Supporting Information

High-Performance Double Ion-buffering Reservoirs of Asymmetric Supercapacitors Based on Flower-like Co$_3$O$_4$-G>N-PEGm Microspheres and 3D rGO-CNT>N-PEGm Aerogels

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Figure S1. (a-b) FT-IR spectra of mPEG, mPEG-OTs, mPEG-N$_3$, G$>$N-PEGm, GO and G. (c) Raman spectra of GO, G and G$>$N-PEGm (the inset shows the ratio of I_D/I_G). (d) XRD patterns of GO, G and G$>$N-PEGm. (e) TGA curves of G$>$N-PEGm and mPEG in N$_2$. (f) The fully scanned XPS spectra, (g) the C/O ratio and (h) C 1s high-resolution XPS spectra of GO, G and G$>$N-PEGm. (i) N 1s high-resolution XPS spectrum of G$>$N-PEGm
**Figure S2.** (a-e) Different magnification SEM images of G>N-PEGm nanosheets. (f) EDS spectrum of G>N-PEGm (the inset shows the ratio of elements).

**Figure S3.** (a-c) Different magnification TEM images of G>N-PEGm nanosheets (the red rings in figure S3c show the aggregation of PEG polymer chains on the surface of the graphene nanosheets). (d) SAED patterns and (e-f) HRTEM images of G>N-PEGm nanosheets.
**Figure S4.** Photographs of G>N-PEGm nanosheets dispersed in water, methanol, ethanol, NMP, DMF and THF (respectively from left to right).

**Figure S5.** XRD patterns of the 3D flower-like hierarchical microspheres of Co(OH)$_2$ and Co(OH)$_2$-G>N-PEGm.
Figure S6. (a-c) Different magnification SEM images of Co(OH)$_2$-G>N-PEGm, (d-i) the EDS elemental mapping analysis of Co-L, O-K, C-K, S-K, and Cl-K for DBS-α-Co(OH)$_2$-G>N-PEGm flower spheres.
Figure S7. (a-c) Different magnification SEM images of G>N-PEGm nanosheets in the Co(OH)$_2$-G>N-PEGm composites, (d-i) the EDS elemental mapping analysis of Co-L, O-K, C-K, S-K, and Cl-K for G>N-PEGm.

Figure S8. (a) TGA-DSC curves of the 3D flower-like hierarchical microspheres DBS-Co(OH)$_2$-G>N-PEGm in air. (b) TGA-DSC curves of the G>N-PEGm nanosheets in air.
Table S1. Temperature ranges of TGA-DSC curves of the flower microspheres Co(OH)$_2$-G>N-PEGm composites in air.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature range</th>
<th>Discussion</th>
<th>Chemical reaction</th>
<th>Weight loss range (%)</th>
<th>Weight loss (%)</th>
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<tr>
<td>S-I</td>
<td>50-120</td>
<td>Adsorbed surface water</td>
<td>-</td>
<td>99.9-98.7</td>
<td>1.2</td>
</tr>
<tr>
<td>S-II</td>
<td>120-200</td>
<td>Intercalated crystallization water</td>
<td>C1</td>
<td>98.7-97.4</td>
<td>1.3</td>
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<tr>
<td>S-III</td>
<td>200-320</td>
<td>Thermal oxidative decomposition of Co(OH)$_2$</td>
<td>C2</td>
<td>97.4-80.5</td>
<td>16.9</td>
</tr>
<tr>
<td>S-IV</td>
<td>320-430</td>
<td>Thermal oxidation of mPEG (on G&gt;N-PEGm)</td>
<td>C3</td>
<td>80.5-75.3</td>
<td>5.2</td>
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<tr>
<td>S-V</td>
<td>430-520</td>
<td>Thermal oxidation of DBS</td>
<td>C4</td>
<td>75.3-72.6</td>
<td>2.7</td>
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<tr>
<td>S-VI</td>
<td>520-650</td>
<td>Thermal oxidation of G</td>
<td>C5</td>
<td>72.6-67.1</td>
<td>5.5</td>
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<tr>
<td>S-VII</td>
<td>650-800</td>
<td>Thermal oxidation of CoSO$_4$</td>
<td>C6</td>
<td>67.1-64.8</td>
<td>2.3</td>
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</tbody>
</table>

