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Supporting Information

An Anticorrosive Zinc Metal Anode with Ultra-long Cycle Life over One Year

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1. Experimental Section

Material Synthesis: The Zn@In anode was prepared by the chemical substitution method, and the procedure was as follows: $InCl_3$•$4H_2O$ (0.59 g) was dispersed in ultra-pure water (100 mL) at room temperature. Then, the Zn plate (100 μm, 10 cm x 10 cm) polished was immersed in the obtained solution for 5 minutes to obtain the Zn@In plate. After that, the obtained Zn@In plate was washed with ultra-pure water and ethanol, respectively. Finally, the Zn@In plate was cut into the suitable size discs (Φ10 mm and Φ14 mm) or strips (1 cm x 2 cm) as electrodes.

Materials Characterization: X-ray diffraction (XRD) patterns of different electrodes were collected by a Bruker D2 PHASER diffractometer using Cu Kα (λ = 1.541 Å) from 10^o to 80^o. Scanning electron microscopy (SEM) and corresponding EDS elemental mapping images were obtained from a scanning electron microscope (FEI Quanta650 FEG). The confocal laser scanning microscope (CLSM) images were collected by the Keyence VK-X200K microscope. The contact angle was measured by Kruss DSA 100. The in-situ optical images were obtained on the optical microscope (OLYMPUS BX51) by using a homemade optical cell.

Cell assembling: The Zn||Zn symmetric cells were assembled using Zn plates with a diameter of 10 mm or 14mm and thickness of 0.1 mm. The glass fiber separators (GF/A, Φ = 16 mm, Whatman) and 2 M $ZnSO_4$ was used as separator and electrolyte respectively. The Zn/MnO_2 full cells were assembled similarly. MnO_2 nanofibers were prepared by the way reported.[1] Active material (MnO_2), Ketjen black, and binder (PTFE) were mixed at a weight ratio of 7:2:1 and formed slurry using isopropanol. Then the slurry was coated on a Ti plate (Φ10 mm) and dried at room temperature for 12 h. After that, the obtained electrodes were the cathode of the Zn/MnO_2 full cells. Meanwhile, 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ were used as the electrolyte.

Electrochemical measurements: The CV data and linear sweep voltammetry (LSV) measurements were conducted on a CH Instruments electrochemical workstation (CHI 760e). Among them, LSV measurements were carried out in 1 M Na_2SO_4 at a sweep rate of 5 mV s^{-1} from −1.1 V to −2.1 V, where Zn plates (1 x 2 cm^2) were used as the working electrode and the counter electrode at the same time and the saturated calomel electrode (SCE) was used as the reference electrode. Galvanostatic charge-discharge and chronopotentiometry tests were performed on a LAND system. Besides, the chronopotentiometry was achieved with Zn plate as the working electrode, counter electrode, and reference electrode at 1 mA cm^{-2} for 1 h in 2 M $ZnSO_4$ aqueous electrolyte. The electrochemical impedance spectroscopy (EIS) data was recorded on the Solartron Electrochemical Interface SI 1287 and SI 1260.

Calculation methods: HER behavior on Zn (101) and In (101) surfaces were investigated by analyzing the free energy of hydrogen adsorption. The energies of all adsorption models were computed by Vienna Ab-initio Simulation Package (VASP). [2] Pseudopotentials and the projector-augmented wave methods were used to simulate the electron-ion interaction. [3, 4] All calculations were done with Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) and the projected augmented wave (PAW) method based on periodically repeated slab models. [5, 6] 450eV and 0.02eV/Å were set as the cut-off energies for plane waves and the convergence tolerance of force on each atom during structure relaxation, respectively.

