Supporting Information

Superior Performance Asymmetric Supercapacitors Based on ZnCo$_2$O$_4$@MnO$_2$ Core-shell Electrode

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Experimental Section:

Synthesis of 3D porous spinous α-Fe$_2$O$_3$ on soft thin Fe substrate

In a typical procedure, a Fe foil (1 cm × 1 cm) was cleaned from a consecutive ultrasonication in acetone, ethanol, distilled water. 5 mL Oleic, 2 mL HCl (36%-38%) and 10 mL Ethanol were added and formed solution. After that the prepared Fe foil being immersed in solution in a 60 mL autoclave. Meanwhile the autoclave was sealed and maintained at 60°C for 4h, and then cooled naturally to room temperature. The Fe substrate attached with brown things was washed with water and ethanol for several times before characterization. Finally as-synthesized materials were subsequent annealing at 400 °C in air.

Calculation methods:
The discharge specific capacitance ($C_{sp}$) or areal capacitance($C_a$) in the three-electrode was calculated from the discharge curves using the following equation:\[^{1,2}\]

\[ C_{sp} = \frac{It}{m\Delta V} \quad C_a = \frac{It}{S\Delta V} \]

where $I$ (A) is the discharge current, $t$ (s) is the discharge time, $\Delta V$ (V) is the voltage interval of the discharge, and $m$ (g) is the active material mass of the electrode. $S$ is the geometrical area of the electrode.

The energy density and power density are calculated according to the following equations respectively:\[^{3,4}\]

\[ E = 0.5C\Delta V^2 \quad P = \frac{E}{t} \]

Where $C$ (F g$^{-1}$) is the specific capacitance, $E$ (Wh kg$^{-1}$) is the energy density, $P$ (W kg$^{-1}$) is the power density, $I$ (A) is the discharge current, $t$ (s) is the discharge time, and $\Delta V$ (V) is the potential window of discharge.

For supercapacitors, the charge balance between the two electrodes will follow the relationship $q^+ = q^-$, where $q^+$ means the charges stored at the positive electrode, $q^-$ means the charges stored at the negative electrode. The charge stored by each electrode usually depends on the specific capacitance ($C$), the potential window for the charge/discharge process ($\Delta E$), and the mass of the electrode ($m$) following Equation: $q = C \times \Delta E \times m$. The mass ratio between the positive and negative electrodes needs to follow: $^{[5]}

\[ \frac{m_+}{m_-} = \frac{C_p \times \Delta E_p}{C_n \times \Delta E_n} \]

Therefore, the optimal mass ratio between such two electrodes can be determined by
the specific capacitance values and potential windows. The ZnCo$_2$O$_4$@MnO$_2$ to α-Fe$_2$O$_3$ mass ratio was adjusted to be 0.92:1. So the total mass of the two active electrode materials is 2.5 mg cm$^{-2}$.

![Figure S1](image1.png)

**Figure S1** Electrochemical characterizations of the hierarchical ZnCo$_2$O$_4$@MnO$_2$ core-shell NTs arrays grown on Ni foam: charge-discharge voltage profiles at different current densities.

![Figure S2](image2.png)

**Figure S2** Impedance Nyquist plots of the ZnCo$_2$O$_4$ NW arrays and the hierarchical ZnCo$_2$O$_4$@MnO$_2$ core-shell NTs arrays grown on Ni foam at open circuit potential.
Figure S3  (a) Typical FESEM images of the 3D porous $\alpha$-Fe$_2$O$_3$; (b) Galvanostatic charging/discharging curves of the 3D porous $\alpha$-Fe$_2$O at different current densities.

Table 1 Summarization of the supercapacitor performance of different electrode material.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Current density</th>
<th>Specific capacitance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo$_2$O$_4$@MnO$_2$ NTs</td>
<td>12 mA cm$^{-2}$</td>
<td>2.32 F cm$^{-2}$</td>
<td>This our work</td>
</tr>
<tr>
<td>Co$_3$O$_4$-MnO$_2$ NW/nanosheet</td>
<td>12 mA cm$^{-2}$</td>
<td>0.56 F cm$^{-2}$</td>
<td>Ref. 6</td>
</tr>
<tr>
<td>MnO$_2$-NiO NWs</td>
<td>12 mA cm$^{-2}$</td>
<td>0.35 F cm$^{-2}$</td>
<td>Ref. 7</td>
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<tr>
<td>Co$_3$O$_4$-NiO NWs</td>
<td>12 mA cm$^{-2}$</td>
<td>1.35 F cm$^{-2}$</td>
<td>Ref. 8</td>
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<tr>
<td>ZnCo$_2$O$_4$NWs</td>
<td>12 mA cm$^{-2}$</td>
<td>0.866 F cm$^{-2}$</td>
<td>Ref. 9</td>
</tr>
</tbody>
</table>

Reference:


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