Supporting Information

Insights into Zn Anode Surface Chemistry for Dendrite-Free Zn Ion Batteries

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1. Supplemental Experimental Details

1.1 *Materials*. Zn foil (~0.1 mm) and Pt were purchased from Haoxuan Metal Material Co. , Ltd. $ZnSO_4 \cdot 7H_2O$ (>99.0%), $CuSO_4 \cdot 5H_2O$ (>99.0%), tetramethylammonium sulfate (TS, >99.98%), Ag/AgCl electrode, Ammonium persulfate (APS, >99.99%) and V_2O_5 powder (>99.99%) were purchased from Sinopharm Chemical ReagentCo., Ltd. All other reagents were analytical grade and used directly without further purification. Deionized water was used to prepare all aqueous electrolytes.

1.2 *Materials Preparation*:

Synthesis of ZnO@Cu/Zn: The commercial Zn foil was cut into Zn ribbons (2 cm × 6 cm), and then one side of the Zn ribbon was carefully polished with sandpaper to remove the passivation layer. A polished Zn ribbons were put into a specially designed tube. The product was rinsed by distilled water and ethanol several times and subsequently calcined at 350 °C for 6 h at a ramp rate of 5 °C min^{-1} under air atmosphere. Prior to the electrodeposition, the treated Zn foil was immersed into 100 mL of a solution containing $CuSO_4 \cdot 5H_2O$ (0.1 M) with an immersed area of 2 cm × 3 cm. During the electrodeposition using an electrochemical workstation (CHI760E, Shanghai, China), the treated Zn foil was used as the working electrode, while platinum (Pt) wire and Ag/AgCl were used as a counter electrode and a reference

electrode, respectively. The deposition was performed for 1,000 s under the static potential of -1.5 V (vs. Ag/AgCl). The material was taken out and rinsed with deionized water and ethanol several times. The resulting Zn foil was dried at 60 °C for 12 h in a vacuum oven.

Synthesis of $NH_4V_3O_8$: 0.4 g V_2O_5 and 0.2 g APS were dissolved in 50 ml of deionized water under magnetic stirring to form solution. The reaction solution was subsequently transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 95 °C for 48 h. After cooled to room temperature, the powder was cleaned with deionized water and ethanol several times.

1.3 *Materials Characterization*:

The micromorphology of the samples was observed using scanning electron microscopy (SEM, FEI-Quanta 250, USA). The elemental analysis of the samples was characterized using a scanning electron microscope (FE-SEM, JSM-7500, Japan) equipped with corresponding energy-dispersive X-ray (EDX) elemental mapping. The crystal structure of the samples was characterized through the X-ray diffraction analysis (XRD, Smart Lab, Riga ku, Japan) with Cu-Kα (λ= 1.540598 Å, Smart Lab) source (scan rate of 2 °min^{-1}) in the 2θ range of 10°~ 80°. The surface element analysis of the samples was carried out by a PHI 5000 VersaProbe XPS instrument (XPS, Thermo ESCALAB 250XI, USA) and Fourier transform infrared spectrum (FTIR, NICOLET iS50, USA).

1.4 *Electrochemical Tests*:

Electrochemical characterization of symmetrical Zn, Zn-TS, ZnO@Cu/Zn and

ZnO@Cu/Zn-TS cells was conducted using both transparent cells and 2032-type coin-cells. Electrochemical impedance spectroscopy (EIS) of these cells were conducted on an electrochemical workstation (CHI660E, Shanghai, China) over the frequency range of 100 kHz to 1 Hz. The cells were galvanostatically charged/discharged in the voltage range of 0.4 – 1.6 V vs. Zn/Zn^{2+} at different current densities on a Land CT5001A battery tester, and the specific capacities were calculated based on the active mass of $NH_4V_3O_8$ cathode. The mass of active material was ~1.1 mg.

1.5 *Transparent Zn Cell and In Situ Dendrite Observation*:

A transparent Zn-Zn cell was designed to observe the Zn dendrite growth. Specifically, a transparent glass dish, two Zn ribbons (0.5 cm × 3 cm), and two plastic clamps form a pool for observing the Zn dendrites. The transparent glass dish is used to store the electrolyte. The Zn dendrites growth was in situ observed by an optical microscope equipped with a digital camera. Meanwhile the transparent Zn cell was tested for Zn stripping/plating using an electrochemical workstation (CHI660E).

1.6 *Theoretical Calculations*:

All calculations were carried out with the Vienna ab initio simulation package (VASP).[1] The electronic exchange-correlation energy was implemented using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[2] A cutoff energy of 500 eV for plane-wave basis set was adopted. As for geometric optimization, the atomic positions were optimized until all components of the forces on each atom were less than -0.05 eV/Å and the total energy converge was set to below 10^{-4} eV. The DFT-D3 correction was used to describe van

der Waals interactions.[3] The bulk phase structure is optimized first, and the surface models are carried out on this basis to adsorb the Zn atom. Table S2 shows the lattice constants and corresponding k-point mesh of the models. A vacuum of 15 Å was set in order to circumvent periodic interactions between the atoms.

2. Supporting Notes

2.1 The strategy for using of TS electrolyte additives and establishment of a dense ZnO@Cu artificial layer on the surface of Zn metal for constructing dendrite-free Zn electrode without side reaction.

The schematic diagram of the production of Zn anode is shown in Fig. S5a. A simple, low-cost, and environmentally friendly method is used to construct the Zn anode with the required surface modification. First, the Zn foil is annealed in high-temperature air to form a thin ZnO layer on its surface. Then, metallic Cu is deposited on the surface of ZnO to form a double-layer heterogeneous interface by using electrodeposition technology. As mentioned above, Zn electrodes are highly unstable with/without electrolyte additives, and the side reactions will occur during the typical charge/discharge process to form $Zn_2SO_4(OH)_2$, which decreases the CE, reversible capacity and cycle life of ZIBs. As a comparison, the Zn metal with ZnO@Cu artificial layer not only effectively suppresses the corrosion reaction by preventing the electrolyte, but also induces the Zn^{2+} stripping/plating together with the TS electrolyte additive, thereby suppressing the Zn dendrites growth and improving the reversibility of Zn electrode (Fig. S5b). The effect of ZnO@Cu layer on the stability of Zn foil is assessed in 2 M $ZnSO_4$ electrolyte, as shown in Figs. S6a and b. After 5 days, the ZnO@Cu/Zn foil still retains a light surface without evident corrosion, which is mainly attributed to the ZnO@Cu protective film isolating to the electrolyte. Similar to Figs. 1d and e, the by-products grow along the Zn metal plane, resulting in a larger size of the deposited Zn plane (Figs. S6c and d), which are further explained in Figs. 2h and 4d. The XRD pattern is gathered after soaking in 2 M $ZnSO_4$ electrolyte (Fig.

