Supplementary information

Dendrite-free Zn anode induced by Sn/NC towards highly efficient Zn-ion battery

Mingyue Wang,[a,c] Shuoshuo Ban,[c] Nanzhe Li,[c] Shengxiang Chen,[c] Mingfu Ye,[c] Jiannan Zhu,*[b] Wenhai Wang*[a,c] and Konglin Wu*[c]

[a]School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, China

[b]Anhui Nandu Huabo New Material Technology Co., Ltd, Fuyang 236500, China

[c]Institute of Clean Energy and Advanced Nanocatalysis (iClean), School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China

*Corresponding authors.

E-mail addresses: wenhaiwang@ahut.edu.cn (W. Wang); zhujiannan0516@163.com (J. Zhu); klwuchem@ahut.edu.cn (K. Wu)

Experimental section

Chemicals

Stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99.0%, Macklin), Urea (CH_4N_2O, 99%, Aladdin), Glucose ($C_6H_{12}O_6$, >99.5%, Aladdin), Sodium borohydride ($NaBH_4$, >98%, Aladdin), Methanol (CH_3OH, 99.5%, Scharlau), Ethanol (CH_3CH_2OH, 99.5%, Scharlau), Water (H_2O, Wahaha Group Co., Ltd), Carbon black (Super P, Timcal), N-Methylpyrrolidone (C_5H_9NO, NMP, 98%, Shanghai Haohong Biomedical Technology Co., Ltd), Polyvinylidene difluorideShandong ($(CH_2CF_2)_n$, PVDF, Shandong Xiya Chemical Co., Ltd), Zinc sulfate ($ZnSO_4$, 99%, Shanghai Haohong scientific Co., Ltd), Manganese sulfate ($MnSO_4$, 99%, Macklin), Ammonium persulphate($(NH_4)_2S_2O_8$, ≥98%, Aladdin), Potassium hydroxide (KOH, ≥99.99%, Aladdin), Sodium sulfate anhydrous (Na_2SO_4, ≥99%, Aladdin), Carbon paper (HCP010N, 0.1 mm, Shanghai Hesen Electric Co., Ltd), Zn foil (0.1mm, Qinghe County Yufa Metal Business Co., Ltd), Cu foil (0.1 mm, Jiangxi Copper Technology Co., Ltd) Glass fiber (GF-A2916, 290 μm, ChongQing Olegeeino Technology Co., Ltd).

Materials synthesis

Synthesis of NC: 10 g urea was placed in a furnace under air atmosphere at 550 °C (ramp: 5 °C min^{-1}) for 4 h to achieve g-C_3N_4. Then 0.375 g g-C_3N_4 was added in 30 mL glucose solution (0.3 M). After sonicating for 6 h, the dispersion was subjected to a hydrothermal reaction (180 °C for 10 h). The achieved product (g-C_3N_4/C) was dried in an oven (70 °C) for 12 h after being individually washed three times with water and ethanol. Finally, g-C_3N_4/C was pyrolyzed in N_2 atmosphere at 900 °C for 1 h to obtain N-doped carbon (NC).

Synthesis of Sn/NC: 30 mg NC was put in a solution containing 140 mg $SnCl_2$ and 30 mL methanol and the mixture was subsequently exposed to ultrasound for 3 h. Then a solution consisting of 160 mg $NaBH_4$ and 2 mL methanol was rapidly introduced in the above mixture. After keeping the reaction for 20 min, the product underwent multiple methanol washes and was dried for 12 h in an oven (70 °C).

Synthesis of MnO_2: 50 mL $MnSO_4$ solution (0.2 M) was put in a 50 mL mixed solution (0.2 M $(NH_4)_2S_2O_8$ + 0.16 M KOH) and the reaction was held for 24 h. The final product was dried in an oven (70 °C) for 12 h after being respectively washed three times with water and ethanol.

Characterization

Scanning Electron Microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F20) were utilized to study the morphologies of samples. The phase composition was analyzed by X-ray diffraction equipment (XRD, Bruker D8 Advance) with Cu K_α radiation. The Sn content of Sn/NC was implemented Thermogravimetric analysis (TGA, NETZSCH STA 449 C) under air atmosphere with 10 °C min^{-1}. The chemical states of products were inspected by X-ray Photoelectron Spectroscopy (XPS, PHI Quantera SXM). Raman spectra were achieved from Renishaw inVia plus with 633 nm laser. N_2 adsorption/desorption measurements were implemented by Micromeritics ASAP 2460.