The free energy of hydrogen adsorption at equilibrium is calculated as

$$\Delta G_{H*} = \Delta E_{\mathrm{H}} + \Delta E_{\mathrm{ZPE}} - T\Delta S_{\mathrm{H}}$$

With

$$\Delta E_H = E_{H+Slab} - E_{Slab} - \frac{1}{2}E_{H_2}$$

Where E_{H2} refers to the energy of a free gas-phase H_2 molecule; E_{Slab} and E_{H+Slab} are energies of a clean Zn (101) or In (101) slab and an H@Zn (101) or H@In (101) slab, respectively. ΔE_{ZPE} represents the gap of the zero point energy for the adsorbed state and the gas phase. Given the vibrational entropy of H* in the adsorbed state is small, the adsorption entropy of 1/2 H_2 is $\Delta S_H \approx$-1/2 S^0_{H2}, where S^0_{H2} is the entropy of H_2 in the gas phase under standard conditions. All the corrections are taken together in

$$\Delta G_{H^*} \approx \Delta E_{\mathrm{H}} + 0.24\mathrm{eV}$$

2. Supplementary Figures and Table

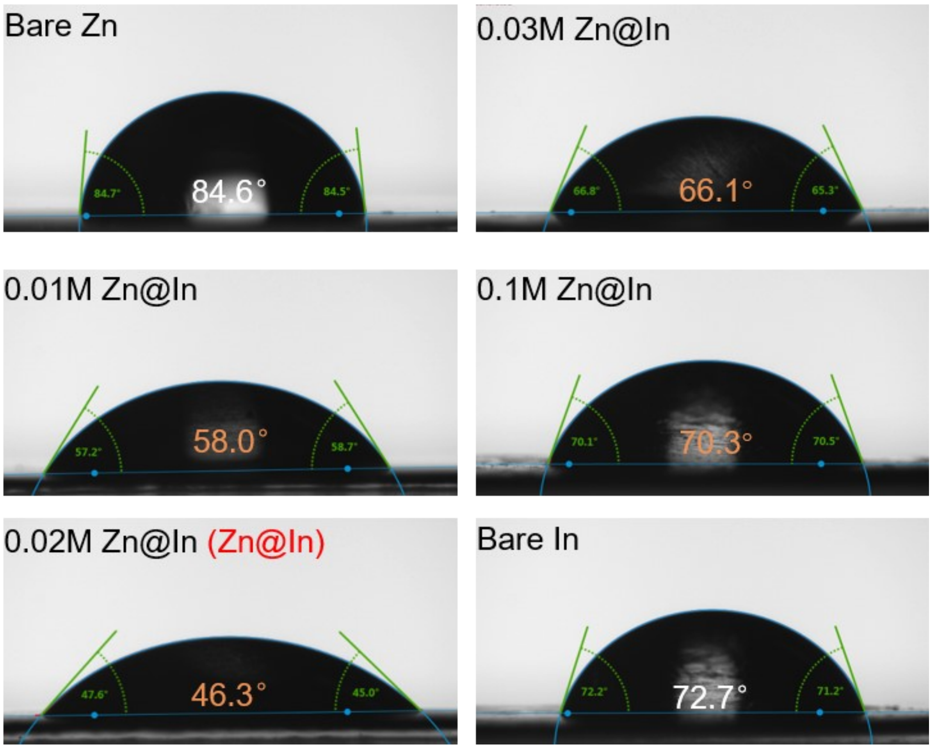

Fig. S1. Images of contact angles on different electrodes.