S7), which is similar to that of ZnO@Cu/Zn foil before immersion and without any peaks for the $Zn_2SO_4(OH)_2$ by-product, demonstrating that the side reactions of the Zn anode with the electrolyte are disrupted.
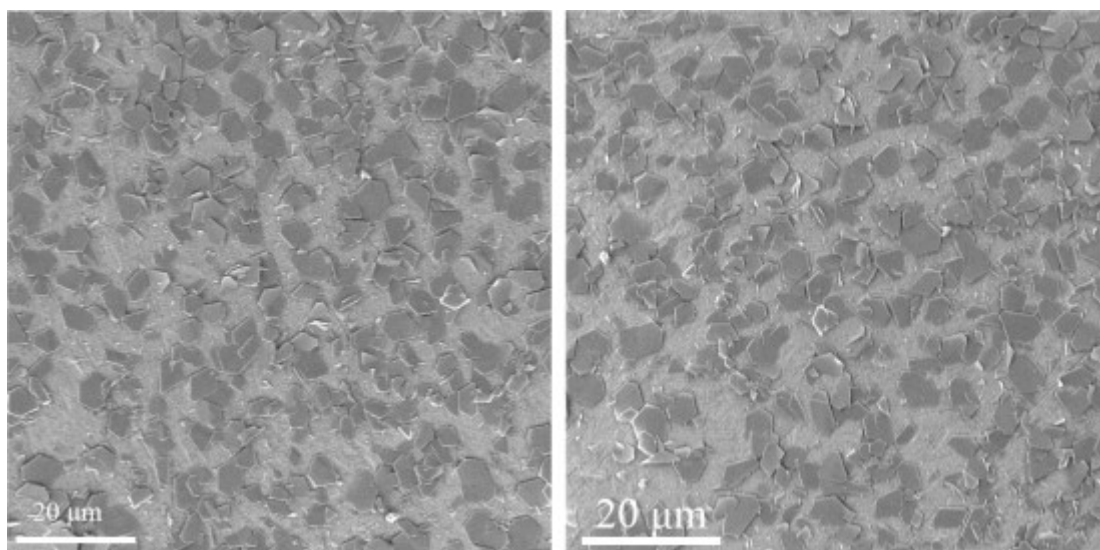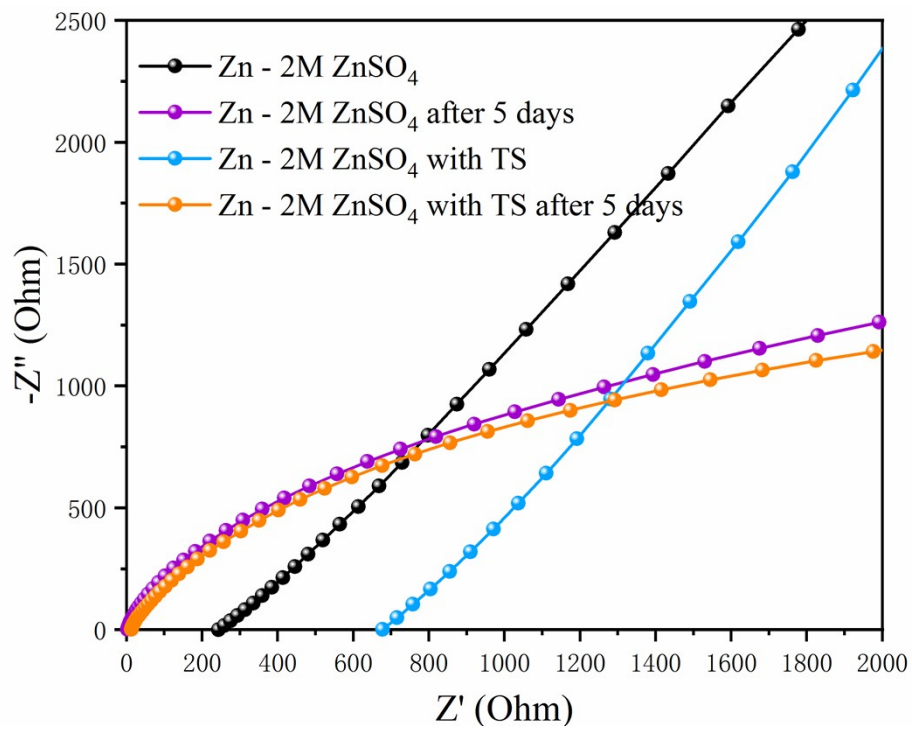
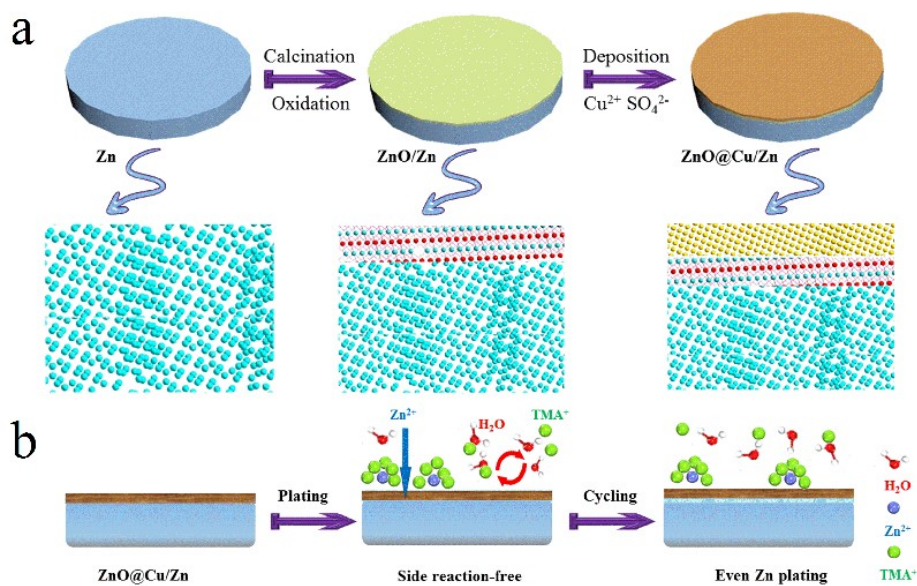# 3. Supporting Fig.s
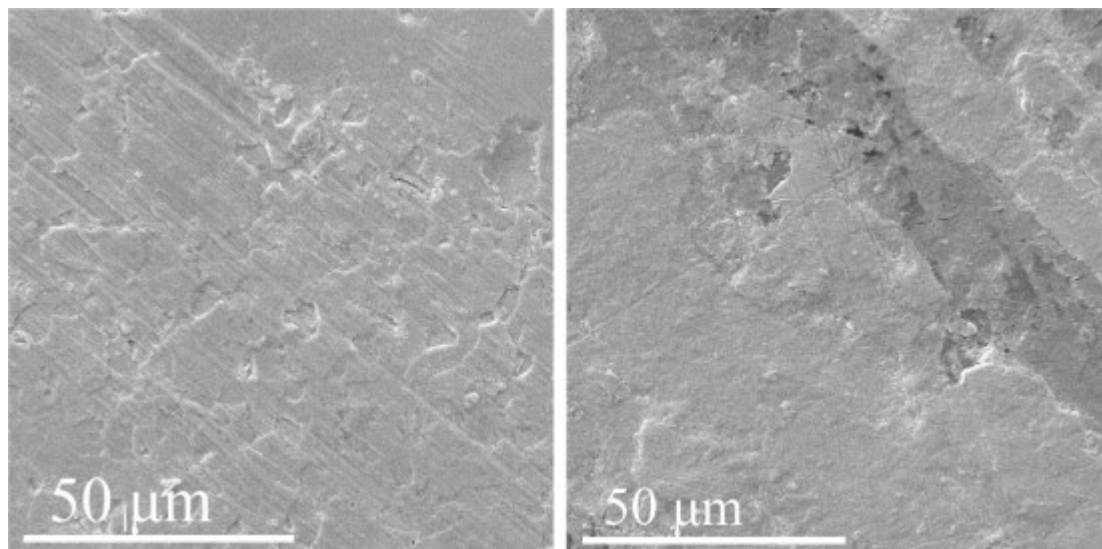
Fig. S1. SEM images of bare Zn foil.
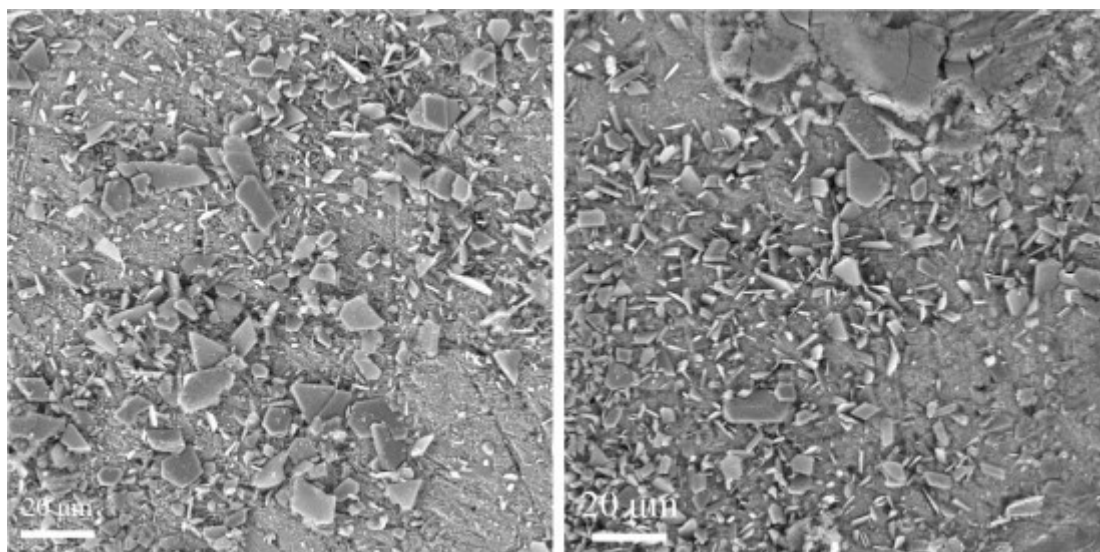
Fig. S2. SEM images of the Zn foil in 2 M ZnSO$_4$ after 5 days.

