

Supplementary Information

Orbital coupling effect enables low-chloride concentration electrolyte for four-electron redox in aqueous zinc||iodine batteries

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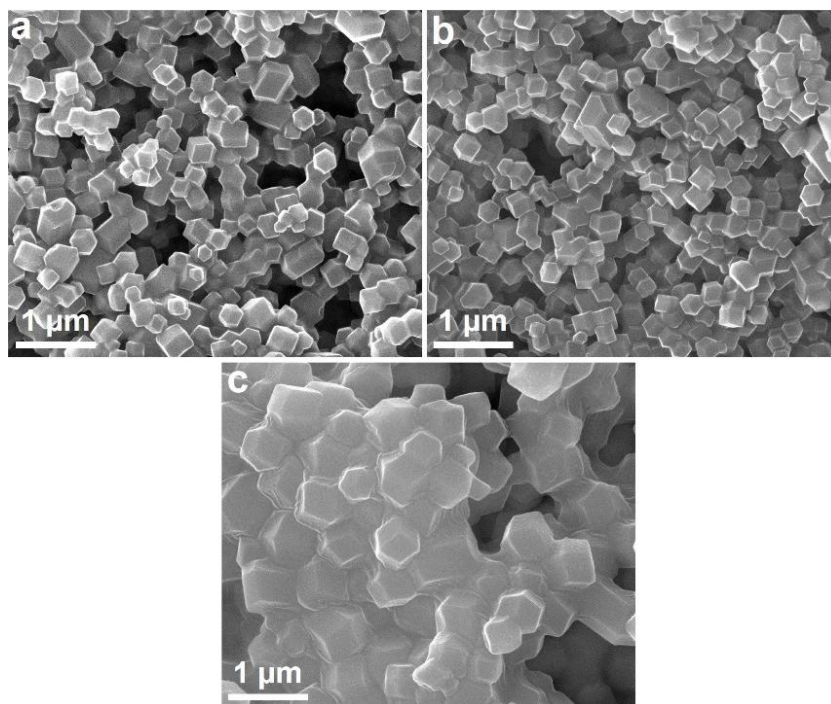
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[#]These authors contributed equally to this work.

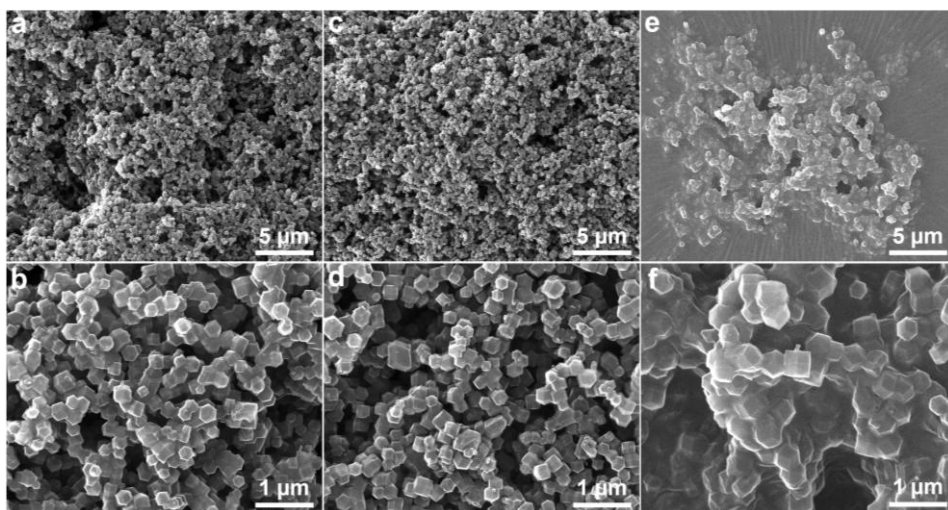
*Corresponding author. E-mail: tcxubg@polyu.edu.hk

Supplementary Figures

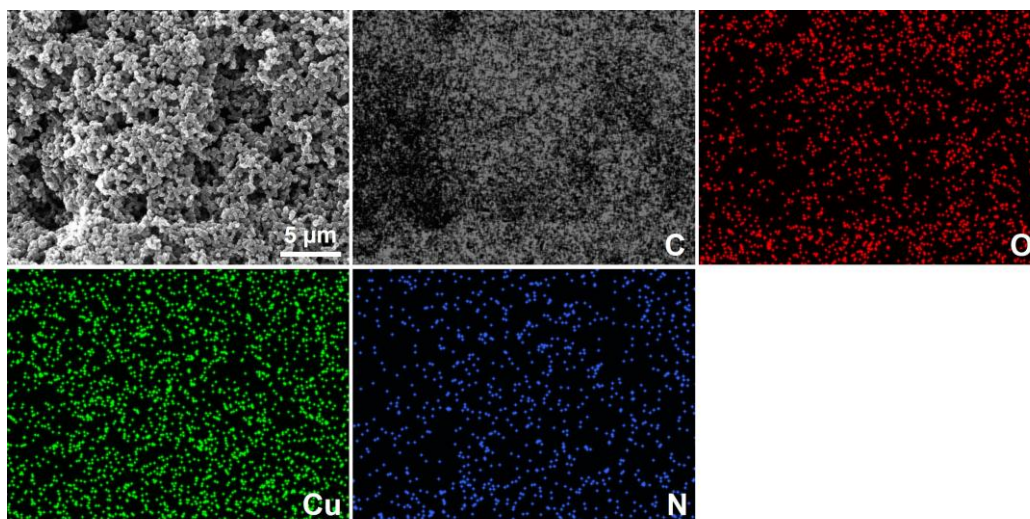


Supplementary Figure 1. SEM images of (a) Cu-ZIF-10%, (b) Cu-ZIF-20%, and (c) Cu-ZIF-30%.

