

Low-temperature ionothermal polymerization of phenazine-based small molecules towards ultrastable and high-capacity anode of aqueous alkaline sodium-ion batteries

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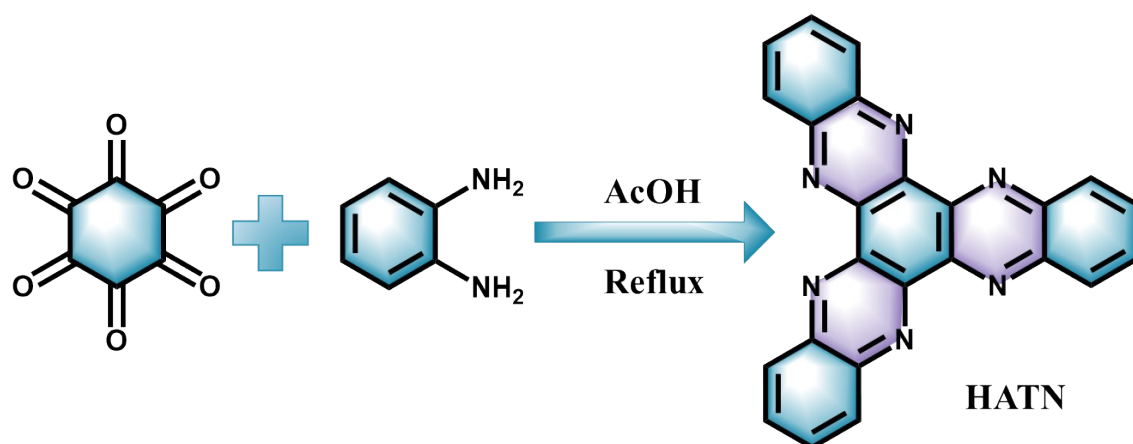


Figure S1. Illustration of the preparation process of HATN.

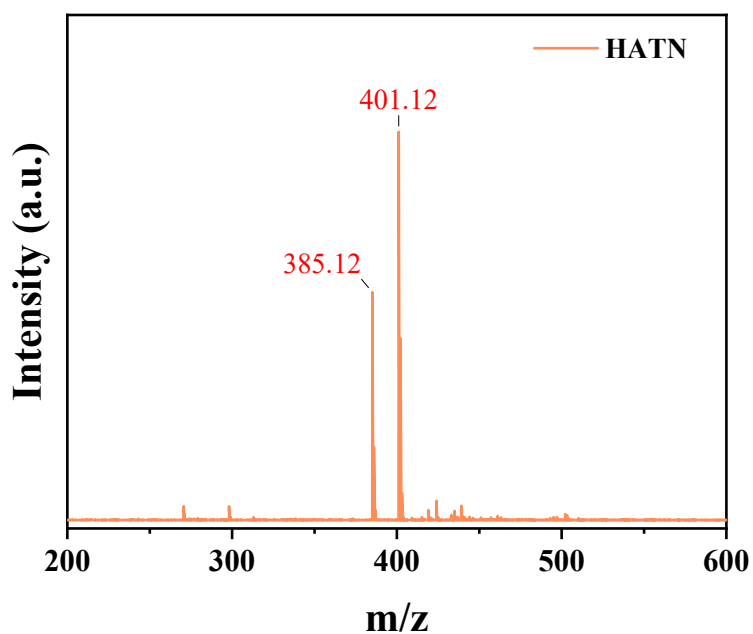


Figure S2. ESI-MS spectrum of HATN. Calculated HATN m/z value: 384, $[\text{HATN}+\text{H}]^+$: 385, found 385.12, $[\text{HATN}+\text{NH}_4]^+$: 401, found 401.12.

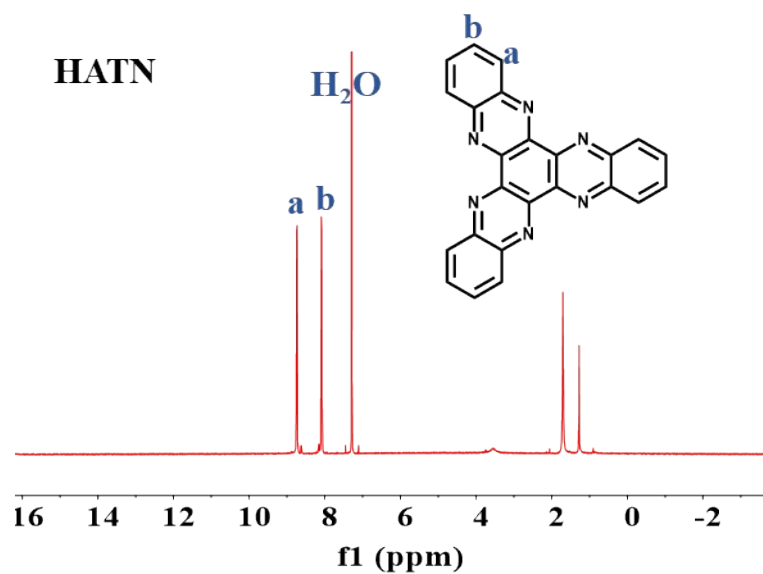


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of HATN.

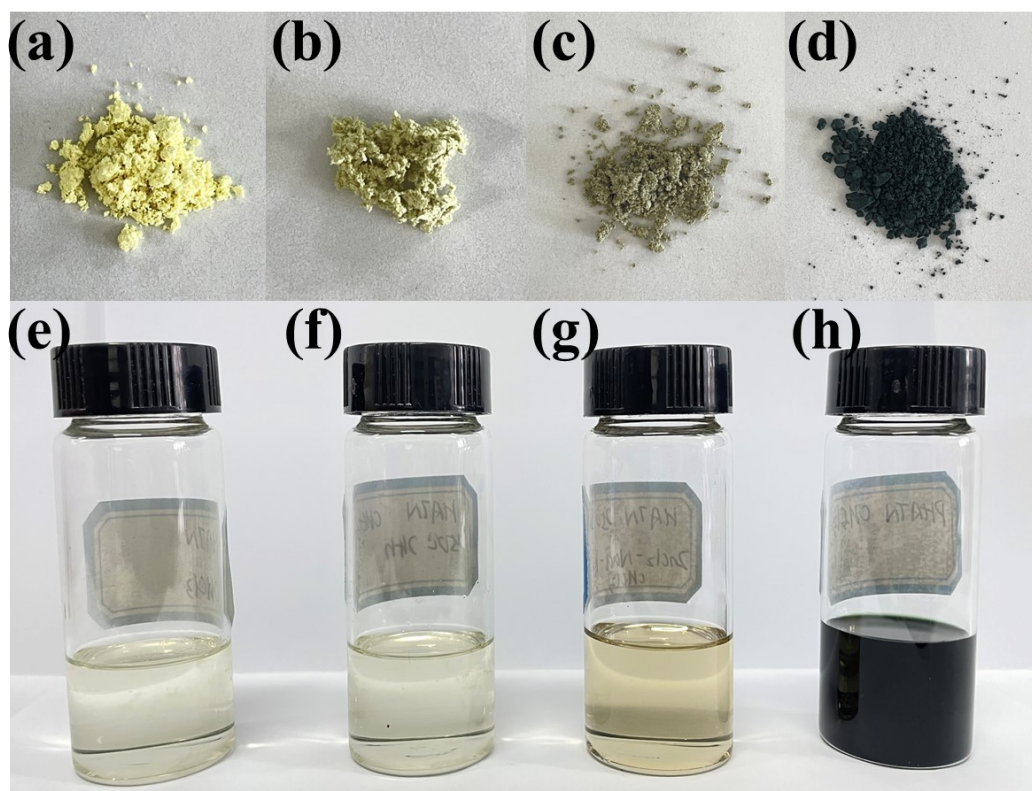


Figure S4. Photographs of products: (a) HATN; (b) the products after heating HATN at 250 °C for 24h; (c) the products after heating the mixture of HATN and ZnCl₂-NaCl-KCl at 250 °C for 24h; (d) PHATN (the products after heating the mixture of HATN and AlCl₃-NaCl-KCl at 250 °C for 24h). Photographs to show the solubility of the products in CHCl₃: (e) the solubility of a; (f) the solubility of b; (g) the solubility of c; (h) the dispersion of d. The results show the PHATN is black and was not well dissolved by CHCl₃.

