

Supplementary Information for

Building fast and selective Zn ion channels for highly stable quasi-solid-state Zn-ion batteries

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1. Materials and Experimental Methods

1.1 Chemicals. Halloysite nanotubes are provided by Andromeda Metal Ltd (Adelaide, Australia). Zn-foil (~0.01 mm) Ti mesh, and Cu-foil were purchased from Shenzhen Kejing Star Technology. Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99.5\%$), Poly(tetrafluoro ethylene) (PTFE, $(\text{CF}_2\text{CF}_2)_n$, 60wt% dispersion in water) Acrylamide (AM, $\text{CH}_2=\text{CHCONH}_2$, $\geq 99\%$), Potassium acetate (KAc, CH_3COOK , $\geq 99\%$), N,N-Ethylenebis(acrylamide) ($(\text{H}_2\text{C}=\text{CHCONHCH}_2)_2$, $\geq 90\%$), Ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\geq 98\%$) Isopropanol (IPA, $\text{C}_3\text{H}_7\text{OH}$, 70% in water), Iodine (I_2 , 99.8%) were purchased from Sigma-Aldrich Chemical Co. All chemicals were used without further purification.

1.2 Synthesis of intercalated halloysite. The halloysite was mixed and ground with KAc at 70:30 (wt:wt) by pestle and mortar. After mixed thoroughly, the mixture was exposed to the air and rested for 3 days. The as-intercalated halloysite was then washed by IPA for three times and freeze dried overnight to obtain i-HNTs.

1.3 PAM electrolyte preparation. 4 g of acrylamide was dissolved in 10 mL of 2.0 M ZnSO_4 solution with vigorous stir in an ice bath. After the solution became transparent, 5 mg of N,N-methylenebisacrylamide was added into the solution and the solution was stirred for another 30 min. After the solution was well-mixed and became clear, 30 mg of APS was added into the solution and keep stirring until dissolved. The polymerization was carried out by using ultraviolet lamp. PAM will be soaked in 2.0 M ZnSO_4 to avoid being dried. The electrolyte was pat-dried before assembly. The i-HNTs@PAM was fabricated by adding halloysite into the initial solution with a ratio of 5 mg-halloysite/ 10 mL-2.0 M ZnSO_4 .

1.4 Electrode preparation. The KB and I_2 was mixed by hand-grinding for 10 min with a weight ratio of 1: 1, then heated under 80°C for 4 h to obtain I_2 @KB. For the preparation of I_2 @KB cathode, the I_2 @KB, KB and PTFE were uniformly mixed at 8:1:1 (wt:wt:wt), and the mixture then was pressed onto Ti mesh and following with drying at 40°C for 2 h. The loading of I_2 in I_2 @KB cathode is controlled at approximately 3 mg cm^{-2} .

1.5 Characterization methods. The morphology of the halloysites was studied by Scanning Electron Microscope (FEI Quanta 450 FEG Environmental and Hitachi SU1510) and Transmission Electron Microscope (FEI Tecnai G2 Spirit). X-ray diffraction (XRD) data were collected by a Rigaku MiniFlex 600 X-ray Diffractometer ($\text{Cu K}\alpha$ $\lambda=1.5418\text{ \AA}$). The test range for XRD is $3.0^\circ \leq 2\theta \leq 80.0^\circ$ with 2° per min. Fourier infrared spectroscopy (FTIR) was collected by a Nicolet 6700 ThermoFisher spectrometer with an MCT detector. Raman spectra

were collected by a HORIBA Scientific Raman spectroscopy ($\lambda = 633$ nm). Collection time is 10 s with 3 repetition. Collection range is 300 cm^{-1} to 4000 cm^{-1} . 50x long focus object was used. Atomic absorption spectroscopy (AAS) was used to measure the Zn ion trapping behavior of i-HNT. 50 mg of i-HNT was dispersed in 10 mL of 2.0 M ZnSO_4 for two days, followed by thorough cleaning with water by centrifugation for 3 times to rinse off the residue Zn salt. The cleaned i-HNT was then dried for further use. The dried i-HNT containing Zn inside was then dissolved by aqua regia to dissolve the trapped Zn ion to the solution for AAS test. After dissolving the i-HNT into aqua regia, the solution was dilute to 100, 1000, 10000 times to fit in the working range of Zn lamp in AAS. For the AAS test, Zn lamp with wavelength of 213.9 nm was used, with working range of 0.01 – 2.00 ppm. Acetylene was used as the fuel gas and air as support gas. The standard Zn solution was used for calibration by dilution to the desired concentration, 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 ppm. The absorbance of 100x, 1000x, and 10000x diluted sample are measured.

