Electronic supplementary information

High-Performance Solid-state Zn Batteries Based on Free-standing Organic Cathode and Metal Zn Anode with Ordered Nano-architecture

Xingchi Xiao, Wenjie Liu, Kai Wang,* Chen Li, Xianzhong Sun, Xiong Zhang, Wenhao Liu, and Yanwei Ma*

Institute of Electrical Engineering, Chinese Academy of Sciences
Beijing 100190, P.R. China
University of Chinese Academy of Sciences
Beijing 100049, PR China
E-mail: wangkai@mail.iee.ac.cn, ywma@mail.iee.ac.cn

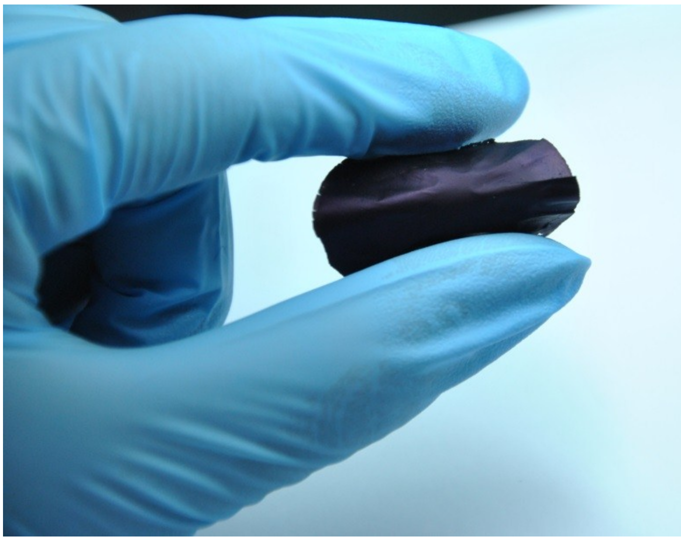

Figure S1. The photography of the PANI@CNT film.