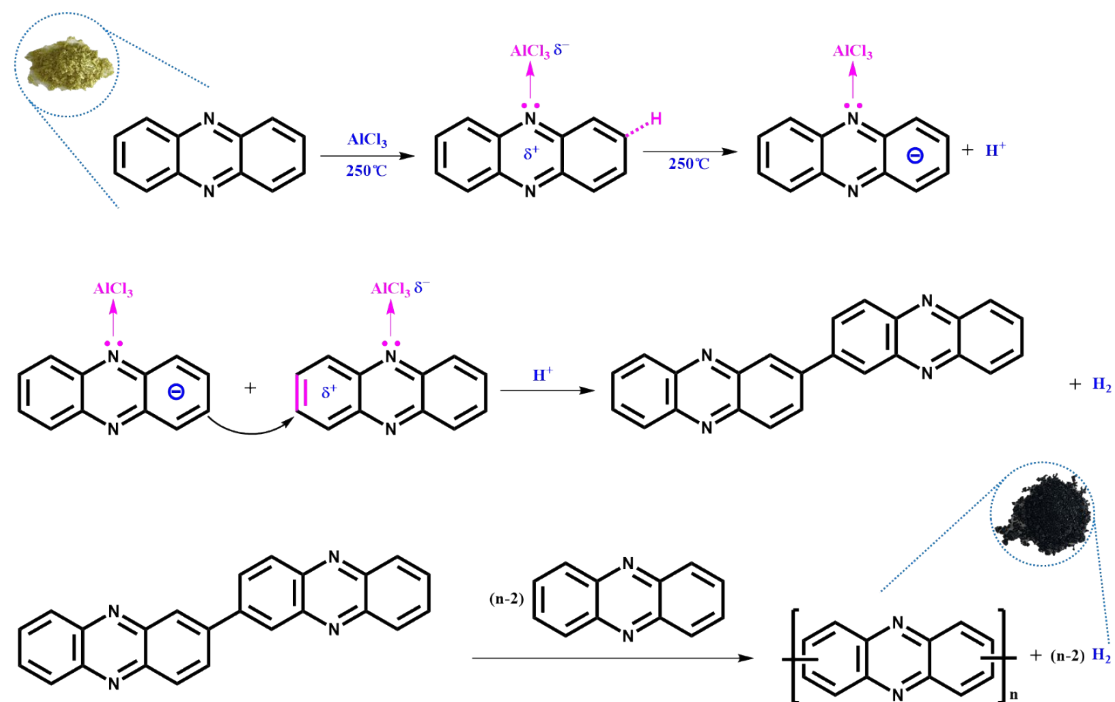


Figure S5. The proposed dehydrocoupling reaction mechanism of PPZ.

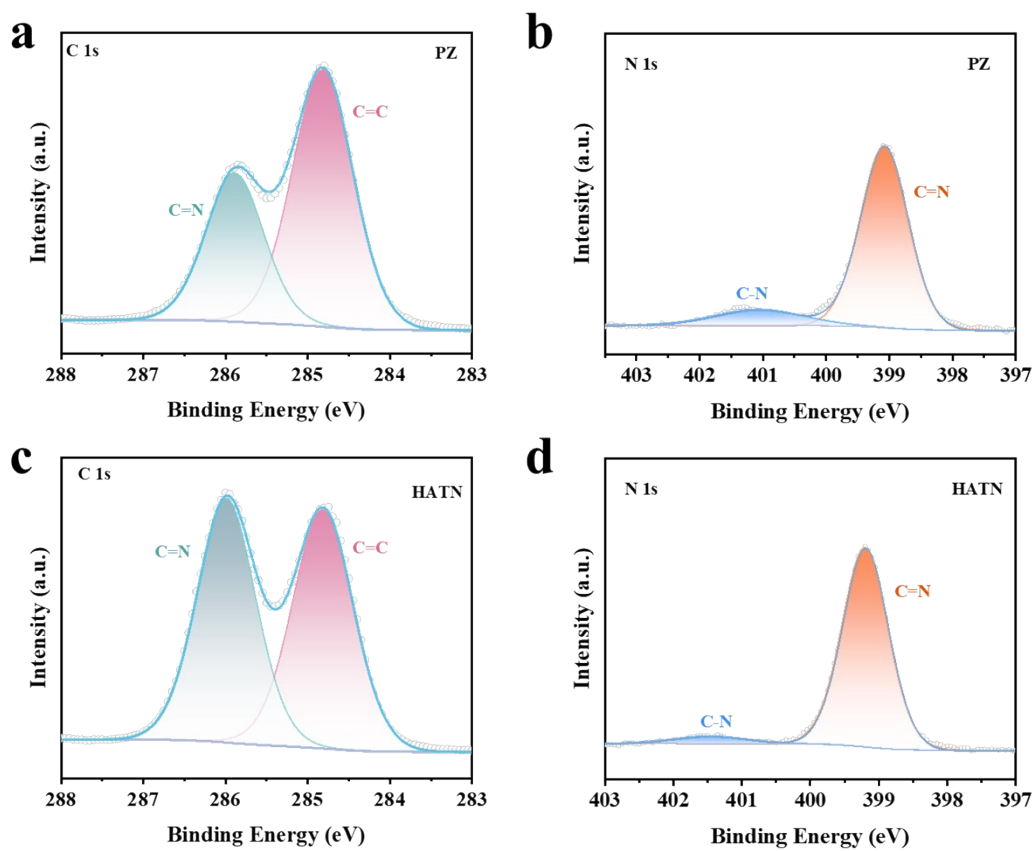


Figure S6. (a) The C 1s XPS spectra of PZ. (b) The N 1s XPS spectra of PZ. (c) The C 1s XPS spectra of HATN. (d) The N 1s XPS spectra of HATN.

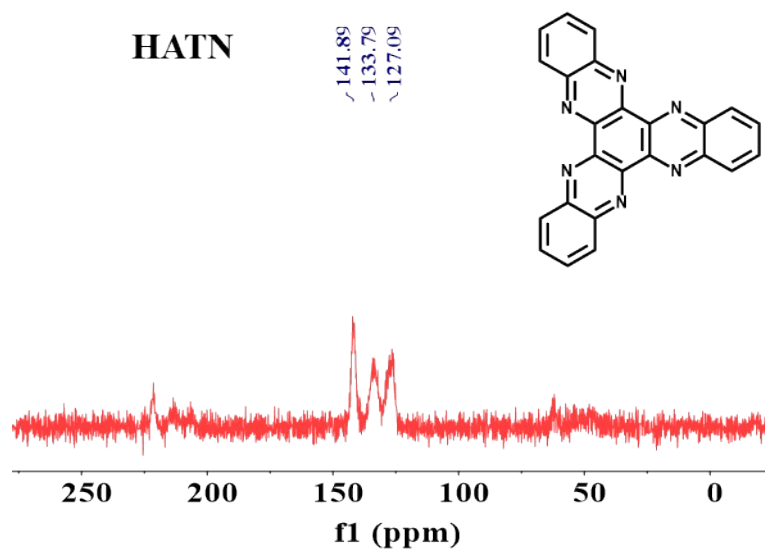


Figure S7. ^{13}C solid-state NMR spectrum of HATN.