Chemical reactions in the stages of TGA-DSC curves of the flower microspheres Co(OH)$_2$-G>N-PEGm composites in air as follows:

\[
\text{Co(OH)}_2\text{DBS}_y\cdot z\text{H}_2\text{O}\cdot \text{G}>\text{N-PEGm} \xrightarrow{120 - 200^\circ C} \text{Co(OH)}_2\text{DBS}_y\cdot \text{G}>\text{N-PEGm} + \text{H}_2\text{O} \quad (C1)
\]

\[
\text{Co(OH)}_2\text{DBS}_y\cdot \text{G}>\text{N-PEGm} + \text{O}_2 \xrightarrow{300 - 320^\circ C} \text{Co}_3\text{O}_{4-y/2}\text{DBS}_y\cdot \text{G}>\text{N-PEGm} + \text{H}_2\text{O} \quad (C2)
\]

\[
\text{Co}_3\text{O}_{4-y/2}\text{DBS}_y\cdot \text{G}>\text{N-PEGm} + \text{O}_2 \xrightarrow{320 - 430^\circ C} \text{Co}_3\text{O}_{4-y/2}\text{DBS}_y\cdot \text{G} + \cdot\text{(CH}_2\text{CH}_2\text{O})\cdot x + \text{H}_2\text{O} + \text{CO}_2 + \text{NO}_2 \quad (C3)
\]

\[
\text{Co}_3\text{O}_{4-y/2}\text{DBS}_y\cdot \text{G} + \text{O}_2 \xrightarrow{430 - 520^\circ C} \text{Co}_3\text{O}_{4-y}(\text{SO}_4)_y\cdot \text{G} + \text{H}_2\text{O} + \text{CO}_2 \quad (C4)
\]

\[
\text{Co}_3\text{O}_{4-y}(\text{SO}_4)_y\cdot \text{G} + \text{O}_2 \xrightarrow{520 - 650^\circ C} \text{Co}_3\text{O}_{4-y}(\text{SO}_4)_y + \text{CO}_2 \quad (C5)
\]

\[
\text{Co}_3\text{O}_{4-y}(\text{SO}_4)_y \xrightarrow{550 - 800^\circ C} \text{Co}_3\text{O}_4 + \text{O}_2 + \text{SO}_2 \quad (C6)
\]
Figure S9. (a) Schematic illustration and (b1-b6) photographs of detecting the concentration of Co$^{2+}$ ions in the reaction process of precursors.

In Figure S9a, the schematic illustration of C, C$_1$ and C$_1$-NaOH represent the centrifugal sedimentation, clarified centrifugate and sedimentation (by adding NaOH solution) of precursors, respectively. As shown in Figure S9b1- S9b6, by the reaction proceeding under different reaction temperatures, the concentration of Co$^{2+}$ ions becomes lower gradually, thus indicating to form the Co(OH)$_2$ microspheres.
Figure S10. (a-c) Different magnification SEM images of Co$_3$O$_4$-G>N-PEGm, (d-i) the EDS elemental mapping analysis of Co-L, O-K, C-K, S-K, and Cl-K for Co$_3$O$_4$-G>N-PEGm flower spheres.

The evenly distributed Co, O, C, S and Cl elements (without Na element else) in the Co$_3$O$_4$-G>N-PEGm flower microsphere can indicate that the DBS-intercalated Co(OH)$_2$-G>N-PEGm composites have been converted to Co$_3$O$_4$-G>N-PEGm with DBS ions doping in the cobalt spinel oxide (Figure S10d-S10i).
Figure S11. (a) O 1s and (b) C 1s XPS spectrum of \( \text{Co}_3\text{O}_4 \) and \( \text{Co}_3\text{O}_4\text{-G>N-PEGm} \).