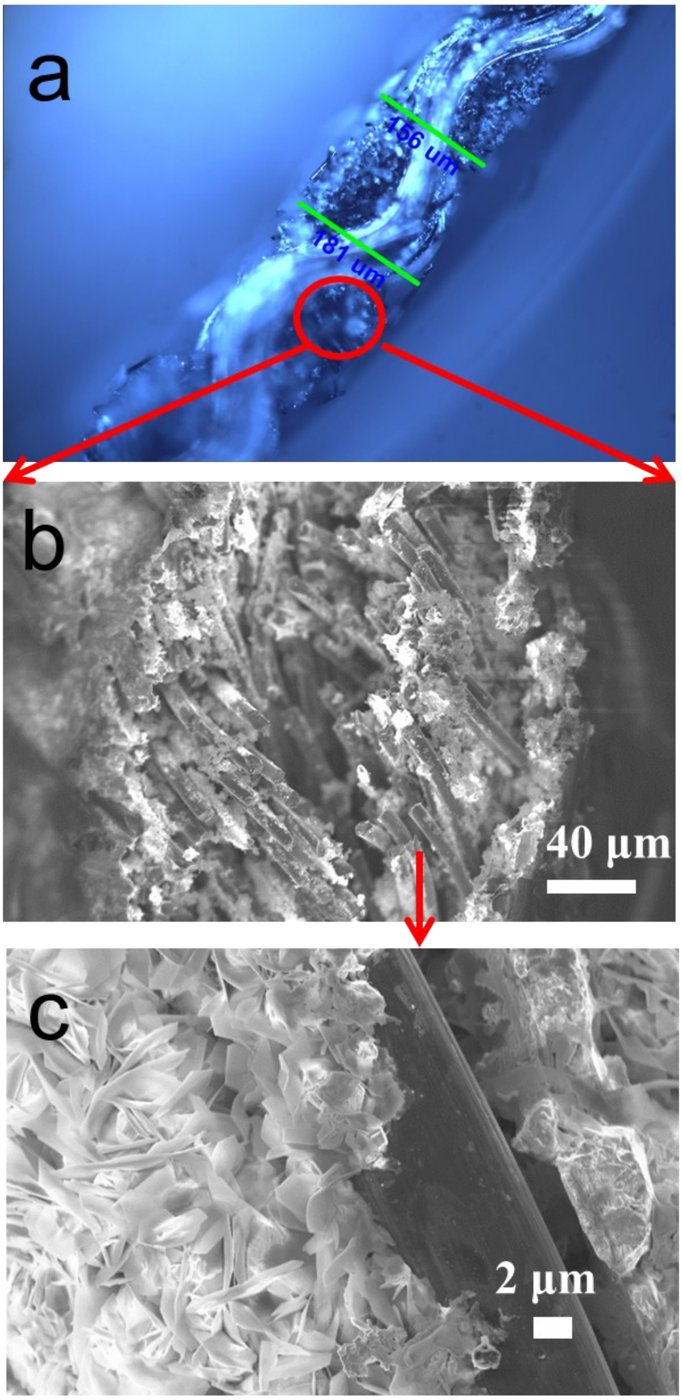

Figure S2. The cross-section of the Zn@CC anode :(a) the optical microscopy, (b) SEM images.

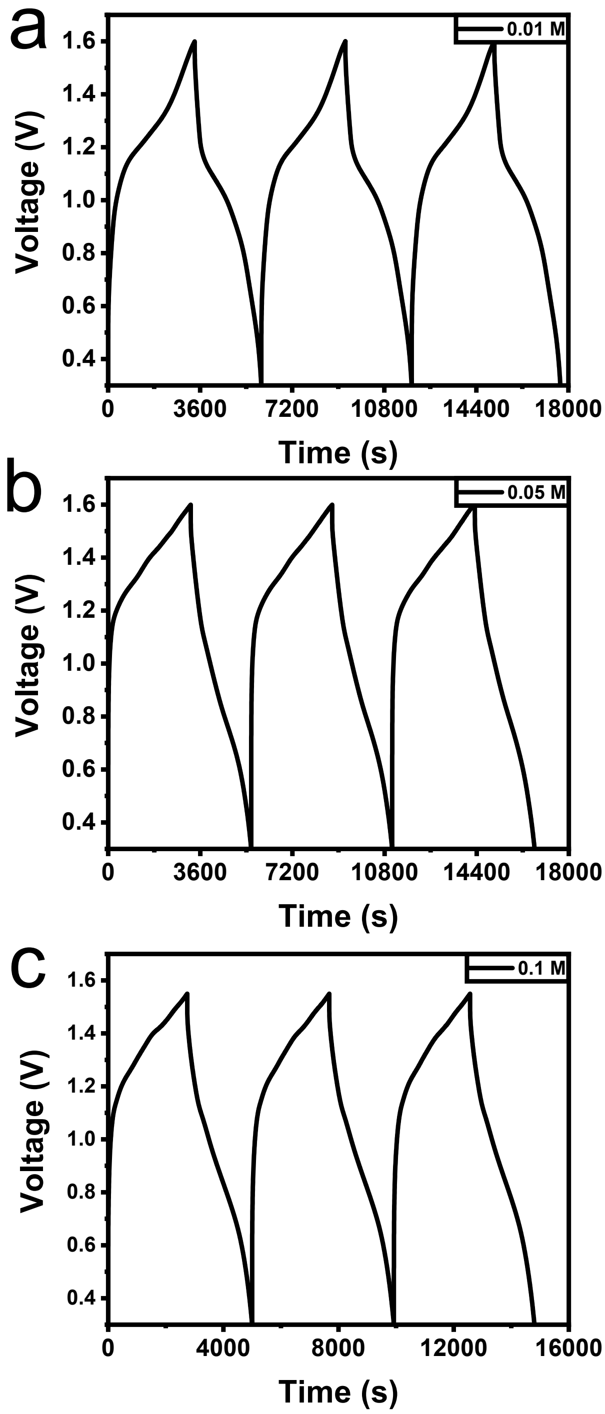

Figure S3. The The initial three galvanostatic charge-discharge curves at a current density of 0.2 A/g for (a) 0.01 M-battery, (b) 0.05 M-battery and (c) 0.1 M-battery.