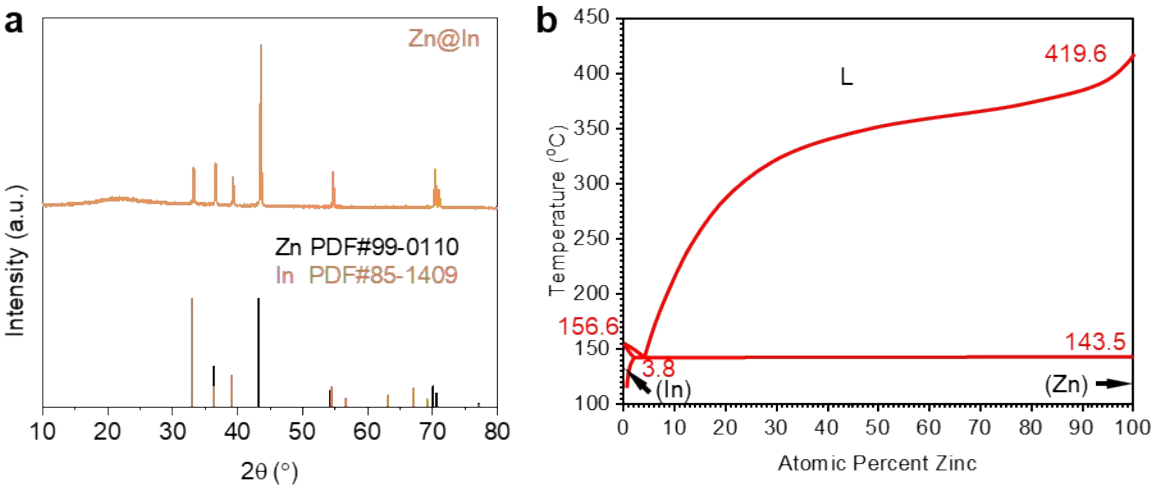

Fig. S2. a) XRD pattern of Zn@In. b) Phase diagrams of Zn with indium. [7]

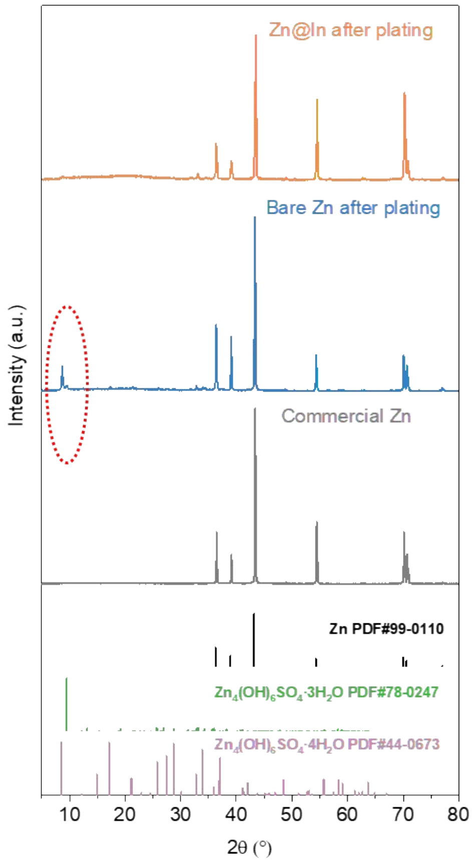

Fig. S3. XRD patterns of commercial Zn foil, bare Zn and Zn@In after plating.

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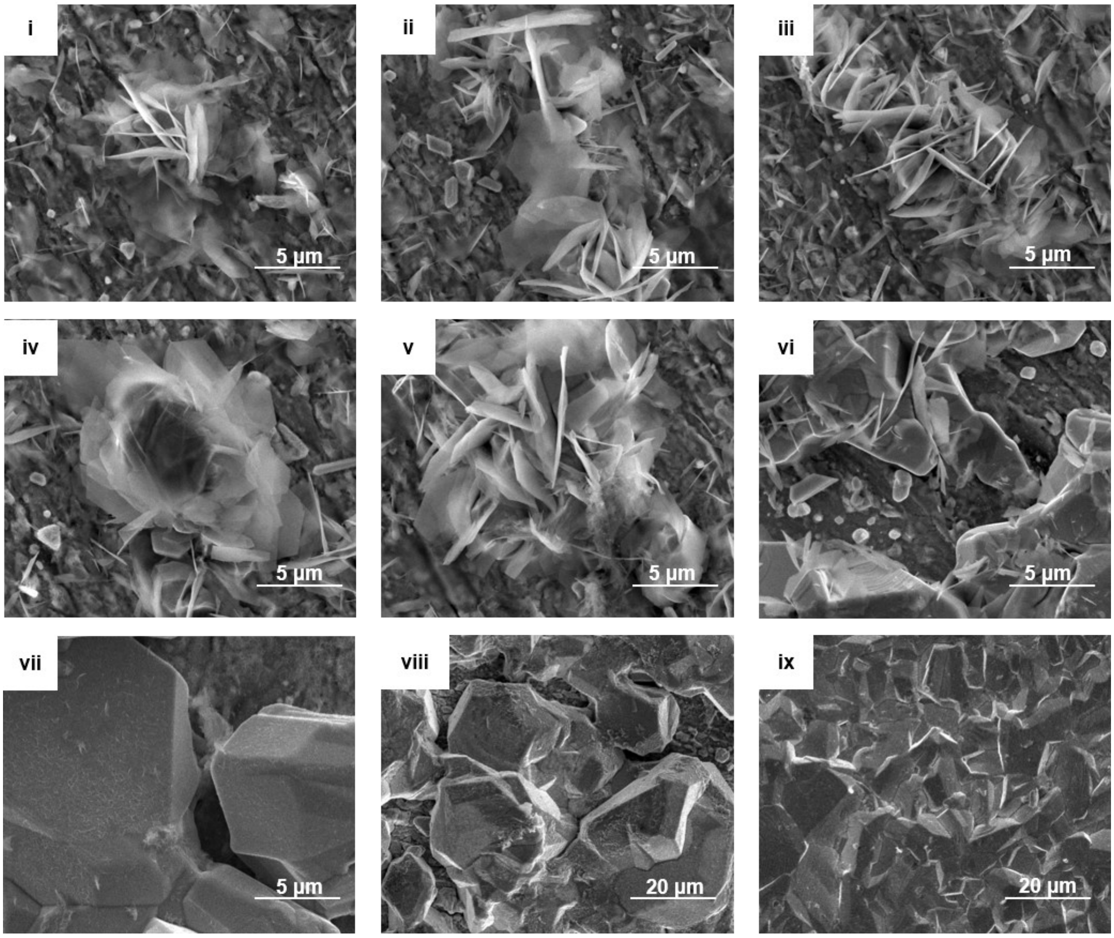