Electrochemical performance

To prepare modified Zn anodes, Sn/NC (or NC) and PVDF were introduced in NMP with a fixed mass ratio (9:1). The slurry was then cast onto bare zinc anodes (BZn) and these Zn anodes were dried for 24 hours at 70 °C in an oven. The loading of Sn/NC or NC on BZn was 1.0 mg cm^{-2}. All battery measurements were conducted with Swagelok cells and these cells were constructed in air. Symmetric cells were fabricated with Zn-based electrodes as electrodes, glass fiber as the separator and 2 M $ZnSO_4$ as the electrolyte. Asymmetric cells were assembled with Cu foil as the cathode, Zn-based electrodes as the anode, glass fiber as the separator and 2 M $ZnSO_4$ as the electrolyte. Full cells were constructed with MnO_2 as the cathode, Zn-based electrodes as the anode, glass fiber as the separator and a mixed solution (2 M $ZnSO_4$+0.2 M $MnSO_4$) as the electrolyte. The cathode was fabricated with MnO_2, Super P and PVDF were mixed in NMP with a mass ratio (7:2:1). Then the slurry was coated on carbon paper and the slurry coated carbon paper was put in an oven (70 °C) for 24 h. The loading of MnO_2

on carbon paper was ~1.0 mg cm^{-2} and the mass of MnO_2 was applied to calculate the capacity of the full cell. The HER activities of Sn/NC@Zn, NC@Zn and BZn were implemented in a three-electrode system, where Zn based electrodes, graphite rod and Ag/AgCl were respectively employed as the working electrode, the counter electrode and the reference electrode. Linear sweep voltammetry (LSV) was conducted in N_2 saturated 1 M Na_2SO_4 with a scan rate of 5 mV s^{-1}. Cyclic voltammetry (CV), LSV and chronoamperometry measurements were performed with a CHI760E electrochemical workstation. The galvanostatic discharge/charge measurements were undertaken with a battery testing system (Neware CT3001A).

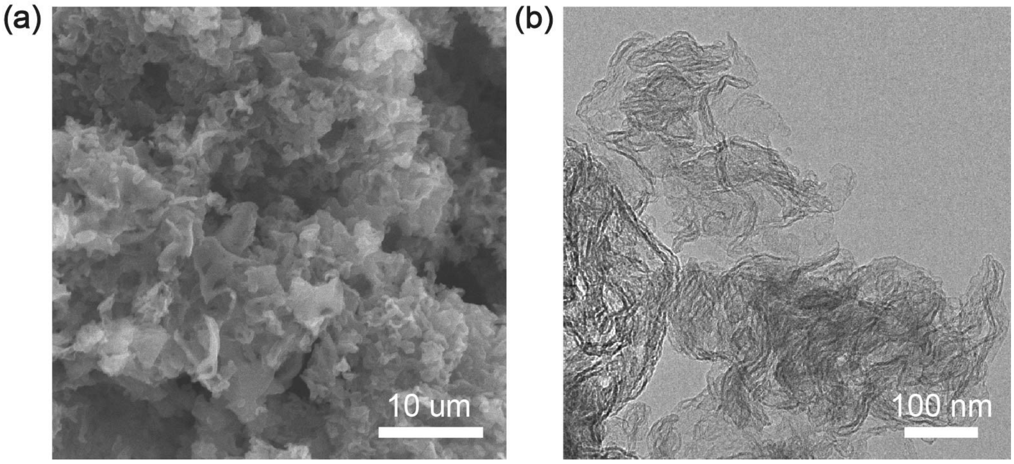

Fig. S1. (a) SEM image of NC and (b) TEM image of NC.

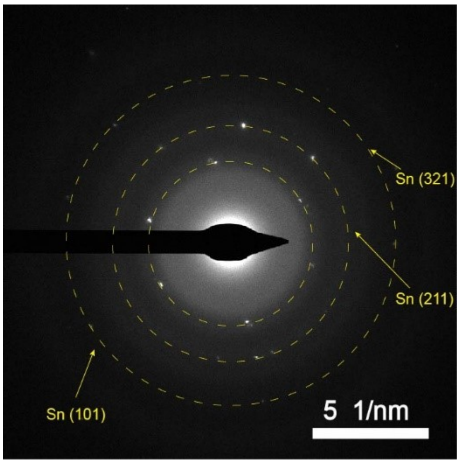

Fig. S2. SAED image of Sn/NC.