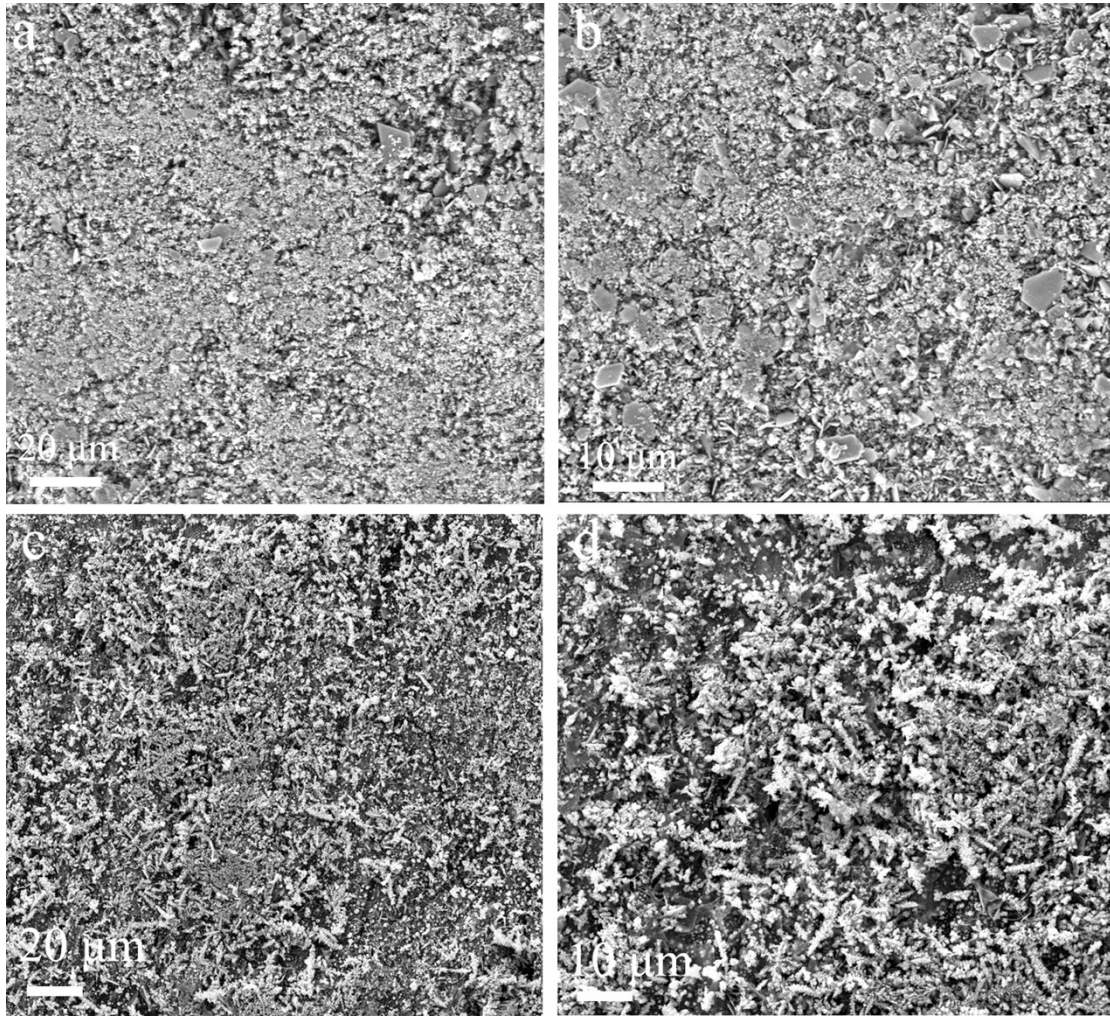**Fig. S3**. SEM image of Zn foil in 2 M ZnSO$_4$ with TS after 5 days.

Fig. S4. Electrochemical impedance spectroscopy measurements of various Zn cells.

Fig. S5. a) Introducing the ZnO@Cu layer on the surface of Zn metal substrate by two-step strategy. b) By incorporating the artificial ZnO@Cu layer on the Zn surface and using TS electrolyte additive, uniform and compact Zn plating behavior without side reactions can be obtained.

Fig. S6. a, b) SEM images of the ZnO@Cu/Zn in pure 2 M $ZnSO_4$ after 5 days; c, d) SEM images

of the ZnO@Cu/Zn in 2 M $ZnSO_4$ with TS after 5 days.
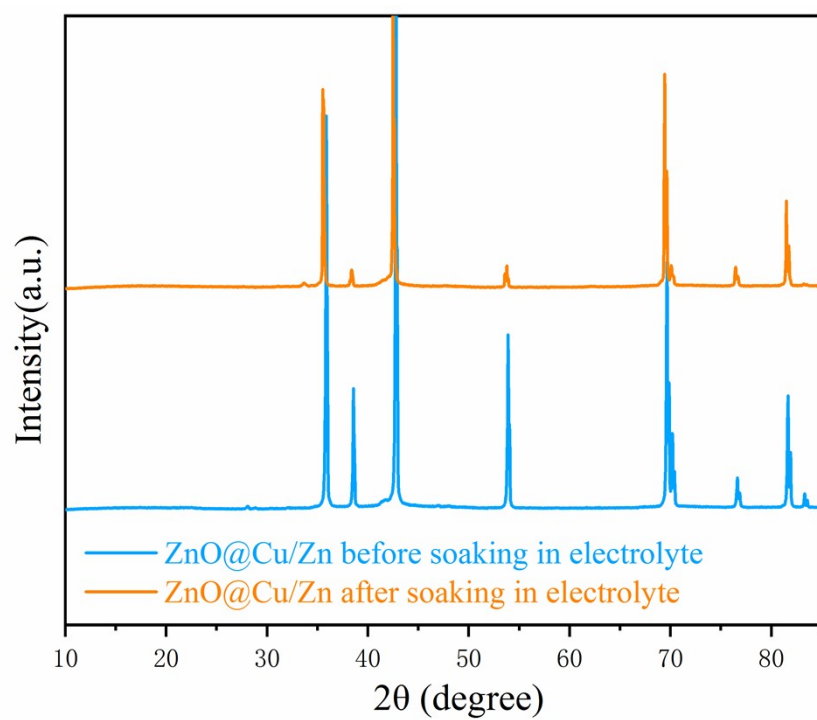
Fig. S7. XRD patterns of ZnO@Cu/Zn foil before and after the soaking in 2 M $ZnSO_4$ for

