

## Supplementary Information

### Interfacial design towards stable zinc metal-free zinc-ion batteries with high energy density

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## **Experimental section**

### **The preparation of P(VDF-TrFE) and its polarization**

P(VDF-TrFE) copolymer powder with a molecular ratio of VDF to TrFE of 30:70 was purchased from Solvay. Zinc trifluoromethane sulphonate ( $\text{Zn}(\text{OTf})_2$ ) powder was purchased from Sigma. A transparent, slightly viscous solution coating solution was prepared by dissolving 3 wt% P(VDF-TrFE) and 1 wt%  $\text{Zn}(\text{OTf})_2$  in N, N-dimethylformamide (DMF) (purchased from Sigma) and magnetic stirring for 4 hours. Then the solution was spin-coated onto a Graphene@Cu foil (Beijing Graphene Institute) at 2000 rpm for 90 seconds in an argon-saturated glove box. The coated P(VDF-TrFE)@graphene@Cu foil was conditioned on a hotplate set at 70°C for 30 minutes to remove any residual DMF solvent before being removed from the glove box. This was followed by annealing at 135 °C for 2 hours in the oven to increase the  $\beta$ -phase crystallinity within the P(VDF-TrFE) copolymers. The polarization of the  $\beta$ -phase P(VDF-TrFE) was carried out by the corona poling technique without altering the material's structure. The coated graphene@Cu foils were mounted on a grounded hot plate stage preheated to 80°C. For this, a potential of +25 kV (-25 kV) was applied to a Pinner charging bar (Chargemaster VCM, purchased from Simco-Ion). The bar was positioned 4 cm above the stage and traversed the sample at 0.1 mm/s, allowing either positive or negative polarization over a large area of the sample. The remnant electric field induced by polarization remains permanent unless exposed to high temperatures (above the Curie temperature) or subjected to a reverse high electric field.

### **The synthesis of $\text{MnO}_2$**

In a standard synthesis procedure, a solution of 50 mL of  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 M) was initially combined with 50 mL of  $\text{K}_2\text{S}_2\text{O}_8$  (0.1 M). Subsequently, 25 mL of NaOH (1.2 M) was introduced into the resulting mixture and stirred for 1 hour, followed by an additional 1 hour aging period. The resultant precipitate was collected, washed with water, and subsequently subjected to freeze-drying to yield  $\text{MnO}_2$  nanosheets.

### **Material characterization**

The surface morphologies and the thickness of the P(VDF-TrFE) film were analyzed using atomic force microscopy (AFM) (Bruker Dimension Icon). The detailed morphology was assessed via scanning electron microscopy (SEM) on a ZEISS SEM Supra 40 (5 kV). The graphene@Cu quality and P(VDF-TrFE) crystallinity were carried out by Raman microscopy (WITec alpha 300R) using a 532 nm laser with a laser spot size of 1  $\mu\text{m}$ . The crystallographic

data of samples were characterized by X-ray diffraction (XRD) on D8 Advance, Bruker, with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The Kelvin probe force microscopy (KPFM) was conducted on Dimension Icon, Bruker. The in-situ observation was conducted with a Nikon Eclipse LV100-ND microscopy.