As shown in Figure S11b, it displays four different peaks at 284.8, 286.2, 286.8 and 288.4 eV, which can be respectively ascribed to non oxygenated C (C=C/C-C) in aromatic rings (284.8 eV), C in C-O-C (286.2 eV), C in C=O (286.8 eV) and C in O-C=O (288.4 eV) bonding compared with the bare \( \text{Co}_3\text{O}_4 \) flower spheres. The peak at 286.0 eV for \( \text{Co}_3\text{O}_4\text{-G>N-PEGm} \) can be mainly attributed to the ether-oxygen groups (C-O-C) of mPEG polymer chains on G>N-PEGm. It is worthy to note that the peak at 285.6 eV for \( \text{Co}_3\text{O}_4\text{-G>N-PEGm} \) may correspond to Co←:O-C coordination bonds.
Figure S12. The long-term stability of Co$_3$O$_4$-G>N-PEGm: (a) the initial 20 times galvanostatic charge-discharge curves, and (b) the cycling performance at a current density of 40 Ag$^{-1}$.

Table S2. BET surface area, pore volume, and BJH pore size distribution of Co$_3$O$_4$-G>N-PEGm-250, Co$_3$O$_4$-G>N-PEGm-350 and Co$_3$O$_4$-G>N-PEGm-450.

<table>
<thead>
<tr>
<th>Name</th>
<th>BET (m$^2$/g)</th>
<th>Pore volume (mL/g)</th>
<th>BJH (nm)</th>
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<tr>
<td>Co$_3$O$_4$-G&gt;PEGm-250</td>
<td>107.79</td>
<td>0.52</td>
<td>4</td>
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<tr>
<td>Co$_3$O$_4$-G&gt;PEGm-350</td>
<td>96.59</td>
<td>0.47</td>
<td>4</td>
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<tr>
<td>Co$_3$O$_4$-G&gt;PEGm-450</td>
<td>73.08</td>
<td>0.44</td>
<td>6.5</td>
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**Figure S13.** Photographs of 3D rGO-CNT>N-PEGm aerogels in different sizes.

**Figure S14.** Photographs of 3D rGO-CNT>N-PEGm hydrogels in water with different ratios of rGO-CNT>N-PEGm respectively from left to right as shown on samples (the inset without water).
Figure S15. (a) XRD patterns of 3D rGO-CNT>N-PEGm aerogels with different mass ratios. (b-h) XRD peaks of 3D rGO-CNT>N-PEGm aerogels with different ratios according to the (002) planes of rGO and CNTs.

Figure S16. (a-f) and (i-j) TEM images of 3D rGO aerogels. (g-h) and (k-l) HRTEM images of 3D rGO aerogels.
**Figure S17.** (a-f) and (i-j) TEM images of 3D rGO-CNT>N-PEGm aerogels. (g-h) and (k-l) HRTEM images of 3D rGO-CNT>N-PEGm aerogels.

**Figure S18.** The electrochemical properties of 3D rGO-CNT>N-PEGm aerogels with various mass ratios (according to rGO / CNT>N-PEGm): (a) CV curves at a scan rate of 100 mV s$^{-1}$. (b)
Galvanostatic charge-discharge curves at current density of 2 A g\(^{-1}\). (c) The specific capacitance at various current densities. The electrochemical properties of 3D rGO-CNT>N-PEGm aerogels (rGO / CNT>N-PEGm = 40:10): (d) Nyquist plots (the inset shows the equivalent circuit), (e) the initial 20 times galvanostatic charge-discharge curves, and (f) the cycling performance at a current density of 15 A g\(^{-1}\).

**Figure S19.** (a) CV curves of 3D rGO-CNT>N-PEGm aerogels and Co\(_3\)O\(_4\)-G>N-PEGm electrodes performed in a three-electrode configuration in 6 M KOH solution at a scan rate of 100 mV s\(^{-1}\). (b) CV curves of the asymmetric supercapacitors measured at different potential windows (at 100 mV s\(^{-1}\)). (c) Galvanostatic charge-discharge curves with the increase of the potential window (at current density of 1 A g\(^{-1}\)). (d) The IR drop at the start point of the discharge curves of Co\(_3\)O\(_4\)-G>N-PEGm // rGO-CNT>N-PEGm asymmetric supercapacitors. (e) The voltage drop (IR drop) of Co\(_3\)O\(_4\)-G>N-PEGm // rGO-CNT>N-PEGm asymmetric supercapacitors. (f) The specific capacitance at various current densities.