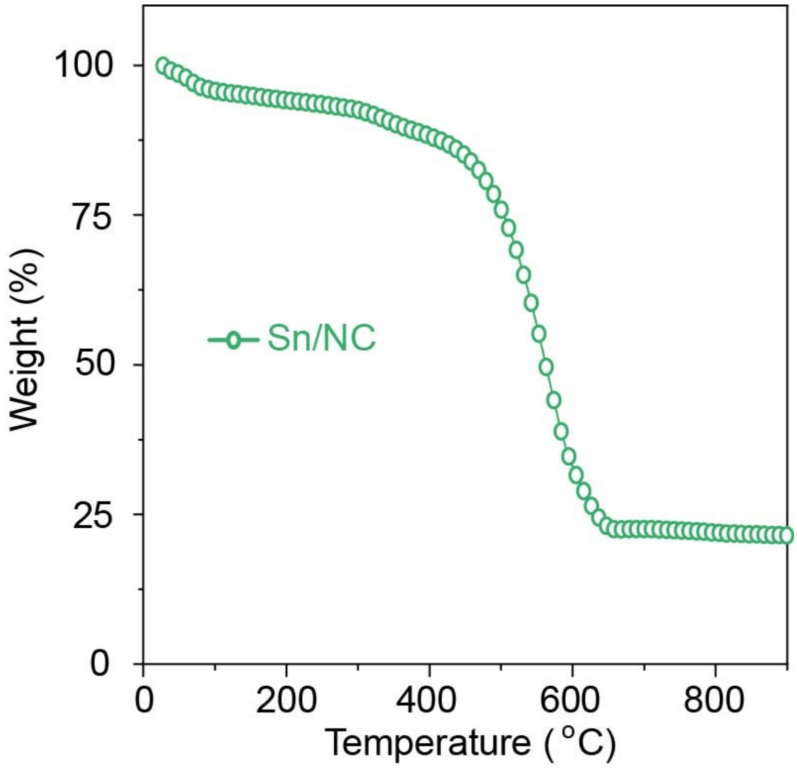

Fig. S3. TG curves of Sn/NC.

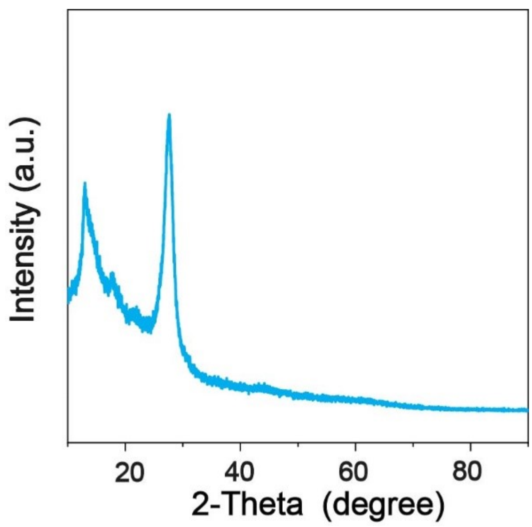

Fig. S4. XRD pattern of g-C_3N_4.

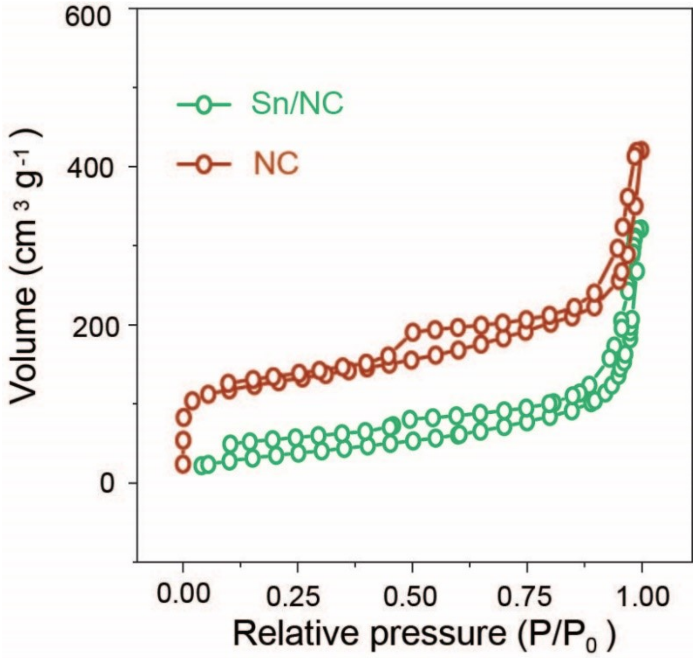

Fig. S5. Nitrogen adsorption/desorption isotherms of Sn/NC and NC.

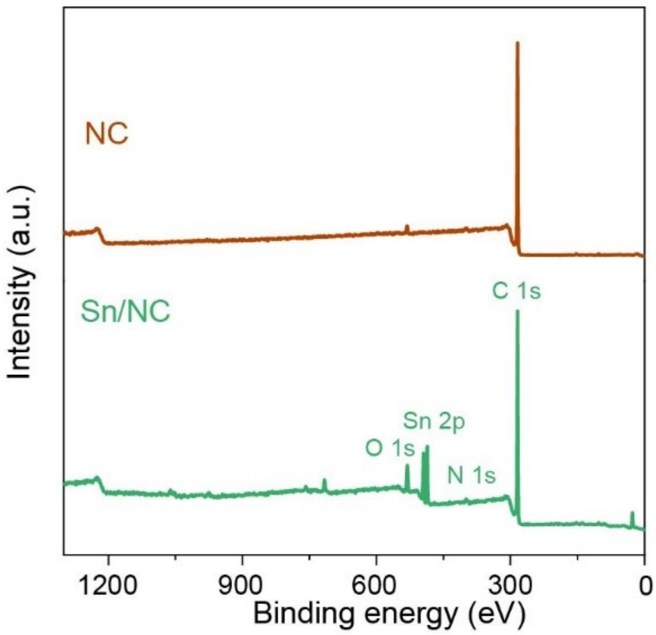

Fig. S6. Full XPS spectra of Sn/NC and NC.