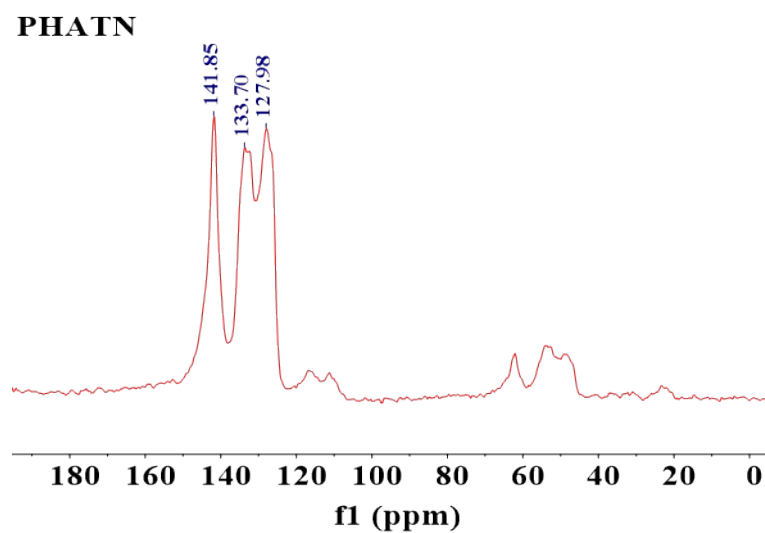


Figure S8. ^{13}C solid-state NMR spectrum of PHATN.

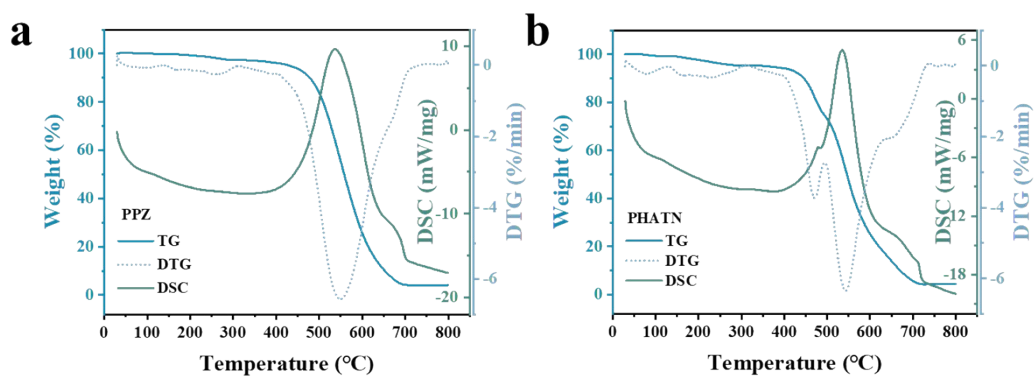


Figure S9. The TGA, DTG and DSC curves of (a) PPZ and (b) PHATN in Air.

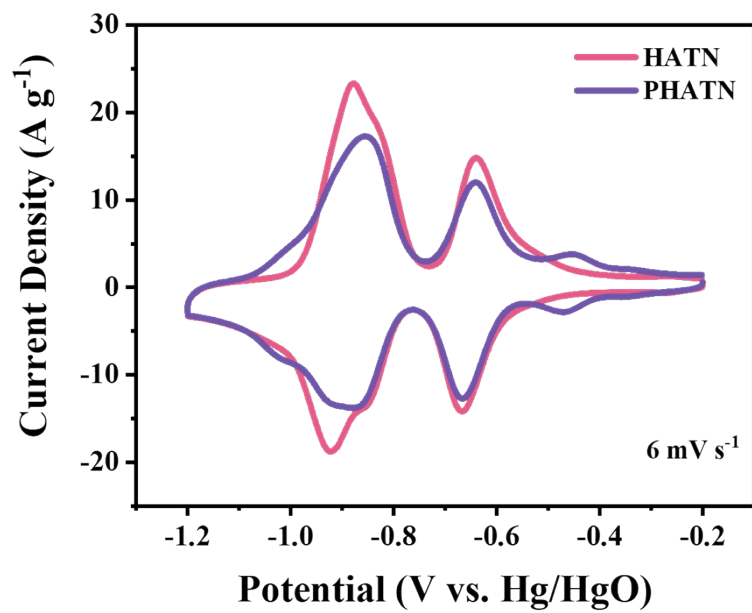


Figure S10. CV curves of HATN and PHATN at 6 mV s^{-1} .

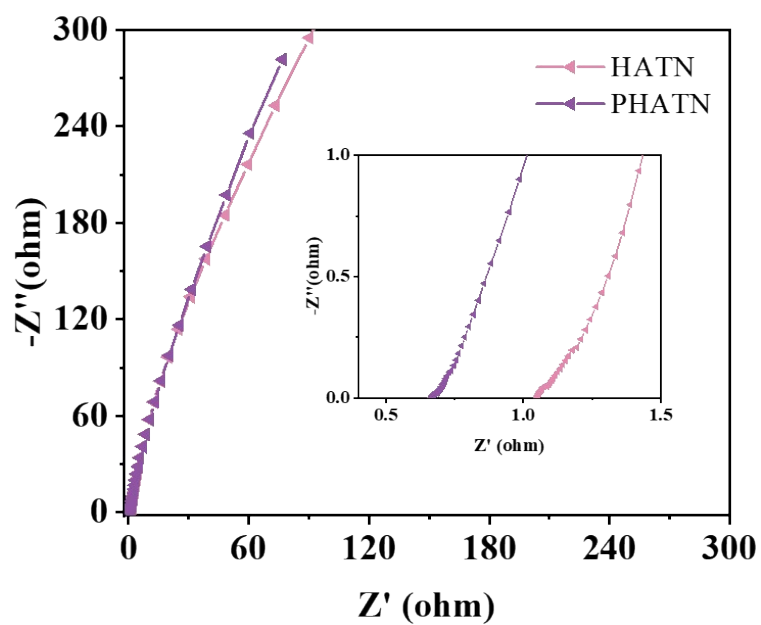


Figure S11. The electrochemical impedance spectrum (EIS) of HATN and PHATN.

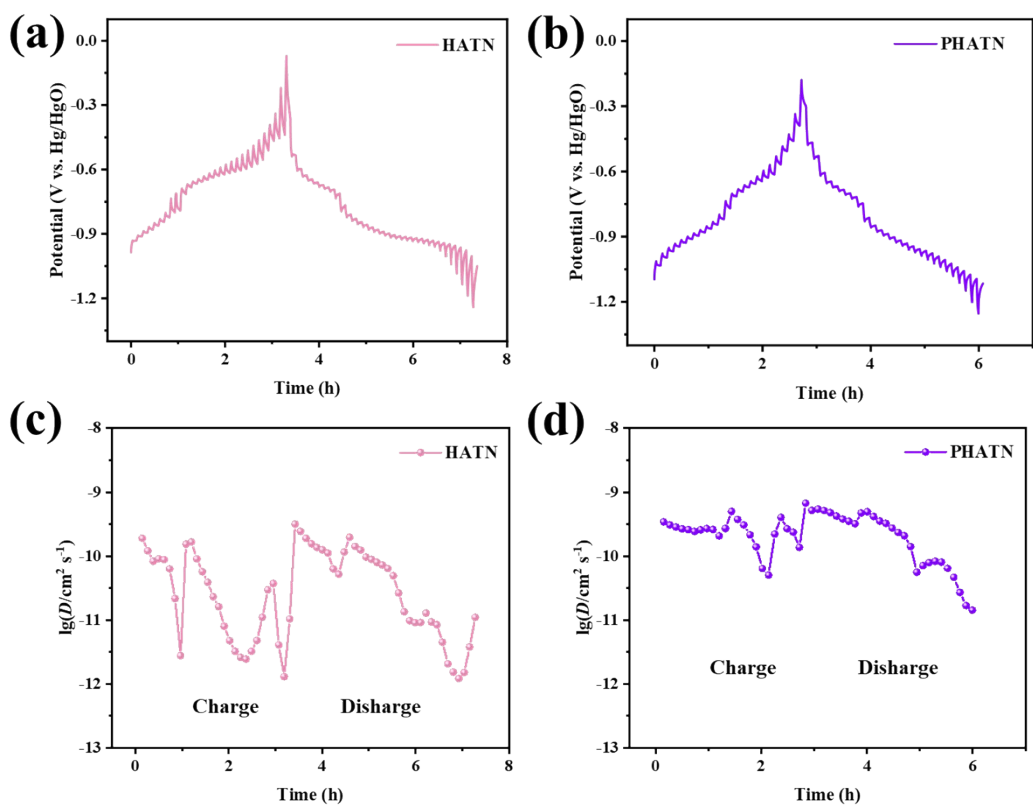


Figure S12. The GITT curves of (a) HATN and (b) PHATN; The ion diffusion coefficients of (c) HATN and (d) PHATN.