### **Electrochemical test**

All electrochemical tests were conducted at room temperature utilizing an electrochemical system (Bio-logic VMP 3) and the Wuhan Landian instrument. The as-prepared MnO<sub>2</sub> nanosheets were blended with carbon and polyvinylidene fluoride in a 7:2:1 ratio, using N-methyl-2-pyrrolidone as the solvent. This mixture was manually ground for a minimum of 10 minutes to create a slurry. The slurry was then uniformly coated onto carbon paper, and subsequently subjected to an overnight heat treatment at 80°C for further utilization. For electrochemical testing of the half-cell, nonwoven fabric paper with thickness of 2 mm was employed as the separator, Zn foil functioned as the counter electrode, Cu or PPG-Cu was the working electrode and 2M ZnSO<sub>4</sub> solution served as the electrolyte. Plating and stripping tests were executed with a stripping cutoff voltage of 1.0 V vs. Zn/Zn<sup>2+</sup>. Coulombic efficiency was determined by evaluating the capacity ratio of Zn stripped to Zn plated. In preparation for the assembly of the zinc metal-free zinc-ion battery, the MnO<sub>2</sub> electrode underwent pre-zincification within a cell utilizing Zn metal as the counter electrode. The cell was charged/discharged for two cycles and then discharged to 1 V at current density of 0.5 mA cm<sup>-2</sup>. Subsequently, the pre-zincified MnO<sub>2</sub> electrode was meticulously rinsed, dried, and coupled with either a Cu or PPG-Cu electrode in a CR2032 coin cell with the electrolyte of 2M ZnSO<sub>4</sub>+0.2M MnSO<sub>4</sub>. Notably, the Cu or PPG-Cu electrode was pre-treated at 10 mA cm<sup>-2</sup> with 10 mAh cm<sup>-2</sup> for 5 cycles to achieve enough nucleation before full cell assembly. Following assembly, the full cell underwent a galvanostatic charge to 1.8 V prior to further testing. For both cyclic voltammetry (CV) and charge/discharge testing of the full cell, the measurement voltage was constrained within the 1–1.8 V range. Charge/discharge measurements employed current densities of 0.5, 0.8, 1, 2, 3, 4, and 5 mA cm<sup>-2</sup> (based on the area of cathode side). Electrochemical impedance spectroscopy (EIS) tests were conducted across a frequency spectrum spanning from 0.01 to 10<sup>5</sup> Hz.

### **Theoretical calculation**

The finite element simulation was used to simulate the electrochemical state of the P(VDF-TrFE) coated Graphene@Cu metal surface. A hexagonal zinc nucleus grown across the coating

was set as the model. The validation simulation experiment is based on the secondary current distribution model in COMSOL.<sup>1,2</sup> By applying this model, the distribution of the negative electrode surface electric field induced by the intrinsic polarization electric field and the potential drop are investigated. Simultaneously, the effect of the intrinsic polarization electric field of P(VDF-TrFE) on the actual electrode field and potential distribution is obtained by incorporating the positive electrode bias. This allows for inferring the diffusion and reaction of ions. In the experiment, the bulk phase conductivity of the cathode plate Cu is  $5.967 \times 10^7$  S/m, the conductivity of the Zn dendritic phase is  $1.731 \times 10^7$  S/m, the conductivity of the zinc sulfate electrolyte is 4.716 S/m, the concentration of Zn ions in the solution is 2 mol/L, the experimental temperature is 298 K, and the polarization potential strength of P(VDF-TrFE) is 200 mV.

In real, electrode reactions follow Faraday's law of electrolysis, and the chemical equilibrium potential is obtained from the Nernst equation, as described below. The chemical equilibrium potential of zinc is -0.76V, with the reference equilibrium electrode potential at 0 V.

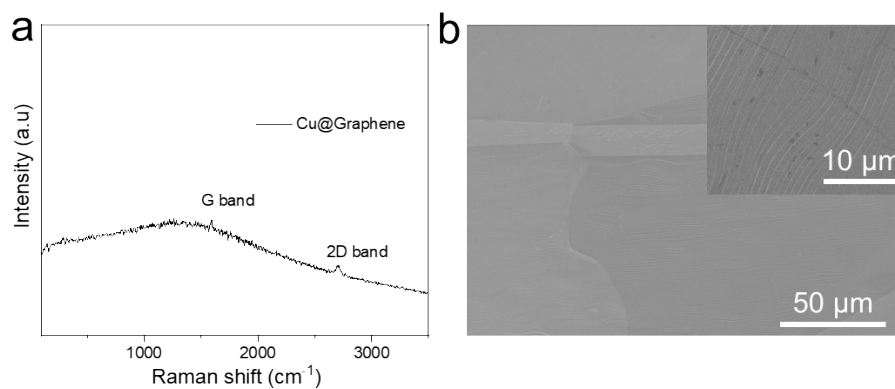


The electrode reactions in the experiment follow the Butler-Volmer equation. The expression for the local cathodic current density is:

