Construction of Strawberry-like Ni$_3$S$_2$@Co$_9$S$_8$ Heteronanoparticle-Embedded Biomass-Derived 3D N-doped Hierarchical Porous Carbon for Ultrahigh Energy Density Supercapacitors

Shifu Wang, a Zuoyi Xiao, a* Shangru Zhai, a Haisong Wang, a Weijie Cai, a Longfei Qin, a Jianying Huang, a Di Zhao, a Zhongcheng Li b and Qingda An a*  

a. Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, P. R. China.  
b. Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

*Corresponding authors.  
E-mail: zyxiao80@163.com (Prof. Z. Xiao), anqingdachem@163.com (Prof. Q. An).
Fig. S1 Nitrogen adsorption-desorption isotherms of Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-600, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-700, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800 and Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-900.
Table S1 Structural parameters of Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-600, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-700, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800 and Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-900.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g$^{-1}$)</th>
<th>$S_{mic}$ (m$^2$/g$^{-1}$)</th>
<th>$V_{pore}$ (cm$^3$/g$^{-1}$)</th>
<th>$V_{mic}$ (cm$^3$/g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-600</td>
<td>122.8</td>
<td>76.7</td>
<td>0.075</td>
<td>0.017</td>
<td>4.58</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-700</td>
<td>274.7</td>
<td>84.6</td>
<td>0.186</td>
<td>0.017</td>
<td>4.98</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800</td>
<td>360.1</td>
<td>73.7</td>
<td>0.258</td>
<td>0.106</td>
<td>5.29</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-900</td>
<td>46.2</td>
<td>12.9</td>
<td>0.068</td>
<td>0.003</td>
<td>6.19</td>
</tr>
</tbody>
</table>
Fig. S2 (a-b) SEM images of Ni$_3$S$_2$@Co$_5$S$_9$/N-HPC-900 at different magnifications.
Fig. S3 Pore distribution diagrams of Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-600, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-700, Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800 and Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-900.
Fig. S4 High-resolution C 1s and N 1s XPS spectra of Ni$_3$S$_2$@Co$_8$S$_8$/N-HPC-800.
Fig. S5 (a-f) EDS mapping of the ZIF-NC-800. Map sum spectrum and the content of different elements on the surface of ZIF-NC-800.
Table S2 The content of different elements on the surface of ZIF-NC-800 and Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800.

<table>
<thead>
<tr>
<th>Element</th>
<th>ZIF-NC-800 (At. %)</th>
<th>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800 (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>83.59</td>
<td>75.62</td>
</tr>
<tr>
<td>N1s</td>
<td>8.35</td>
<td>3.65</td>
</tr>
<tr>
<td>O1s</td>
<td>6.12</td>
<td>14.54</td>
</tr>
<tr>
<td>S2p</td>
<td>0.00</td>
<td>1.66</td>
</tr>
<tr>
<td>Co2p</td>
<td>1.38</td>
<td>1.57</td>
</tr>
<tr>
<td>Ni 2p</td>
<td>0.00</td>
<td>2.96</td>
</tr>
</tbody>
</table>
Fig. S6 XRD pattern of HPC.
<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{pore}}$ (cm$^3$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPC-700</td>
<td>438.1</td>
<td>0.758</td>
<td>8.54</td>
</tr>
</tbody>
</table>
Table S4. Comparison of the specific capacitance of Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800 with other reported works.

<table>
<thead>
<tr>
<th>materials</th>
<th>capacitance (F g$^{-1}$)</th>
<th>current density (A g$^{-1}$)</th>
<th>electrolyte</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoS$_x$/S</td>
<td>618</td>
<td>2</td>
<td>1 M KOH</td>
<td>1</td>
</tr>
<tr>
<td>CoS nanocages</td>
<td>1475</td>
<td>1</td>
<td>1 M KOH</td>
<td>2</td>
</tr>
<tr>
<td>Ni$<em>{12}$Co$</em>{3.3}$S$_4$</td>
<td>696</td>
<td>1</td>
<td>6 M KOH</td>
<td>3</td>
</tr>
<tr>
<td>Ni-Co-S/NF</td>
<td>1406.9</td>
<td>0.5</td>
<td>1 M KOH</td>
<td>4</td>
</tr>
<tr>
<td>Co$_9$S$_8$/NS-C</td>
<td>734</td>
<td>1</td>
<td>6 M KOH</td>
<td>5</td>
</tr>
<tr>
<td>NiCo-MOF</td>
<td>1202.1</td>
<td>1</td>
<td>2 M KOH</td>
<td>6</td>
</tr>
<tr>
<td>Ni$_3$S$_2$</td>
<td>1370.4</td>
<td>2</td>
<td>6 M KOH</td>
<td>7</td>
</tr>
<tr>
<td>Ni@rGO-Ni$_3$S$_2$</td>
<td>987.8</td>
<td>1.5</td>
<td>6 M KOH</td>
<td>8</td>
</tr>
<tr>
<td>NF@rGO/Ni$_3$S$_2$</td>
<td>816.8</td>
<td>0.98</td>
<td>6 M KOH</td>
<td>9</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800</td>
<td>1970.5</td>
<td>0.5</td>
<td>6 M KOH</td>
<td>This work</td>
</tr>
</tbody>
</table>
Fig. S7 (a) CV curves at different scan rates from 5 to 100 mV s$^{-1}$, (b) GCD curves at various current densities for Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-600.
Fig. S8 (a) CV curves at different scan rates from 5 to 100 mV s$^{-1}$, (b) GCD curves at various current densities for Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-700.
Fig. S9 (a) CV curves at different scan rates from 5 to 100 mV s$^{-1}$, (b) GCD curves at various current densities for Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-900.
Fig. S10 (a) CV curves at different scan rates from 5 to 100 mV s\(^{-1}\), (b) GCD curves at various current densities for Co\(_9\)S\(_8\)/N-HPC-800.
Fig. S11 (a) CV curves at different scan rates from 5 to 100 mV s\(^{-1}\), (b) GCD curves at various current densities for Ni\(_2\)S\(_3\)/N-HPC-800.
Fig. S12 (a) CV curves at different scan rates from 5 to 100 mV s$^{-1}$, (b) GCD curves at various current densities for ZIF-NC-800.
Fig. S13 (a) CV curves at different scan rates from 5 to 100 mV s$^{-1}$, (b) GCD curves at various current densities for HPC.
**Fig. S14.** Comparison of the cycling stability of Ni$_3$S$_2$/N-HPC-800, Co$_9$S$_8$/N-HPC-800 and Ni$_3$S$_2$@Co$_9$S$_8$/N-HPC-800.
Fig. S15 (a) CV curves at different scan rates and (b) GCD curves at different current densities of the Co$_9$S$_8$/N-HPC-800//HPC asymmetrical supercapacitor.
Fig. S16 (a) CV curves at different scan rates and (b) GCD curves at different current densities of the Ni$_3$S$_2$/N-HPC-800//HPC asymmetrical supercapacitor.
Fig. S17 (a) CV curves at different scan rates and (b) GCD curves at different current densities of the ZIF-NC-800//HPC asymmetrical supercapacitor.