Fig. S4. SEM images of Zn deposits evolution at different growth states along with different deposition capacities at a current density of 2 mA cm^{-2} on Zn@In anode.

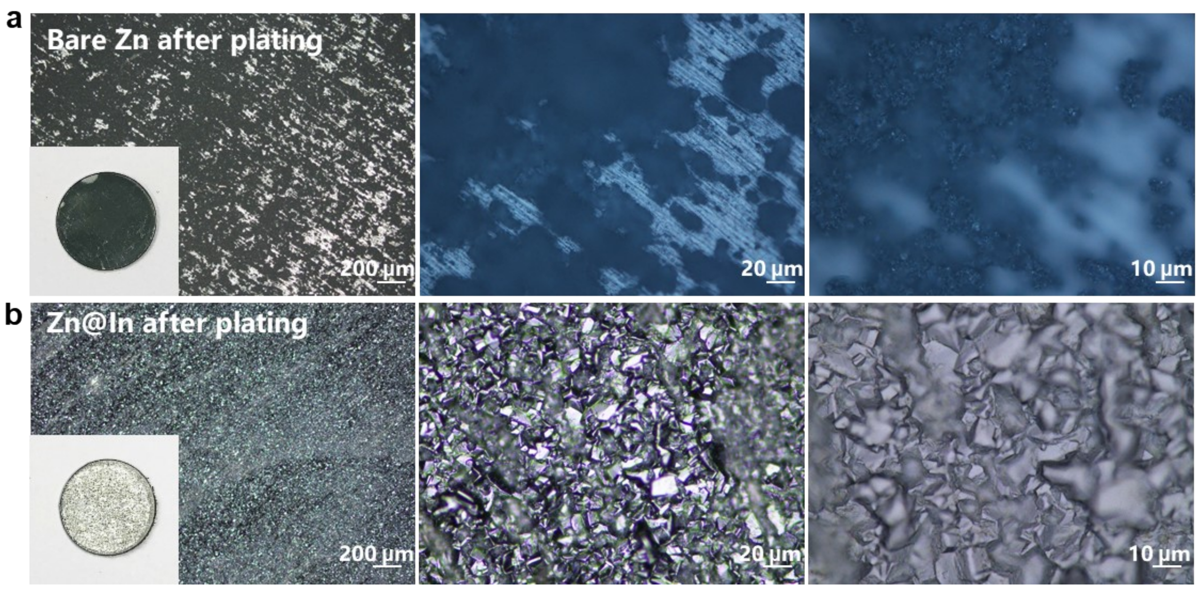

Fig. S5. Optical microscope images of the a) bare Zn and b) Zn@In after plating at a current density of 2 mA cm^{-2} for 1 h at different magnifications.