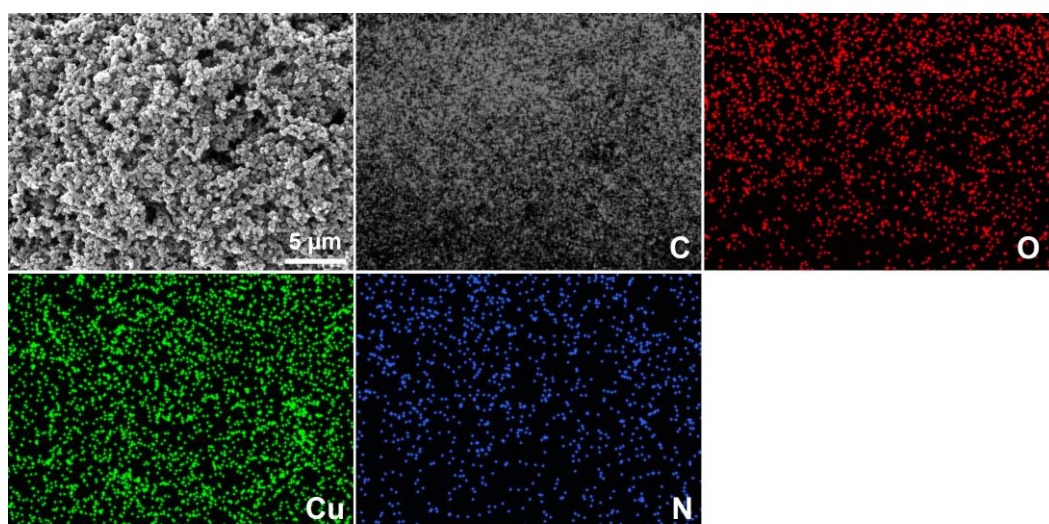
Supplementary Figure 1 displays the SEM images of the synthesized Cu-ZIF precursors with different Cu concentrations. The Cu-ZIF-10% and Cu-ZIF-20% particles exhibit a well-defined polyhedral morphology, predominantly ranging from 100-200 nm in size, with sharp edges and smooth surfaces, indicating high crystallinity and uniform nucleation. When the molar ratio of copper increases to 30%, severe particle aggregation becomes evident. The primary particles lose their discrete polyhedral structure, merging into large irregular clusters exceeding 500 nm in size. This pronounced aggregation suggests that excessive copper incorporation disrupts the crystalline growth of Cu-ZIF, due to the altered coordination kinetics and nucleation density during synthesis.



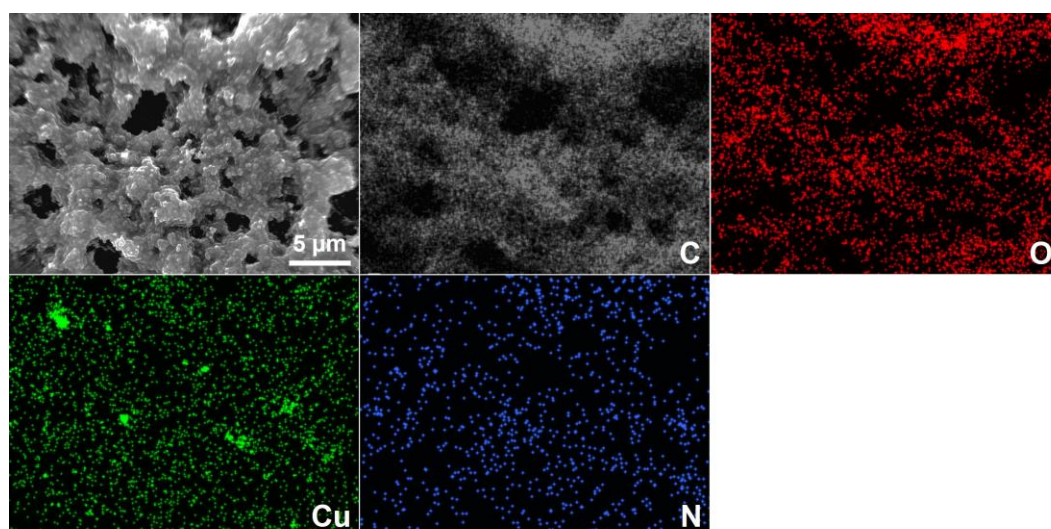
Supplementary Figure 2. SEM images of (a-b) Cu-N/PC-1, (c-d) Cu-N/PC-2, and (e-f) Cu-N/PC-3.