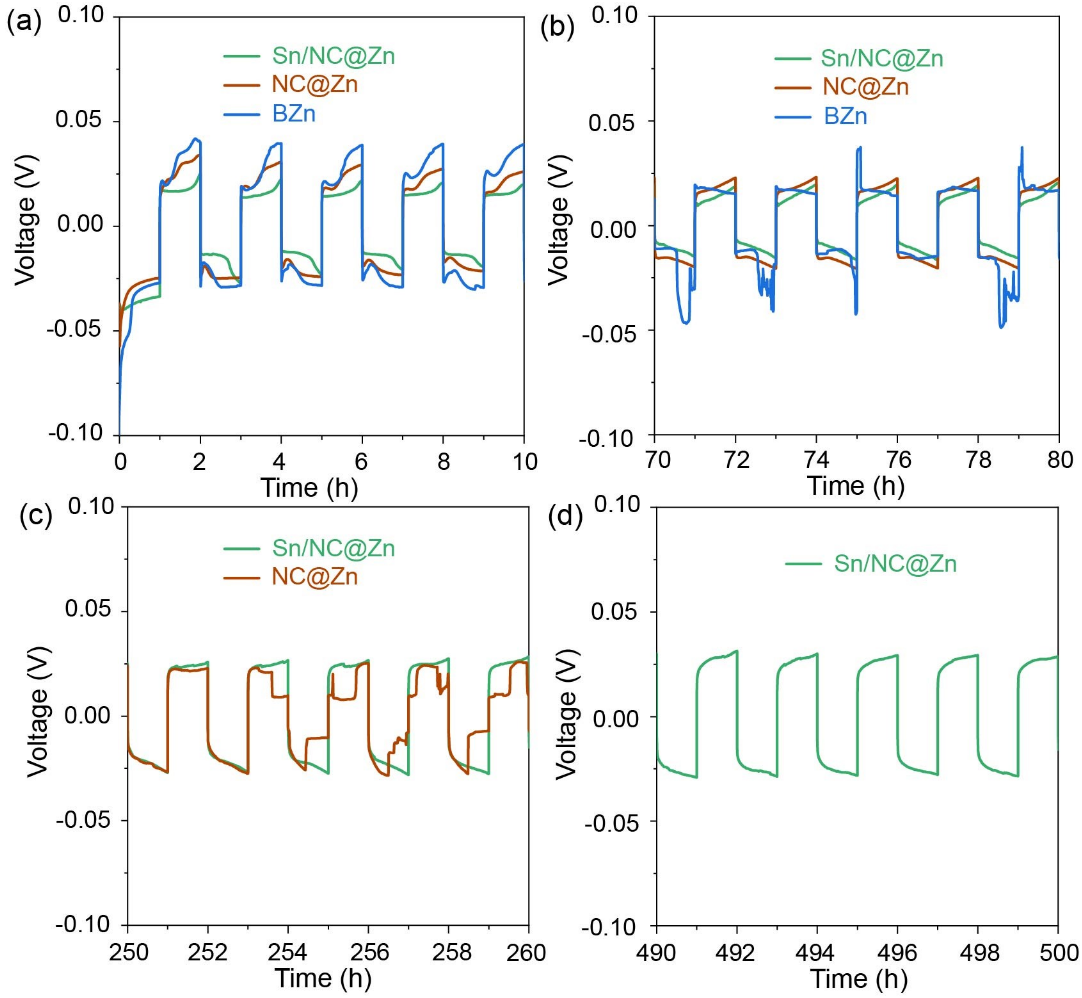

Fig. S7. Magnified regions of symmetric cells at 1 mA cm^{-2} with 1 mAh cm^{-2}: (a) 0 to10 h; (b) 70 to80 h; (c) 250 to260 h; (d) 490 to500 h.