**Figure S19b** shows a series of CV curves measured with different potential windows from 0-0.8 V to 0-1.6 V at 100 mV s\(^{-1}\). At the operating potential window of 1.0 V, the pseudocapacitive redox-peaks in the region from 0.6 to 1.0 V are attributed to the reversible Faradaic redox reactions of the Co\(_3\)O\(_4\)-G>N-PEGm positive electrode.
material. When the operating potential window increases to 1.6 V, more redox reactions occur for the larger current response. In Figure S19c, the galvanostatic charge-discharge curves are measured with the increase of the potential window at current density of 1 A g$^{-1}$, which correspond to the CV curves of Figure S19b with different potential windows. Moreover, they also combine the pseudocapacitance of Co$_3$O$_4$-G>N-PEGm and electrical double-layer capacitance of the 3D rGO-CNT>N-PEGm aerogels.
<table>
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<th>Positive electrode</th>
<th>morphology (structure)</th>
<th>Capacitance (F g⁻¹)</th>
<th>Current density (A g⁻¹)</th>
<th>Negative electrode</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Power density (W Kg⁻¹)</th>
<th>Retention (%)</th>
<th>Cycle numbers</th>
<th>Ref</th>
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<tr>
<td>Co₃O₄@CoWO₄</td>
<td>core/shell nanoneedles</td>
<td>384.7</td>
<td>0.5</td>
<td>rGO</td>
<td>19.1</td>
<td>531.2</td>
<td>88.8</td>
<td>5000</td>
<td>Ref.1</td>
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<td>Co₃O₄@MnO₂</td>
<td>core/shell arrays</td>
<td>560</td>
<td>0.2</td>
<td>MEGO porous carbon</td>
<td>17.7</td>
<td>158</td>
<td>81.1</td>
<td>10,000</td>
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<td>Co₃O₄@RGO</td>
<td>aerogel</td>
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<td>0.5</td>
<td>AC</td>
<td>40.65</td>
<td>340</td>
<td>92.92</td>
<td>2000</td>
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<td>nanoflakes</td>
<td>1112</td>
<td>3.3</td>
<td>AC</td>
<td>23.3</td>
<td>2300</td>
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<td>20,000</td>
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<td>hybrid nanorods</td>
<td>847.2</td>
<td>1</td>
<td>AC</td>
<td>38</td>
<td>275</td>
<td>94.7</td>
<td>5000</td>
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<td>1</td>
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<td>Co₃O₄</td>
<td>MOF (ZIF-67)</td>
<td>504</td>
<td>5 mV cm⁻³</td>
<td>rGO</td>
<td>36</td>
<td>8000</td>
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<td>2000</td>
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<td>41.90</td>
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<td>TiO₂/C/Co₃O₄</td>
<td>ternary hybrid nanocomposites in situ coating method</td>
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<td>1</td>
<td>AC</td>
<td>18.54</td>
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<td>1</td>
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<td>5000</td>
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<td>Co₃O₄@NiMoO₄</td>
<td>nanocomposites on Ni foam</td>
<td>2041</td>
<td>0.5</td>
<td>AC</td>
<td>41.9</td>
<td>68.7</td>
<td>94.2</td>
<td>1000</td>
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<td>1</td>
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<td>35.7</td>
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<td>95</td>
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<td>CS aerogel</td>
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<td>34.4</td>
<td>400</td>
<td>84.7</td>
<td>10,000</td>
<td>Our work</td>
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MEGO: activated microwave exfoliated graphite oxide activated graphene.

CS aerogel: carbon aerogel microspheres.

3D GCA: 3D rGO-CNT>N-PEGm aerogels.
Figure S20. The CV curves (at the scan rate of 100 mVs$^{-1}$) and charge-discharge curves (at the current density of 1 Ag$^{-1}$) of the 1$^{st}$ and 10000$^{th}$ cycle for the asymmetric supercapacitors.

References