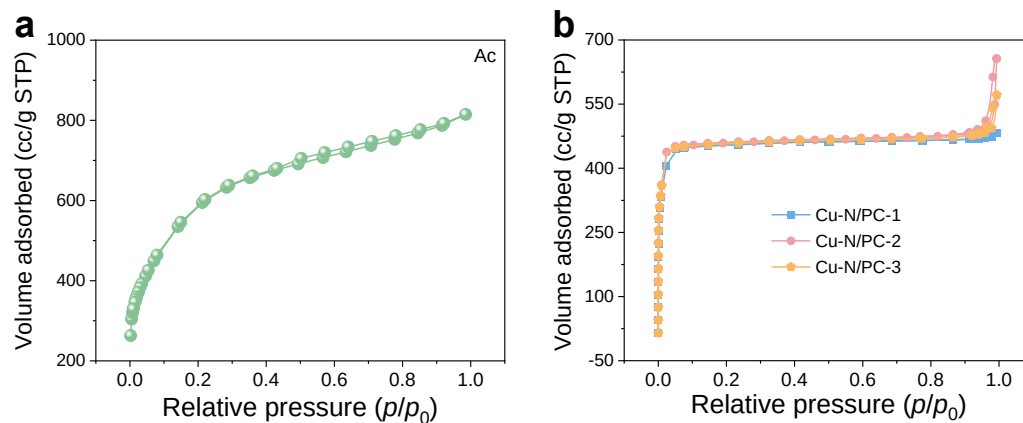
Supplementary Figure 3. SEM and the corresponding element mapping images of Cu-N/PC-1.



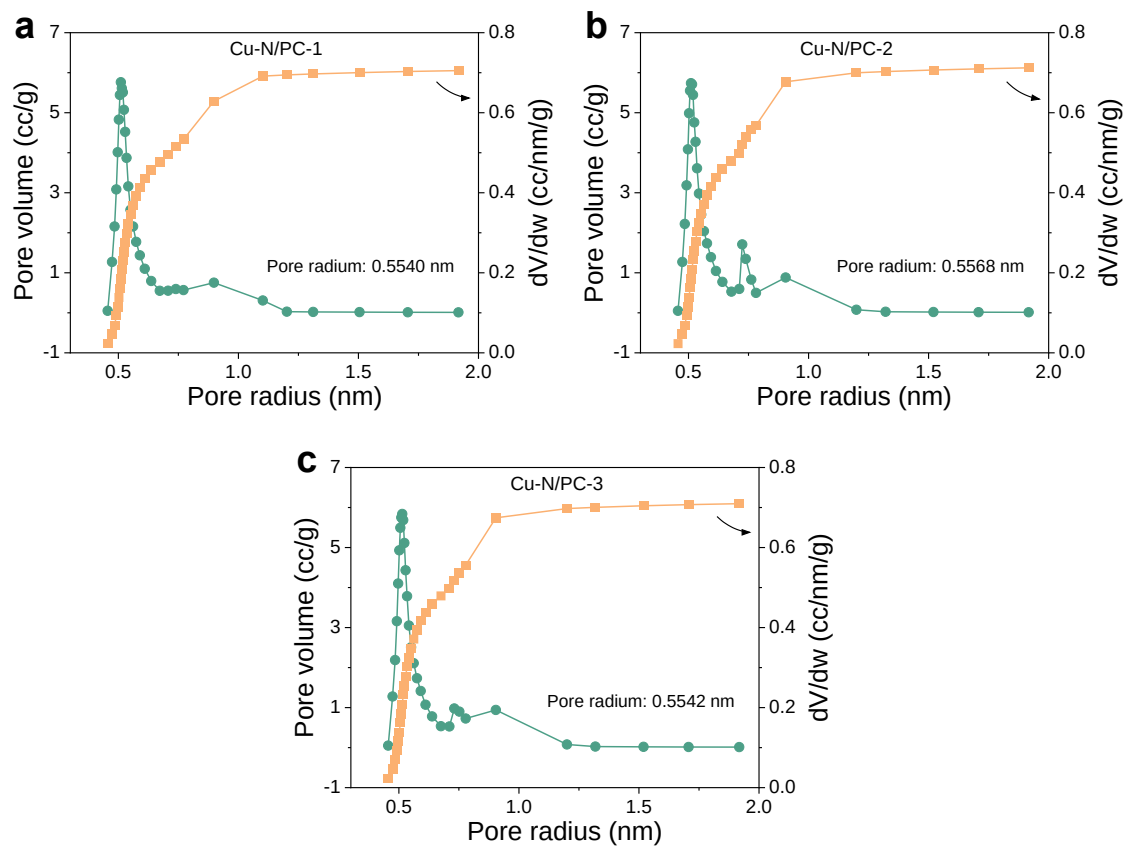
Supplementary Figure 4. SEM and the corresponding element mapping images of Cu-N/PC-2.