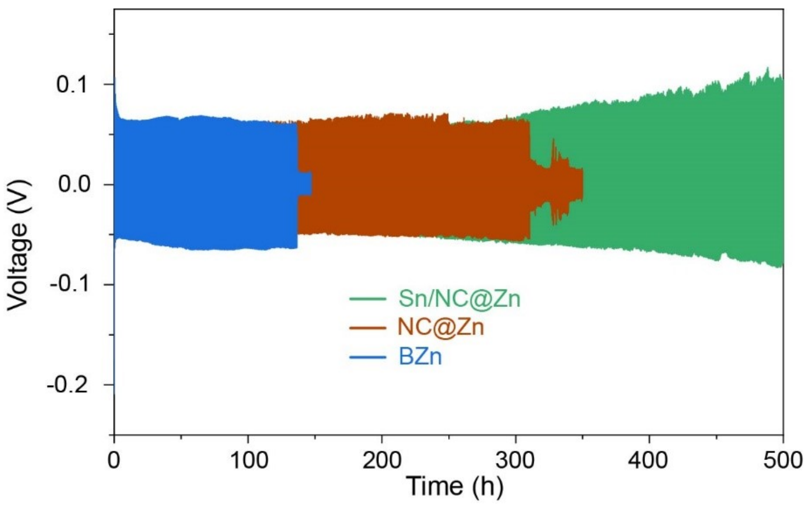

Fig. S8. Symmetric cells at 5 mA cm^{-2} with a capacity of 1 mA h cm^{-2}.

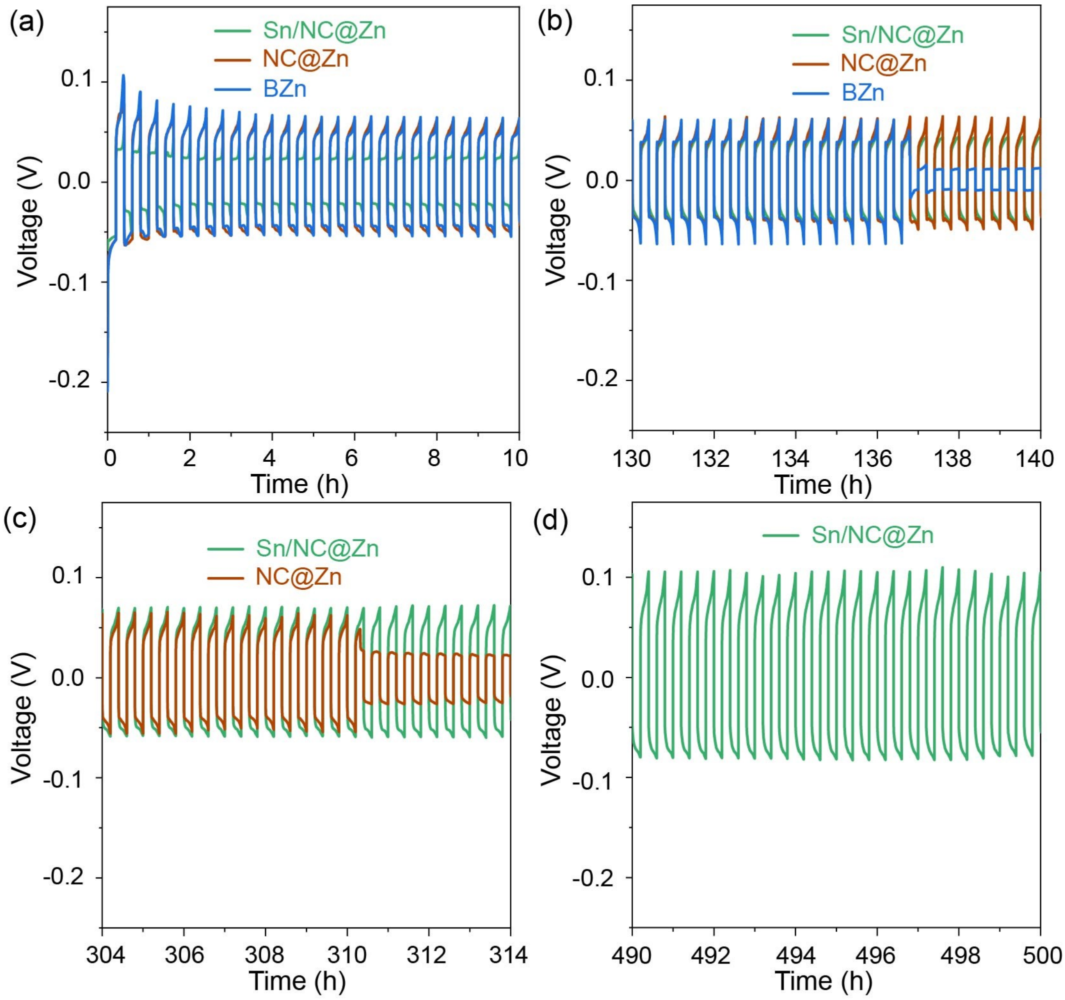

Fig. S9. Magnified regions of symmetric cells at 5 mA cm^{-2} with 1 mAh cm^{-2}: (a) 0 to10 h; (b) 130 to 140 h; (c) 304 to 314 h; (d) 490 to 500 h.