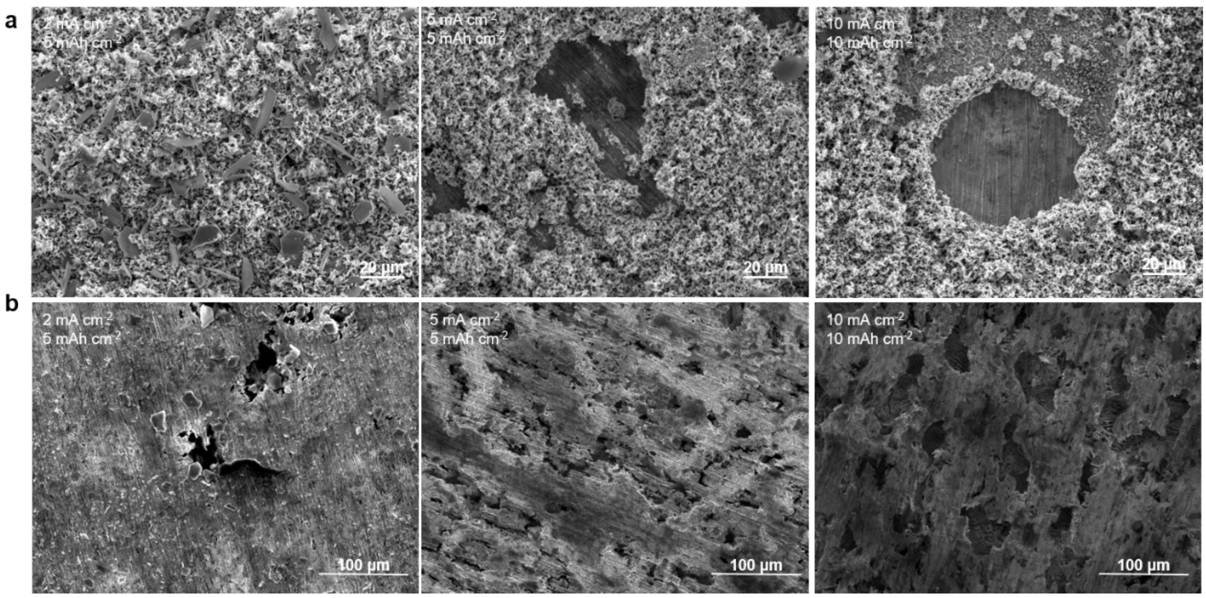

Fig. S6. SEM images of bare Zn a) after plating; and b) after stripping at the selected current density.