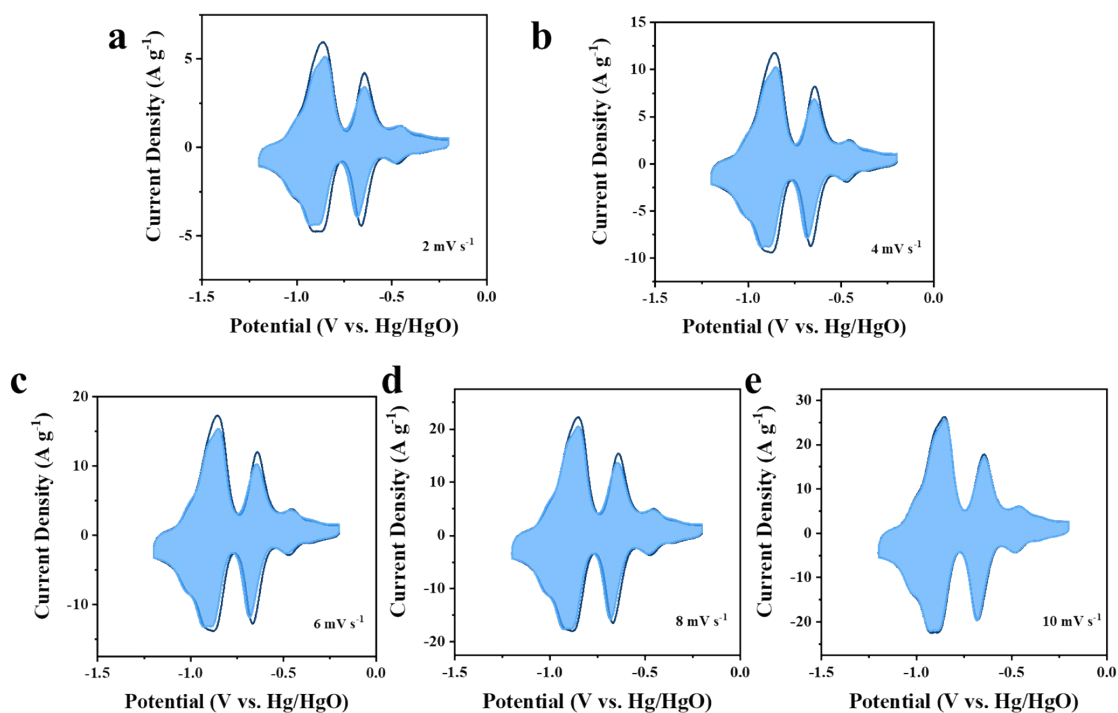


Figure S13. The calculated capacitive current curves (blue regions) at different scan rates (2mV s^{-1} ; 4mV s^{-1} ; 6mV s^{-1} ; 8mV s^{-1} ; 10mV s^{-1}) of PHATN.

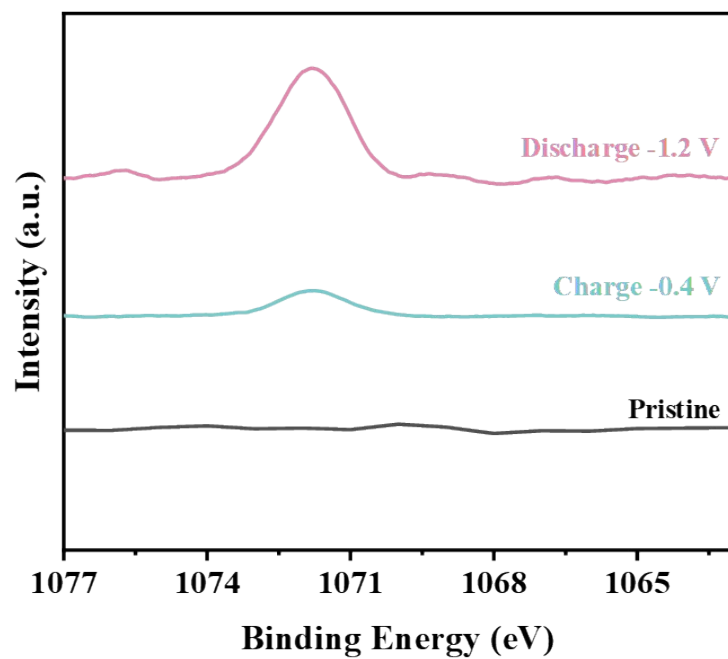


Figure S14. Na 1s XPS spectra of PHATN at different discharge and charge states.

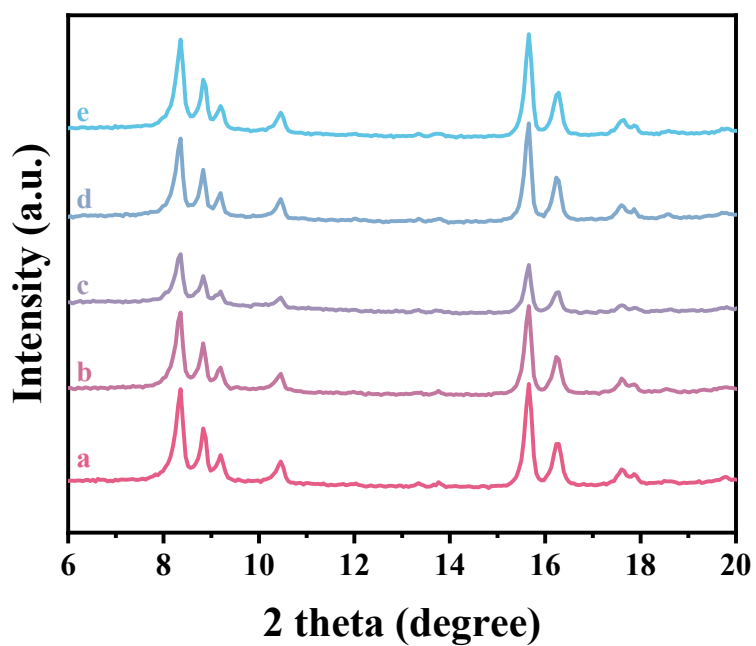


Figure S15. Ex-situ XRD of PHATN electrode as the anode at different discharge and charge states.