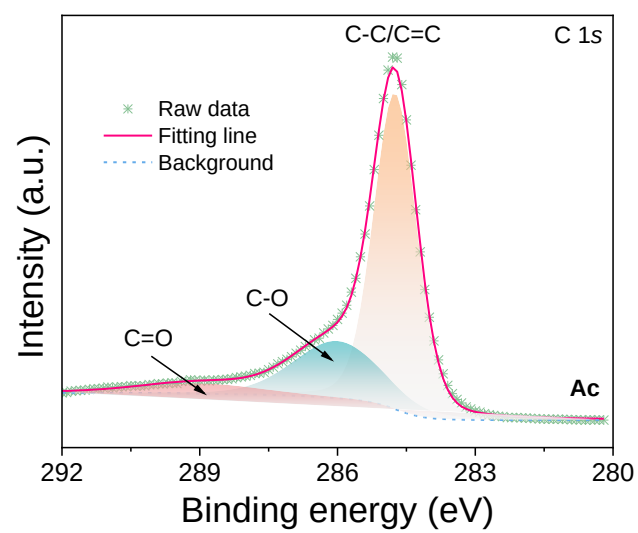
Supplementary Figure 5. SEM and the corresponding element mapping images of Cu-N/PC-3.



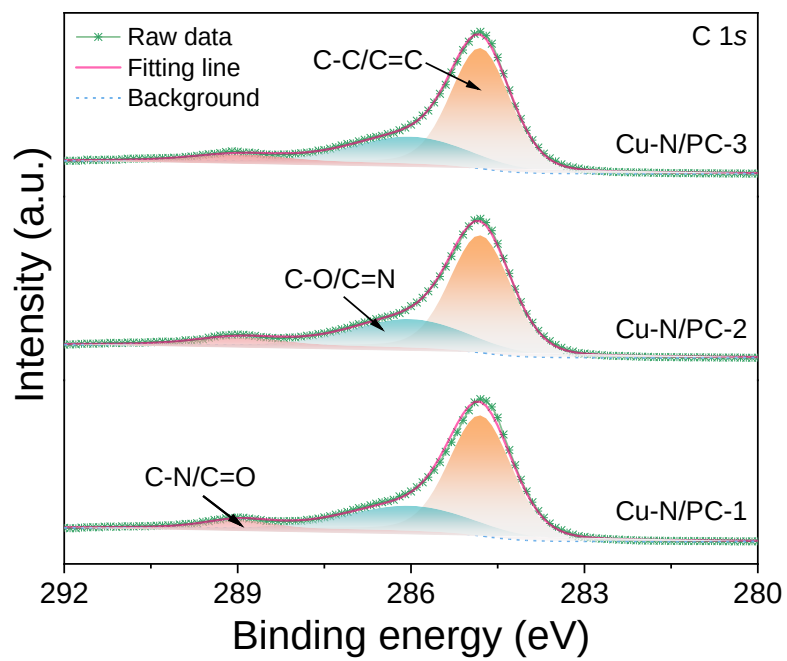
Supplementary Figure 6. Nitrogen adsorption/desorption isotherms of (a) Ac and (b) Cu-N/PC materials.



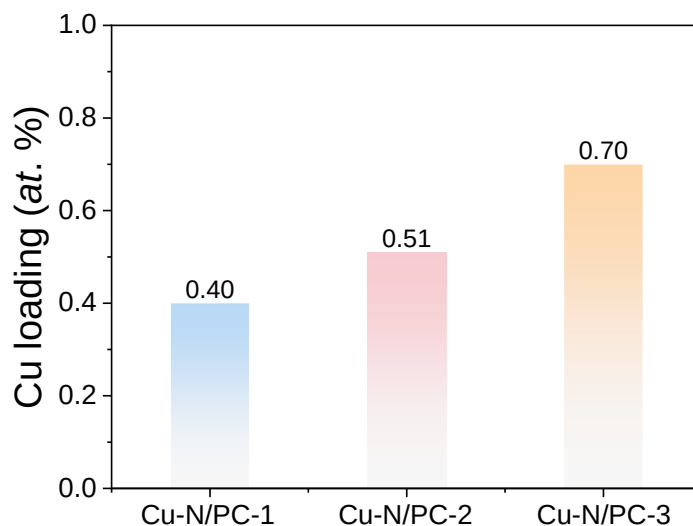
Supplementary Figure 7. Micropore-size distributions of (a) Cu-N/PC-1, (b) Cu-N/PC-2, and (c) Cu-N/PC-3.



Supplementary Figure 8. XPS C 1s spectra of Ac.