5 days.
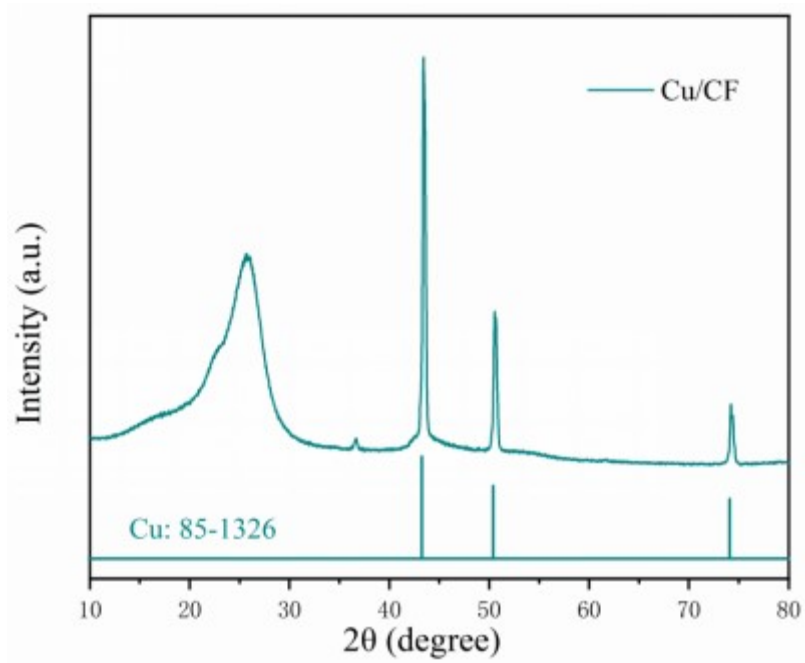
Fig. S8. f) X-ray diffraction (XRD) patterns of Cu on Carbon cloth.

Fig. S9. EDS mapping images of ZnO@Cu/Zn including Zn, Cu and O element.
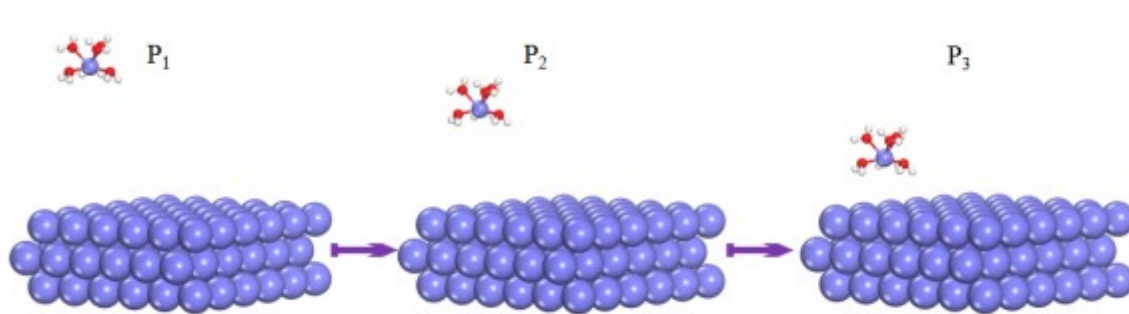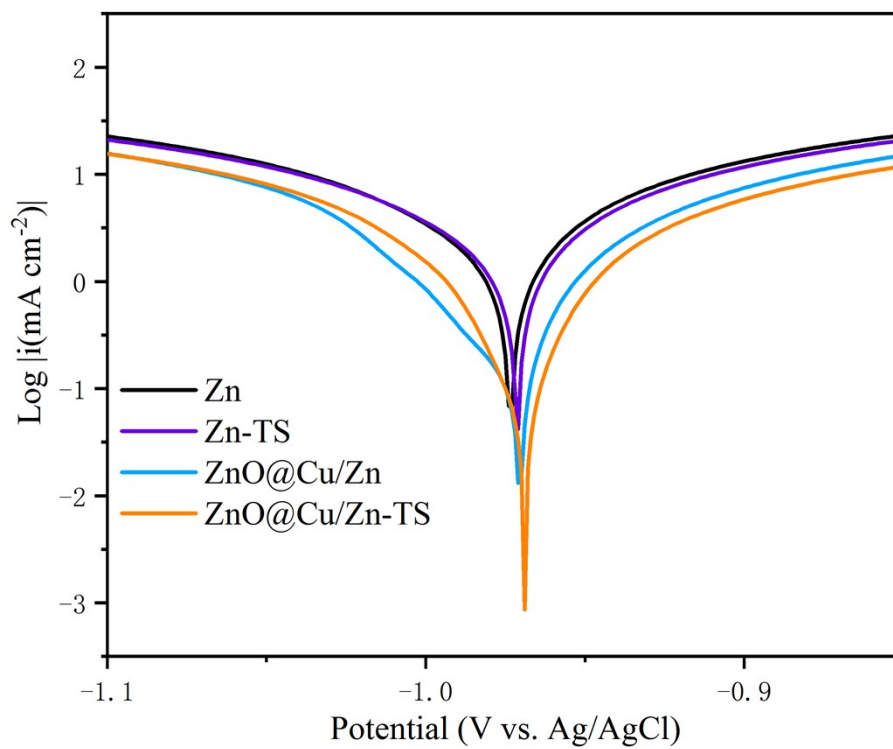
Fig. S10. SEM, TEM and HR-TEM images of ZnO@Cu/Zn.

Fig. S11. Transmission mapping images of ZnO@Cu/Zn including Zn, Cu and O element.

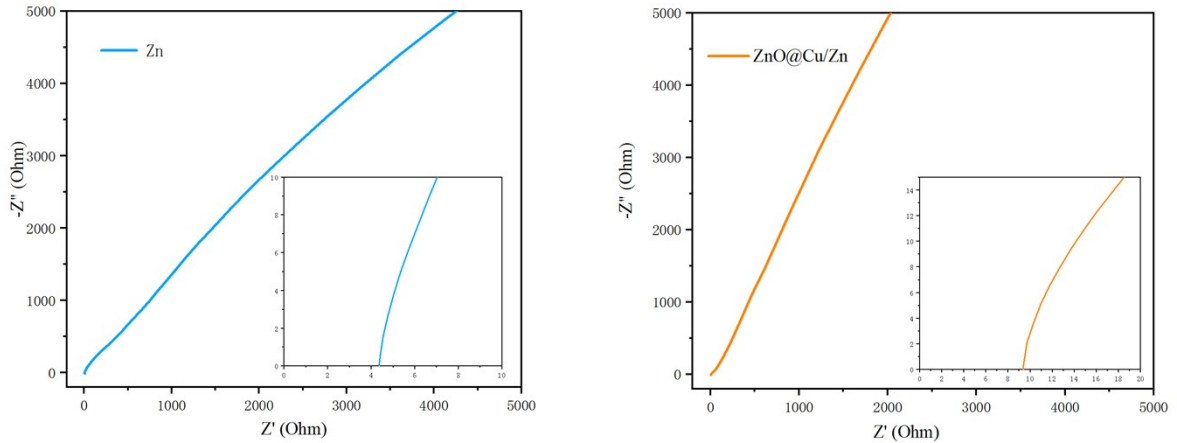**Fig. S12**. High-resolution XPS spectra of Cu in ZnO/Zn and ZnO@Cu/Zn.

Fig. S13. Model of DFT calculations, showing a hydrated Zn^{2+} ion passing on a Zn surface.

