Supporting Information

One-step synthesis of MnO$_x$/PPy nanocomposite as a high-performance cathode for rechargeable zinc-ion battery and insight into its energy storage mechanism

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Fig. S1. Pore size distribution of the MnO$_x$/PPy composite.
Fig. S2. Mn 3s XPS spectrum of the MnO\textsubscript{x}/PPy composite.

The XPS of the Mn 3s regions was further performed. As shown in Fig. S2, the energy differences of Mn 3s multiplet splittings for MnO\textsubscript{x}/PPy is 5.1 eV. The value is consistent with the mixed (III and IV) valences of Mn (5.5 eV for Mn\textsubscript{2}O\textsubscript{3}; 4.5 eV for MnO\textsubscript{2}) [1,2].
Fig. S3. SEM image of pure PPy electrode.
The MnO$_x$/PPy composite was heat treated at 500 °C in air to remove the shielding of PPy. The XPS and XRD results of MnO$_x$ (Fig. S4) verified the coexistence of Mn$^{3+}$ and Mn$^{4+}$ in the MnO$_x$. However, compared with XPS result of MnO$_x$/PPy, the Mn$^{3+}$/Mn$^{4+}$ ratio in the MnO$_x$ is higher than that in the MnO$_x$/PPy composite. Moreover, the crystallinity of MnO$_x$ increases.

**Fig. S4.** (a) XPS and (b) XRD pattern of the MnO$_x$. 
Fig. S5. (a) Cyclic voltammetry curves of Zn-MnOₓ/PPy and Zn-MnOₓ batteries. (b) Discharge/charge profiles of Zn-MnOₓ/PPy and Zn-MnOₓ batteries at a 0.15 A g⁻¹. (d) Rate capability of Zn-MnOₓ/PPy and Zn-MnOₓ batteries. (f) Long-term cycling performance of Zn-MnOₓ/PPy and Zn-MnOₓ batteries at 6 A g⁻¹.

Fig. S5 shows that the MnOₓ electrodes show poor capacity and rate performance when compared with MnOₓ/PPy electrodes.
The reactions of the rechargeable aqueous Zn- MnO$_x$/PPy batteries can be formulated as below. [3-7]

**MnO$_x$/PPy Cathode reactions:**
\[
\begin{align*}
H_2O & \leftrightarrow H^+ + OH^- \\
MnO_x + 2xH^+ + (2x - 2)e^- & \leftrightarrow Mn^{2+} + xH_2O \\
3Zn^{2+} + 6OH^- + ZnSO_4 + yH_2O & \leftrightarrow ZnSO_4[Zn(OH)_2]_3 \cdot yH_2O \\
PPy + Zn^{2+} & \leftrightarrow PPy.Zn^{2+}
\end{align*}
\]

**MnO$_x$/PPy Anode reaction:**
\[
Zn \leftrightarrow Zn^{2+} + 2e^-
\]

Reference: