

Electronic Supplementary Information

## Ultra-trace polyvinyl alcohol induced interfacial solvation regulation for stable zinc metal anodes

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## 1. Experimental

### 1.1 Materials

Polyvinyl alcohol (PVA, Aladdin Biochemical Technology Co., Ltd, alcoholysis degree: 98.0-99.0%, viscosity: 5.2-6.0 mPa.s),  $C_4H_6O_4Zn$  (Aladdin Biochemical Technology Co., Ltd, 99%),  $C_2H_3NaO_2 \cdot 3H_2O$  (Aladdin Biochemical Technology Co., Ltd, 99.5%),  $Na_2SO_4$  (Aladdin Biochemical Technology Co., Ltd, 99%),  $H_2SO_4$  (Xilong scientific, 95%~98%), aniline (Aladdin Biochemical Technology Co., Ltd, 99.9%), zinc foils (Thickness: 70  $\mu m$ ) and fiberglass separator (Whatman, No.1823-090) were used as received without further treatment. Ultra-pure water (resistivity  $\sim 18.2 M\Omega cm$ ) was obtained through the LIDING STAR-10 system.

### 1.2 Materials Preparation

**Preparation of PVA-containing zinc acetate electrolytes:** 0.3 g of PVA powder was dissolved in 30 mL of ultra-pure water under continuous magnetic stirring at 80 °C to prepare a homogeneous 10 g L<sup>-1</sup> PVA stock solution, which was then diluted with ultra-pure water forming solutions with different concentrations of PVA including 1 g L<sup>-1</sup>, 10<sup>-2</sup> g L<sup>-1</sup>, 10<sup>-5</sup> g L<sup>-1</sup> and 10<sup>-8</sup> g L<sup>-1</sup>. Subsequently, 5.56 g of zinc acetate anhydrous ( $Zn(Ac)_2$ ) was dissolved in 3 mL of 10<sup>-2</sup> g L<sup>-1</sup> PVA solution, and the mixture was diluted to 30 mL with ultra-pure water and stirred vigorously at 25 °C to obtain  $Zn(Ac)_2$  electrolyte containing 10<sup>-3</sup> g L<sup>-1</sup> PVA (denoted as ppm-PVA). Similarly,  $Zn(Ac)_2$  electrolytes containing 10<sup>-6</sup> g L<sup>-1</sup> and 10<sup>-9</sup> g L<sup>-1</sup> PVA (denoted as ppb-PVA and ppt-PVA, respectively) were prepared with the same procedure using 10<sup>-5</sup> g L<sup>-1</sup> and 10<sup>-8</sup> g L<sup>-1</sup> PVA solutions, respectively. The  $Zn^{2+}$  concentration in all electrolyte formulations maintained 1 M.

For comparison, pure 1 M  $Zn(Ac)_2$  electrolyte was also prepared by dissolving 5.56 g of  $Zn(Ac)_2$  into 30 mL of ultra-pure water, which was named as w/o-PVA. Besides, 1 M  $Zn(Ac)_2$  electrolyte with a high concentration of PVA (1 g L<sup>-1</sup>) was obtained by dissolving 5.56 g of anhydrous  $Zn(Ac)_2$  in 3 mL of 10 g L<sup>-1</sup> PVA, which was then diluted to 30 mL with ultra-pure water (denoted as 1000 ppm-PVA). For repeated parallel experiments, the homogeneous 10 g L<sup>-1</sup> PVA stock solution was additionally diluted with ultra-pure water forming solutions with different concentrations of PVA including 10<sup>-3</sup> g L<sup>-1</sup>, 10<sup>-4</sup> g L<sup>-1</sup>, 10<sup>-6</sup> g L<sup>-1</sup> and 10<sup>-7</sup> g L<sup>-1</sup>.  $Zn(Ac)_2$  electrolytes containing 10<sup>-4</sup> g L<sup>-1</sup>, 10<sup>-5</sup> g L<sup>-1</sup>, 10<sup>-7</sup> g L<sup>-1</sup> and 10<sup>-8</sup> g L<sup>-1</sup> PVA (denoted as 100 ppb-PVA, 10 ppb-PVA, 100 ppt-PVA and 10 ppt-PVA, respectively) were prepared with the same procedure using 10<sup>-3</sup> g L<sup>-1</sup>, 10<sup>-4</sup> g L<sup>-1</sup>, 10<sup>-6</sup> g L<sup>-1</sup> and 10<sup>-7</sup> g L<sup>-1</sup> PVA solutions, respectively.

**Preparation of PVA-containing sodium acetate electrolytes:** The PVA-containing  $C_2H_3NaO_2$  electrolytes were prepared with the same procedure as that used to prepare  $Zn(Ac)_2$  electrolytes, except that the amount of  $C_2H_3NaO_2$  was 4.10 g to keep the concentration of  $Na^+$  in electrolytes being 1 M.

**Preparation of positive electrodes:** Carbon nanotube (CNT) supported polyaniline (PANI) was used as the positive electrode of AZIBs. To prepare PANI@CNT cathode, 17.755 g of  $Na_2SO_4$ , 6.8 mL of  $H_2SO_4$ , and 4.56 mL of aniline were first mixed in 400 mL of ultra-pure water under continuous stirring, yielding a transparent

solution, which was then diluted to 500 mL with ultra-pure water to prepare a 2 M aniline solution. The continuous CNT films, synthesized by the blown aerosol chemical vapor deposition method,<sup>1</sup> were cut into small pieces with a dimension of  $1 \times 2 \text{ cm}^2$  for use as current collectors. Electrodeposition was performed in a three-electrode system using a platinum foil as the working electrode, the CNT current collector as the counter electrode, and a saturated calomel electrode (SCE) as the reference. The electrodeposition was carried out in 2 M aniline solution using cyclic voltammetry (CV) by sweeping the potential in the range of 0 – 0.8 V at  $60 \text{ mV s}^{-1}$  for 80 cycles. Afterward, the counter electrode was carefully rinsed with ultra-pure water and dried in an oven at  $40 \text{ }^\circ\text{C}$  for 10 min to obtain the PANI@CNT cathode with a loading of approximately  $1 \text{ mg cm}^{-2}$ .

### 1.3 Structural Characterization

The crystal structure of ZMAs was examined by X-ray diffractometry (XRD, Bruker-D8, Cu  $K\alpha$  radiation). The surface chemistry was probed by X-ray photoelectron spectrometry (XPS, ThermoFisher Scientific ESCALAB Xi<sup>+</sup>). The morphology of samples was inspected by a scanning electron microscope (SEM, Thermo Fisher Phenom ProX). The hydrogen gas evolution in various electrolyte systems was monitored by differential electrochemical mass spectrometry (Hidden, HPR-40 DEMS). In-situ optical microscopic observation was performed using a benchtop high-resolution microscope (AOSW AO-21TZ). The roughness of ZMAs was characterized by a profilometer (Bruker DektakXT). Furthermore, the surface topography fluctuation was measured by a MXFMS-BD LY-WN-YH400 ultra depth microscope. The contact angle was measured on a KRUSS DSA25S drop shape analyzer. Raman spectra of the electrolytes were acquired on a LabRAM HR Evolution Raman spectrometer with a 532 nm laser.

### 1.4 Electrochemical Characterization

Linear sweep voltammetry (LSV) was performed on a CHI 660e electrochemical workstation in the three-electrode system comprising a Zn foil as the working electrode, a Pt foil as the counter electrode, and a Hg/HgCl<sub>2</sub> electrode (saturated KCl, 0.2415 V vs. SHE) as the reference. The electrolyte consisted of PVA-containing C<sub>2</sub>H<sub>3</sub>NaO<sub>2</sub> solution. CV studies were carried out in the PVA-containing Zn(Ac)<sub>2</sub> electrolyte using two pieces of Pt foils as the working and counter electrodes and the Hg/HgCl<sub>2</sub> electrode as the reference.

Symmetric Zn||Zn cells were assembled using custom-made stainless steel cells. Specifically, a piece of Whatman glass fiber separator was sandwiched by two identical zinc electrodes, and then PVA-containing Zn(Ac)<sub>2</sub> electrolyte was injected into the cell. The ratio of the electrolyte volume to the area of the Zn anode foil is  $200 \text{ } \mu\text{L cm}^{-2}$ . The electrochemical impedance spectroscopy (EIS) measurements were performed on a Biologic SP50e electrochemical workstation in the frequency range from 0.01 Hz to 100 kHz to comprehensively analyze the interfacial charge transfer processes. The chronoamperometry (CA) was conducted at the voltage of  $-150 \text{ mV}$ .

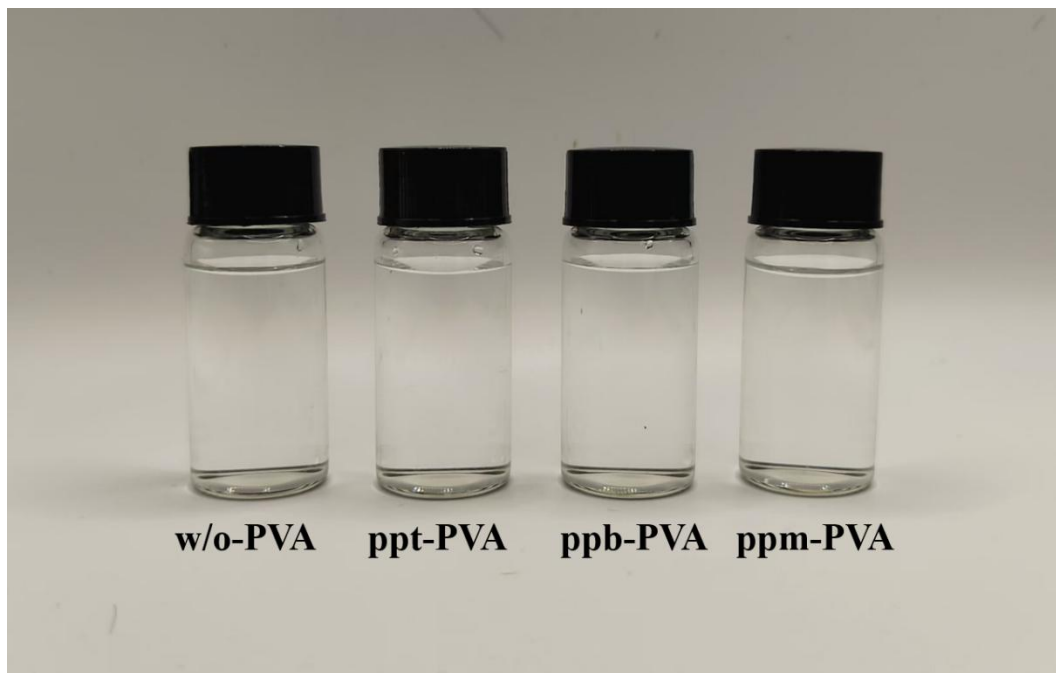
Zn||PANI@CNT full cells were fabricated with a zinc foil anode, a PANI@CNT film cathode, and a glass fiber separator. Either w/o-PVA or ppb-PVA Zn(Ac)<sub>2</sub> was employed as the electrolyte. Cyclic voltammetry (CV) was conducted using an electrochemical workstation (Biologic SP50e). The Zn||PANI@CNT battery was tested in a voltage range of 0.5 to 1.6 V at a scan rate of 0.6 mV s<sup>-1</sup>. Galvanostatic charge-discharge characteristics, cycle stability, and rate capability were evaluated using a battery tester (LANHE CT3002A).

### *1.5 Theoretical Calculations*

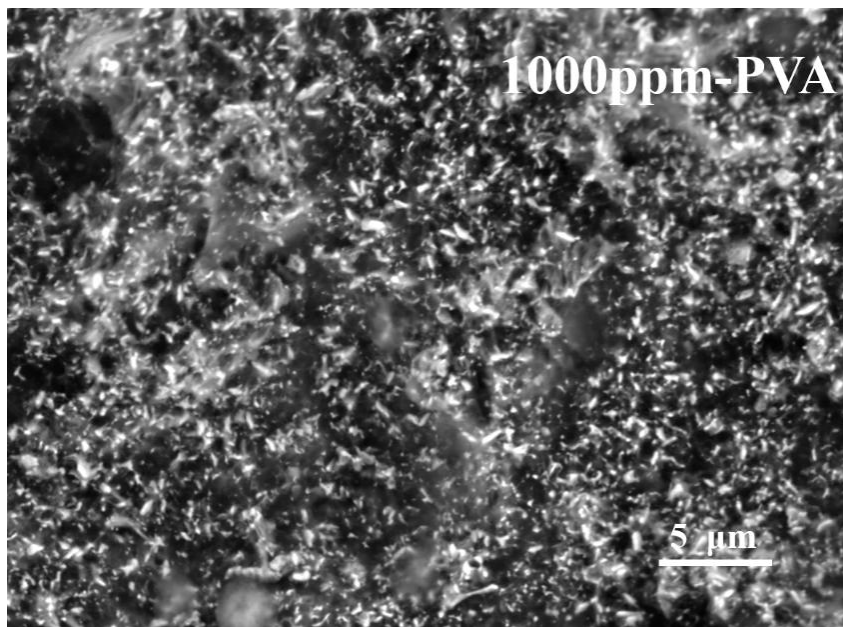
The DFT calculations were conducted using the VASP software.<sup>2</sup> The PAW (Projector Augmented Wave) pseudopotential and the GGA PBE (Perdew - Burke - Ernzerhof) functional were used for the calculations.<sup>3-5</sup> The energy cutoff was fixed to 520 eV. The electronic convergence was set at  $1 \times 10^{-5}$ , while the geometric convergence was set to  $1 \times 10^{-4}$  eV. The Monkhorst-Pack method was employed for k-point sampling.<sup>6</sup> The VESTA software was utilized to analyze the geometric and electronic structures of samples.<sup>7</sup>

In the realm of classical molecular dynamics simulations, the Forcite module within the Materials Studio 2020 software was employed. The potential function selected was COMPASS II (a Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies).<sup>8</sup> The simulation parameters were carefully chosen: the time step was set to 1 fs, and the temperature was maintained at 298 K. The Nose thermostat was used to regulate the temperature. Specifically, the electrolyte model first underwent a 2000 ps run under the NPT ensemble to achieve a stable structure, with the pressure held at 0.1 GPa. Following this initial equilibration, the model was simulated for 5000 ps under the NVT ensemble. During simulations, the structure was sampled every 0.5 ps for the purpose of analyzing the radial distribution function and mean squared displacement.

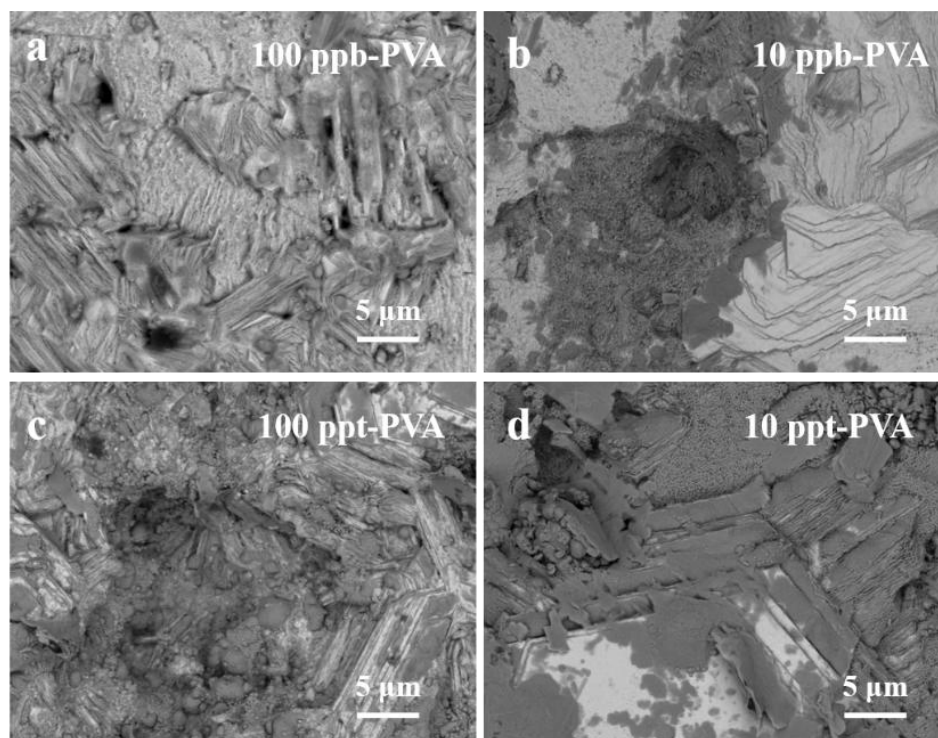
## 2. Supplementary Figures



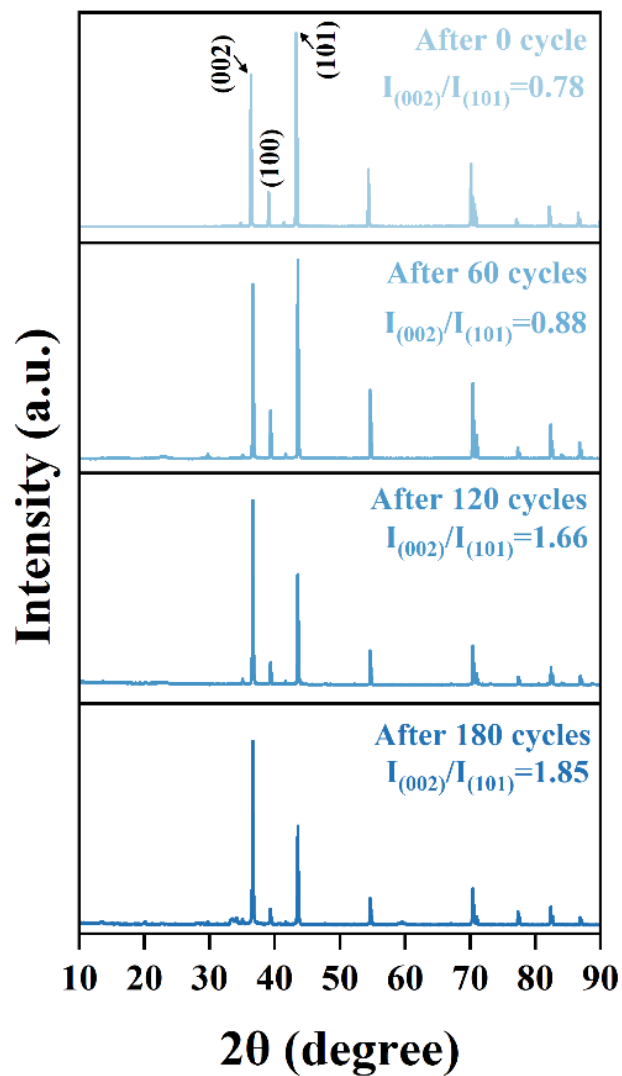
**Fig. S1** Digital photographs of electrolytes with different PVA concentrations.



