Electronic Supplementary Information

A polydopamine coating enabling the stable cycling of MnO_2 cathode materials in aqueous zinc batteries

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1 Experimental section

1.1 Material synthesis

MnO_2 and MnO_2/PDA materials were obtained with the modified steps of previous studies.[1,2] Typically, 0.35 g $KMnO_4$ was dissolved in 35 mL deionized water, and 3.3 mL HCl (36%~38%) was added. The mixture was stirred for 10 min, transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 140 °C for 16 h. The MnO_2 product was collected by centrifugation, washed with deionized water and ethanol for three times, respectively, and dried at 60 °C overnight. To obtain PDA coating, the above MnO_2 product without drying was dispersed and sonicated for 10 min in 50 mL buffer solution of 40 mg PEO-PPO-PEO (P123) triblock copolymer and 60 mg 2-amino-2-(hydroxymethyl)-1,3-propanedio (Tris). Subsequently, 20 mg dopamine hydrochloride was added and the mixture was stirred for 10 h at room temperature. The product was collected by centrifugation, washed with deionized water and ethanol for three times, respectively, and dried at 60 °C overnight. The solid was finally heated at 300 °C for 5 h under Ar to obtain the MnO_2/PDA product.

1.2 Characterizations

X-ray diffraction (XRD) was carried out on a PANalytical Empyrean diffractometer with Cu-Kα radiation. The morphologies were investigated by HITACHI SU 8010 scanning electron microscope. The high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-ARM200F transmission electron microscope. Raman spectra were performed on a confocal laser micro-Raman spectrometer (XPLORA, HORIBA Scientific, France) with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was measured on an XPS spectrometer (ESCALAB 250Xi, Thermo Scientific Escalab, USA) with Al-Kα radiation (8.34 Å) as the excitation source. The data was analyzed using Avantage software and calibrated by referencing the C 1s peak to 284.8 eV. The Fourier transform infrared spectroscopy (FT-IR) was conducted with a Vertex-70 spectrometer (BRUKER, Germany). The Mn concentrations in electrolytes were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a PerkinElmer 8300 instrument. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TA Instruments TAG Q500/MS Discovery) at a heating rate of 5 °C min^{-1} in an air atmosphere. Gel permeation chromatography (GPC) measurements were performed by PL GPC 50. Zeta potential was measured by a Nanoparticle size analyzer (Nano-S90). The powder was dispersed in the H_2SO_4 solutions with the pH of 4.3, which was the same as the 1 M $ZnSO_4$ electrolyte. The cathodes and electrolytes for ex-situ characterizations were cycled at 0.1 A g^{-1} for 20 cycles, and then charged/discharged to the destinated states.

1.3 Electrochemical measurements

The cathodes were prepared by mixing the MnO_2/PDA or MnO_2 active material with Ketjen black and PVDF at a mass ratio of 7:2:1 in NMP solvent. The slurry was dropped casted on carbon paper substrate and dried at 90 °C under vacuum for 12 hours. Coin cells were assembled with filter paper separators. Galvanostatic charge/discharge tests were carried out with the voltage window of 0.8 V-2.0 V. Electrochemical impedance spectroscopy (EIS) was performed with 5 mV amplitudes in the frequency range of 300 kHz to 100 mHz in T-shaped three-electrode PFA Swagelok cells with saturated calomel electrode (SCE) as the reference. All electrochemical measurements were carried out on the LAND or Biologic VMP3 battery test systems.

2 Supplementary Figures

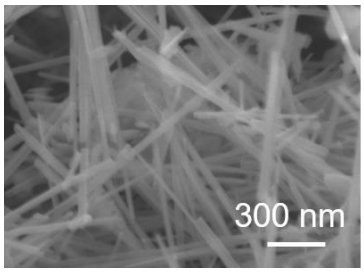

Figure S1. SEM image of MnO_2.