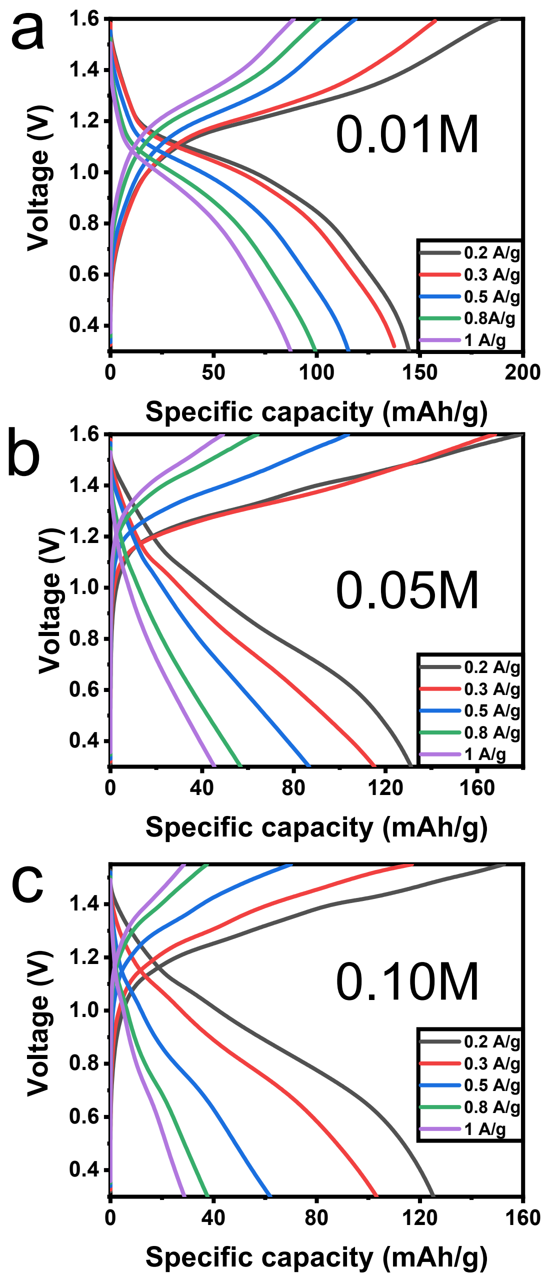

Figure S4. The galvanostatic charge-discharge profiles at various current densities for (a) 0.01 M-battery, (b) 0.05 M-battery and (c) 0.1 M-battery.