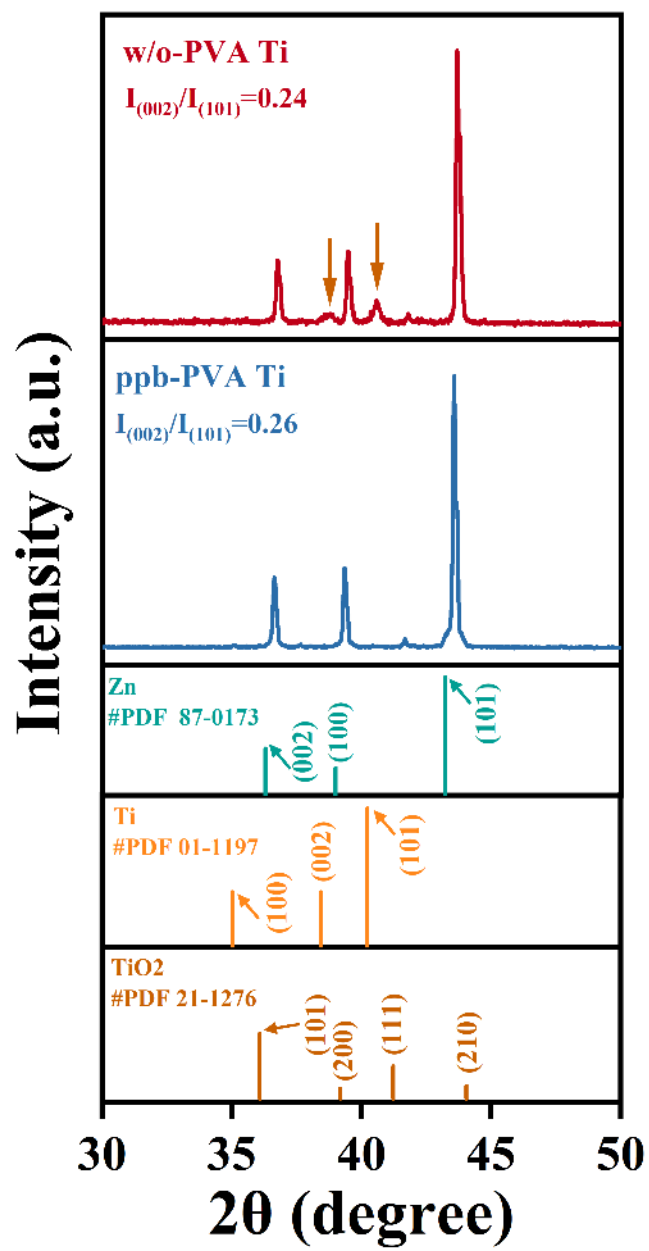
**Fig. S2** *Ex-situ* SEM image of the Zn electrode cycled in 1000 ppm-PVA Zn(Ac)<sub>2</sub> electrolyte at 1 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup> for 5 days.



**Fig. S3** SEM images of the Zn electrodes from Zn||Zn symmetric cells cycled in Zn(Ac)<sub>2</sub> electrolytes containing (a) 100 ppb-PVA, (b) 10 ppb-PVA, (c) 100 ppt-PVA, and (d) 10 ppt-PVA at 1 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup> for 5 days.



**Fig. S4** *Ex-situ* XRD patterns of the Zn electrodes from Zn||Zn symmetric cells cycled in Zn(Ac)<sub>2</sub> electrolytes containing ppb-PVA at 1 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup> after different cycles.



**Fig. S5** XRD patterns of the Ti foil after electrolytic deposition in Zn(Ac)<sub>2</sub> electrolytes containing w/o-PVA and ppb-PVA.