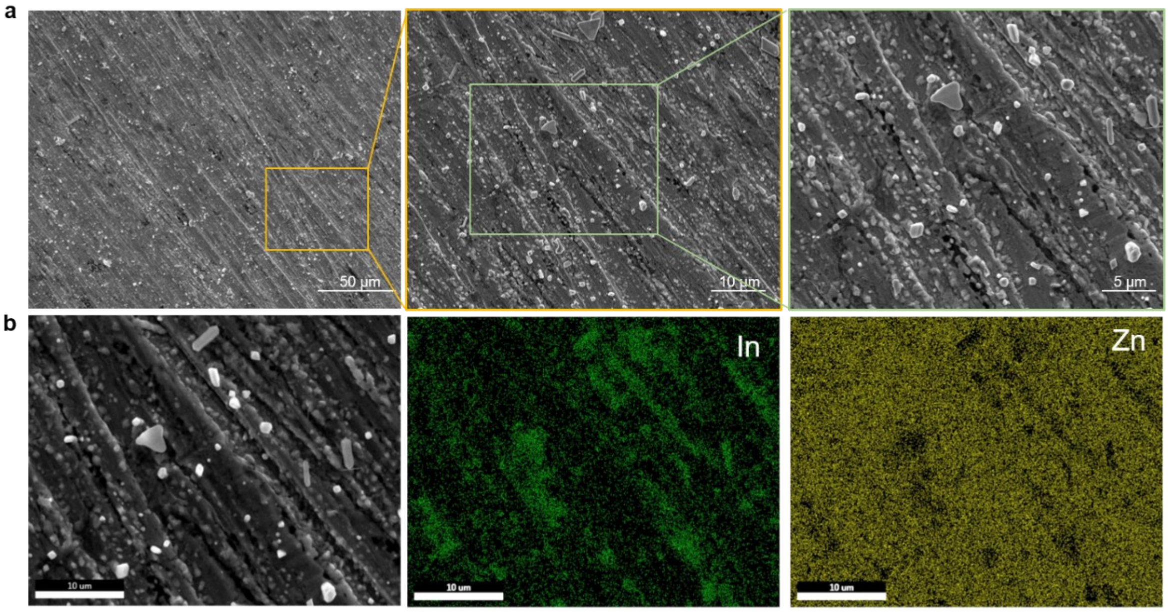

Fig. S7. Top-view SEM and corresponding EDS elemental mapping images of Zn@In.

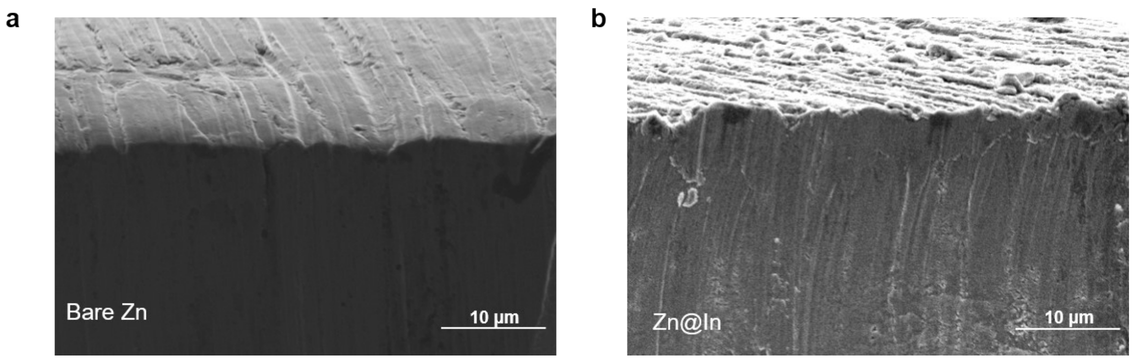

Fig. S8. Cross-section SEM images of a) bare Zn and b) Zn@In anode.

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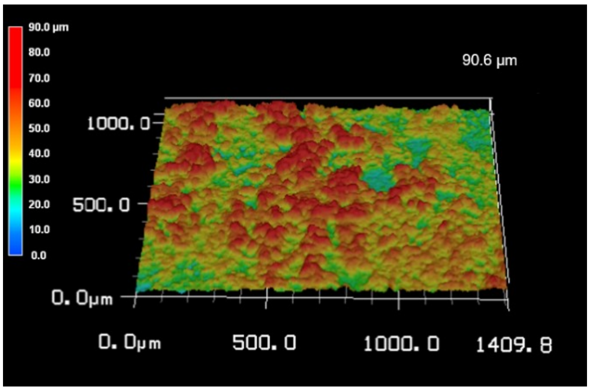

Fig. S9. CLSM optical images for bare Zn after 30 cycles.

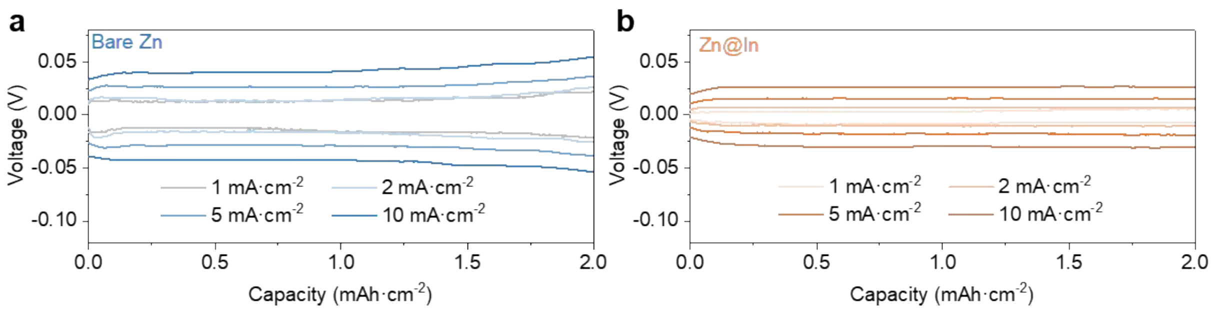

Fig. S10. The voltage hysteresis profiles of a) bare Zn and b) Zn@In at selected current density.