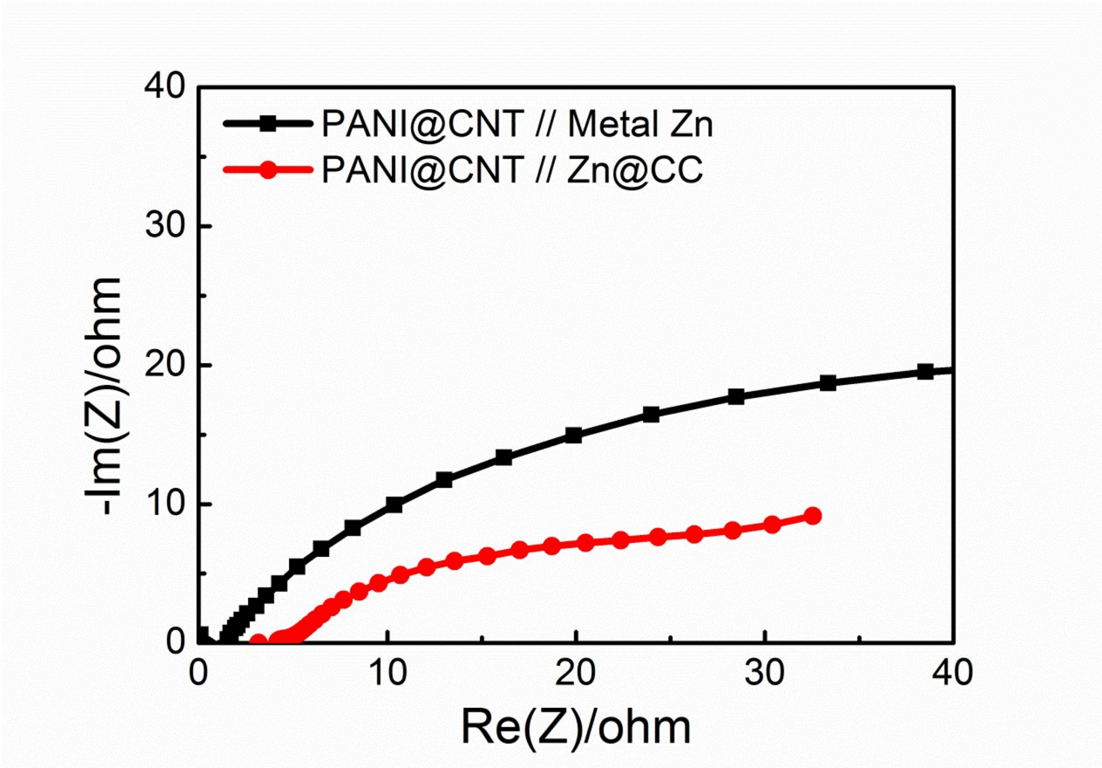

Figure S5. The EIS plot of the Zn ions batteries based on different anode: metal Zn foil and Zn@CC anode.

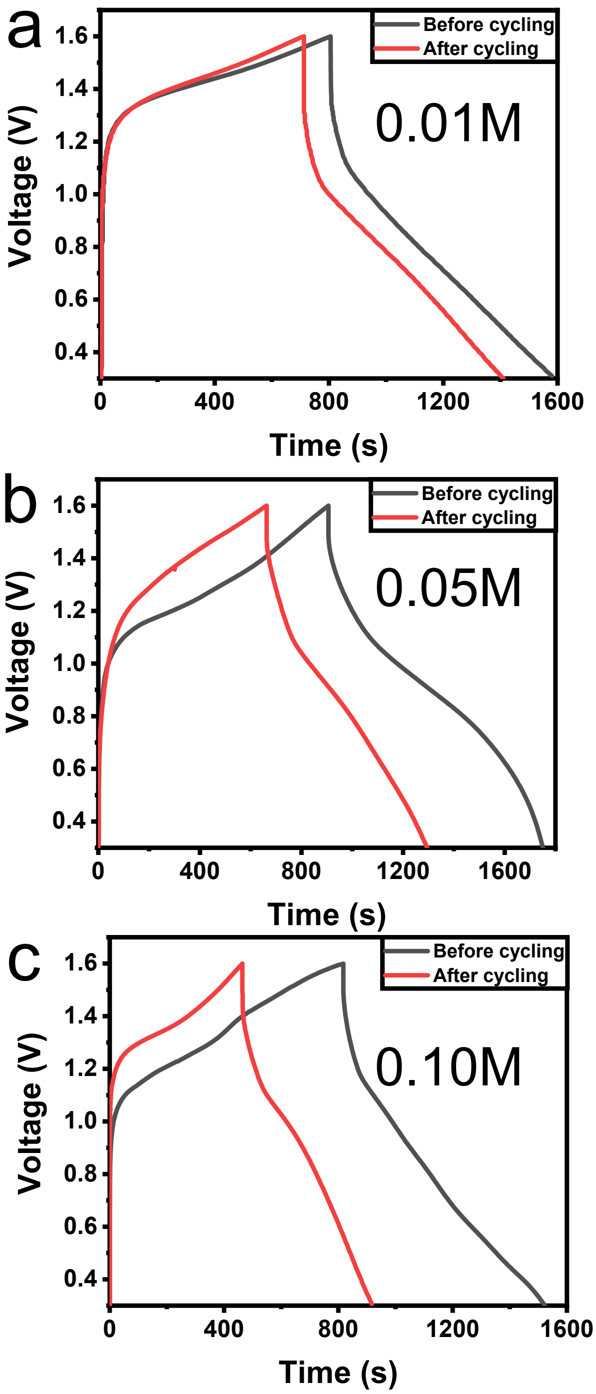

Figure S6. The galvanostatic charge-discharge curves before and after cycling at a current density of 0.5 A/g for (a) 0.01 M-battery, (b) 0.05 M-battery and (c) 0.1 M-battery.

