Electronic Supplementary Information

Ultrathin MnO$_2$ nanoflakes grown on N-doped hollow carbon spheres for high-performance aqueous zinc ion batteries

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Preparation of the Xanthan gum electrolyte

Xanthan gum electrolyte was prepared by a similar method mentioned in the previous research. Typically, 10 g of xanthan gum powder (Aladdin, UPS class) was mixed with 50 mL aqueous solution consisted of 3 M ZnSO$_4$ and 0.15 M MnSO$_4$ at room temperature. After continuous mechanical agitation, a homogeneous gel electrolyte with good flexibility was obtained, which was utilized for the assembly of the flexible battery.

Fabrication of flexible Zn-MnO$_2$ battery

The flexible Zn-MnO$_2$ battery was assembled by separating the MnO$_2$-NHCSs cathode and Zn anode with PP nonwoven separator and xanthan gum electrolyte. After that, the battery was sealed by hot-pressing two pieces of polyethylene oxide films. The MnO$_2$-NHCSs cathode was prepared by coating a slurry consisted of 70 wt.% active material, 20 wt.% conductive agent (Super P) and 10 wt.% PTFE binder onto 0.1 mm stainless steel foil. The active area of the cathode was about 1.5×8 cm$^2$, and the total active material mass loading was about 20 mg (~1.67 mg cm$^{-2}$). A zinc foil (0.1 mm thickness) that was cut into 1.5 cm wide and 8 cm length was used as the anode.
**Fig. S1** Schematic illustration of the preparation of MnO$_2$-NHCSs.
Fig. S2 (a,b) HRTEM images and (c) SAED pattern of the MnO$_2$-NHCSs sample.
Fig. S3 SEM image of prepared SiO$_2$ spheres.
Fig. S4 TGA curves of MnO$_2$-NHCSs and MnO$_2$-HSs.
The average voltage calculation based on the (a) discharge and (b) charge profiles of MnO$_2$-NHCSs in the 5th cycle at 0.1 A g$^{-1}$.

The average discharge/charge voltage ($\bar{U}$) can be estimated by the following formula:

$$\bar{U} = \frac{1}{Q_t} \int_0^{Q_t} U \, dQ$$  \hspace{1cm} (1)$$

Where $U$ is the voltage, $Q$ is specific capacity, and $Q_t$ is the total capacity.

According to the constant current discharge and charge curves shown in Fig. S5, the average discharge and charge voltage were calculated to be 1.362 and 1.569 V, respectively.
Fig. S6 Nyquist spectra of (a) MnO$_2$-NHCSs and (b) MnO$_2$-HSs, the cycled samples were controlled at the same charge state of 1.85 V. Inset of (a) shows the equivalent circuit diagram, Rs: solution resistance, Rct: charge transfer resistance, CPE: constant-phase element, Zw: Warburg impedance.
Fig. S7 (a) Demarcation of the discharge platform by turning point, (b) the capacity contribution of platform I and II to the total capacity.
Fig. S8 Logarithmic diagrams of current (i) and scan rate (v) at specific peak currents.
**Fig. S9** Single GITT profiles and linear behaviour of the transient voltage changes $E$ vs. $\tau^{1/2}$ for the MnO$_2$-NHCSs electrode during the discharge (a,b) and charge (c,d) process.

In order to gain the Zn$^{2+}$ diffusion coefficient of the MnO$_2$-NHCSs electrode, GITT tests were carried out during the 6th cycle. In GITT measurement, the cell was charged or discharged at 0.05 A g$^{-1}$ for 10 min, followed by an open circuit stand for 90 min, allowing the cell voltage to relax to its steady-state value. The procedure was repeated until the battery reached to the cut off voltage (1.85 or 1.0 V). The diffusion coefficient of Zn$^{2+}$ ($D_{Zn}$, cm$^2$ s$^{-1}$) are calculated based on the following equation:

$$D_{Zn} = \frac{4}{\pi\tau} \left( \frac{m_p}{M_g \gamma_m S} \right)^2 \left( \frac{\Delta E_{\tau}}{\Delta E_{\tau}} \right)^2$$  \hspace{1cm} (1)
Where, $\tau$ (s) is the pulse duration of constant current, $m_n$ (g), $M_B$ (g mol$^{-1}$), and $\nu_m$ (cm$^3$ mol$^{-1}$) correspond to the quality, molar mass, and molar volume of the active material, respectively, $S$ (cm$^2$) is the contacting area of electrode with electrolyte (taken as the geometric area of electrode for better comparison with literatures), $\Delta E_S$ is the voltage change of the termination voltage of two adjacent relaxation steps, $\Delta E_\tau$ is the potential change during the constant current pulse after eliminating the IR-drop.
Fig. S10 Nyquist spectra of MnO$_2$-NHCSs taken at different discharge states.
Fig. S11 The cyclic performance of NHCSs at 1.0 A g$^{-1}$ and 2.0 A g$^{-1}$. 
Fig. S12 SEM images of the MnO$_2$-NHCSs electrode after 100 cycles at 1.0 A g$^{-1}$. 
Fig. S13 SEM images of (a,b) pristine Zn plate and (c,d) Zn anode after charging and discharging at 1.0 A g$^{-1}$ for 100 cycles.
**Fig. S14** Ex-situ XRD patterns of the MnO$_2$-NHCSs electrode at different charge/discharge states.
Fig. S15 Ex-situ XRD patterns of the MnO$_2$-NHCSs electrode after different cycles.
Fig. S16 Ex-situ XPS spectra of the MnO$_2$-NHCSs electrode at fully discharged/charged states, (a) Zn 2p, (b) Mn 2p, (c) Mn 3s.
**Table S1.** Specific surface area and pore size parameters of MnO$_2$-NHCSs and MnO$_2$-HSs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$-NHCSs</td>
<td>213.12</td>
<td>0.61</td>
<td>13.52</td>
</tr>
<tr>
<td>MnO$_2$-HSs</td>
<td>141.24</td>
<td>0.83</td>
<td>25.98</td>
</tr>
</tbody>
</table>