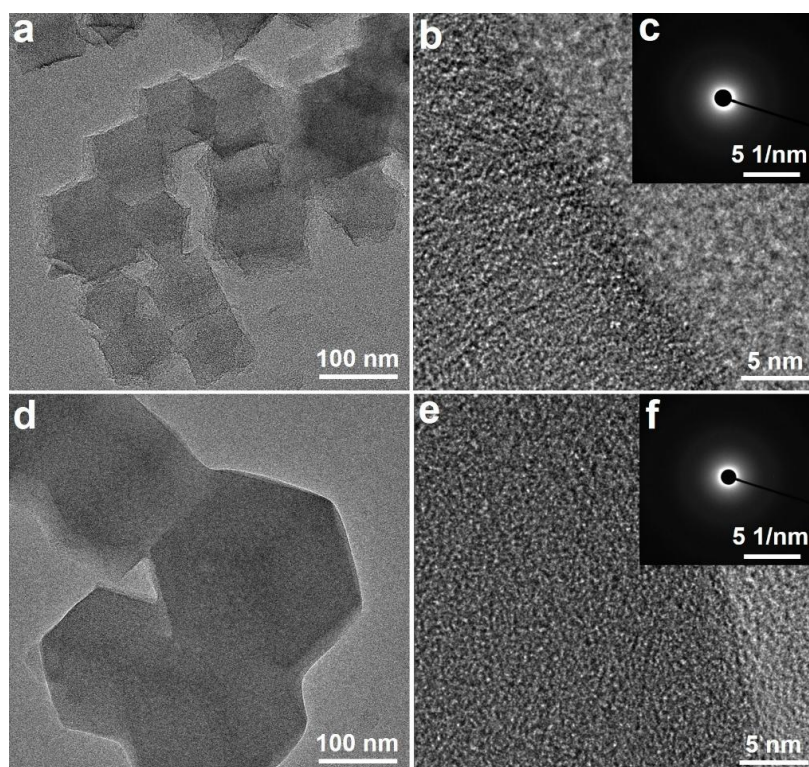


Supplementary Figure 9. XPS C 1s spectra of Cu-N/PC materials.

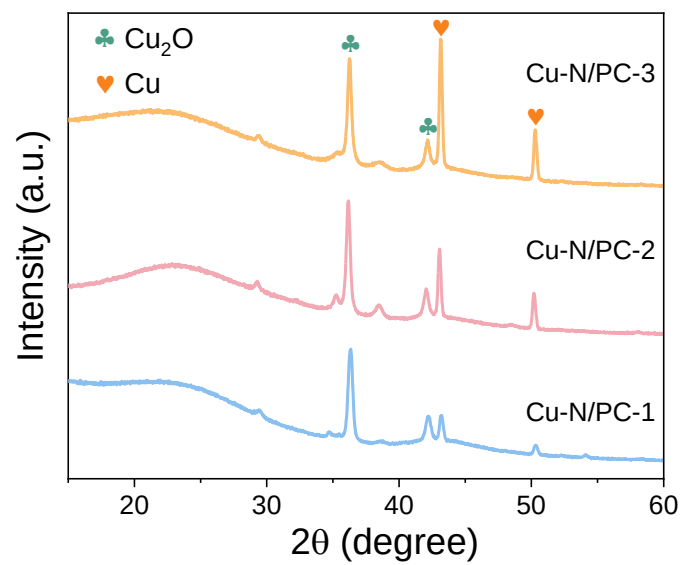


Supplementary Figure 10. The Cu loading values (*at.*%) of the Cu-N/PC-*x* samples.

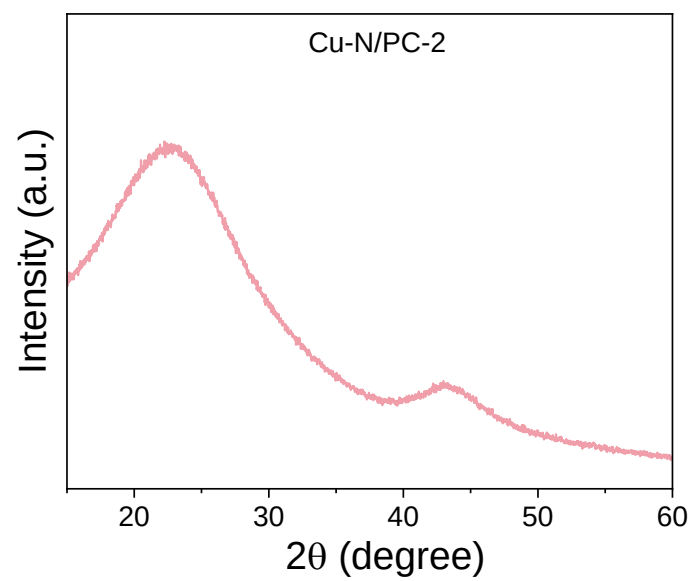
As expected, the Cu loading increases progressively from Cu-N/PC-1 to Cu-N/PC-3, consistent with the increasing amount of copper source added during the synthesis of the Cu-ZIF precursors. Among these, Cu-N/PC-2 exhibits an optimal Cu loading (approximately 0.51 *at.*%), which balances the density of active sites against the preservation of the well-defined ZIF-derived porous structure. Excessive Cu loading in Cu-N/PC-3 leads to partial aggregation of the precursor crystallization and ZIF-derived carbon, as observed in the SEM images (Supplementary Figs. 1 and 2), which explains its inferior electrochemical performance despite possessing the highest Cu content. These Cu loading values clarify the correlation between structure and activity: Cu-N/PC-2 has a moderate and dispersed Cu single-atom density, providing sufficient active sites for iodine adsorption and catalysis, while maintaining the structural integrity and high surface area of the carbon host. This balance is crucial for achieving the four-electron iodine conversion chemistry.