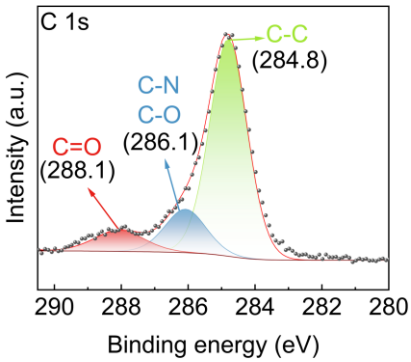

Figure S2. C 1s XPS of MnO_2/PDA.

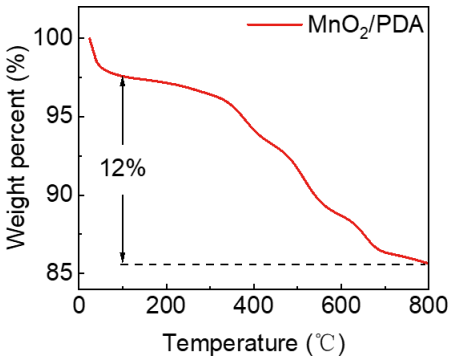

Figure S3. TGA of MnO_2/PDA.

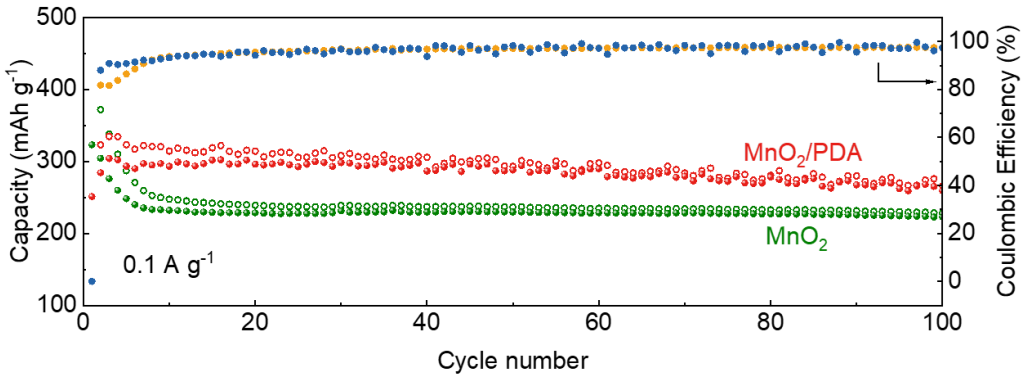

Figure S4. Cycling performance of MnO_2 and MnO_2/PDA at 0.1 A g^{-1}.

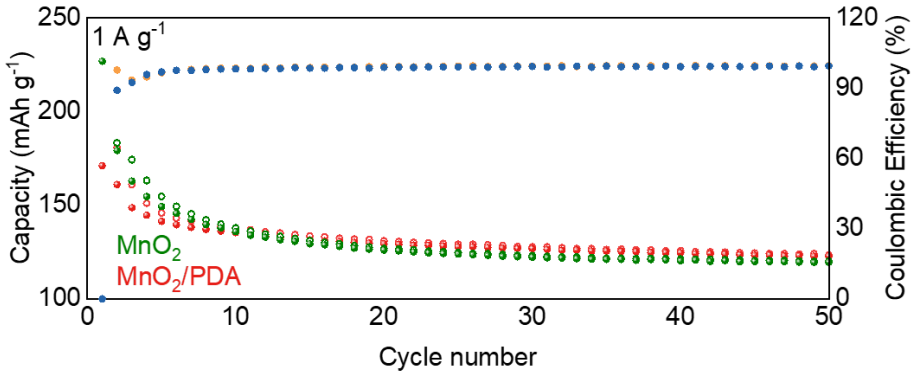

Figure S5. The enlarged figure for the early 50 cycles of MnO_2 and MnO_2/PDA at 1 A g^{-1}.

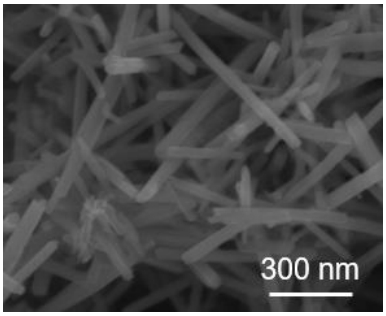

Figure S6. SEM image of MnO_2/PDA after 1000 cycles at 1 A g^{-1}.