1.6 Electrochemical measurements. The 2032-type coin-cells were used for battery testing. Zn foil is used for tests as anode. Glass fiber filter papers are used as the separator when using 2M ZnSO_4 as the electrolyte. For quasi-solid-state cells, i-HNTs@PAM or PAM will be used as electrolyte, and no separator is needed. The symmetric cells for stability tests were assembled with the Zn foil as both electrodes. The Zn//Cu cells for the Coulombic efficiency test were assembled with Cu foil as the counter electrode. For the testing of Zn- I_2 battery, the I_2 @KB cathode was matched with Zn anode, and i-HNTs@PAM or PAM were used as electrolytes. In a typical assembly process, the full batteries are assembled using 80 μL of aqueous solution and 120 μL of polymer prior to curing. The battery was tested under a voltage range of 0.6-1.6 V. All current density was calculated based on the mass of I_2 . and 1 C was defined as 211 mA g^{-1} . For the ionic conductivity test, Ti symmetric cells were used. For ion transference number test, Zn symmetric cells were used. The galvanostatic charge/discharge measurements were performed using a LANHE battery tester and the potentiostatic and EIS tests were performed by a VMP3 Multichannel potentiostatic (Biologic Inc.). The EIS measurements were carried out at 10 mV AC oscillation amplitude, over a frequency range of 100 mHz to 200 KHz.

2. Supplementary Figures

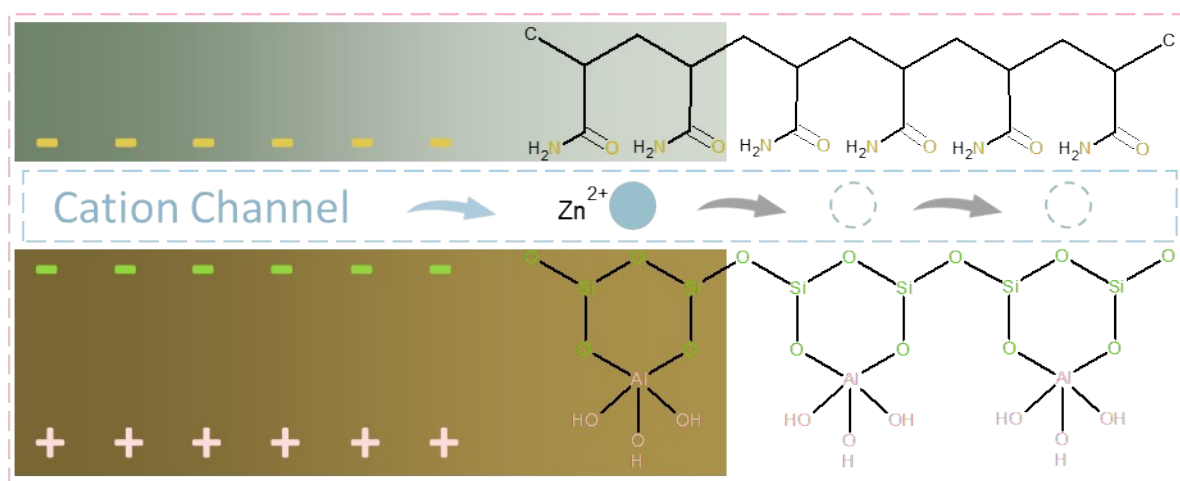


Figure S1. Schematic illustration of the ion channel formation in i-HNTs@PAM.