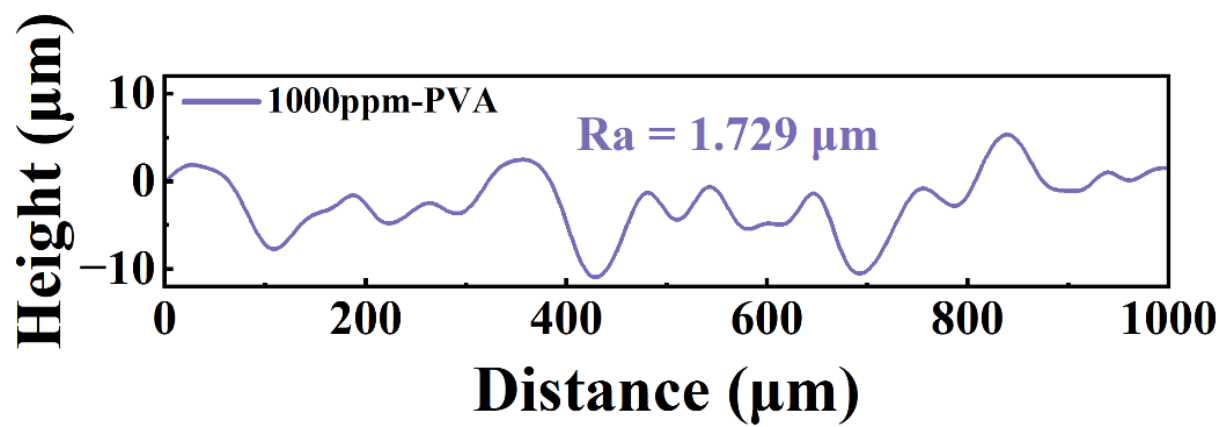
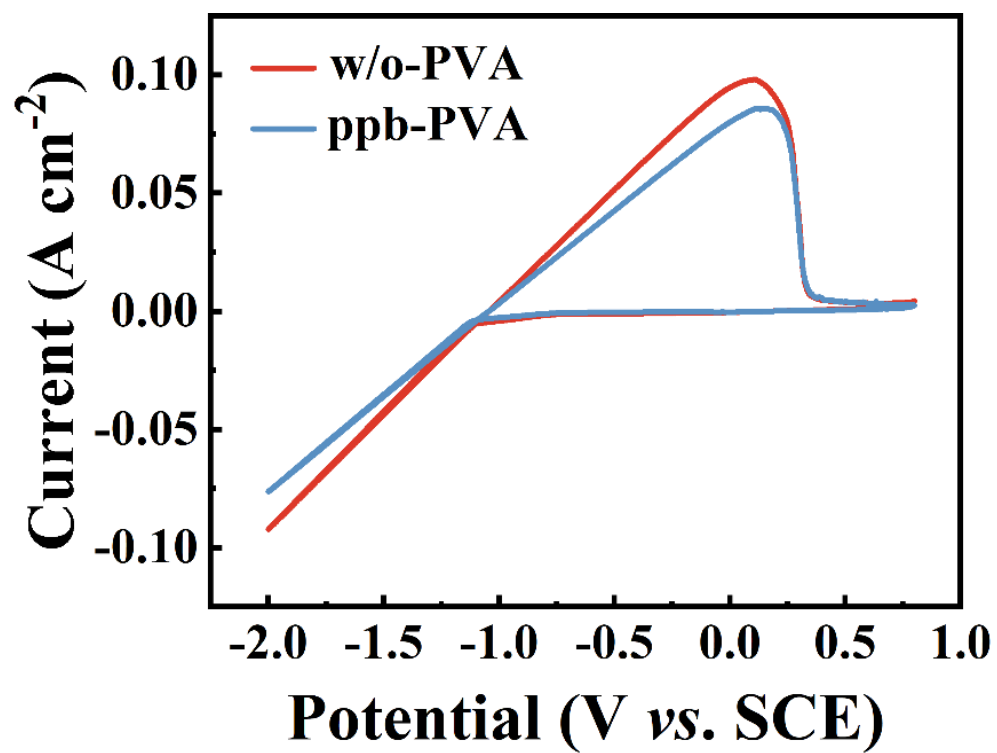
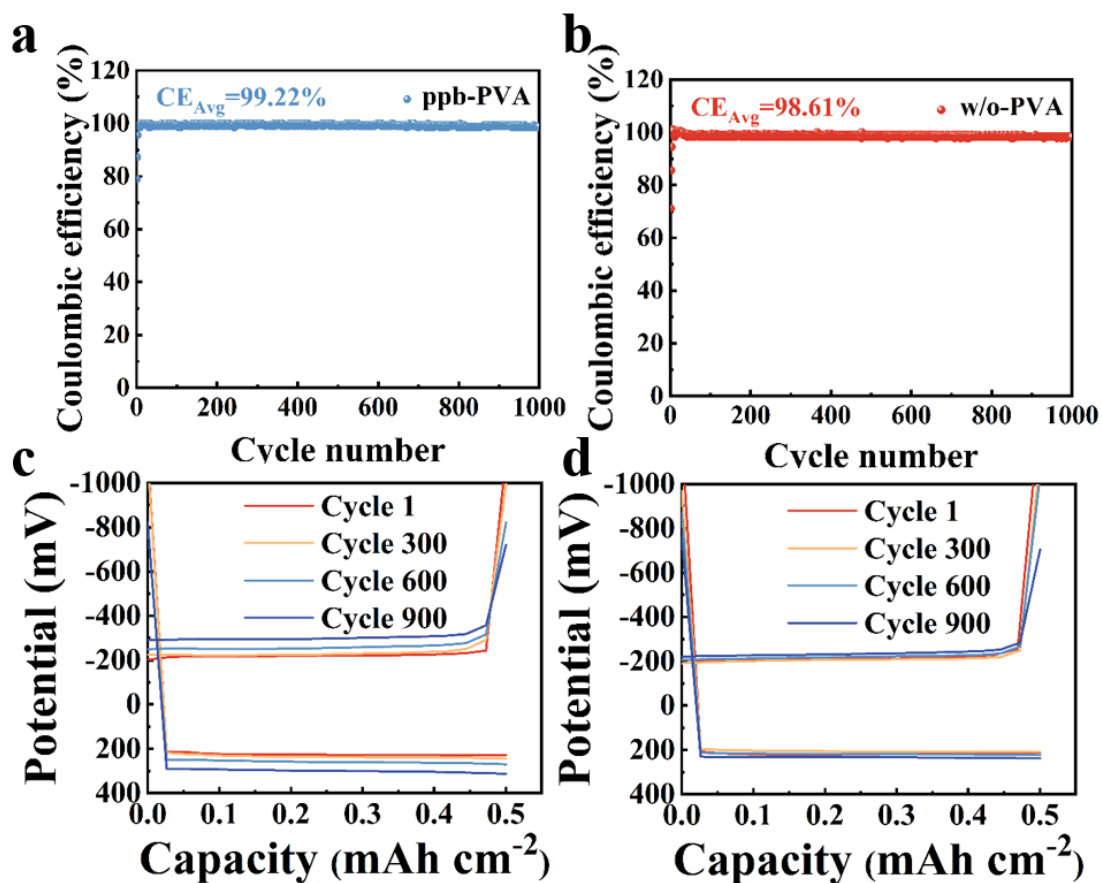


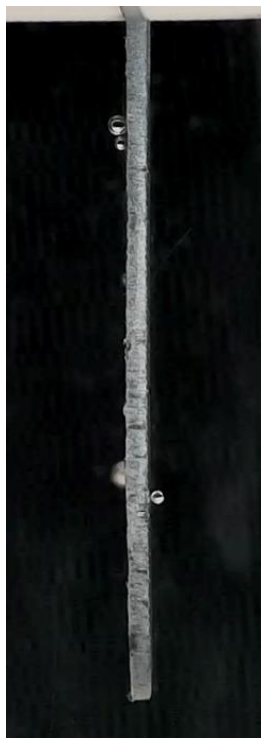
Fig. S6 Roughness of the zinc anode after cycling in 1000 ppm-PVA Zn(Ac)<sub>2</sub> electrolyte.



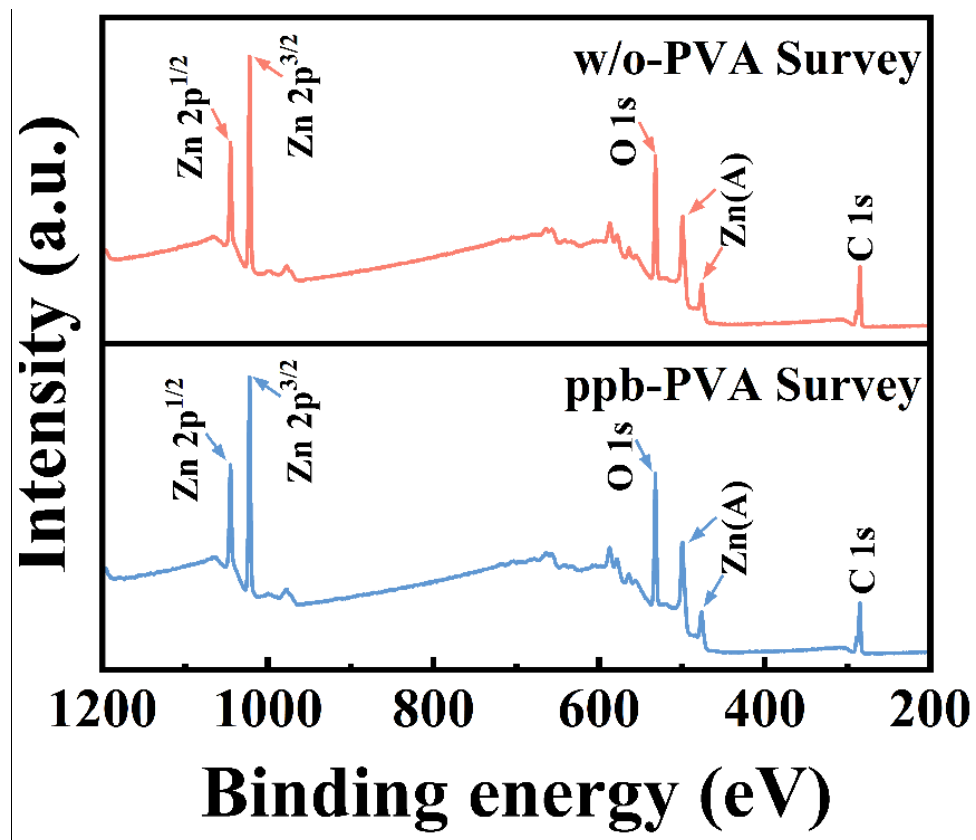
**Fig. S7** CV curves illustrating the plating/stripping of the zinc ions on the platinum electrode in different electrolytes.