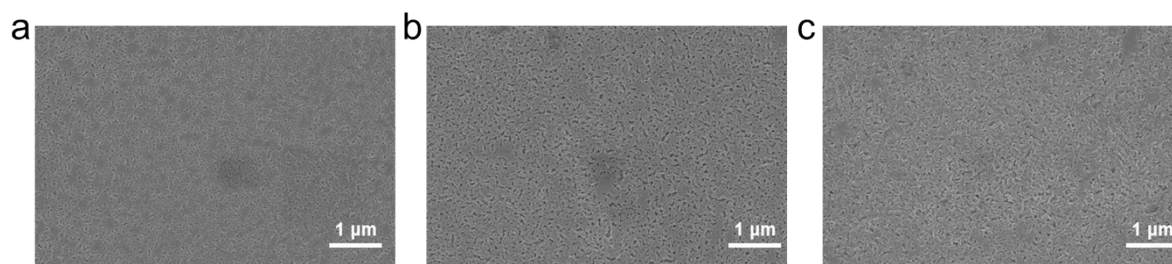
$$i_{ioc,exp} = i_0 \left[ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_a F \eta}{RT}\right) \right] \quad \backslash * \text{MERGEFORMAT (0.2)}$$

The calculation of equilibrium potential in the experiment is based on the Nernst equation.

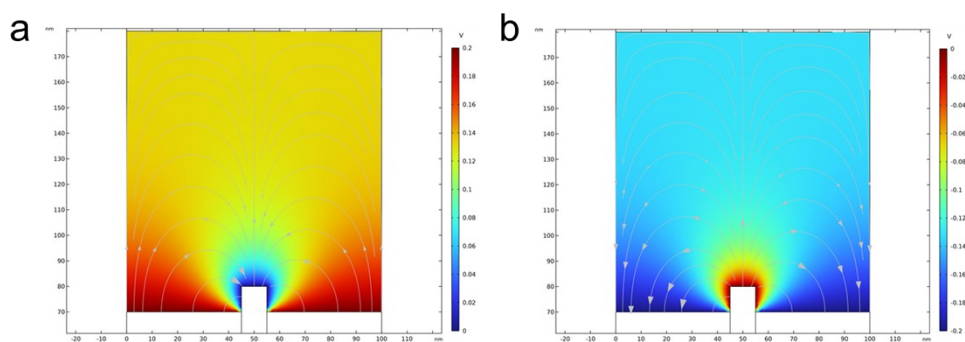
$$E_{eq} = E_{eq,ref}(T) - \frac{RT}{nF} \ln \frac{C_R}{C_0} \quad \backslash * \text{MERGEFORMAT (0.3)}$$



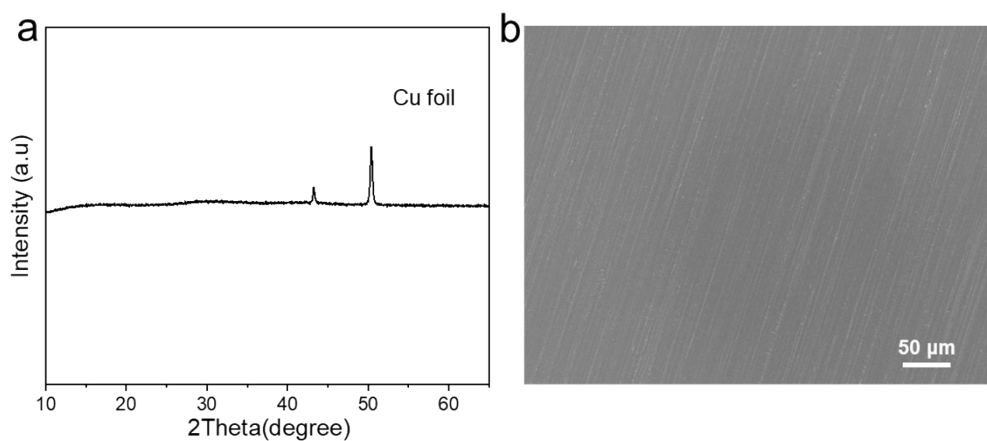
**Fig. S1** (a) Raman spectrum and (b) SEM image of the Cu@Graphene foil.