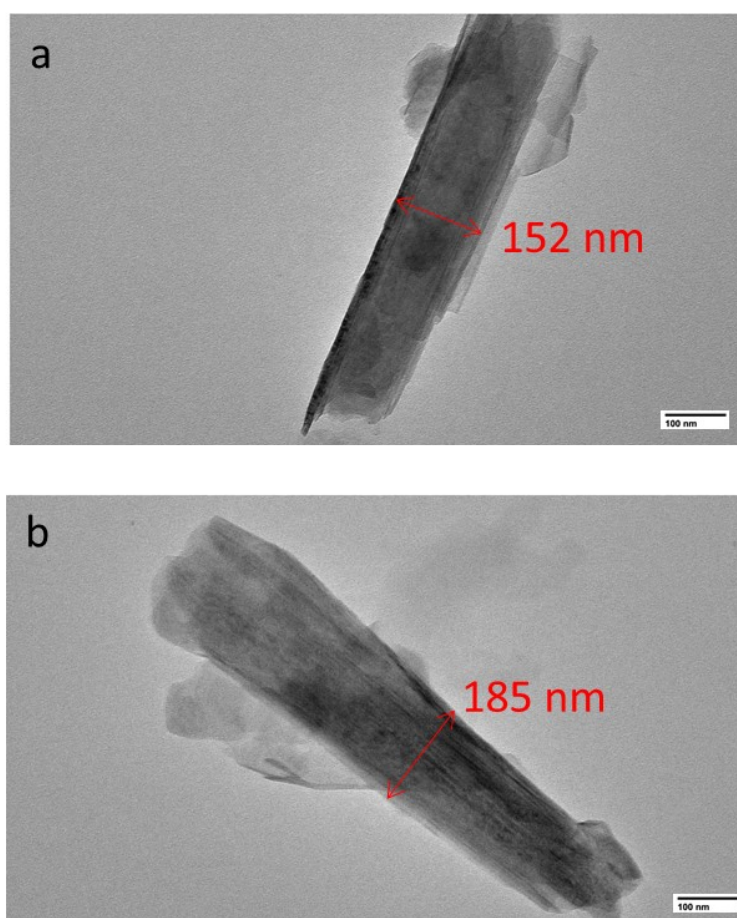


Figure S2. TEM images of pristine HNTs and i-HNTs.

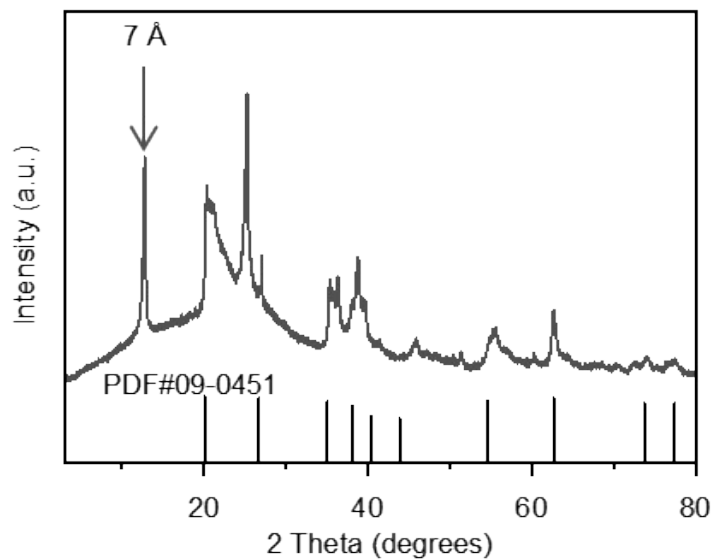


Figure S3. XRD pattern of pristine HNTs.

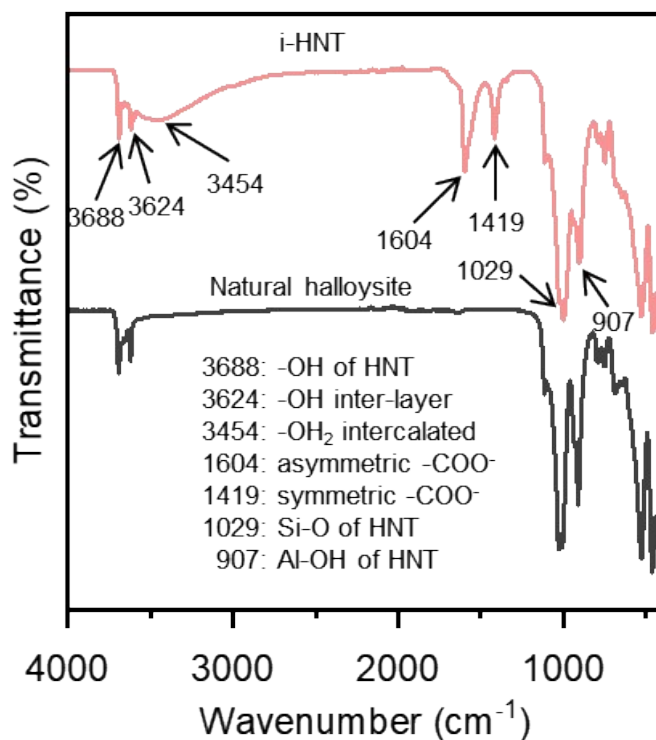


Figure S4. FTIR spectra of pristine HNT and i-HNTs. Two major bands at 3688 and 3624 cm^{-1} for hydroxyl stretching vibration of HNT can be observed. 3688 cm^{-1} is the inter-layer-OH stretching band, while 3624 cm^{-1} is assigned to inner-tubular-space -OH stretching band.¹