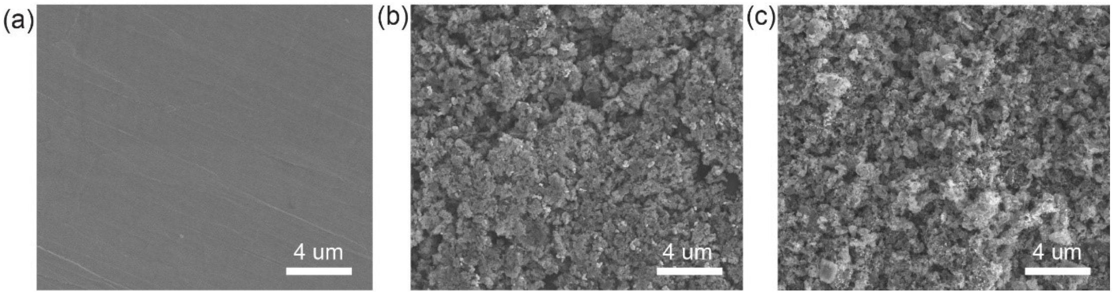

Fig. S10. SEM images of pristine electrodes: (a) bare Zn, (b) NC@Zn and (c) Sn/NC@Zn.

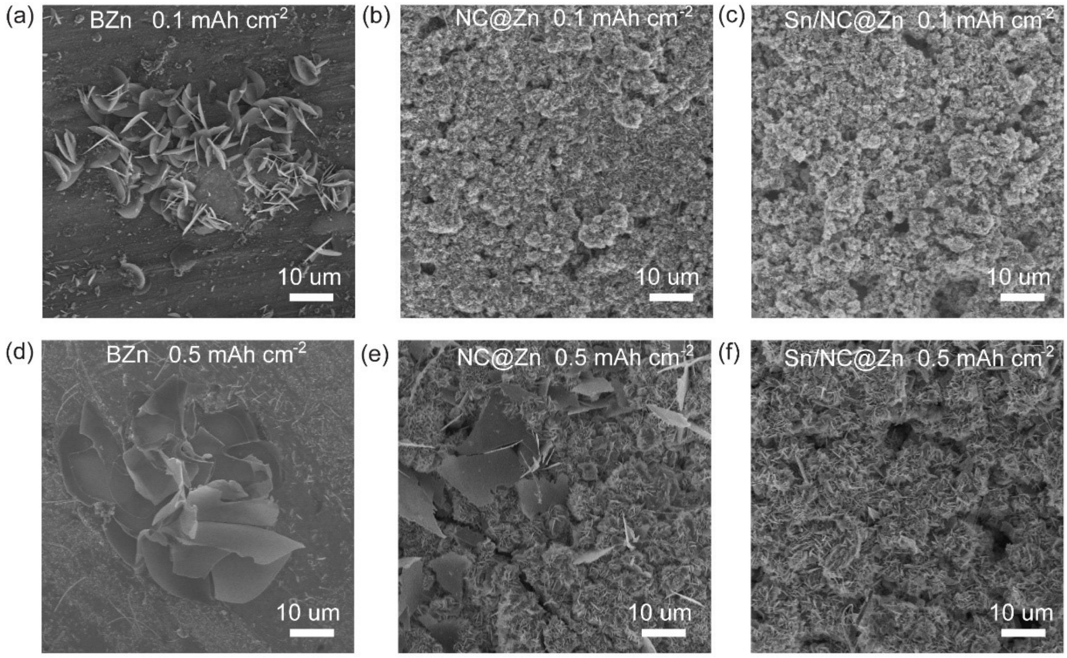

Fig. S11. SEM images of electrodes at 1 mA cm^{-2} after plating Zn with various capacities: (a, d) BZn, (b, e) NC@Zn and (c, f) Sn/NC@Zn.

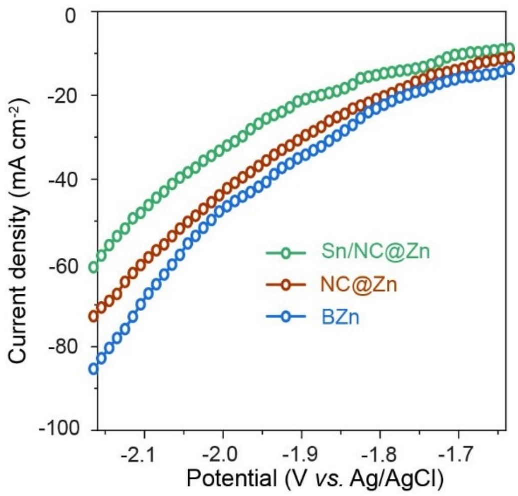

Fig. S12. LSV curves of Zn based electrodes for HER.