Fig. S14. Linear polarization curves showing the corrosion on bare Zn, Zn-TS, ZnO@Cu/Zn and
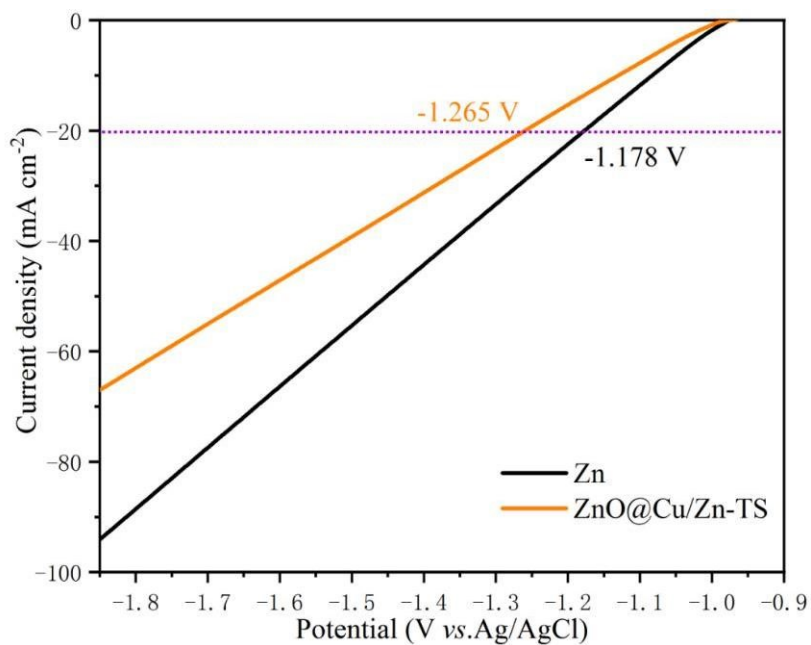
ZnO@Cu/Zn-TS.

Fig. S15. (a) Nyquist plots collected at open circuit voltage (OCV) over the frequency range of

100 kHz to 1 Hz. a) Zn symmetrical cell with glass fibre as separator (inset: enlargement of

indicated range). b) ZnO@Cu coated Zn symmetrical cell with glass fibre as separator (inset:

enlargement of indicated range).

For the Zn/Zn cell with glass fibre, the ionic conductivity of the glass fibre separator could be

calculated from the bulk electrolyte resistance (Fig. S15a) by the following equation:

$$\sigma = \frac{L}{R_b S}$$

where L is the thickness of the glass fibre separator (0.675 mm), S is the contact area (1 cm^2), and

R_b (glass fibre) = ~4.4 ohm at room temperature. Thus, $\sigma_{glass\ fibre}$ = 1.53 × 10^{-2} S cm^{-1}. For the

ZnO@Cu coated Zn symmetrical cell, R_b (ZnO@Cu) = R_b – R_b (glass fibre) = 9.4 ohm (Fig.

S15b). Therefore, the ionic conductivity of the ZnO@Cu film can be evaluated as $\sigma_{ZnO@Cu}$ = ~1.9
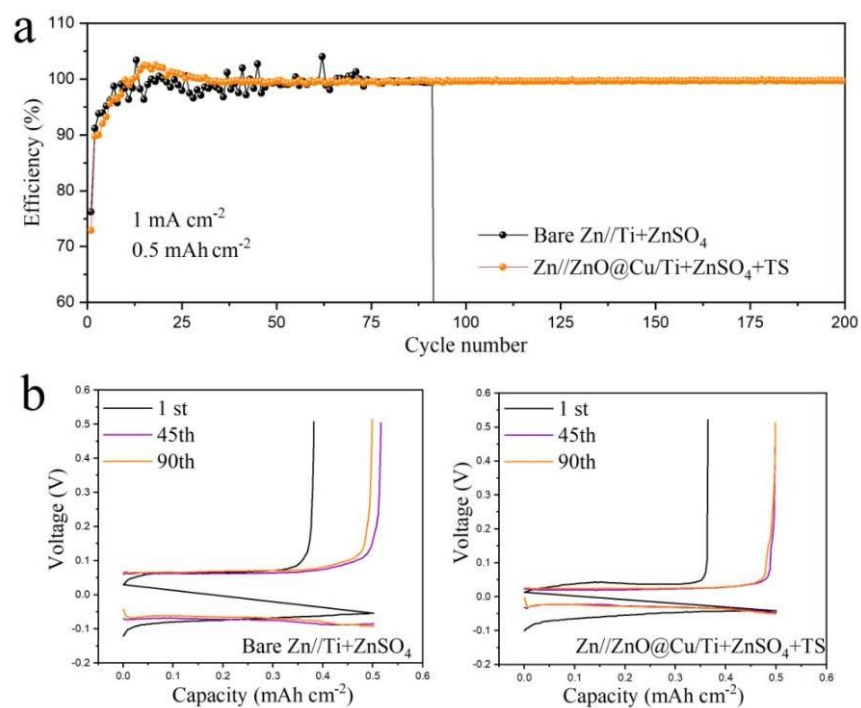
× 10^{-4} S·cm^{-1}.

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Fig. S16. Comparison of HER performance under Zn and ZnO@Cu/Zn-TS electrodes systems.
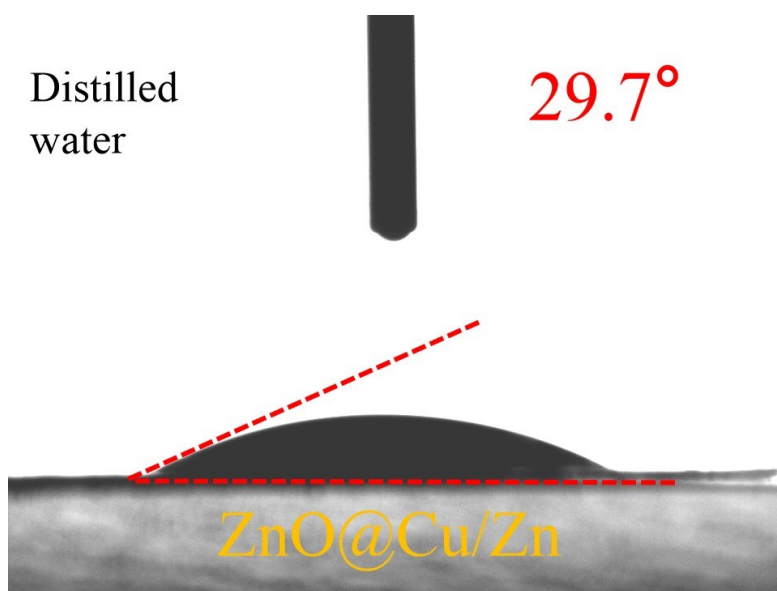

Fig. S17. The contact angle measurement results for the fabricated ZnO@Cu/Zn anodes using

distilled water.
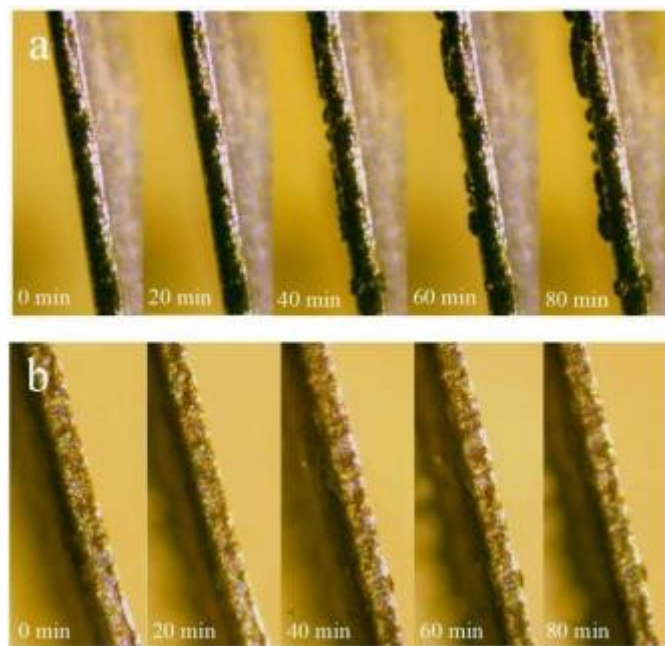
Fig. S18. a) Zn-TS and b) ZnO@Cu/Zn electrodes in symmetric transparent cells, along with the

specified numbers of plating/stripping cycles.