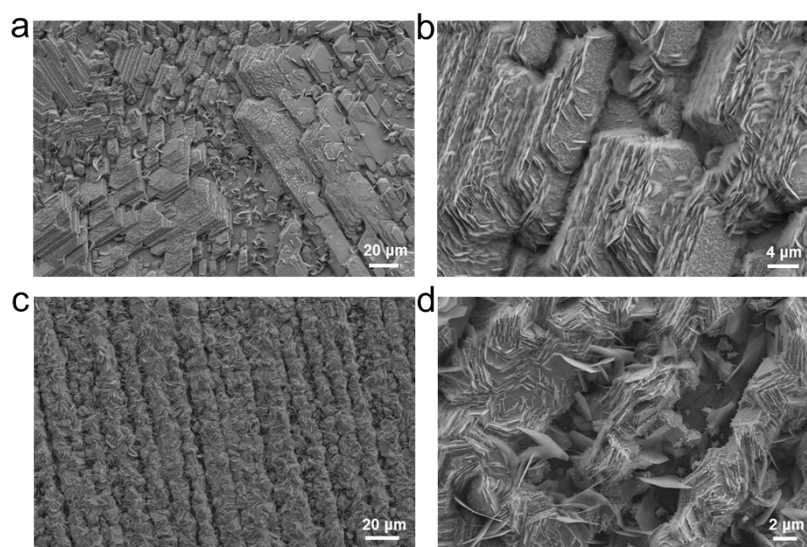
**Fig. S2** SEM images of Cu@Graphene coated with (a) non-polarized P(VDF-TrFE) layer, (b) positively polarized P(VDF-TrFE) layer and (c) negatively polarized P(VDF-TrFE) layer.



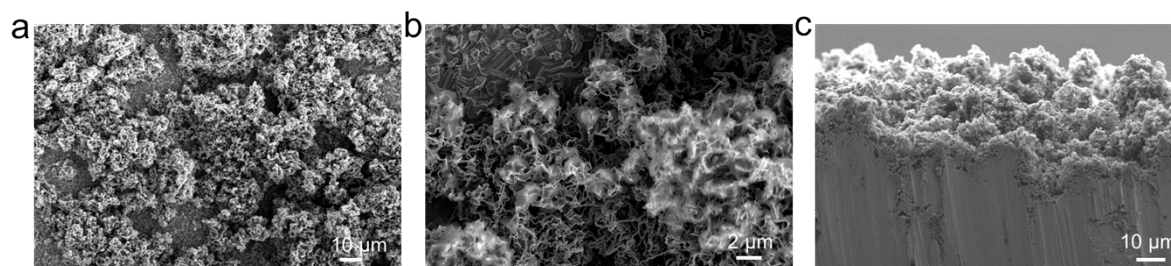
**Fig. S3** (a) Electrochemical potential distribution simulations of P(VDF-TrFE)-coated Graphene@Cu foil with negative polarization and (b) with positive polarization.