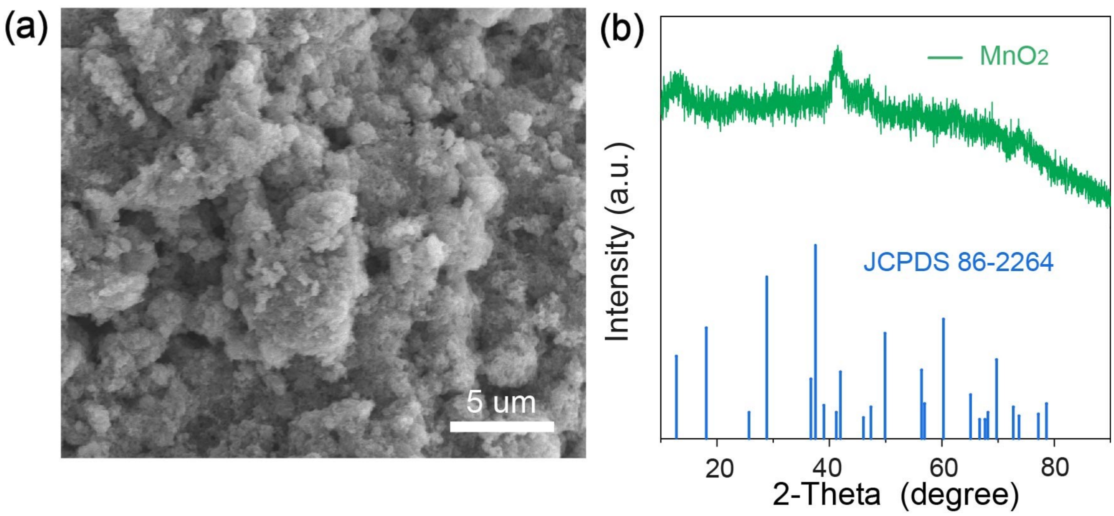

Fig. S13. Characterization of MnO_2: (a) SEM image and (b) XRD pattern.

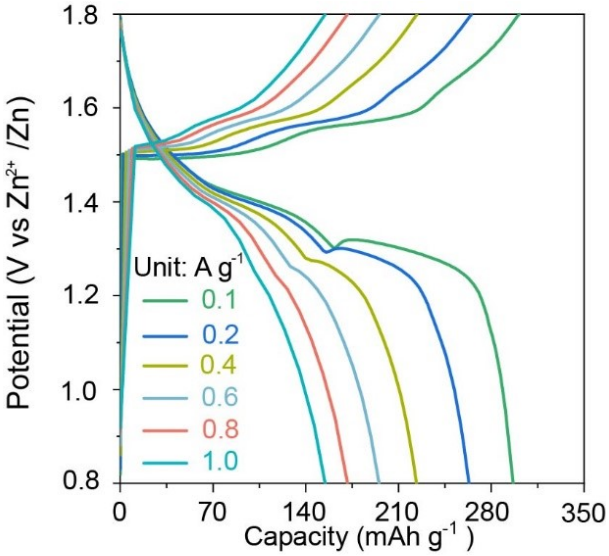

Fig. S14. Galvanostatic discharge/charge profiles of BZn at different current densities.

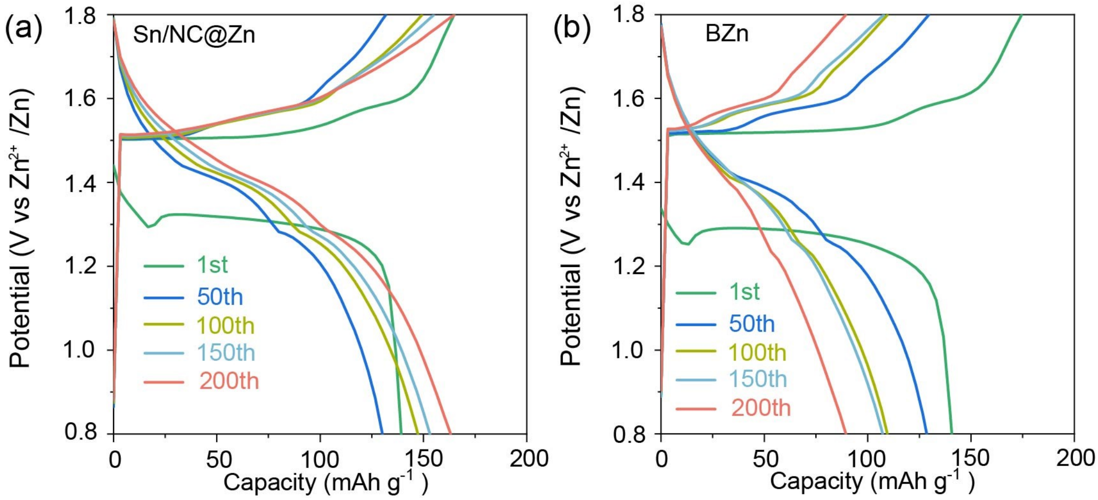

Fig. S15. Galvanostatic discharge/charge profiles at 0.4 A g^{-1}: (a) Sn/NC@Zn; (b) BZn.