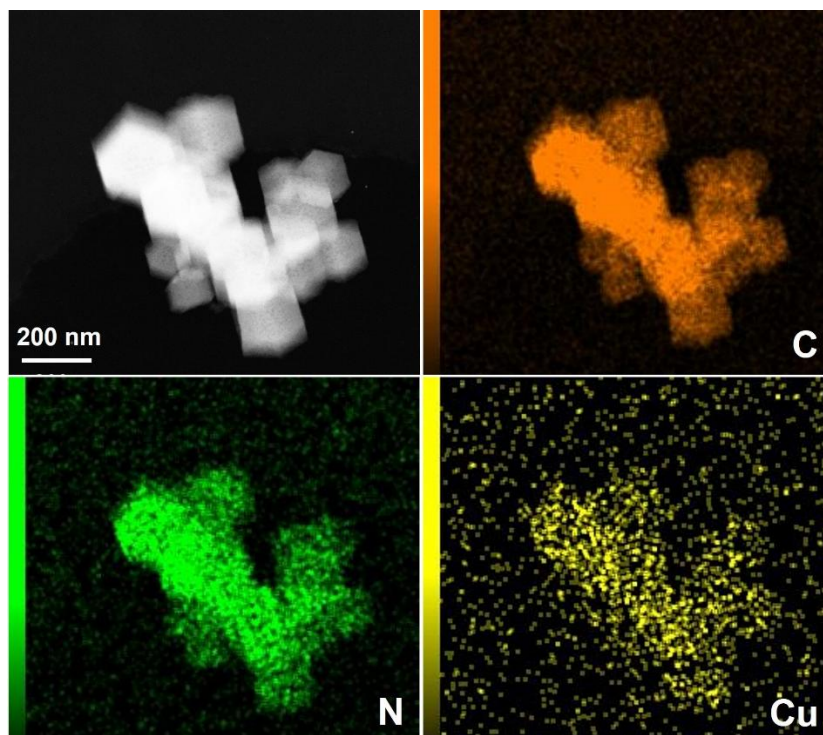
Supplementary Figure 11. TEM, HRTEM images, and the corresponding SAED patterns of (a-c) Cu-N/PC-1, and (d-f) Cu-N/PC-3.



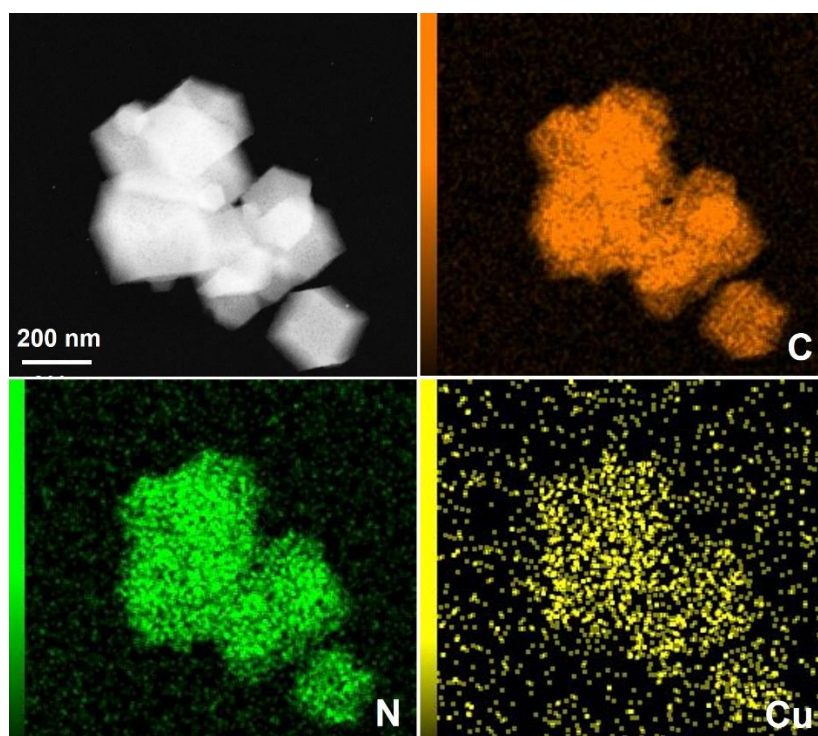
Supplementary Figure 12. XRD patterns of the Cu-N/PC samples before acid washing.



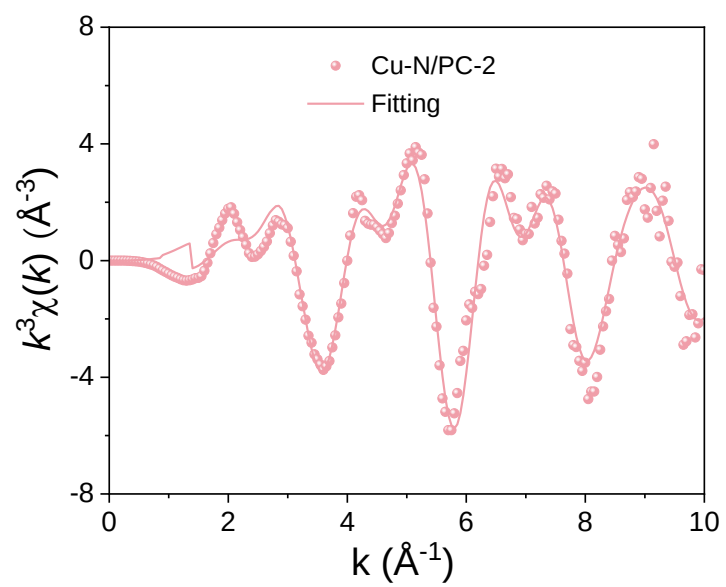
Supplementary Figure 13. XRD pattern of the Cu-N/PC-2 after acid washing.