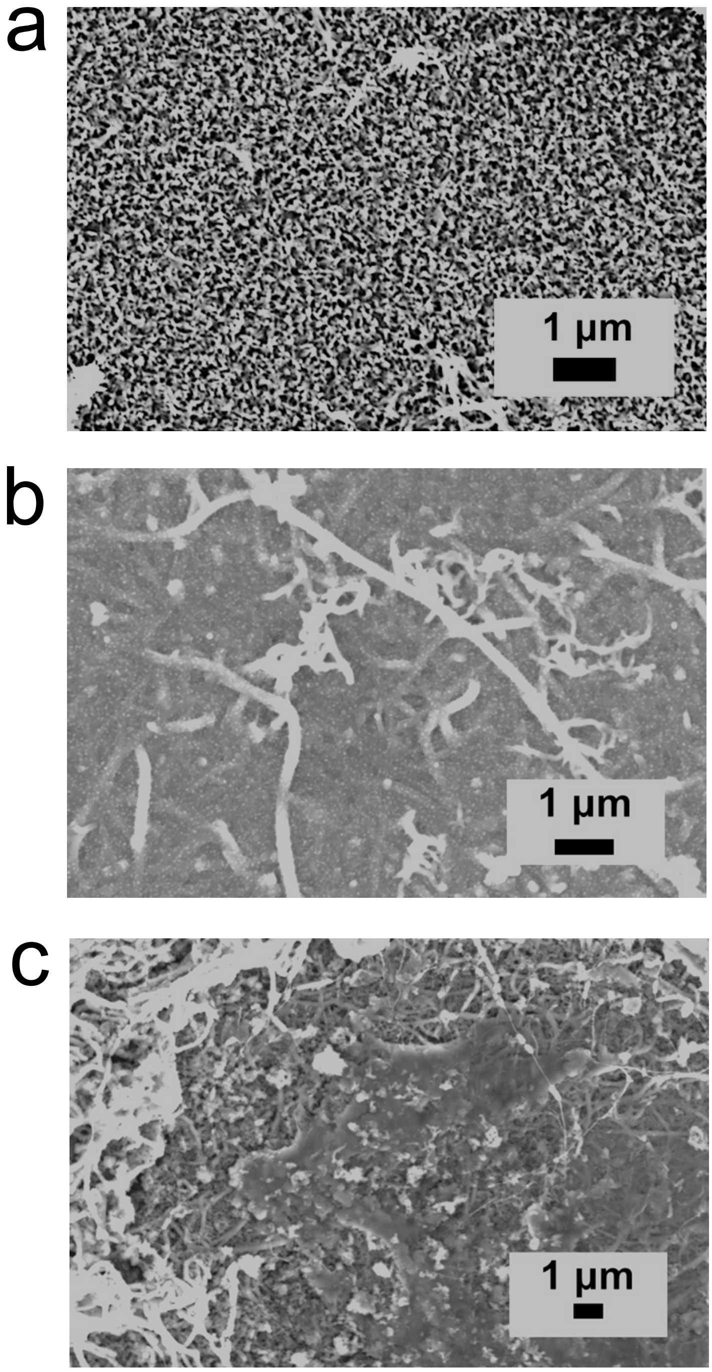

Figure S7. Morphologies in SEM top view of PANI@CNT film prepared by using aniline with various concentrations of (a)0.01M, (b) 0.05 M and (c) 0.1 M.