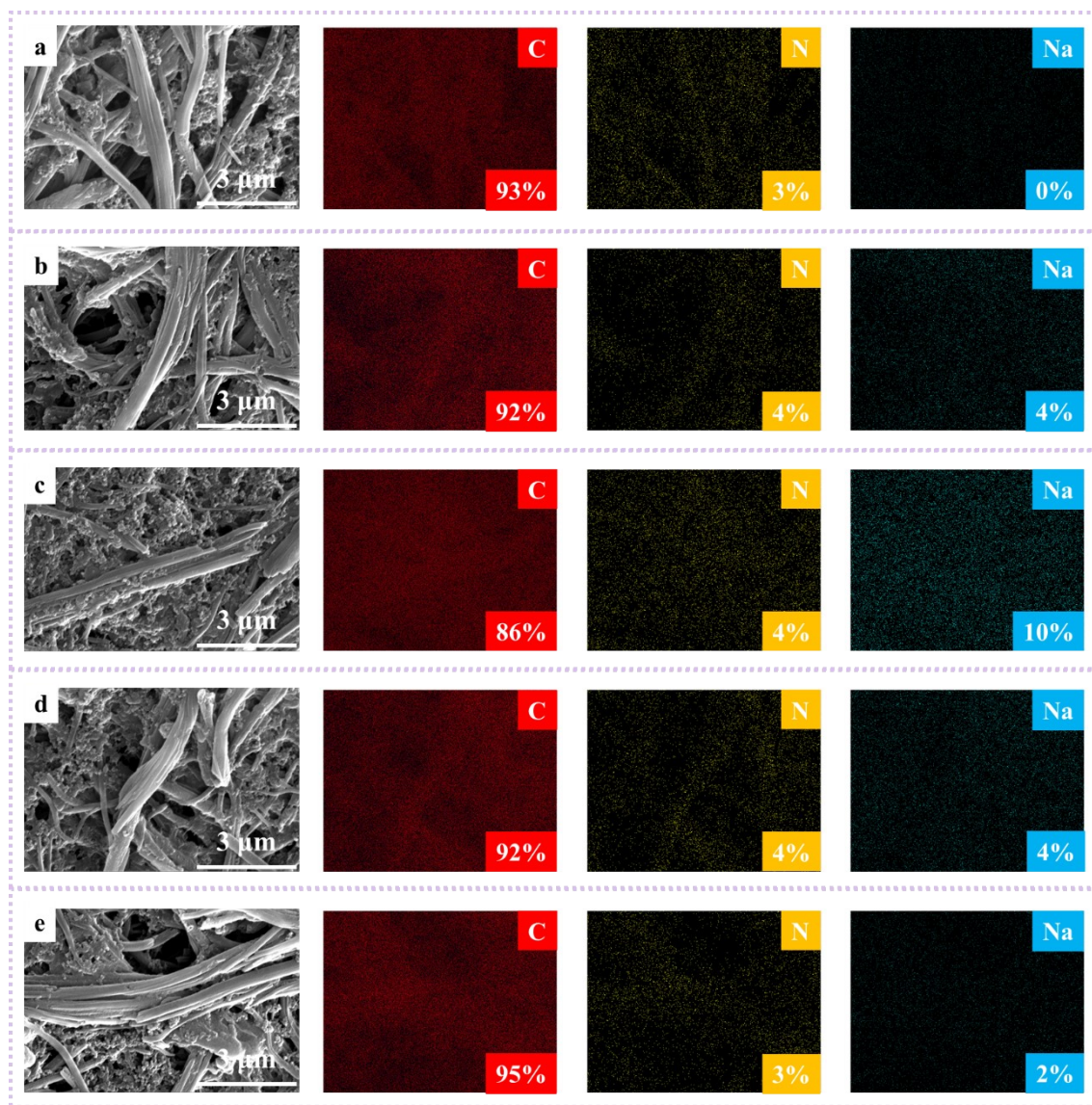


Figure S16. The SEM-EDS mapping images of PHATN electrodes at different charge/discharge states.

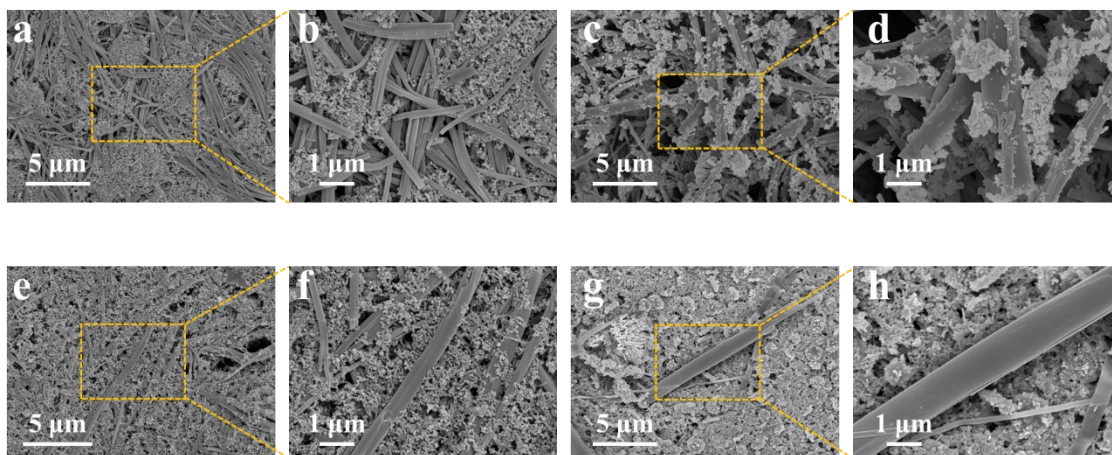


Figure S17. The SEM images of (a, b) pristine electrodes and (c, d) electrodes after 10000 cycles of HATN, and (e, f) pristine electrodes and (g, h) electrodes after 10000 cycles of PHATN.

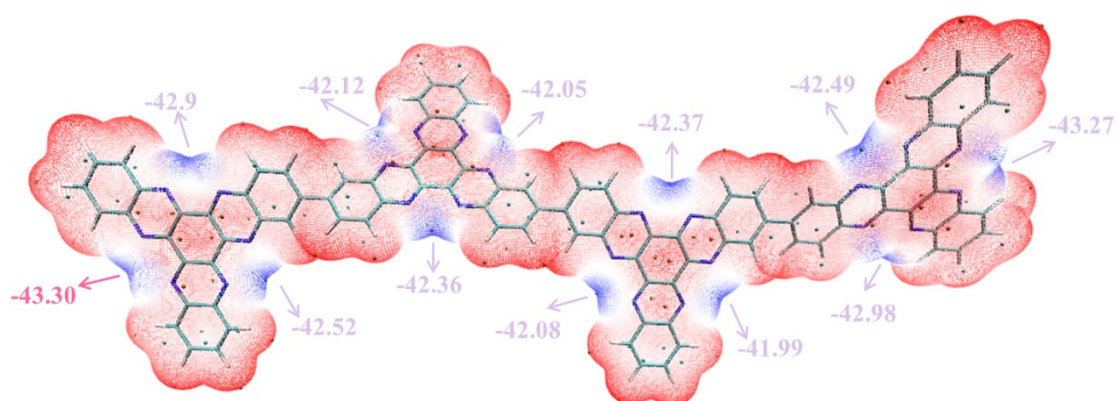


Figure S18. Electrostatic potential diagrams of the tetramer of HATN.