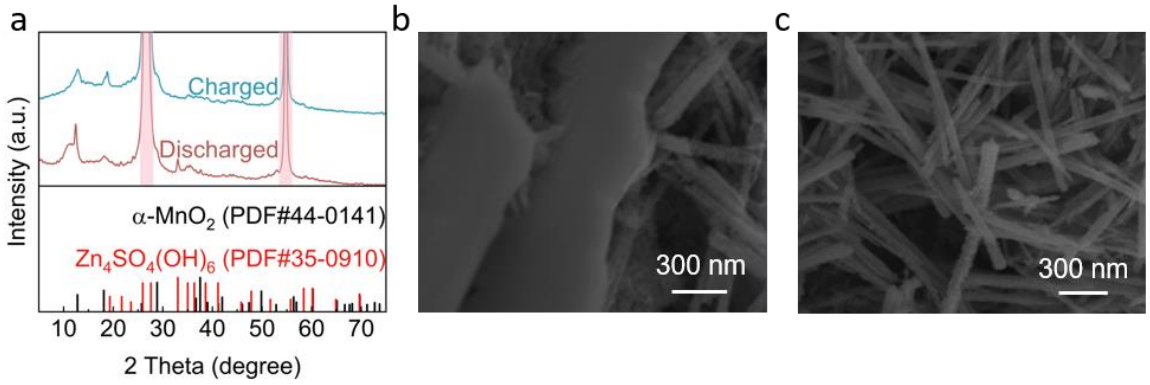

Figure S7. a) XRD patterns of the MnO_2 cathode at different states. SEM images of the b) discharged and c) charged MnO_2 cathode.

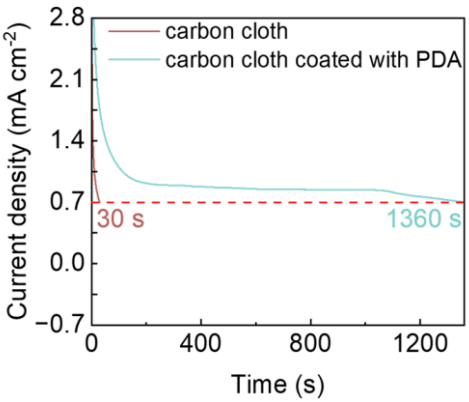

Figure S8. Current response of different cathodes with 2 V constant voltage hold in the 1 M $ZnSO_4$ + 0.1 M $MnSO_4$ electrolyte.

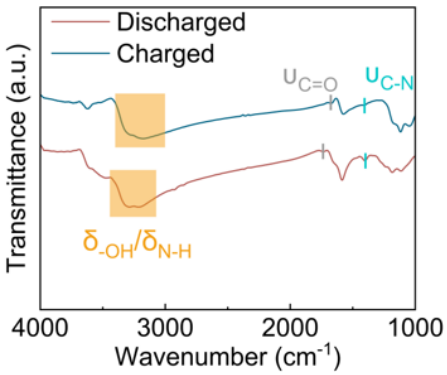

Figure S9. FT-IR of MnO_2/PDA at different states.

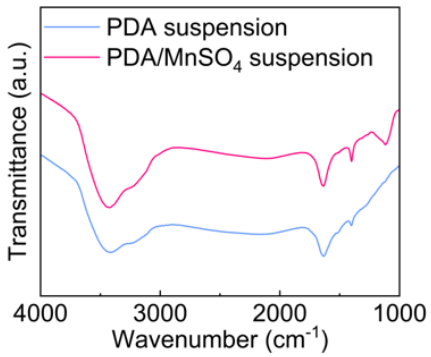

Figure S10. FT-IR of PDA suspension in water and $MnSO_4$ solution.

3 References

1. W. Chen, R. B. Rakhi, H. N. Alshareef, J. *Mater. Chem. A*, 2013, **1**, 3315-3324.

2. H. Jiang, Y. Hu, S. Guo, C. Yan, P. S. Lee, C. Li, *ACS Nano*, 2014, **8**, 6038-6046.