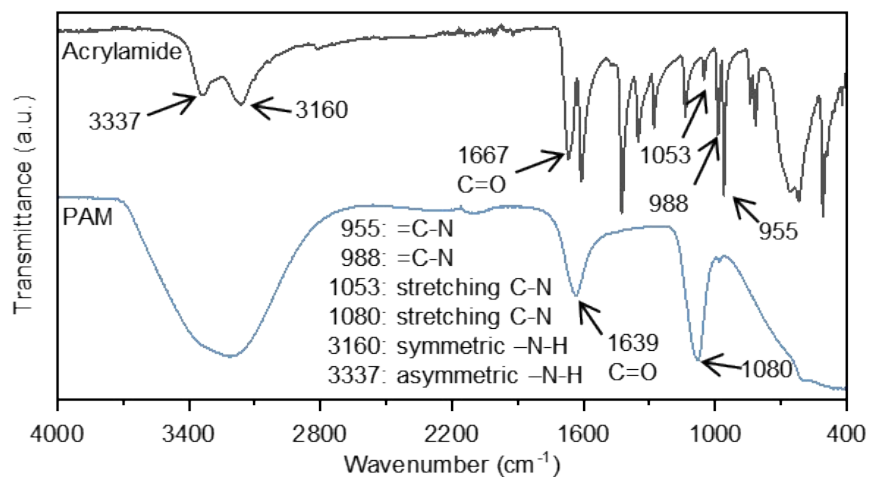


Figure S5. FTIR spectra of acrylamide and PAM. The bands at 3337 and 3160 cm⁻¹ are corresponded to N-H asymmetric and symmetric stretching vibrations. The peaks at 988 and 955 cm⁻¹ can be assigned to out-of-plane bending vibrations of =C-H.

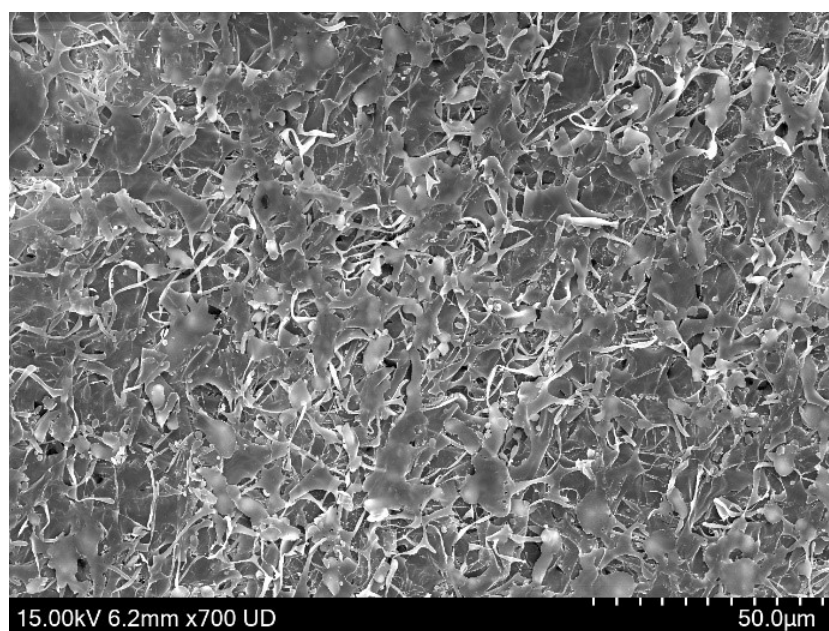


Figure S6. SEM image of PAM.

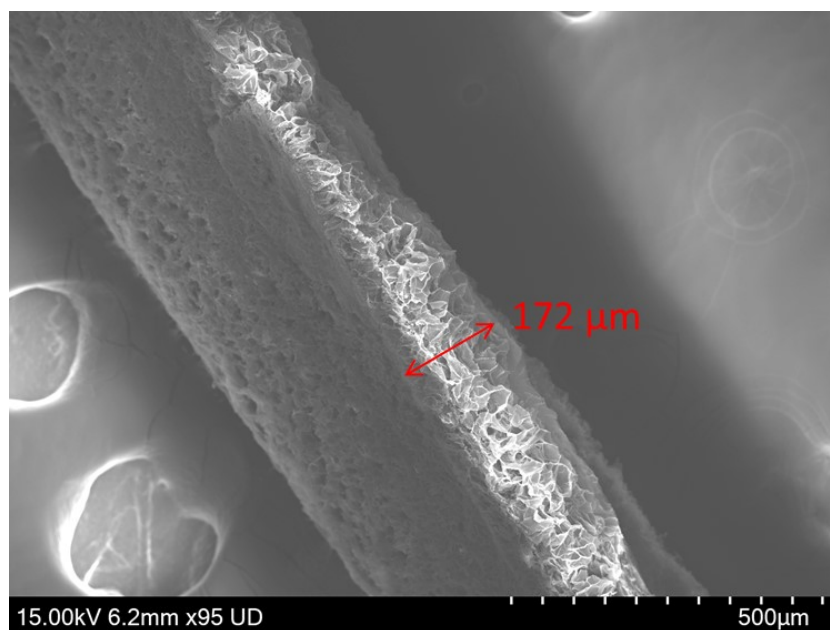


Figure S7. SEM cross-sectional view of PAM.