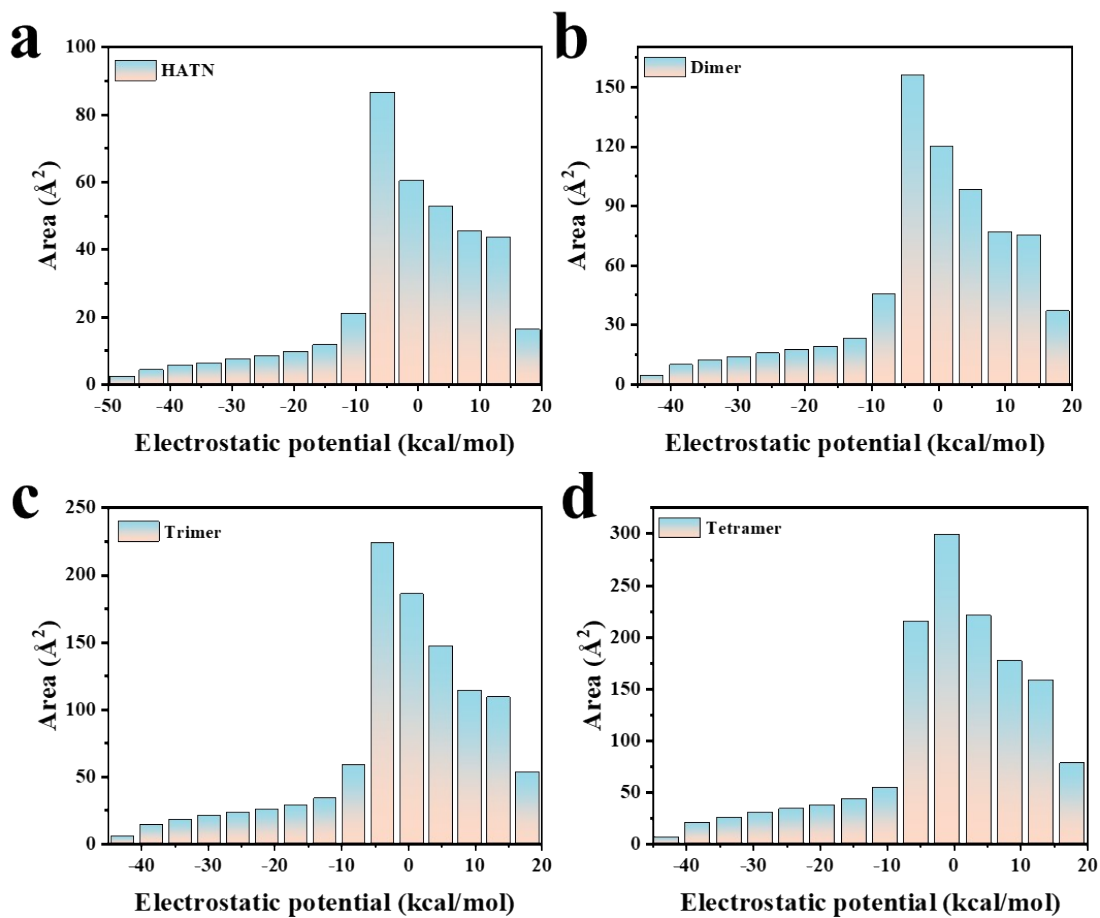


Figure S19. Quantitative distribution of electrostatic potential of HATN, dimer, trimer and tetramer.

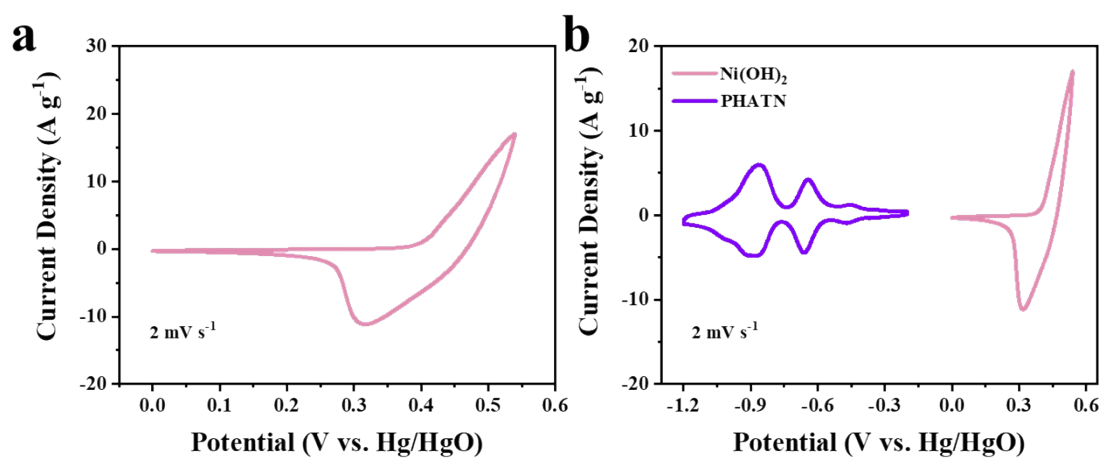


Figure S20. (a) CV curves of Ni(OH)_2 at 2 mV s^{-1} . (b) CV curves of PHATN and Ni(OH)_2 at 2 mV s^{-1} .

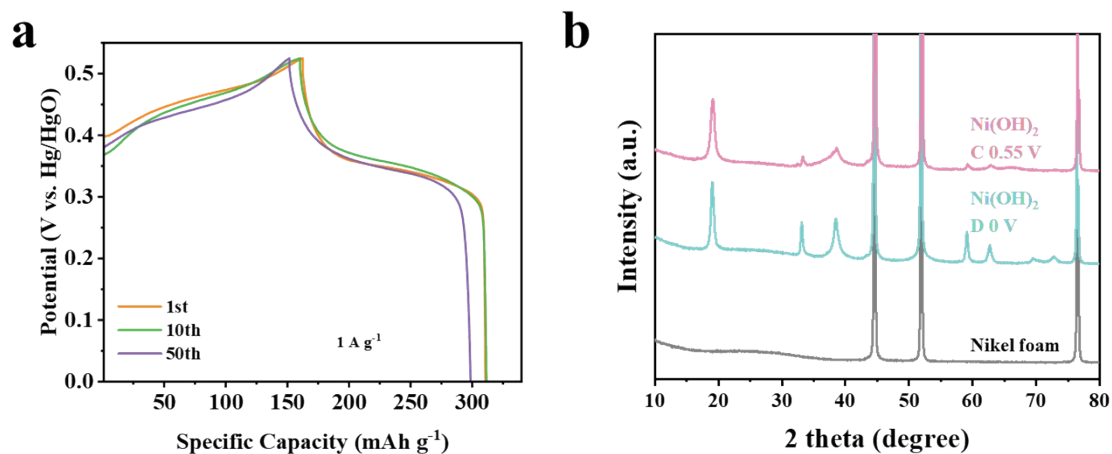


Figure S21. (a) Charge-discharge curves of $\text{Ni}(\text{OH})_2$ electrodes at different cycles. (b) XRD patterns of $\text{Ni}(\text{OH})_2$ electrodes at different charge/discharge states.

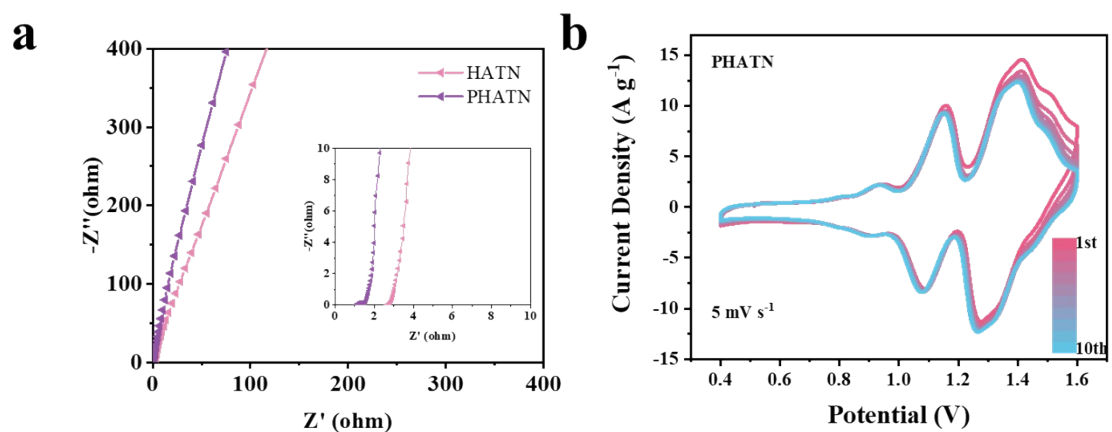


Figure S22. (a) EIS of HATN/ $\text{Ni}(\text{OH})_2$ and PHATN/ $\text{Ni}(\text{OH})_2$. (b) CV curves of PHATN/ $\text{Ni}(\text{OH})_2$ at 5 mV s^{-1} .