**Fig. S8** Coulombic efficiency of Zn||Cu cells assembled with (a) ppb-PVA and (b) w/o -PVA Zn(Ac)<sub>2</sub> electrolytes tested at 8 mA cm<sup>-2</sup>. Corresponding voltage-capacity curves recorded for the Zn||Cu cells with (c) ppb-PVA and (d) w/o -PVA Zn(Ac)<sub>2</sub> electrolytes in cycles 1, 300, 600, and 900.



**Fig. S9** Optical microscopy image showing the cross-section of the zinc anode upon plating at  $3 \text{ mA cm}^{-2}$  in the ppb-PVA/NaAc electrolyte after 30 min.



**Fig. S10** XPS survey spectra of the zinc anodes after immersion in w/o-PVA and ppb-PVA Zn(Ac)<sub>2</sub> electrolytes for one day.

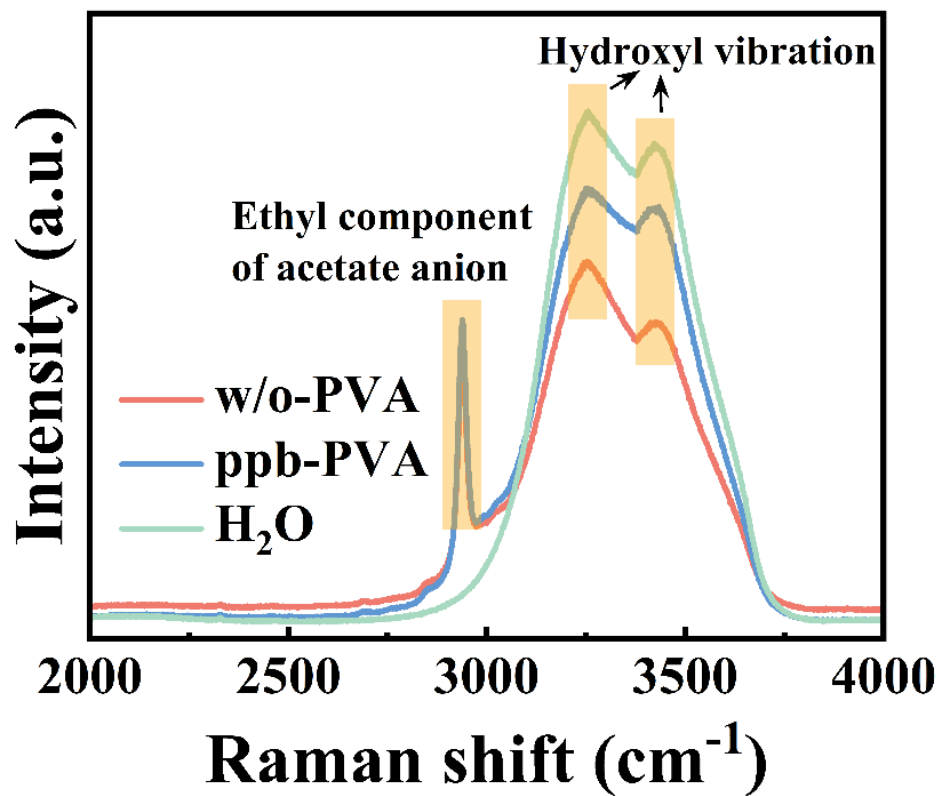
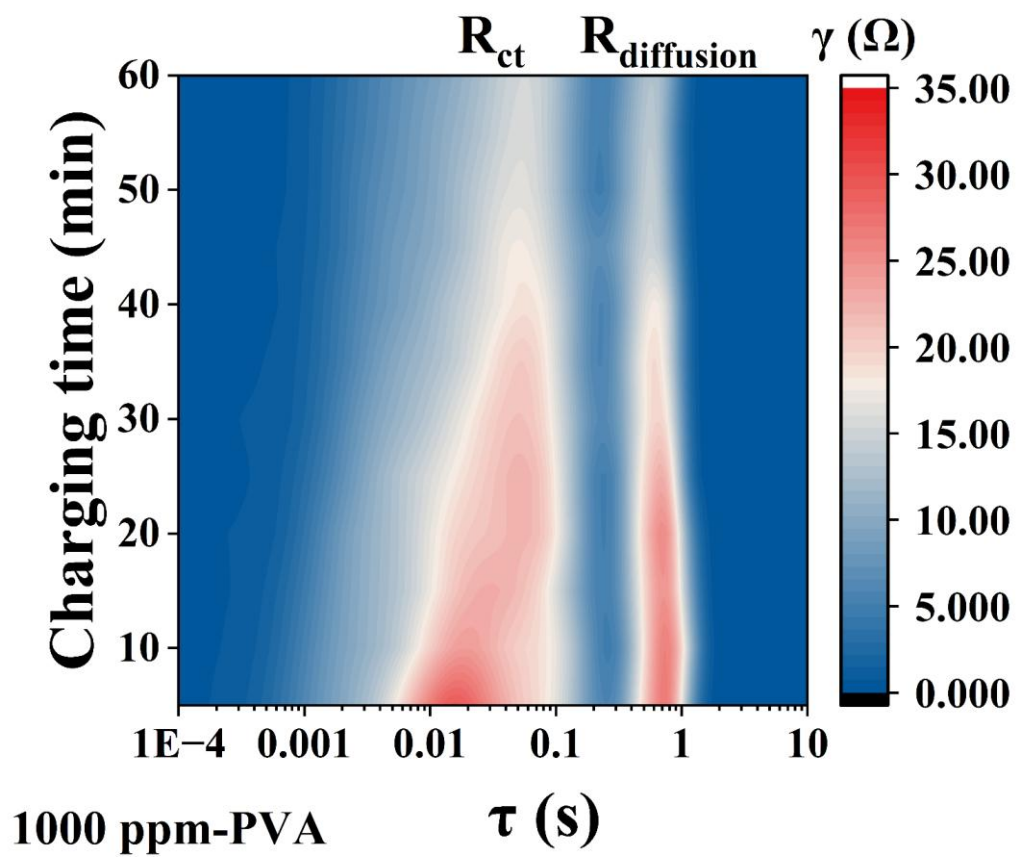
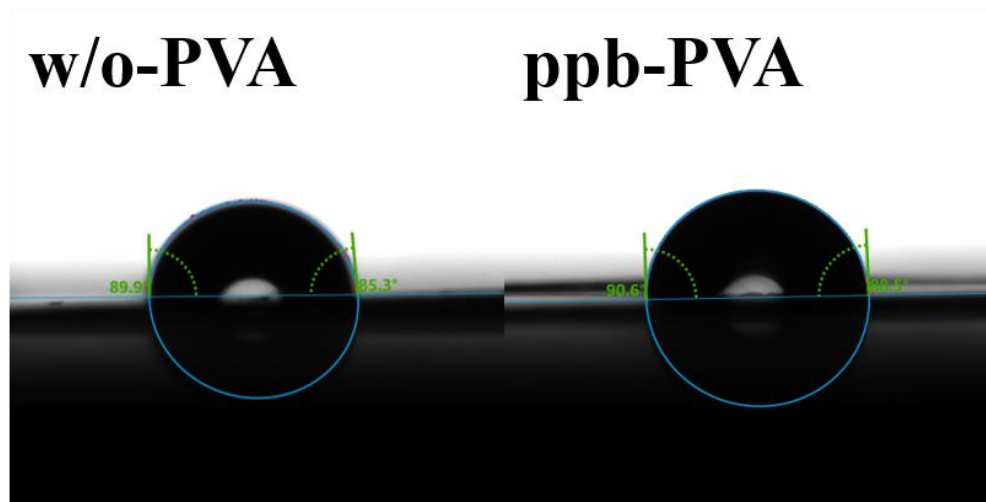