Fig. S19. Coulombic efficiency (CE) measurements of Zn//Ti and Zn//ZnO@Cu/Ti-TS cells under

different electrolyte system and b) corresponding voltage profiles at various cycles.
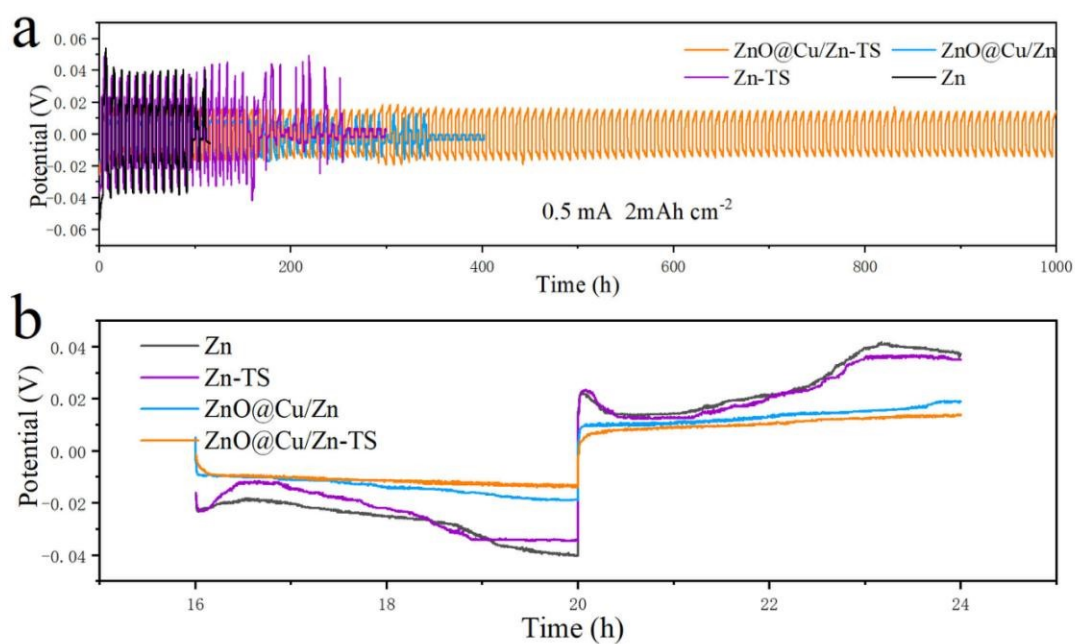
Fig. S20. a) Comparison of the cycling stability of Zn, Zn-TS, ZnO@Cu/Zn and ZnO@Cu/Zn-TS

symmetric cell at 0.5 mA cm^{-2} with the capacity of 2 mA h cm^{-2}; b) High-resolution voltage