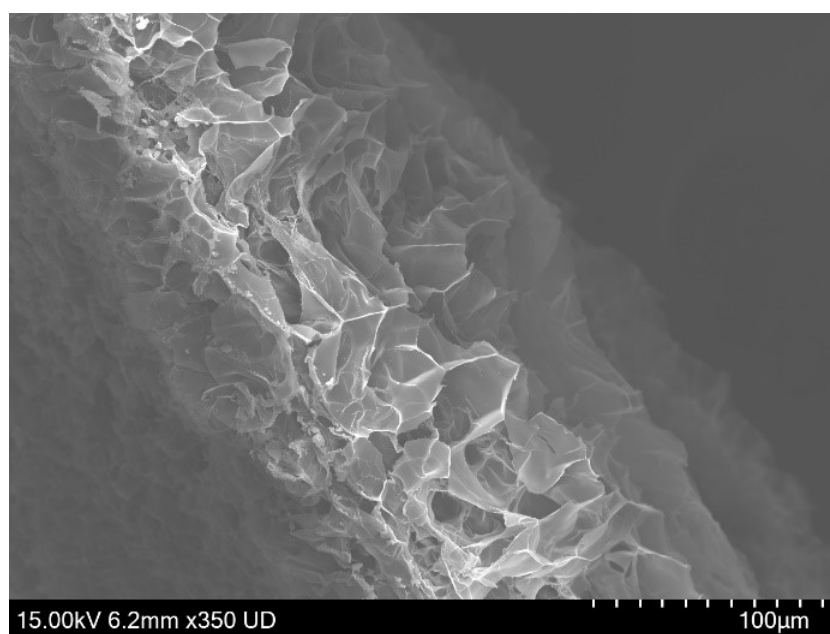


Figure S8. Enlarged SEM cross-sectional view of PAM.

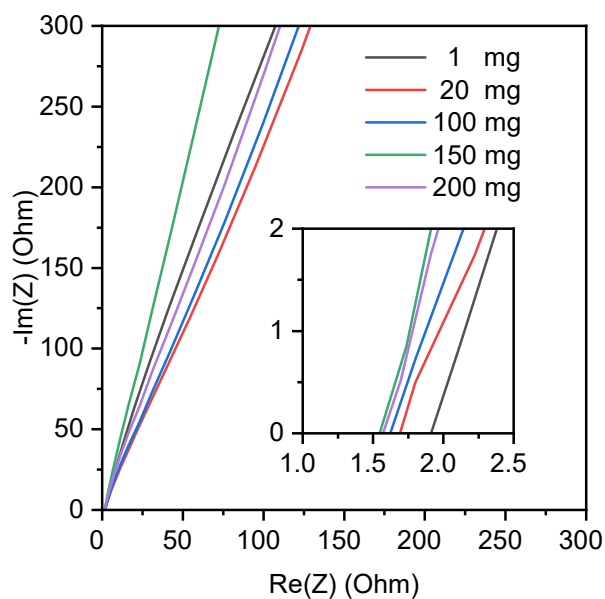


Figure S9. Nyquist plots of the Ti symmetric batteries assembled with the i-HNTs@PAM at different concentration as the electrolyte. The inset shows the resistance when the imaginary part is zero.