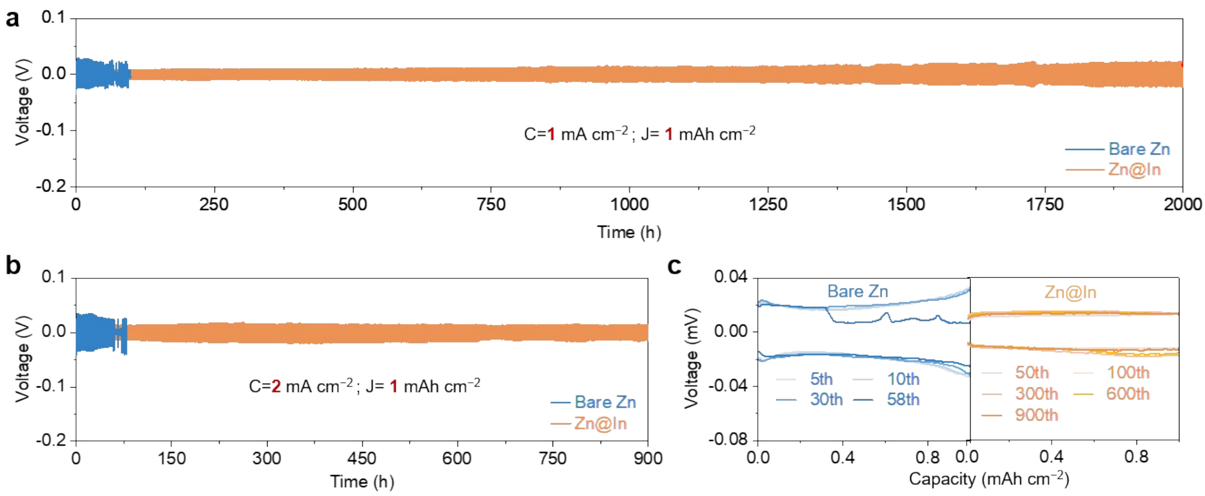

Fig. S11. Long-term galvanostatic cycling performance of Zn||Zn symmetric cells at a) 1 mA cm^{-2} for 1 mAh cm^{-2}; and b) 2 mA cm^{-2} for 1 mAh cm^{-2}; c)the corresponding voltage hysteresis profiles of bare Zn and Zn@In at the current density of 2 mA cm^{-2}.

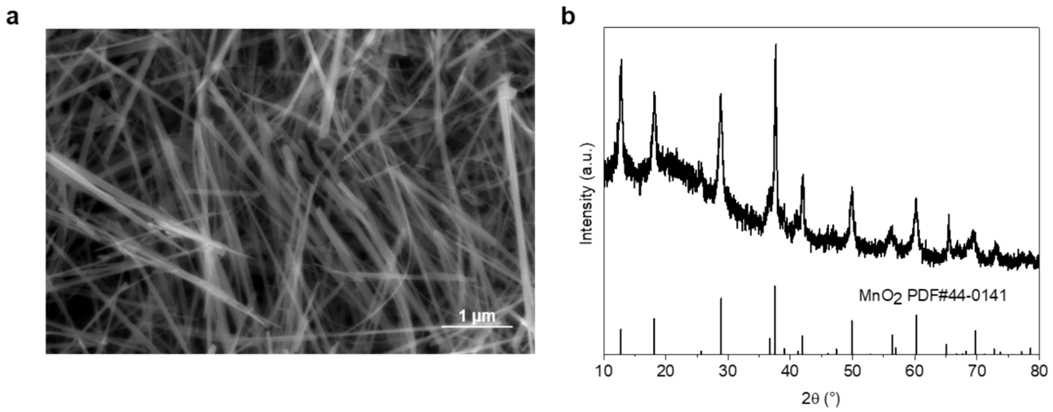

Fig. S12. a) SEM images and b) XRD patterns of the prepared MnO_2.