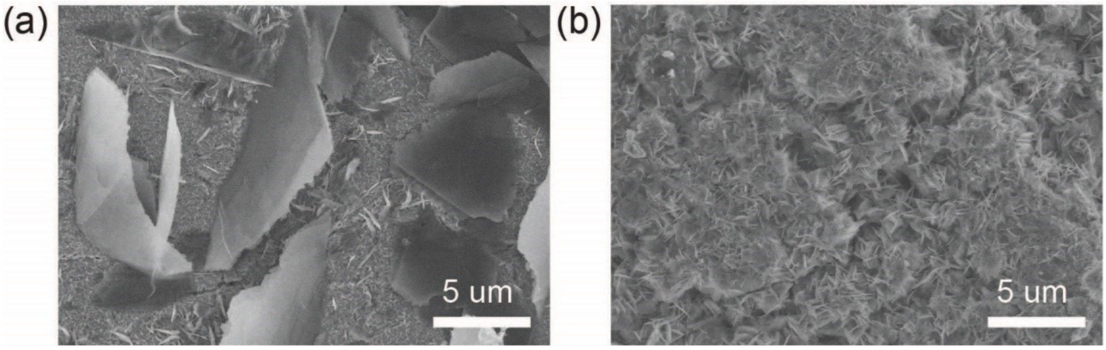

Fig. S16. SEM images of anodes after 50 cycles at 0.4 A g^{-1}: (a) BZn; (b) Sn/NC@Zn.

Table S1. Comparison of electrochemical performances of Sn/NC@Zn with reported anodes in symmetric cells.

Electrode	Current density (mA cm^{-2})	Capacity (mAh cm^{-2})	Cycle time (h)	Voltage hysteresis (mV)	Reference
Sn/NC@Zn	1	1	500	56	This work
At-Sn@HCN @Zn	1	1	150	~50	1
CNT@Zn	0.5	0.15	400	80	2
O, N-CC@Zn	1	1	320	~50	3
MOF-PVDF/Zn	1	0.5	500	90	4
ZnSn-1	1	1	400	~150	5
Zn@ZnF_2	0.5	1	400	50	6
Lignin@ Nafion/Zn	0.2	0.1	376	82	7
100TiO_2@Zn	1	1	150	81.8	8
Zn@ZnO HPA-2.0	1	1	400	~150	9
MXene@Zn	1	1	150	~50	10
ZF@F-TiO_2@Zn	1	1	460	42	11
60alucone@ Zn	1	1	500	46	12

References

1. X. Zhang, C. Qu, X. Zhang, X. Peng, Y. Qiu, Y. Su, J. Zeng, Z. Liu, X. Liu, W. Qi, H. Wang and F. Xu, *Adv. Energy Mater.*, 2024, **14**, 2401139.
2. M. Li, Q. He, Z. Li, Q. Li, Y. Zhang, J. Meng, X. Liu, S. Li, B. Wu, L. Chen, Z. Liu, W. Luo, C. Han and L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1901469.
3. M. Zhou, G. Sun and S. Zang, *J. Energy Chem.*, 2022, **69**, 76-83.
4. M. Liu, L. Yang, H. Liu, A. Amine, Q. Zhao, Y. Song, J. Yang, K. Wang and F. Pan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 32046-32051.
5. L. Wang, W. Huang, W. Guo, Z. H. Guo, C. Chang, L. Gao and X. Pu, *Adv. Funct. Mater.*, 2021, **32**, 2108533.
6. Y. Yang, C. Liu, Z. Lv, H. Yang, Y. Zhang, M. Ye, L. Chen, J. Zhao and C. Li, *Adv. Mater.*, 2021, **33**, 2007388.
7. D. Yuan, W. Manalastas, Jr., L. Zhang, J. J. Chan, S. Meng, Y. Chen and M. Srinivasan, *ChemSusChem*, 2019, **12**, 4889-4900.
8. K. Zhao, C. Wang, Y. Yu, M. Yan, Q. Wei, P. He, Y. Dong, Z. Zhang, X. Wang and L. Mai, *Adv. Mater. Interfaces*, 2018, **5**, 1800848.
9. J. Y. Kim, G. Liu, G. Y. Shim, H. Kim and J. K. Lee, *Adv. Funct. Mater.*, 2020, **30**, 2004210.
10. N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao and Z. Niu, *Angew. Chem. Int. Ed.*, 2021, **60**, 2861-2865.
11. Q. Zhang, J. Luan, X. Huang, Q. Wang, D. Sun, Y. Tang, X. Ji and H. Wang, *Nat. Commun.*, 2020, **11**, 3961.
12. H. He and J. Liu, *J. Mater. Chem. A.*, 2020, **8**, 22100-22110.