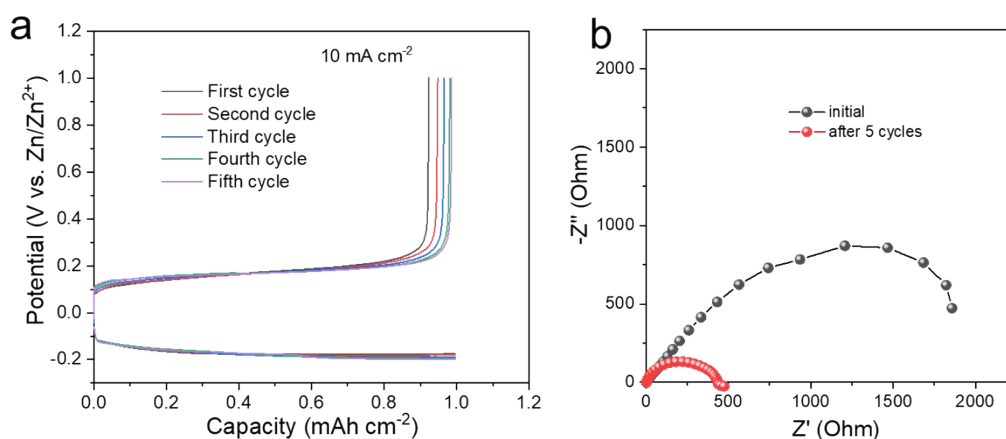
**Fig. S4** (a) XRD pattern and (b) SEM image of the bare Cu foil.



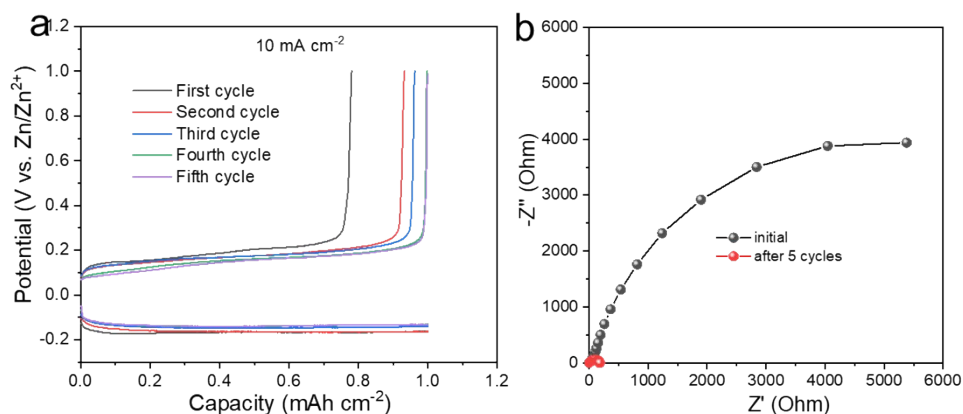
**Fig. S5** SEM images of (a, b) Graphene@Cu deposited with Zn and (c, d) positively polarized P(VDF-TrFE)@Cu deposited with Zn.



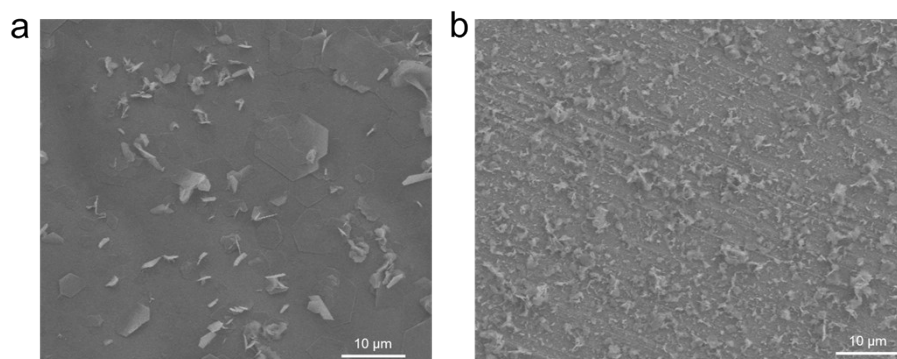
**Fig. S6** (a,b) SEM images and (c) cross section SEM images of the bare Cu after 30min deposition of Zn.