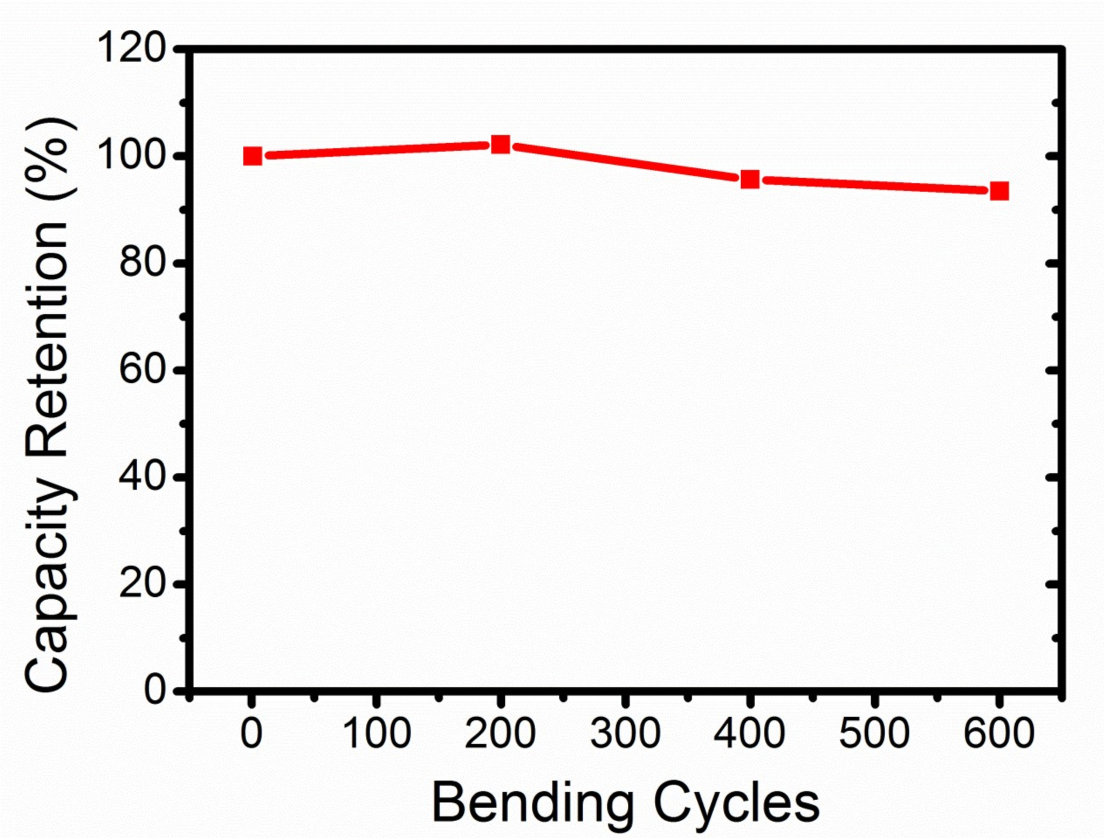

Figure S8. The bending cycles of the as-prepared Zn ions battery.

Table S1. The ionic conductivity of common cellulosic film with 1M ZnSO4 solution and Gel film, respectively.

	Cellulosic -1M ZnSO4	Gel Film
Thickness (μm)	53	83
Resistance (Ohm)	0.95	1.58
Conductivity (mS/cm)	5.90	5.56

Table S2. Comparison of as-prepared 0.01M- \battery with previously reported Zn ions batteries based on organic cathode.

Ref	Year	Electrode	Capacity	Flexible
This work		**Zn@CC // PANI@CNT**	**144mAh/g**	**Flexible Cathode**
S1	2014	Zn // ZnHCF	65 mAh/g	No
S2	2014	Zn // $Na_{0.95}MnO_2$	60 mAh/g	No
S3	2015	Zn//$Zn^{2+}Al^{3+}$//Graphite	94 mAh/g	No
S4	2016	Mo_6S_8//Zn^{2+}//Carbon	62 mAh/g	No
S5	2016	$ZnMn_2O_4$ // Carbon	120 mAh/g	No
S6	2017	Zn@CF // HQ-NaFe	81 mAh/g	No
S7	2018	Zn / /PPy	123 mAh/g	Yes
S8	2018	Zn//CMK-3-p-chloranil	118 mAh/g	No
S9	2018	Zn@NT//MnO_2@SS-PPy	136.4 mAh/g	Yes
S10	2019	Zn//MnO_x@$Ti_3C_2T_x$-CNTs	88 mAh/g	Yes
S11	2019	Zn@Fiber//ZnHCF@CNTs	94.9 mAh/g	Yes
S12	2019	Zn//Polydopamine@CNT	88 mAh/g	Flexible Cathode