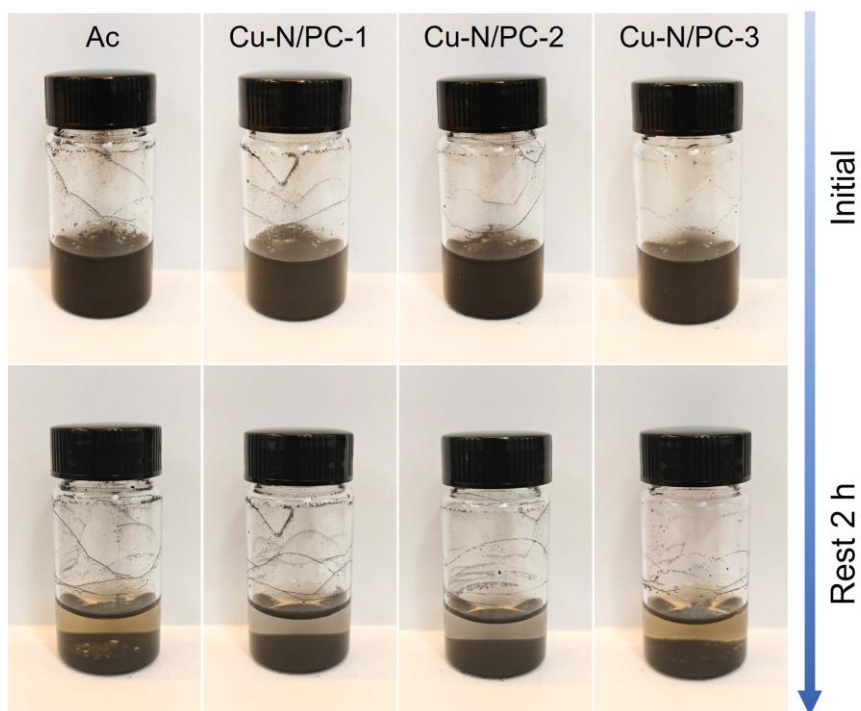
Supplementary Figure 14. EDS mapping images of Cu-N/PC-1.



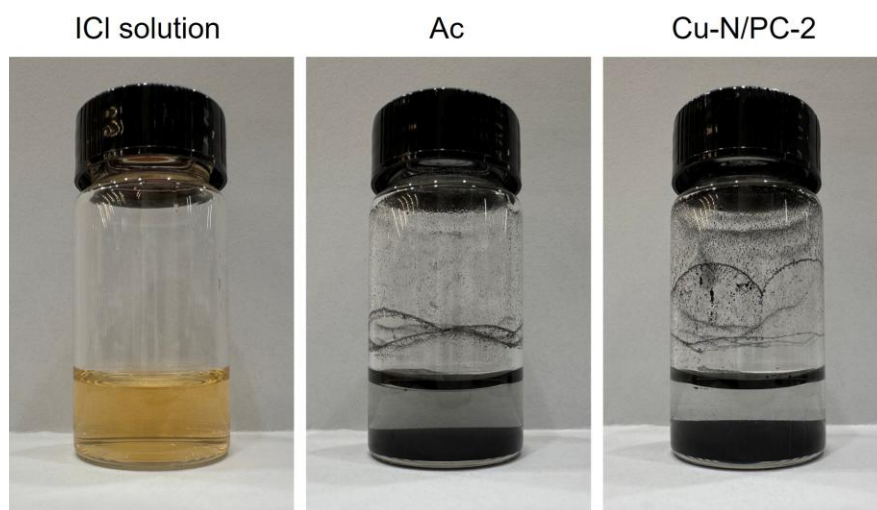
Supplementary Figure 15. EDS mapping images of Cu-N/PC-3.



Supplementary Figure 16. FT-EXAFS fitting curves of Cu-N/PC-2 at the Cu K-edge in k -space.

