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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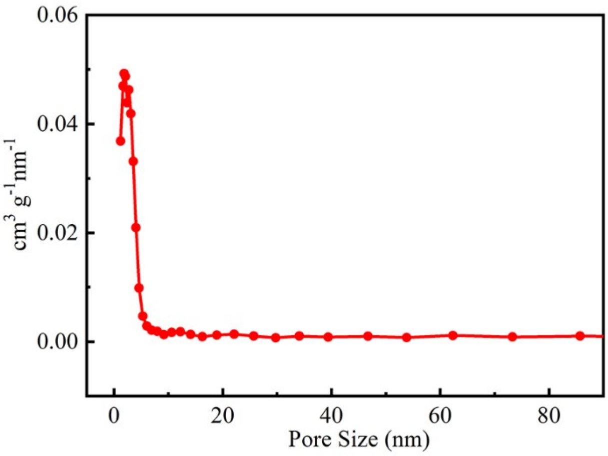

Fig. S1. Pore size distribution of the MnO_x/PPy composite.

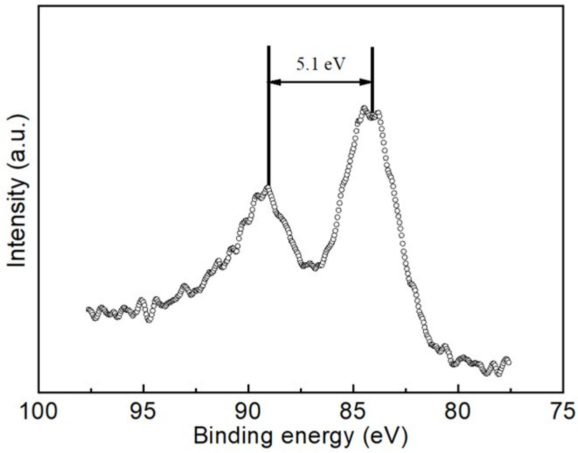

Fig. S2. Mn 3s XPS spectrum of the MnO_x/PPy composite.

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_x/PPy is 5.1 eV. The value is consistent with the mixed (III and IV) valences of Mn (5.5 eV for Mn_2O_3; 4.5 eV for MnO_2) [1,2].

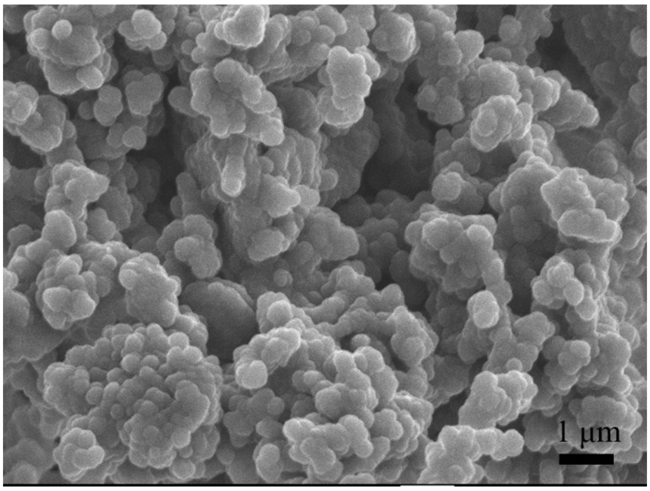

Fig. S3. SEM image of pure PPy electrode.

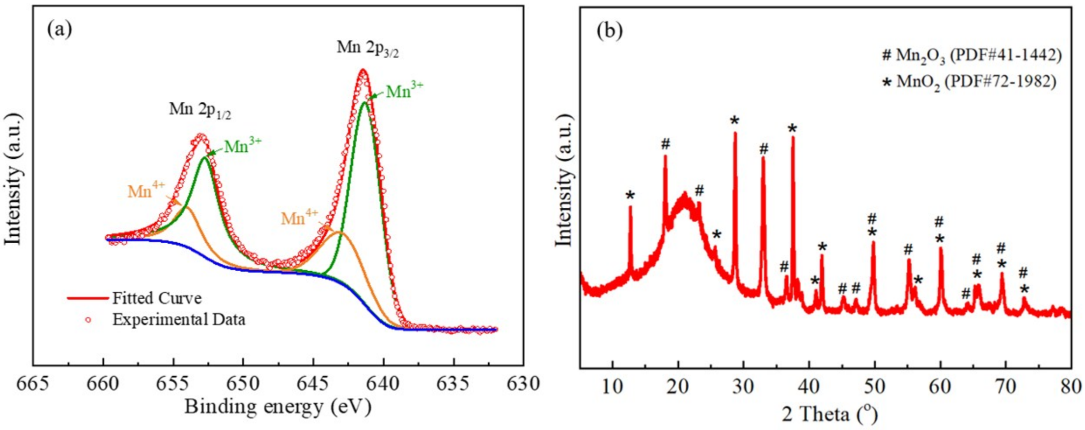

Fig. S4. (a) XPS and (b) XRD pattern of the MnO_x**.**

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.

