test,

$^\text{c}C_{\text{m}}\%_T$, retention rate of specific capacitance after cycle life test.