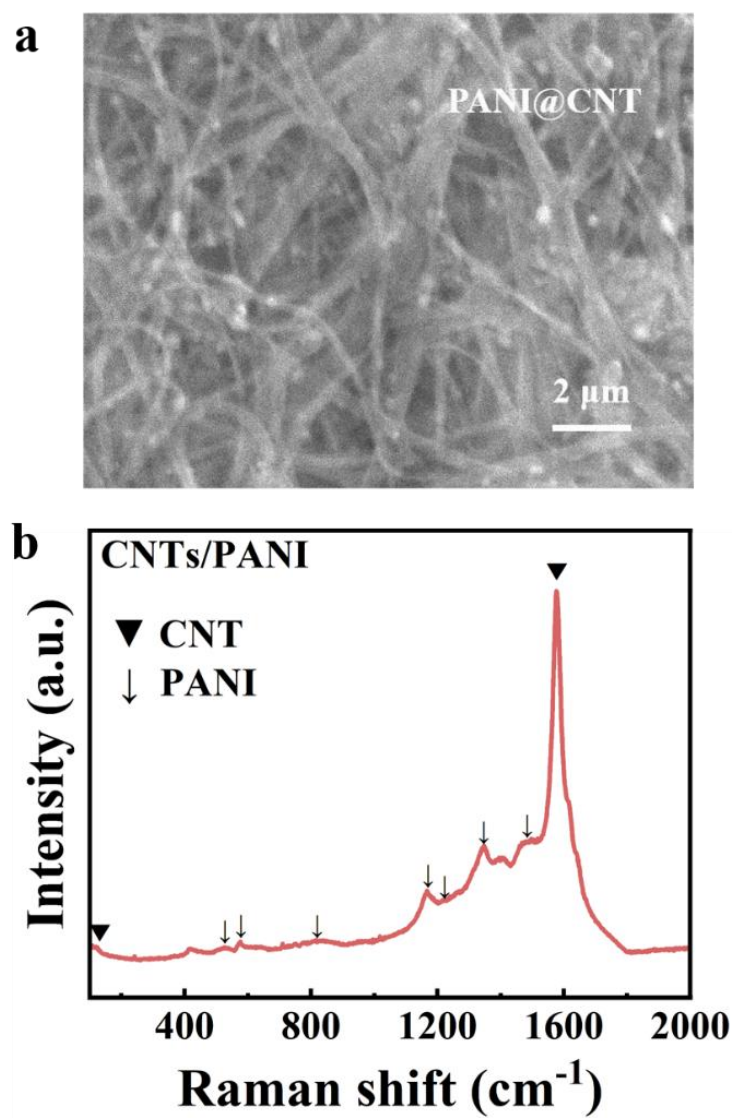
Fig. S11 Raman spectra of the w/o-PVA/Zn(Ac)<sub>2</sub>, ppb-PVA/Zn(Ac)<sub>2</sub>, and pure H<sub>2</sub>O solutions.



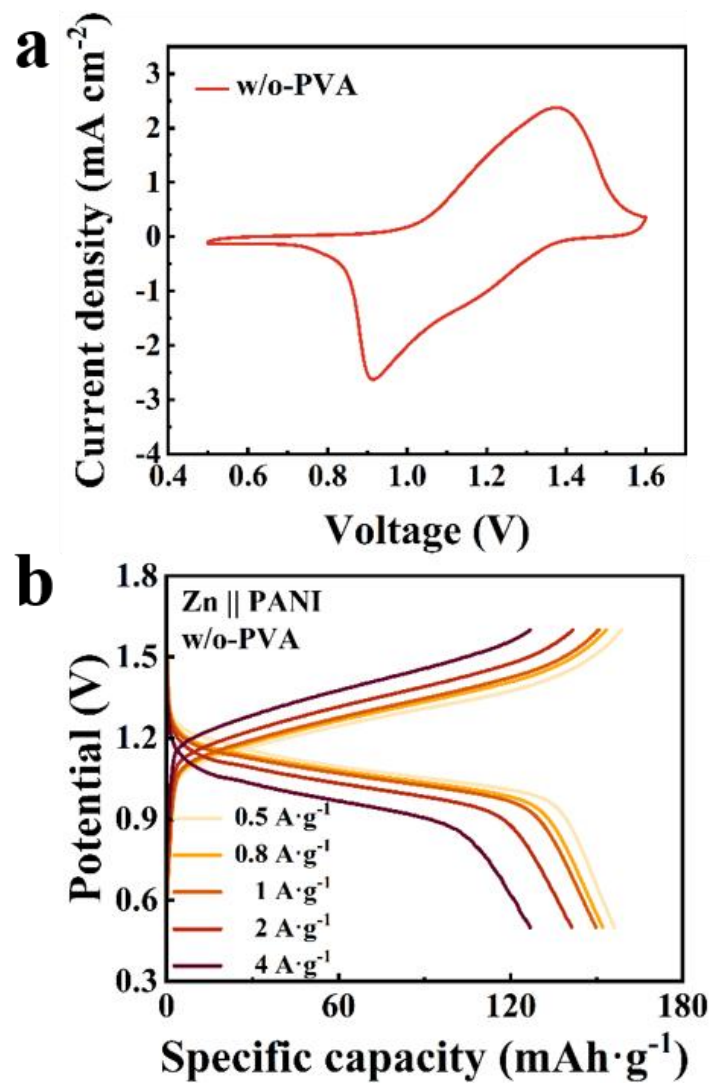
**Fig. S12** DRT analysis of the Zn||Zn symmetric cell assembled with 1000 ppm-PVA Zn(Ac)<sub>2</sub> electrolyte.