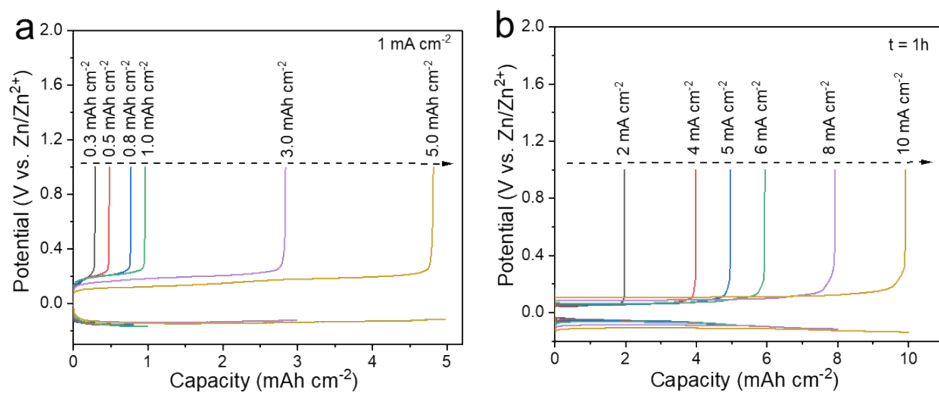
**Fig. S7** (a) The plating and stripping for bare Cu at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  for five cycles. (b) Impedance spectra of bare Cu before and after test at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  for five cycles.



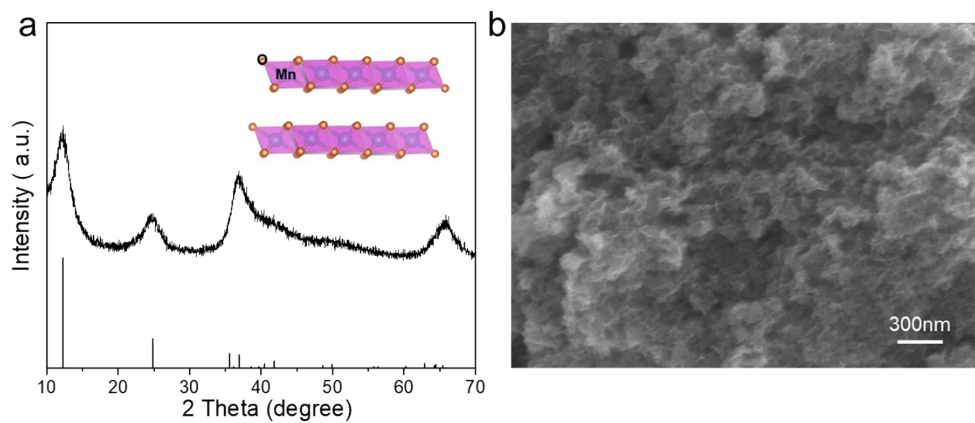
**Fig. S8** (a) The plating and stripping for PPG-Cu at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  for five cycles. (b) Impedance spectra of PPG-Cu before and after test at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  for five cycles.



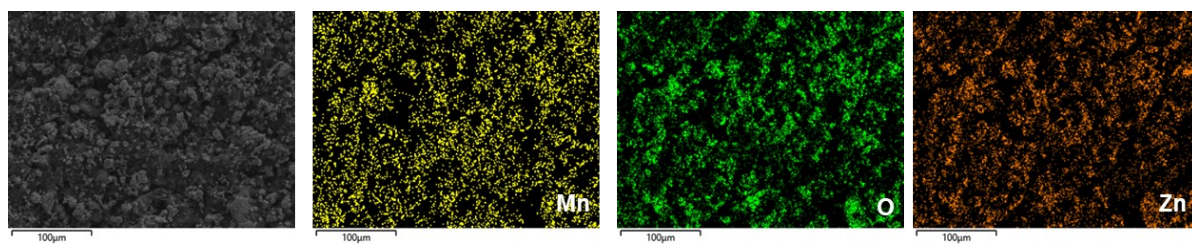
**Fig. S9** SEM images of the (a) PPG-Cu and (b) bare Cu after test at  $10 \text{ mA cm}^{-2}$  with  $1 \text{ mAh cm}^{-2}$  for five cycles.