profiles at 0.5 mA cm^{-2} with the capacity of 2 mA h cm^{-2} for the first cycle.
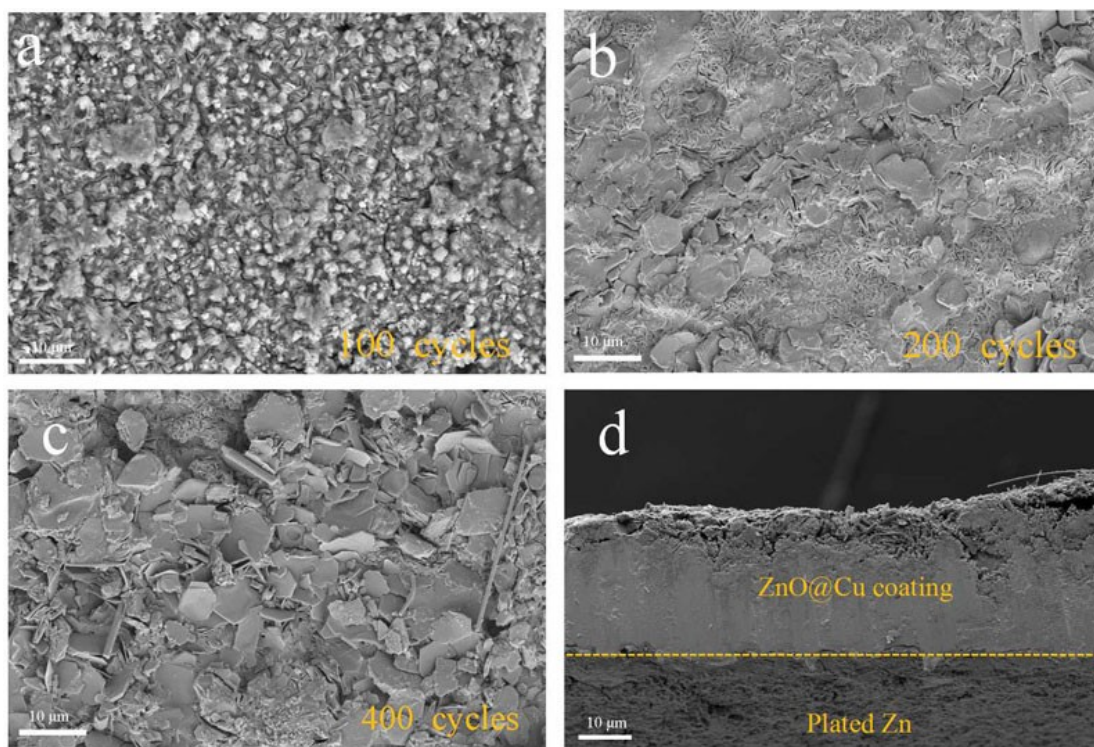
Fig. S21. Top-view SEM images of Zn deposition for ZnO@Cu/Zn-TS electrodes after a) 100 cycles, b) 200 cycles and c) 400 cycles; d) Cross-sectional SEM image of Zn deposition for ZnO@Cu/Zn-TS electrodes after 400 cycles at 10 mA cm^{-2} and 2 mAh cm^{-2}.
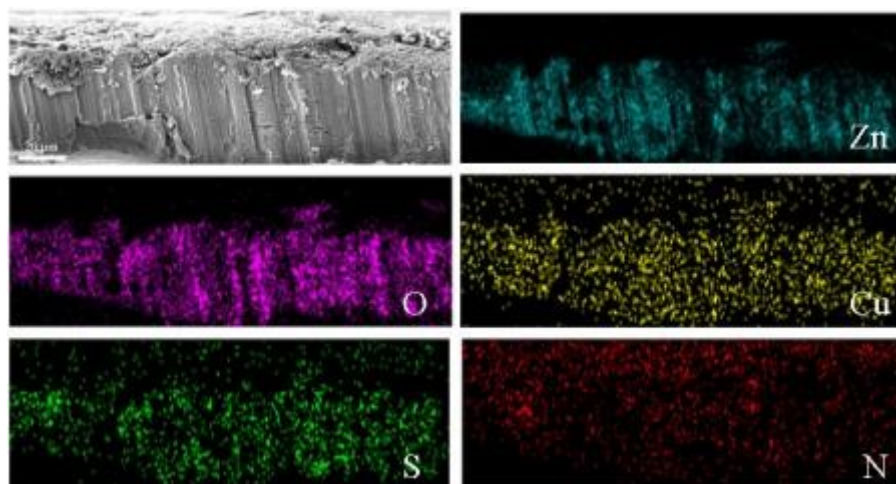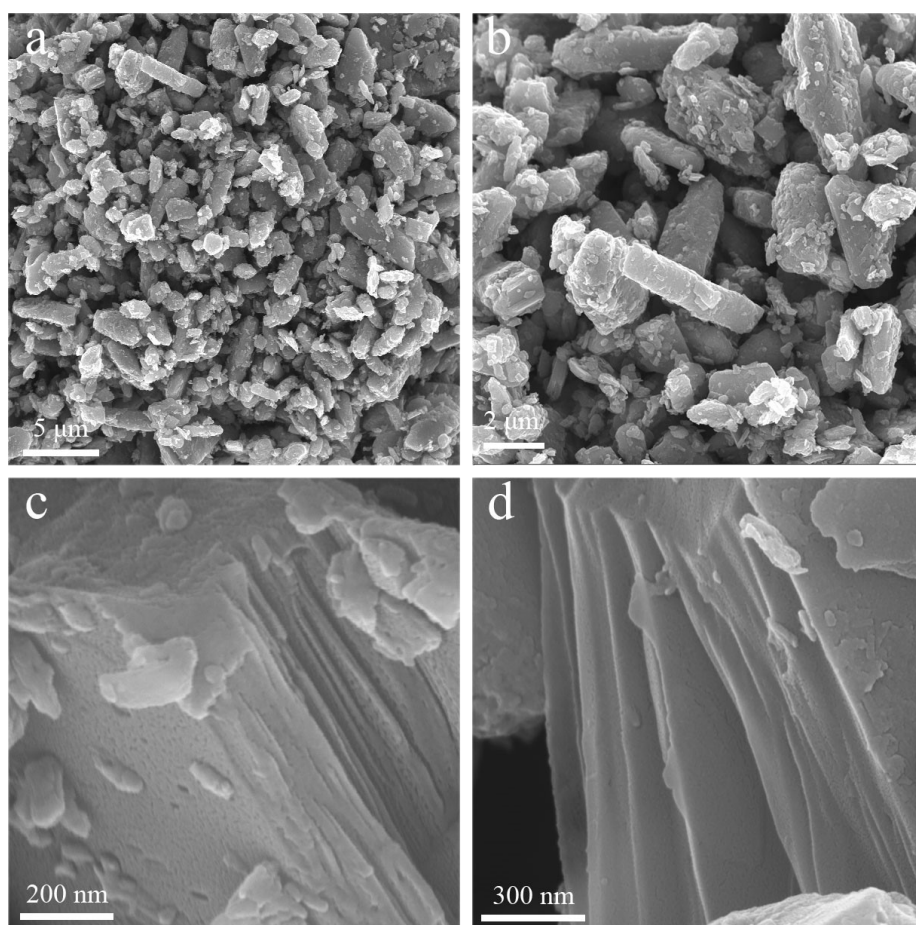
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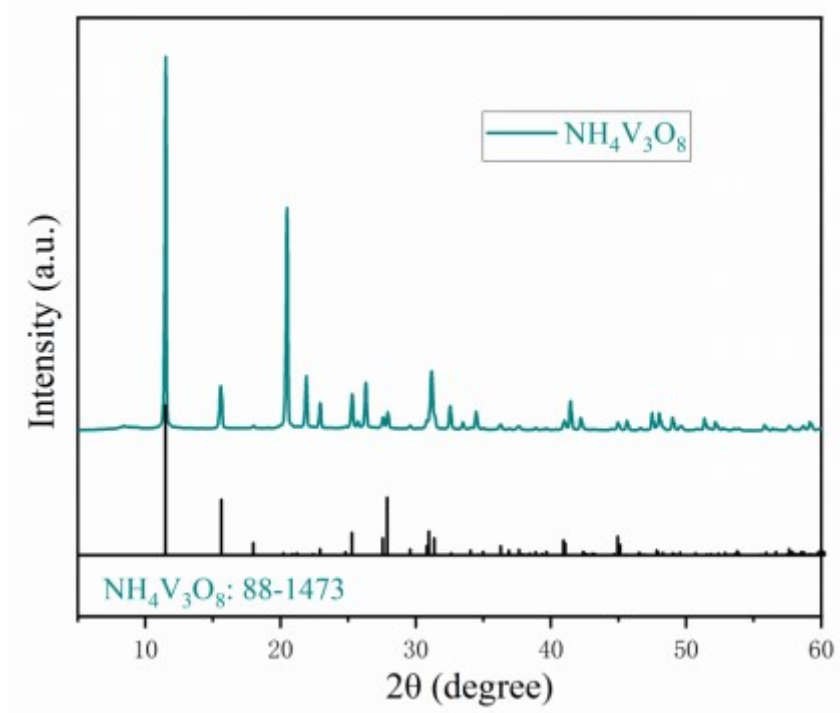
Fig. S23. XRD pattern of $NH_4V_3O_8$.