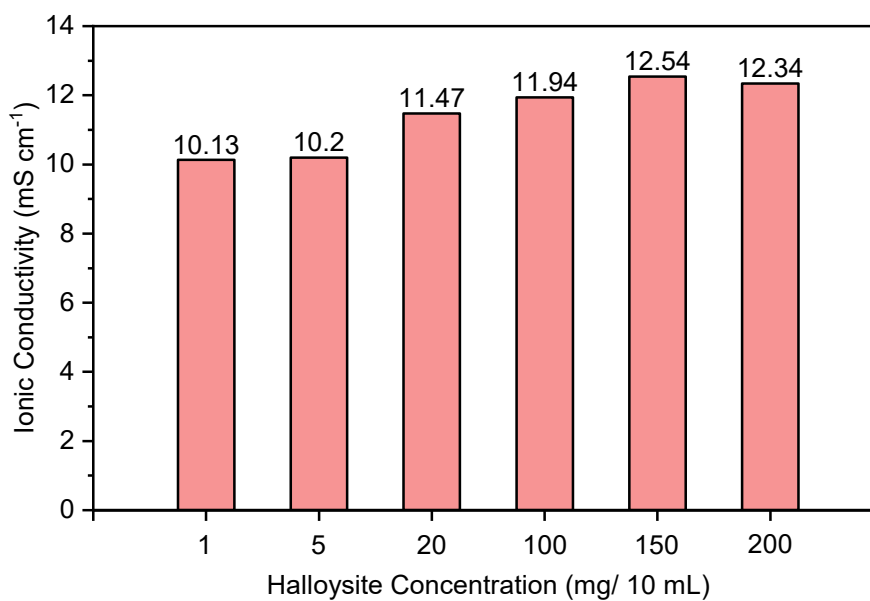


Figure S10. Corresponding ionic conductivity of i-HNT@PAM with different concentration.

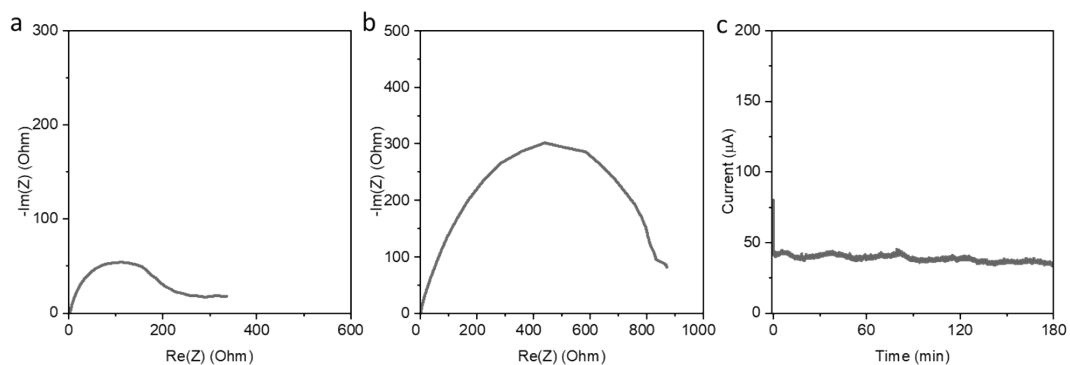


Figure S11. The EIS of the Zn symmetric battery assembled with the i-HNTs@PAM with 20 mg i-HNT in 10 mL PAM as the electrolyte at the initial state (a) and steady state(b). (c) Room temperature chronoamperometry of the same cell at a potential step of 50 mV.

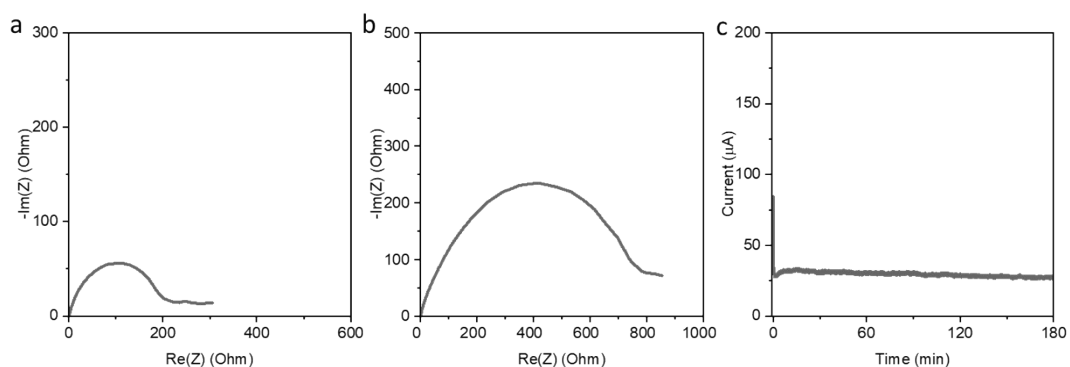


Figure S12. The EIS of the Zn symmetric battery assembled with the i-HNTs@PAM with 100 mg i-HNT in 10 mL PAM as the electrolyte at the initial state (a) and steady state(b). (c) Room temperature chronoamperometry of the same cell at a potential step of 50 mV.