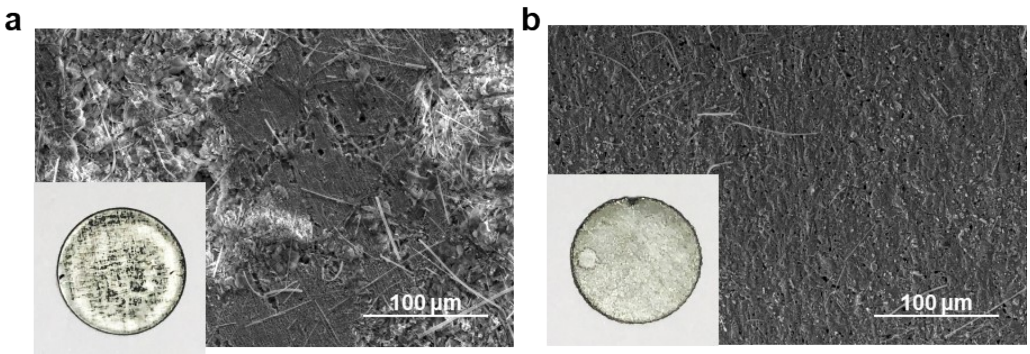

Fig. S13. Optical images and corresponding SEM images of a) bare Zn and b) Zn@In after 300 cycles.

Table S1 Comparison in voltage hysteresis and cycling life between our Zn@In electrode and previously reported Zn metal electrodes on Zn symmetric cells.

Sample	Electrolytes	Current density areal capacity	Voltage hysteresis at 1st cycle	Cycling life	Reference
Zn@In	**2 M $ZnSO_4$**	**1 mA cm^{-2} 0.5 mAh cm^{-2}; 1 mA cm^{-2} 1mAh cm^{-2}**	**18 mV**	**9400 h; 2000 h**	**This work**
Nano-$CaCO_3$-coated Zn	3 M $ZnSO_4$ + 0.1 M $MnSO_4$	1 mA cm^{-2} 0.1 mAh cm^{-2}	70 mV	80 h	Adv. Energy Mater. 2018, 8, 1801090.
MXene-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	100 mV	150 h	Angew. Chem. Int. Ed. 2020, 60, 2861.
502-coated Zn	2 M $ZnSO_4$	0.5 mA cm^{-2} 0.25 mAh cm^{-2}	50 mV	800 h	Energy Storage Mater. 2021, 36, 132.
Indium hydroxide sulfate-coated Zn	3 M $ZnSO_4$	1 mA cm^{-2} 0.5 mAh cm^{-2}	40 mV	700 h	J. Am. Chem. Soc. 2021, 143, 3143.
Montmorillonite-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 0.25 mAh cm^{-2}	45 mV	1000 h	Adv. Energy Mater. 2021, 11, 2100186.
Nafion-Zn-X-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 0.5 mAh cm^{-2}	~30 mV	1000 h	Angew. Chem. Int. Ed. 2020, 59, 16594.
$NaTi_2(PO_4)_3$-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	~45 mV	260 h	Adv. Funct. Mater. 2020, 30, 2004885.
F-TiO_2-coated Zn	0.5 M $Zn(CH_3COO)_2$	1 mA cm^{-2} 1 mAh cm^{-2}	20 mV	460 h	Nat. Commun. 2020, 11, 3961.
Zn|In	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	120 mV	500 h	Small 2020, 16, 2001736.
C-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	100 mV	400 h	Adv. Energy Mater. 2020, 10, 1904215.
ZnF_2-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	~30 mV	800 h	Adv. Mater. 2021, 33, 2007406.
COF-coated Zn	2 M $ZnSO_4$	1 mA cm^{-2} 1 mAh cm^{-2}	36 mV	420 h	Adv. Mater. 2021, 33, 2101726.

3. Reference

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[6] B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* **1999**, *59*, 7413.
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