Supplementary Figure 1. XRD pattern of the as-synthesized NiCo-glycerate precursor.
Supplementary Figure 2. FESEM images of samples. (a) NiCo-glycerate spheres, and the products obtained after sulfidation of NiCo-glycerate solid spheres at 160 °C for different durations: (b) 0.5 h; (c) 2 h; (d) 6 h. Scale bars, 1 µm.
Supplementary Figure 3. FESEM images of the NiCo-glycerate spheres prepared at different temperatures. (a) 150 °C; (b) 210 °C. Scale bars, 200 nm.
Supplementary Figure 4. XRD analysis of sulfided samples. XRD patterns of the products after sulfidation of NiCo-glycerate solid spheres at 160 °C for different durations. (a) 0.5 h, (b) 2 h, and (c) 6 h.
Supplementary Figure 5. TEM analysis of sulfided samples using different TAA amounts. TEM images of the products after sulfidation of NiCo-glycerate solid spheres at 160 °C with different amounts of TAA. (a) 15 mg and (b) 100 mg. Scale bars, 200 nm.
Supplementary Figure 6. TEM analysis of sulfided samples with different reaction durations. TEM images of the products after sulfidation of NiCo-glycerate solid spheres at 120 °C for different durations: (a, b) 6 h. Scale bars, 500 and 200 nm, respectively. (c, d) 12 h. Scale bars, 500 and 200 nm, respectively.
Supplementary Figure 7. TEM images of NiCo$_2$S$_4$ hollow spheres. The sample was prepared at 200 °C for 6 h. Scale bars are 500 and 200 nm in (a) and (b), respectively.
Supplementary Figure 8. HRTEM image of annealed NiCo$_2$S$_4$ ball-in-ball hollow spheres. Scale bar, 5 nm.
Supplementary Figure 9. TEM image and EDX-elemental mapping images of several NiCo$_2$S$_4$ ball-in-ball hollow spheres. (a) TEM image. Scale bar, 500 nm. (b-d) EDX-elemental mapping images shown in (b) cobalt, (c) nickel, and (d) sulfur. Scale bars, 500 nm.
**Supplementary Figure 10. BET analysis.** $\text{N}_2$ adsorption-desorption isotherms at 77 K and pore size distribution (inset) of NiCo$_2$S$_4$ ball-in-ball hollow spheres.
Supplementary Figure 11. Microstructure of MnCo$_2$S$_4$ ball-in-ball hollow spheres. (a) FESEM image. Scale bar, 1 µm. (b) TEM image. Scale bar, 200 nm. (The amount of TAA used is 80 mg).
Supplementary Figure 12. Electrochemical characterizations of the single-shelled NiCo$_2$S$_4$ hollow spheres electrode. (a) Galvanostatic charge/discharge voltage profiles; (b) specific capacitance as a function of current density.
Supplementary Figure 13. Microstructure of NiCo$_2$S$_4$ ball-in-ball hollow spheres after cycling for 2000 cycles at a current density of 5 A g$^{-1}$. (a-c) FESEM images. Scale bars, 1 µm (a, b) and 200 nm (c). (d) TEM image. Scale bar, 100 nm.
Supplementary Figure 14. Microstructure and electrochemical performance of G/CS paper. (a) FESEM image of G/CS paper. Scale bar, 1 μm; inset in (a) shows a digital photograph of flexible G/CS paper. (b) TEM image of G/CS. Scale bar, 100 nm. (c) CV curve at 5 mV s⁻¹. (d) Galvanostatic charge/discharge voltage profiles at a current density of 1 A g⁻¹.
Supplementary Figure 15. Galvanostatic charge/discharge voltage profiles of the ASC device at different current densities from 5 to 20 A g$^{-1}$. 
Supplementary Figure 16. Ragone plots of ASC devices. The reported values for other ASC devices are added for comparison.
Supplementary Table 1. Electrochemical performance of different Ni-Co sulfides based electrodes.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type of materials</th>
<th>Loading mass</th>
<th>Specific capacitance</th>
<th>Capacitance retention</th>
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<tr>
<td>This work</td>
<td>NiCo$_2$S$_4$ spheres</td>
<td>5 mg cm$^{-2}$</td>
<td>705 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>68% from 1 to 20 A g$^{-1}$</td>
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<td>2</td>
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<td>231 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>53% from 1 to 20 A g$^{-1}$</td>
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<td>NiCo$_2$S$_4$ nanoprisms</td>
<td>1.0 mg cm$^{-2}$</td>
<td>585 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>65% from 1 to 20 A g$^{-1}$</td>
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<td>9</td>
<td>NiCo$_2$S$_4$ nanotubes</td>
<td>4~6 mg cm$^{-2}$</td>
<td>550 at 5 A g$^{-1}$</td>
<td>50% from 0.2 to 5 A g$^{-1}$</td>
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<td>NiCo$_2$S$_4$ nanotubes on Ni foam</td>
<td>4.2 mg cm$^{-2}$</td>
<td>608 F g$^{-1}$ at 15 A g$^{-1}$</td>
<td>78% from 2 to 15 A g$^{-1}$</td>
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<td>11</td>
<td>NiCo$_2$S$_4$ nanosheets/graphene</td>
<td>Not reported</td>
<td>760 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>52% from 3 to 20 A g$^{-1}$</td>
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<td>12</td>
<td>NiCo$_2$S$_4$ nanosheets/carbon cloth</td>
<td>0.8 mg cm$^{-2}$</td>
<td>1418 F g$^{-1}$ at 5 A g$^{-1}$</td>
<td>91% from 5 to 100 A g$^{-1}$</td>
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<td>NiCo$_2$S$_4$ mesoporous nanoparticles</td>
<td>Not reported</td>
<td>840 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>86.8% from 2 to 20 A g$^{-1}$</td>
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<td>2~3 mg cm$^{-2}$</td>
<td>888 F g$^{-1}$ at 20 A g$^{-1}$</td>
<td>66.2% from 1 to 20 A g$^{-1}$</td>
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<td>15</td>
<td>CoS$_2$ hollow spheres</td>
<td>Not reported</td>
<td>522 F g$^{-1}$ at 5 A g$^{-1}$</td>
<td>76% from 0.5 to 5 A g$^{-1}$</td>
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<td>CoS nanowire arrays</td>
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<td>102 F g$^{-1}$ at 40 A g$^{-1}$</td>
<td>79% from 2 to 40 A g$^{-1}$</td>
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<td>17</td>
<td>NiS$_2$ nanocube</td>
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<td>158 F g$^{-1}$ at 12.5 A g$^{-1}$</td>
<td>23% from 1.25 to 12.5 A g$^{-1}$</td>
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<td>18</td>
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<td>579 F g$^{-1}$ at 5 A g$^{-1}$</td>
<td>64% from 0.5 to 5 A g$^{-1}$</td>
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Supplementary References