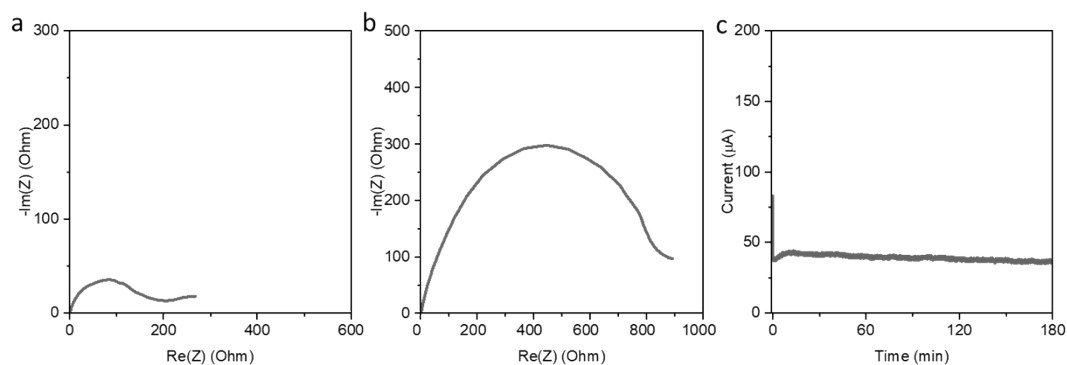


Figure S13. The EIS of the Zn symmetric battery assembled with the i-HNTs@PAM with 150 mg i-HNT in 10 mL PAM as the electrolyte at the initial state (a) and steady state(b). (c) Room temperature chronoamperometry of the same cell at a potential step of 50 mV.

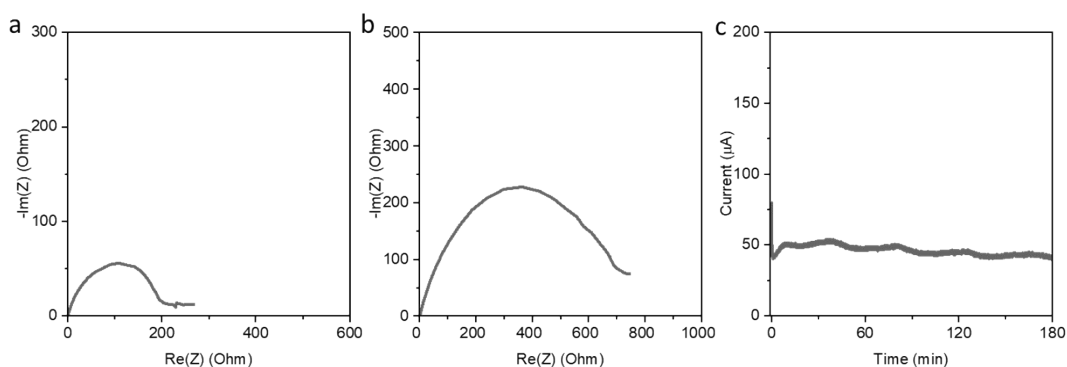


Figure S14. The EIS of the Zn symmetric battery assembled with the i-HNTs@PAM with 200 mg i-HNT in 10 mL PAM as the electrolyte at the initial state (a) and steady state(b). (c) Room temperature chronoamperometry of the same cell at a potential step of 50 mV.

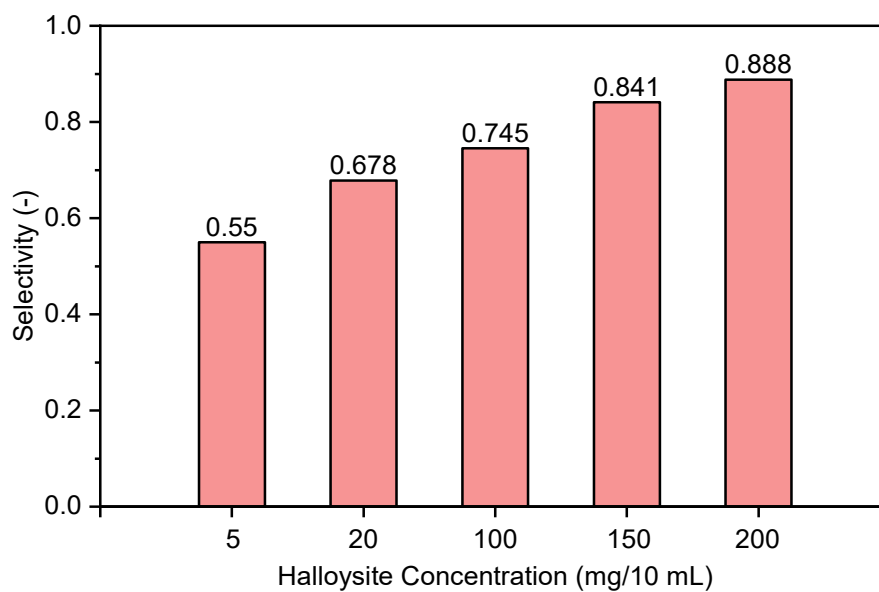


Figure S15. Corresponding selectivity of i-HNT@PAM with different concentration.