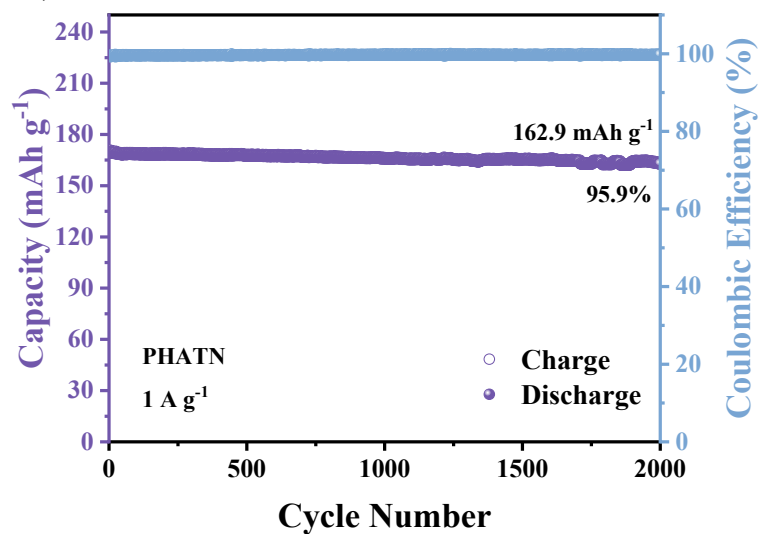
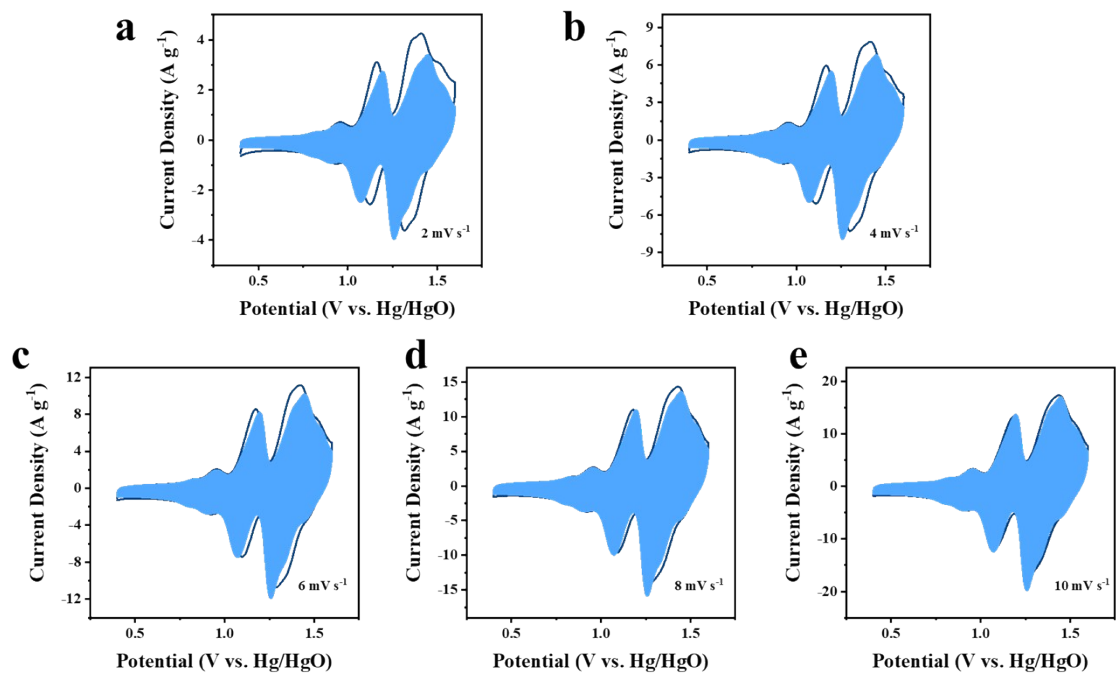
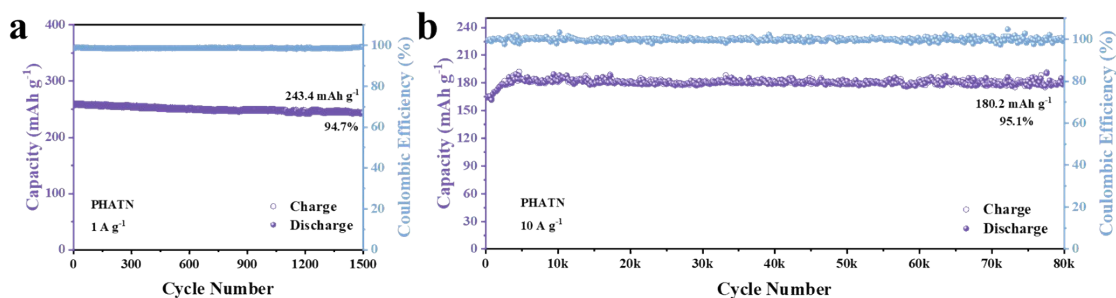
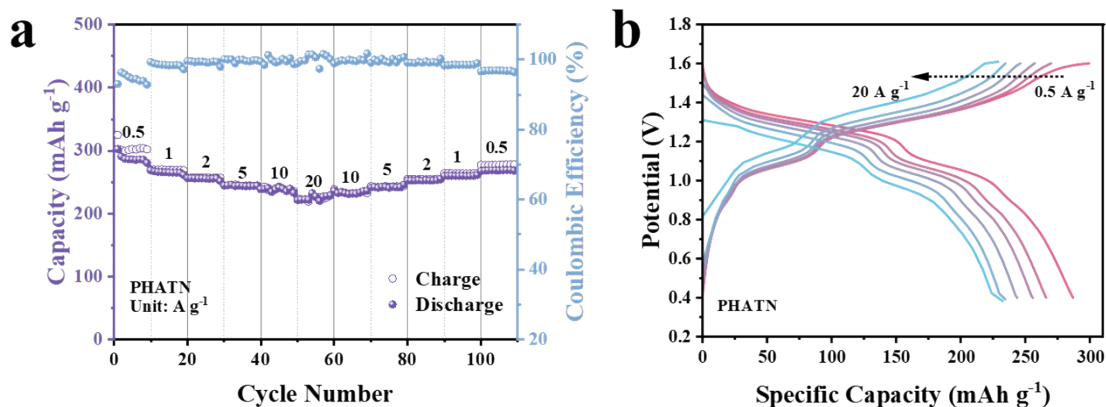


Figure S23. Cycle performance of PHATN/ $\text{Ni}(\text{OH})_2$ at 1 A g^{-1} .



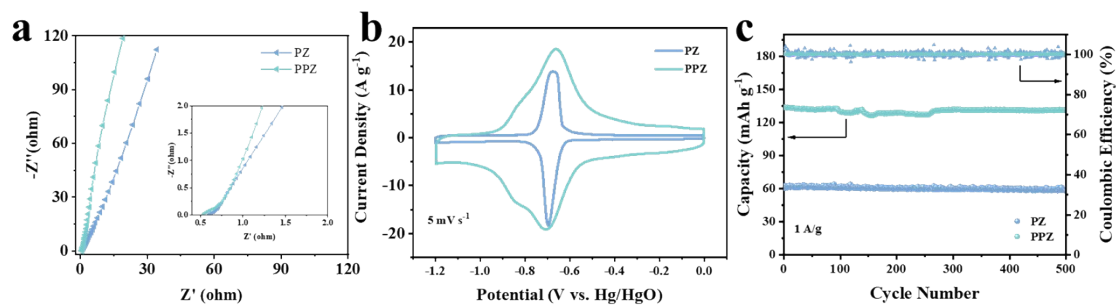


Figure S27. (a) EIS of PZ and PPZ as anode. (b) CV curves of PZ and PPZ as the anode at 5 mV s^{-1} . (c) Cycling performance of PZ and PPZ as anode at 1 A g^{-1}