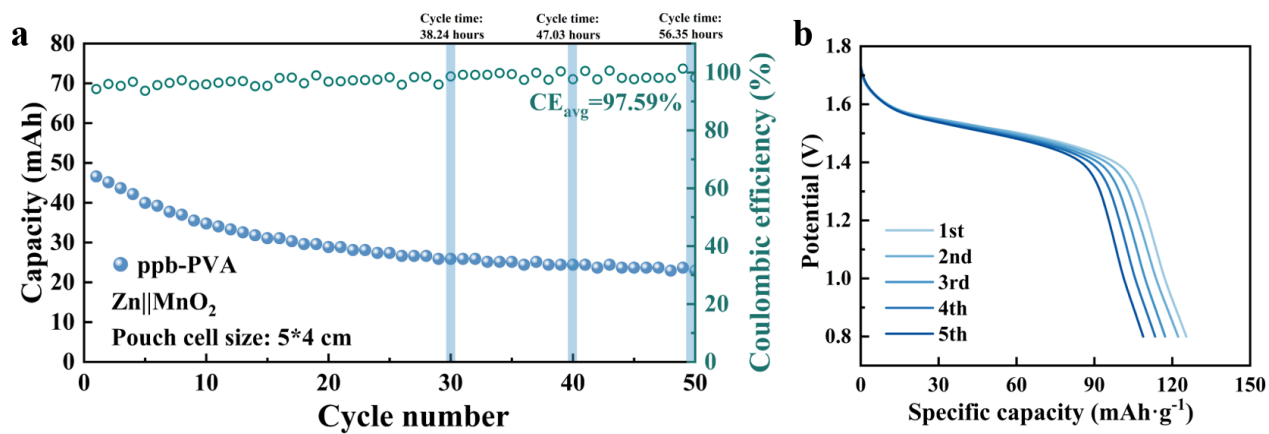
**Fig. S13** Contact angle tests of the w/o-PVA/ $\text{Zn}(\text{Ac})_2$  and ppb-PVA/ $\text{Zn}(\text{Ac})_2$  electrolytes on zinc foils.



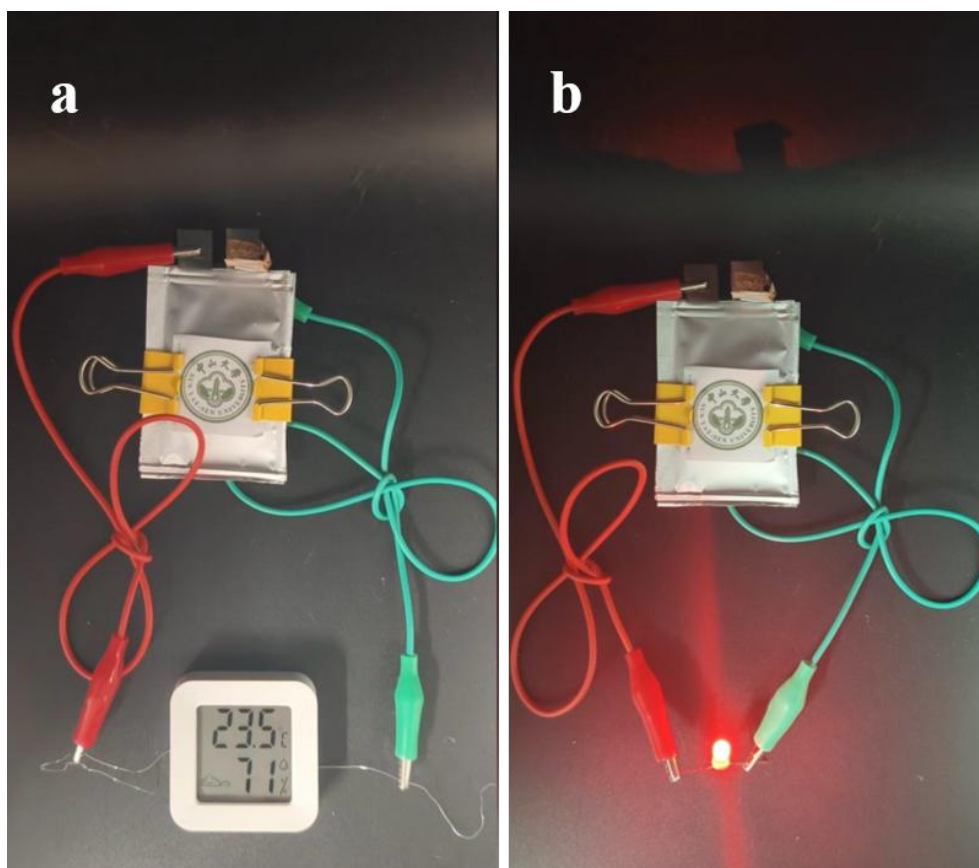
**Fig. S14** (a) SEM image and (b) Raman spectrum of the PANI@CNT cathode.



**Fig. S15** (a) CV curve of Zn||PANI@CNT batteries assembled with the w/o-PVA  $\text{Zn}(\text{Ac})_2$  electrolyte recorded at a scan rate of  $0.6 \text{ mV s}^{-1}$ . (b) Galvanostatic charge/discharge curves of Zn||PANI@CNT batteries assembled with the w/o-PVA  $\text{Zn}(\text{Ac})_2$  electrolyte acquired at different current densities.



**Fig. S16a-b** (a) Cycling stability of the Zn||MnO<sub>2</sub> pouch battery employing ppb-PVA electrolyte (0.2 A g<sup>-1</sup>), (b) GCD curves of the pouch battery at different cycles.



**Fig. S17** Digital photographs illustrating the Zn||MnO<sub>2</sub> pouch battery fabricated with the ppb-PVA Zn(Ac)<sub>2</sub> electrolyte powering (a) a thermometer and (b) an LED bulb.

## References

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