**Fig. S10** (a) Charge–discharge profiles of the bare Cu//Zn cell at 1 mA cm<sup>-2</sup>. (b) Charge–discharge profiles of the bare Cu//Zn cell at different current densities (electrodeposition time: 1h).

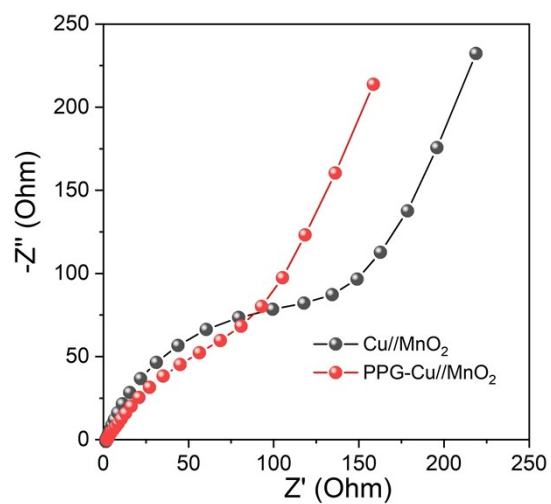


**Fig. S11** (a) XRD pattern and (b) SEM image of the MnO<sub>2</sub>.

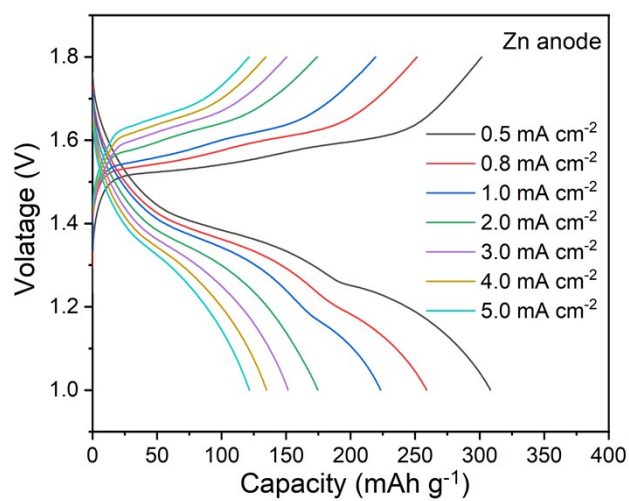


**Fig. S12** EDX mapping images of the Zn<sup>2+</sup> ions pre-inserted MnO<sub>2</sub>.





**Fig. S13** Impedance spectra of the bare  $\text{Cu//MnO}_2$  and  $\text{PPG-Cu//MnO}_2$ .



**Fig. S14** Charge-discharge curves of the  $\text{Zn//MnO}_2$  battery.

**Table S1.** The comparison of this work with recently reported asymmetric half cells for Zn ion battery.

Active material	Electrolytes	Test condition	Cycle numbers	Ref.
PPG-Cu//Zn	2M ZnSO <sub>4</sub>	10 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	3000	This work
Cu//Zn	50%PC-sat.	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	500	3
Stainless steel (SS)//Zn	0.5 M Zn(OTf) <sub>2</sub> -TEP	0.5 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	1000	4
Cu//Zn	Anti-M-50%	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	900	5
Zn  Cu	2M ZnSO <sub>4</sub>	1 mA cm <sup>-2</sup> 1 mAh cm <sup>-2</sup>	350	6
Gr-Cu//Zn	2M ZnSO <sub>4</sub>	5 mA cm <sup>-2</sup> 5 mAh cm <sup>-2</sup>	400	7
Cu-Ag//Zn	3M Zn(TFSI) <sub>2</sub> /EMC	0.5 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	200	8
C/Cu//Zn	3 M Zn(OTf) <sub>2</sub>	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	300	9
BTO/PVT@Cu//Zn	2 M ZnSO <sub>4</sub>	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	950	10
Ti/MOF-coated Zn	1 M Zn(TFSI) <sub>2</sub> /H <sub>2</sub> O	1 mA cm <sup>-2</sup> 0.5 mAh cm <sup>-2</sup>	350	11

## Reference

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