Electronic supplementary information

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

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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 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-Zn battery with previously reported Zn ions batteries based on organic cathode.

| Ref | Year | Electrode | Capacity | Flexible |
|-----|------|-----------|----------|----------|
| This work | Zn@CC // PANI@CNT | 144 mAh/g | Flexible Cathode |
| S1 | 2014 | Zn // ZnHCF | 65 mAh/g | No |
| S2 | 2014 | Zn // Na0.95MnO2 | 60 mAh/g | No |
| S3 | 2015 | Zn//Zn2+Al3+/Graphite | 94 mAh/g | No |
| S4 | 2016 | Mo5S8//Zn2+/Carbon | 62 mAh/g | No |
| S5 | 2016 | ZnMn2O4//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//MnO2@SS-PPy | 136.4 mAh/g | Yes |
| S10 | 2019 | Zn//MnO4@Ti3C2Tx-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.