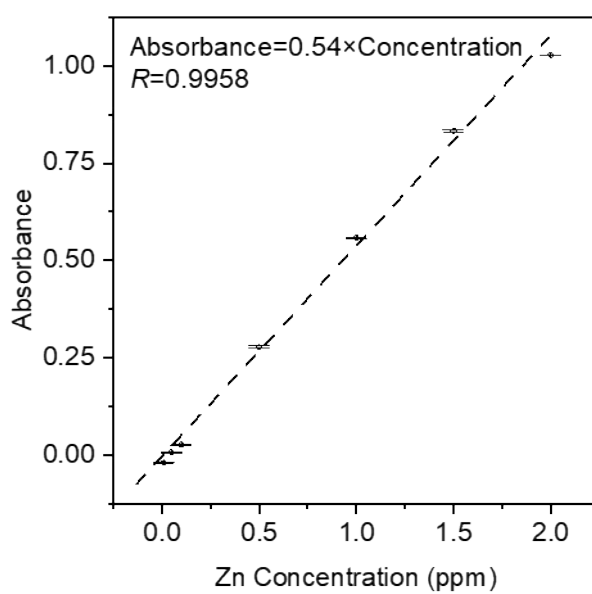


Figure S16. The calibration curve for Zn AAS.

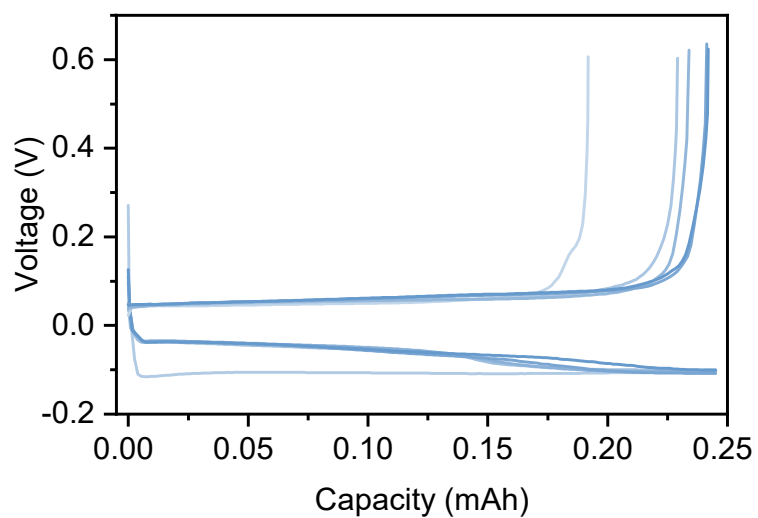


Figure S17. The capacity-voltage profiles of Zn/Cu cell with the PAM as the electrolyte at the 1st, 5th, 10th, 50th, and 100th cycles. The voltage polarization is around 124 mV.

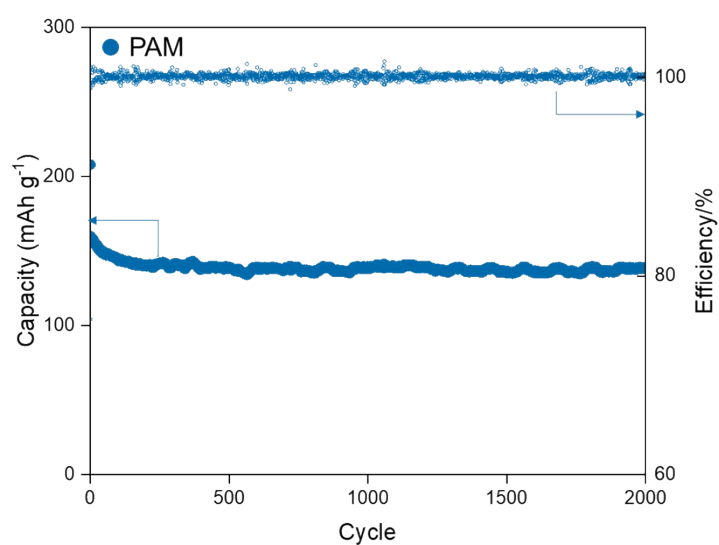


Figure S18. Cycling reversibility and CEs of Zn/I₂ cells at 8C with the PAM as the electrolyte.

3. Supplementary Table

Table S1. The AAS result for Zn trapping.

	100x		1000x		10000x	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Absorbance	1.1178	1.0621	0.1489	0.1484	0.0145	0.0149
Concentration (ppm)	2.0646	1.9617	0.2750	0.2741	0.0267	0.0275
Original concentration (ppm)	206	196	275.0	274.1	267.0	275.0

Reference:

1. S. Letaief, T. A. Elbokl and C. Detellier, *J. Colloid. Interface Sci.*, 2006, **302**, 254-258.