**Table S2.** Electrochemical performance comparisons of the MnO$_2$-NHCSs electrode with other previously reported manganese-based oxide cathodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Rate capability</th>
<th>Cycling stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-MnO$_2$ nanorod</td>
<td>1 M ZnSO$_4$</td>
<td>233/0.083, 31/1.666</td>
<td>147/63%/0.083/50</td>
<td>4</td>
</tr>
<tr>
<td>Todorokite-type MnO$_2$</td>
<td>1 M ZnSO$_4$</td>
<td>108/0.05</td>
<td>-/100%/0.05/50</td>
<td>5</td>
</tr>
<tr>
<td>δ-MnO$_2$ nanoflake</td>
<td>1 M ZnSO$_4$</td>
<td>252/0.083, 30/1.333</td>
<td>112/-/0.083/100</td>
<td>6</td>
</tr>
<tr>
<td>Cation-Deficient ZnMn$_2$O$_4$</td>
<td>3 M Zn(CF$_3$SO$_3$)$_2$</td>
<td>150/0.05, 72/2.0</td>
<td>80/94%/0.5/500</td>
<td>7</td>
</tr>
<tr>
<td>a-MnO$_2$ nanorod</td>
<td>1 M ZnSO$_4$</td>
<td>323/0.016, 47/1.666</td>
<td>104/-/0.083/75</td>
<td>8</td>
</tr>
<tr>
<td>V-doped MnO$_2$</td>
<td>1 M ZnSO$_4$</td>
<td>266/0.066</td>
<td>131/49.2%/0.066/100</td>
<td>9</td>
</tr>
<tr>
<td>α-MnO$_2$@C</td>
<td>1 M ZnSO$_4$</td>
<td>272/0.066</td>
<td>189/69.5%/0.066/50</td>
<td>10</td>
</tr>
<tr>
<td>ZnHCF@MnO$_2$</td>
<td>0.5 M ZnSO$_4$</td>
<td>118/0.1, 75.2/1.0</td>
<td>~70/77%/0.5/1000</td>
<td>11</td>
</tr>
<tr>
<td>ZnMn$_2$O$_4$</td>
<td>1 M ZnSO$_4$+0.05, M MnSO$_4$</td>
<td>70.2/3.2</td>
<td>106.5/100%/0.1/300</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Solution composition</td>
<td>Rate capability</td>
<td>Cycling stability</td>
<td>This work</td>
</tr>
<tr>
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<tr>
<td>MnO$_2$@CFP</td>
<td>2 M ZnSO$_4$+0.2 M MnSO$_4$</td>
<td>290/0.09</td>
<td>50−70/100%/1.885/10000</td>
<td>13</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2 M ZnSO$_4$+0.1 M MnSO$_4$</td>
<td>137/2.0, 38/2.0</td>
<td>82.2/~/2.0/1000</td>
<td>14</td>
</tr>
<tr>
<td>SSWM@Mn$_3$O$_4$</td>
<td>2 M ZnSO$_4$+0.1 M MnSO$_4$</td>
<td>296/0.1, 125/0.5</td>
<td>296/98%/0.1/50</td>
<td>15</td>
</tr>
<tr>
<td>MnO$_2$-NHCSs</td>
<td>3 M ZnSO$_4$+ 0.15 MnSO$_4$</td>
<td>348/0.1, 127/3.0</td>
<td>349/100%/0.1/80</td>
<td>This work</td>
</tr>
</tbody>
</table>

Explanation of the above data implications: take the first a-MnO$_2$ nanorod as an example, i) Rate capability, 233/0.083, 31/1.666 present that 233 mAh g$^{-1}$ at 0.083 A g$^{-1}$, and 31 mAh g$^{-1}$ at a high rate of 1.666 A g$^{-1}$; ii) Cycling stability, 147/63%/0.083/50 present that 147 mAh g$^{-1}$ (capacity retention of 63%) was retained at 0.083 A g$^{-1}$ after 50 cycles.
References