Reference:

- S1. Zhang, L., Chen, L., Zhou, X., & Liu, Z. (2015). Towards High‐Voltage Aqueous Metal‐Ion Batteries Beyond 1.5 V: The Zinc/Zinc Hexacyanoferrate System. *Advanced Energy Materials*, *5*(2), 1400930.
- S2. Zhang, B., Liu, Y., Wu, X., Yang, Y., Chang, Z., Wen, Z., & Wu, Y. (2014). An aqueous rechargeable battery based on zinc anode and Na 0.95 MnO 2. *Chemical Communications*, *50*(10), 1209-1211.
- S3. Wang, F., Yu, F., Wang, X., Chang, Z., Fu, L., Zhu, Y., ... & Huang, W. (2016). Aqueous rechargeable zinc/aluminum ion battery with good cycling performance. *ACS applied materials & interfaces*, *8*(14), 9022-9029.
- S4. Cheng, Y., Luo, L., Zhong, L., Chen, J., Li, B., Wang, W., ... & Liu, J. (2016). Highly reversible zinc-ion intercalation into chevrel phase Mo6S8 nanocubes and applications for advanced zinc-ion batteries. *ACS applied materials & interfaces*, *8*(22), 13673-13677.
- S5. Zhang, N., Cheng, F., Liu, Y., Zhao, Q., Lei, K., Chen, C., ... & Chen, J. (2016). Cation-deficient spinel ZnMn2O4 cathode in Zn (CF3SO3) 2 electrolyte for rechargeable aqueous Zn-ion battery. *Journal of the American Chemical Society*, *138*(39), 12894-12901.
- S6. Wang, L. P., Li, N. W., Wang, T. S., Yin, Y. X., Guo, Y. G., & Wang, C. R. (2017). Conductive graphite fiber as a stable host for zinc metal anodes. *Electrochimica Acta*, *244*, 172-177.
- S7. Wang, J., Liu, J., Hu, M., Zeng, J., Mu, Y., Guo, Y., ... & Huang, Y. (2018). A flexible, electrochromic, rechargeable Zn//PPy battery with a short circuit chromatic warning function. *Journal of Materials Chemistry A*, *6*(24), 11113-11118.

- S8. Kundu, D., Oberholzer, P., Glaros, C., Bouzid, A., Tervoort, E., Pasquarello, A., & Niederberger, M. (2018). Organic cathode for aqueous Zn-ion batteries: taming a unique phase evolution toward stable electrochemical cycling. *Chemistry of materials*, *30*(11), 3874-3881.
- S9. Wang, Z., Ruan, Z., Liu, Z., Wang, Y., Tang, Z., Li, H., ... & Zhi, C. (2018). A flexible rechargeable zinc-ion wire-shaped battery with shape memory function. *Journal of Materials Chemistry A*, *6*(18), 8549-8557.
- S10. Luo, S., Xie, L., Han, F., Wei, W., Huang, Y., Zhang, H., ... & Wang, L. (2019). Nanoscale Parallel Circuitry Based on Interpenetrating Conductive Assembly for Flexible and High - Power Zinc Ion Battery. *Advanced Functional Materials*, 1901336.
- S11. Zhang, Q., Li, C., Li, Q., Pan, Z., Sun, J., Zhou, Z., ... & Wang, X. (2019). Flexible and High-Voltage Coaxial-Fiber Aqueous Rechargeable Zinc-Ion Battery. *Nano letters*.
- S12. Yue, X., Liu, H., & Liu, P. (2019). Polymer grafted on carbon nanotubes as a flexible cathode for aqueous zinc ion batteries. *Chemical communications*, *55*(11), 1647-1650.