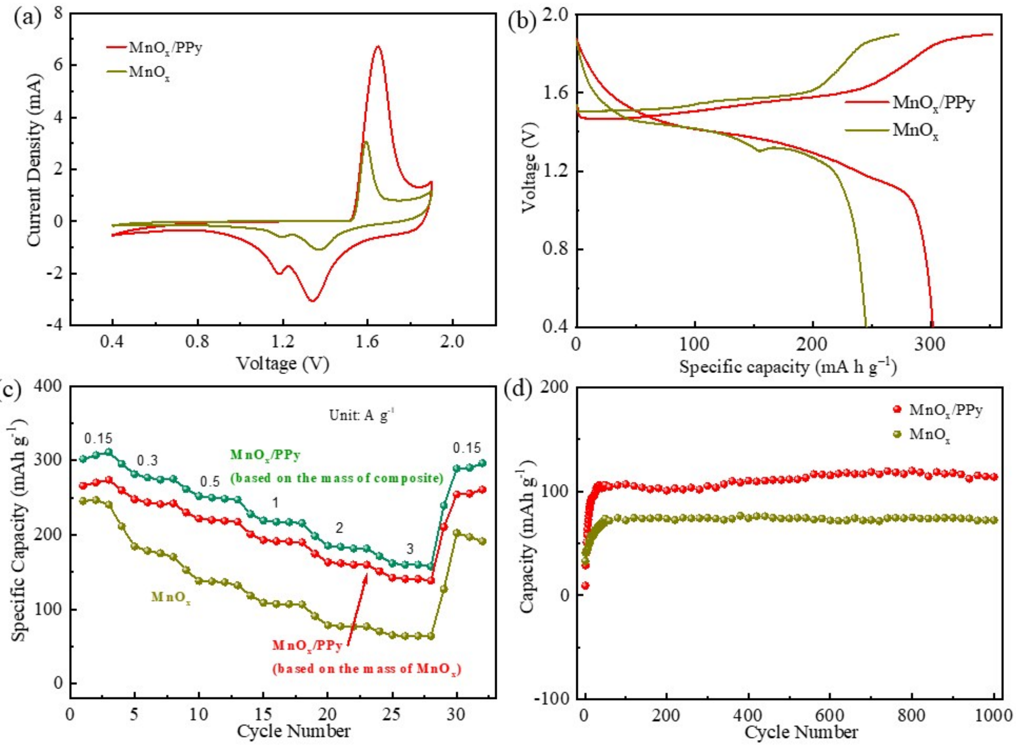

Fig. S5. (a) Cyclic voltammetry curves of Zn-MnO_x/PPy and Zn-MnO_x batteries. (b) Discharge/charge profiles of Zn-MnO_x/PPy and Zn-MnO_x batteries at a 0.15 A g^{-1}. (d) Rate capability of Zn-MnO_x/PPy and Zn-MnO_x batteries. (f) Long-term cycling performance of Zn-MnO_x/PPy and Zn-MnO_x batteries at 6 A g^{-1}.

Fig. S5 shows that the MnO_x electrodes show poor capacity and rate performance when compared with MnO_x/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:

$$H_2O \leftrightarrow H^+ + OH^-$$

$$MnO_x + 2xH^+ + (2x-2)e^- \leftrightarrow Mn^{2+} + xH_2O$$

$$3Zn^{2+} + 6OH^- + ZnSO_4 + yH_2O \leftrightarrow ZnSO_4[Zn(OH)_2]_3 \cdot yH_2O$$

$$PPy + Zn^{2+} \leftrightarrow PPy\_Zn^{2+}$$

MnO_x/PPy Anode reaction:

$$Zn \leftrightarrow Zn^{2+} + 2e^-$$

Reference:

[1] L. Du, S. Yu, X. Liu and Y. Ding, *Appl. Surf. Sci.*, 2019, 486, 460-465.
[2] W. Tang, H. Liu, X. Wu and Y. Chen, *Ozone-Sci. Eng.*, 2104, 36, 502-512.
[3] Z. Guo, Y. Ma, X. Dong, J. Huang, Y. Wang and Y. Xia, *Angew. Chem.*, 2018, 130, 11911-11915.
[4] N. Palaniyandy, M. Kebede, K. Raju, K. Ozoemena, L. le Roux, M. Mathe and R. Jayaprakasam, *Mater. Chem. Phys.*, 2019, 230, 258-266.
[5] J. Hao, J. Mou, J. Zhang, L. Dong, W. Liu, C. Xu and F. Kang, *Electrochim. Acta*, 2018, 259, 170-178.
[6] H. Pan, Y. Shao, P. Yan, Y. Cheng, K. Han and Z. Nie, *Nat. Energy*, 2016, 1, 16039.
[7] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu and J. Chen, *Nat. Commun.*, 2017, 8, 405.