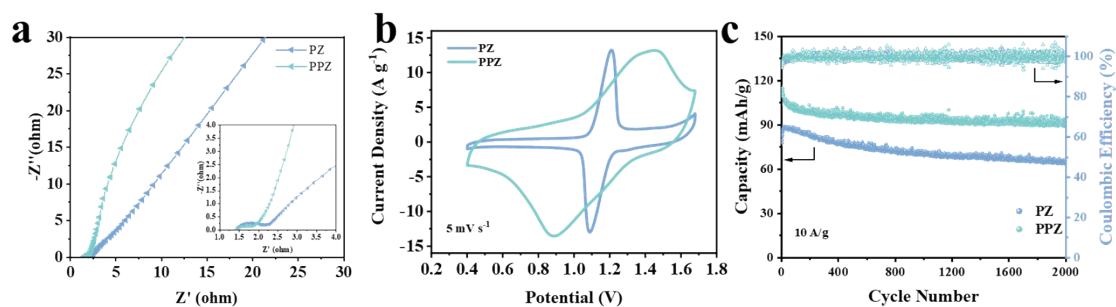


Figure S28. (a) EIS of PZ//Ni(OH)₂ and PPZ//Ni(OH)₂. (b) CV curves of PZ//Ni(OH)₂ and PPZ//Ni(OH)₂ at 5 mV s^{-1} . (c) Cycling performance of PZ//Ni(OH)₂ and PPZ//Ni(OH)₂ at 1 A g^{-1}

Table S1. The electronic conductivity of the obtained samples.

Sample	Test content	Test methods	Results			units
			2 Mpa	4 Mpa	6 Mpa	
PZ	Electrical conductivity	Quadrupole probe	1.39E-07	1.89E-07	2.19E-07	S / m
PPZ	Electrical conductivity	Quadrupole probe	1.33E-04	1.92E-04	2.46E-04	S / m
HATN	Electrical conductivity	Quadrupole probe	2.47E-09	3.82E-09	5.44E-09	S / m
PHATN	Electrical conductivity	Quadrupole probe	1.91E-06	3.60E-06	4.80E-06	S / m

Table S2. Rate performance and cycling performance comparison of PHATN//Ni(OH)₂ with other materials-based aqueous sodium-ion batteries reported in the literature.

Sample	electrolyte	Discharge capacity (mAh g ⁻¹)	Cycling performance (Current density)	Ref.
CDPZ@G // Ni-MOF	10 M NaOH	130.5 (0.5 A g ⁻¹) based on the anode mass	91.3% / After 1500 cycles (6 A g ⁻¹)	1
3CN-DPZ // Ni-BTA	10 M NaOH	323.6 (2 A g ⁻¹) based on the anode mass	96.4% / After 5000 cycles (8 A g ⁻¹)	2
PBA // CrCrPBA	17 M NaClO ₄	52.8 (0.125 A g ⁻¹) based on the anode mass	93.01% / After 500 cycles (3.75 A g ⁻¹)	3
N-NaVTP // N-NaVTP	Saturated NaClO ₄	49.7 (0.2 A g ⁻¹) based on the total mass of cathode and anode	60% / After 1000 cycles (5 A g ⁻¹)	4
Na ₃ MnTi(PO ₄) ₃ // Na ₃ MnTi(PO ₄) ₃	1 M Na ₂ SO ₄	57.9 (0.029 A g ⁻¹) based on the total mass of cathode and anode	98% / After 100 cycles (0.0587 A g ⁻¹)	5
NaTi ₂ (PO ₄) ₃ // Na ₂ NiFe(CN) ₆	0.5 M Na ₂ SO ₄	77 (0.06 A g ⁻¹) based on the total mass of cathode and anode	96% / After 300 cycles (0.06 A g ⁻¹)	6
NaTi ₂ (PO ₄) ₃ // Na ₂ NiFe(CN) ₆	0.5 M Na ₂ SO ₄ // 0.1M Na ₄ Fe(CN) ₆	110 (0.06 A g ⁻¹) based on the total mass of cathode and anode	84.7% / After 1000 cycles (0.09 A g ⁻¹)	6
NaTi ₂ (PO ₄) ₃ // Na ₂ MnFe(CN) ₆	NaClO ₄	61 (0.118 A g ⁻¹) based on the total mass of cathode and anode	74.3% / After 13000 cycles (1.18 A g ⁻¹)	7
LTP@C/CNTs // Na _{0.44} MnO ₂	5 M NaNO ₃	83.36 (0.2 A g ⁻¹) based on the anode mass	79.4% / After 500 cycles (3 A g ⁻¹)	8
NaTi ₂ (PO ₄) ₃ @C // NaVPO ₄ F@C	17 M NaClO ₄	43.9 (0.1 A g ⁻¹) based on the total mass of cathode and anode	48.8% / After 100 cycles (0.5 A g ⁻¹)	9

Na ₃ V ₂ (PO ₄) ₃ // Na ₃ V ₂ (PO ₄) ₃	NaClO ₄ -H ₂ O-urea ratio of 1-3-2	37 (0.01 A g ⁻¹) base on the total mass of cathode and anode	72%/After 1000 cycles (0.5 A g ⁻¹)	10
NaTi ₂ (PO ₄) ₃ // Na ₃ V ₂ (PO ₄) ₃	NaTFSI: H ₂ O:acetonitrile ratio of 1:1:2.5	96 (0.01 A g ⁻¹) base on the anode mass	71% / After 1000 cycles (0.5 A g ⁻¹)	11
NaTi ₂ (PO ₄) ₃ // Na _{0.44} MnO ₂	NaClO ₄ -H ₂ O-urea ratio of 1-3-2	74.5 (0.02 A g ⁻¹) base on the cathode mass	90% / After 3500 cycles (0.5 A g ⁻¹)	12
NaTi ₂ (PO ₄) ₃ @C// m-NiHCF	5M NaClO ₄	61.4 (0.1 A g ⁻¹) base on the cathode mass	83% / After 600 cycles (0.1 A g ⁻¹)	13
Na ₃ (PO ₄) ₃ // Na ₃ V ₂ (PO ₄) ₃	19 M NaClO ₄ -NaOTF -H ₂ O	40 (0.117 A g ⁻¹) base on the total mass of cathode and anode	87.5% / After 100 cycles (0.117 A g ⁻¹)	14
NaTi ₂ (PO ₄) ₃ // KMnHCF	polyethylene glycol: H ₂ O ratio of 92:8	105 (0.1 A g ⁻¹) base on the cathode mass	80% / After 3500 cycles (0.8 A g ⁻¹)	15
NaTi ₂ (PO ₄) ₃ @C// HEPBA	1 M Na ₂ SO ₄	75 (0.05 A g ⁻¹) base on the cathode mass	87% / After 1000 cycles (0.1 A g ⁻¹)	16
NaTi ₂ (PO ₄) ₃ // Na ₂ Zn ₃ [Fe(CN) ₆] ₂	17 M NaClO ₄	55 (0.12 A g ⁻¹) base on the cathode mass	100% / After 1000 cycles (0.6 A g ⁻¹)	17
FeHCF // CuHCF	Saturated NaNO ₃	50 (0.06 A g ⁻¹) base on the cathode mass	86% / After 250 cycles (0.3 A g ⁻¹)	18
NaTi ₂ (PO ₄) ₃ -C // AC	1 M Na ₂ SO ₄	100 (0.1 A g ⁻¹) base on the anode mass	61%/After 500 cycles (0.2 A g ⁻¹)	19
Na ₂ VTi(PO ₄) ₃ /C/ / Na ₂ VTi(PO ₄) ₃ /C	1 M Na ₂ SO ₄	55 (0.05 A g ⁻¹) base on the cathode mass	83% / After 600 cycles (0.4 A g ⁻¹)	20
PHATN // Ni(OH) ₂	6 M NaOH	302.5 (0.5 A g ⁻¹) base on the anode mass	95.1% / After 80000 cycles (10 A g ⁻¹)	This work

Notes and references

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