Fig. S24. SEM images of $NH_4V_3O_8$.
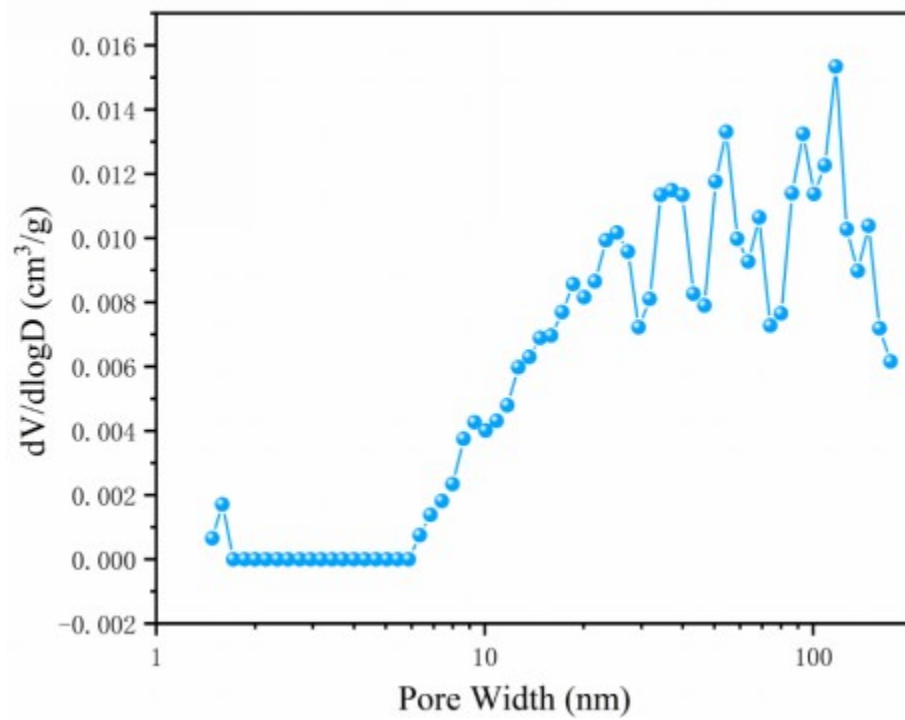
Fig. S25. Pore size distribution curves of $NH_4V_3O_8$.
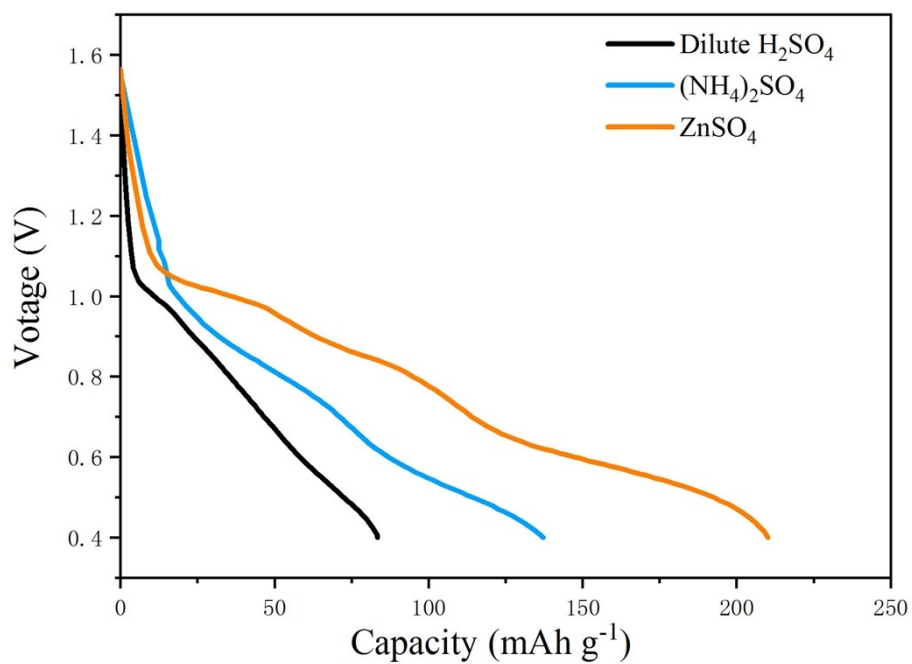
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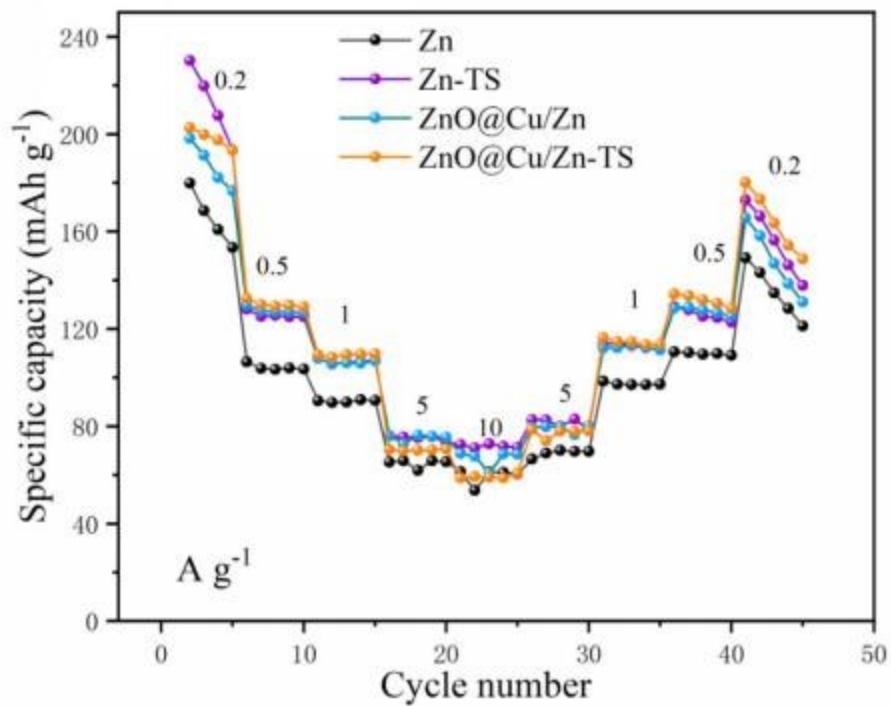
Fig. S27. Rate performance based on charging/discharging curves of the $NH_4V_3O_8|Zn$,

$NH_4V_3O_8|Zn$-TS, $NH_4V_3O_8|ZnO@Cu/Zn$ and $NH_4V_3O_8|ZnO@Cu/Zn$-TS battery.

Table S1. Comparison of the adsorption energy of Zn^{2+} ions of Zn, ZnO and Cu at bridge, top and hole view.

Zn (111)		Cu (111)		ZnO(001)	
Bridge (eV)	-0.484	Bridge	-1.368	O-hole	-4.640
Top (eV)	-0.630	Top	-1.113	Zn-hole	-4.677
Hole (eV)	-0.498	Hole	-1.405		

Table S2. The calculated lattice constants and corresponding k-point mesh of the bulk and surface structures.

	a /Å	b /Å	c /Å	α /°	β /°	γ /°	k-point
Zn	2.566	2.566	5.035	90.00	90.00	90.00	11×11 ×5
Cu	3.545	3.545	3.545	90.00	90.00	90.00	7×7×7
ZnO	4.238	4.238	4.238	90.00	90.00	90.00	6×6×6
Zn(001)	5.133	5.133	/	90.00	90.00	120.00	6×6×1
Cu(111)	5.014	5.014	/	90.00	90.00	120.00	6×6×1
ZnO(111)	5.190	5.190	/	90.00	90.00	120.00	6×6×1

Table S3. Results of electrical conductivity measurement performed on Zn foil, ZnO@Cu/Zn and ZnO@Cu powder.

Electrode Materials	Resistivity (Ω•cm)
Zn foil	0.0626
ZnO@Cu/Zn	0.0715
ZnO@Cu powder	16.54

Table S4. Comparison of the electrolyte additives or artificial layer of symmetric cells for Zn dendrite inhibition.

Artificial layer/additives (ZnSO$_4$ solution)	Current density with capacity	cycle life	Ref.
Zif-67 layer	2 mA cm^{-2} with 1 mAh cm^{-2}	1200 h	[4] *Adv. Sci.* **2020**, 2002173
polyvinyl butyral layer	0.5 mA cm^{-2} with 0.5 mAh cm^{-2}	2200 h	[5] *Adv. Funct. Mater.* **2020**, 2001263
polyacrylamide electrolyte additive	1 mA cm^{-2} with 1 mAh cm^{-2}	280 h	[6] *Angew. Chem, Int. Ed.* **2019**, *58*, 15841–15847

3D-ZnO layer	5 mA cm^{-2} with 1.25 mAh cm^{-2}	500 h	[7] *Energy Environ. Sci.* **2020**, *13*, 503-510
Anhydrous Acetonitrile electrolyte additive	1 mA cm^{-2} with 1 mAh cm^{-2}	1,300 h	[8] *Electrochimica Acta.* **2020**, *358*, 136937
ethylene glycol electrolyte additive	5 mA cm^{-2} with 0.5 mAh cm^{-2}	800 h	[9] *Nano Energy.* **2021**, *80*, 105478
tetrabutylammonium sulfate electrolyte additive	5 mA cm^{-2} with 2 mAh cm^{-2}	500 h	[10] *ACS Energy Lett.* **2020**, *5*, 3012−3020
NaTi$_2$(PO$_4$)$_3$ layer	1 mA cm^{-2} with 1 mAh cm^{-2}	260 h	[11] *Adv. Funct. Mater.* **2020**, *30*, 2004885
ZnS layer	2 mA cm^{-2} with 2 mAh cm^{-2}	1,100 h	[12] *Adv. Mater.* **2020**, 2003021
Glucose electrolyte additive	1 mA cm^{-2} with 1 mAh cm^{-2}	2,000 h	[13] *Angew. Chem. Int. Ed.* **2021**, *60*, 2–1
ZrO$_2$ layer	0.25 mA cm^{-2} with 0.125 mAh cm^{-2}	3,800 h	[14] *Adv. Funct. Mater.* **2020**, *30*, 1908528
ZnO@Cu layer and TS additive	10 mA cm^{-2} with 2 mAh cm^{-2}	over 1000h	Present work
ZnO@Cu layer and TS additive	0.5 mA cm^{-2} with 2 mAh cm^{-2}	over 1000h	Present work
ZnO@Cu layer and TS additive	0.25 mA cm^{-2} with 0.125 mAh cm^{-2}	over 4,500 h	Present work

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