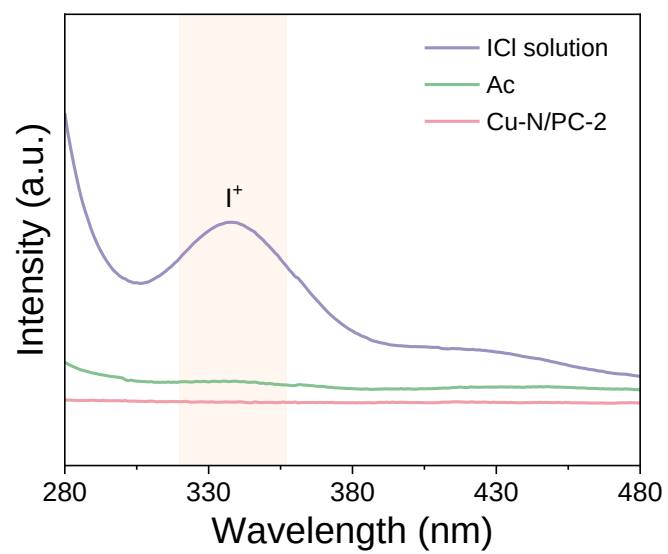


Supplementary Figure 17. Digital photos for the solubility and adsorption tests of the different samples in the iodine solution.

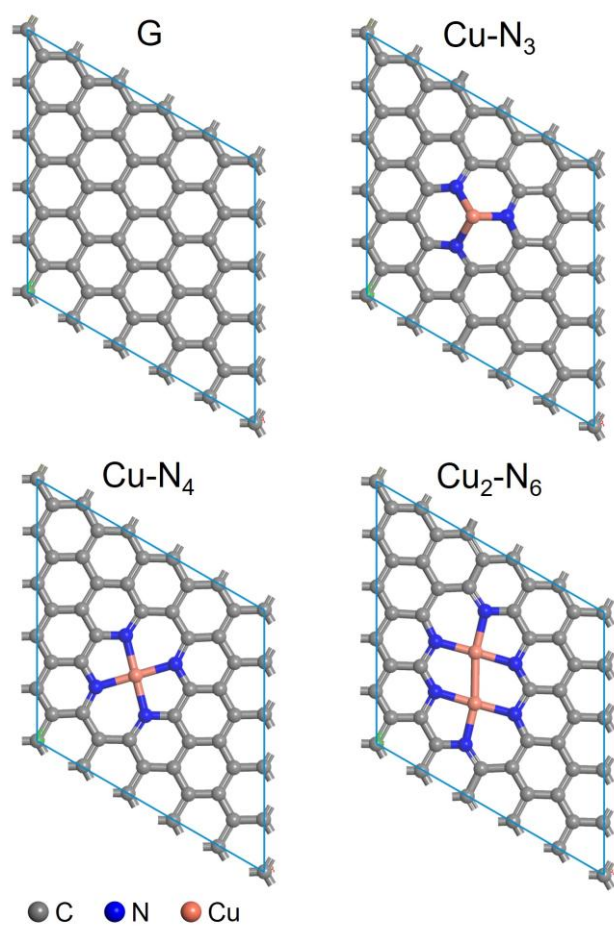


Supplementary Figure 18. Digital photos for the adsorption tests of the different samples in the ICl solution after resting for 2 h (solution: 2M ZS + 0.1M ChCl).

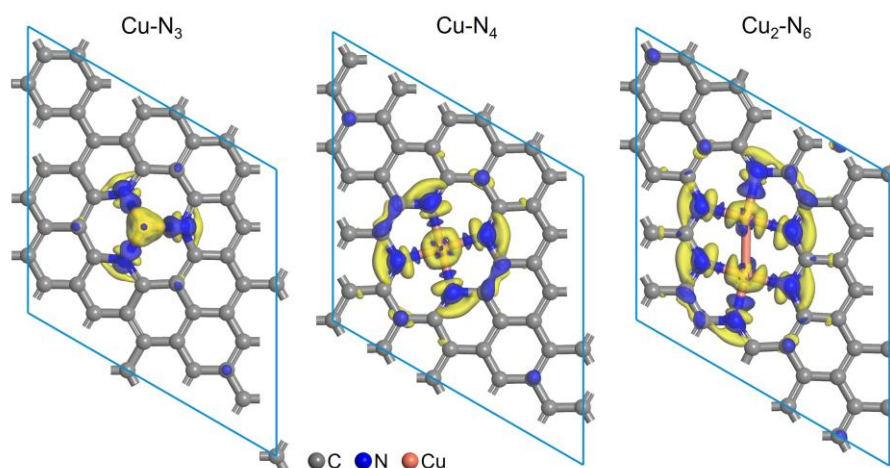
The adsorption capacity of Ac and Cu-N/PC-2 host materials for ICl has been investigated through visualization and spectroscopic experiments. Equal amounts of Ac and Cu-N/PC-2 powder were added into the same concentration of ICl solutions. After standing for two hours, both solutions became transparent (Supplementary Fig. 18), indicating their strong adsorption capacity for ICl due to their high specific surface area. Notably, the Cu-N/PC-2 sample, which contains abundant Cu single-atom sites, exhibits stronger ICl adsorption capacity due to the synergistic effect of its high specific surface area and the Cu single-atom sites. Additionally, the UV-vis spectra were utilized to confirm the ICl adsorption capacity (Supplementary Fig. 19). These results experimentally confirm that the Cu-N/PC-2 single-atom catalyst possesses a strong adsorption capacity for ICl.



Supplementary Figure 19. UV-vis spectra of Ac and Cu-N/PC-2 after being immersed in ICl solution for 2 h.

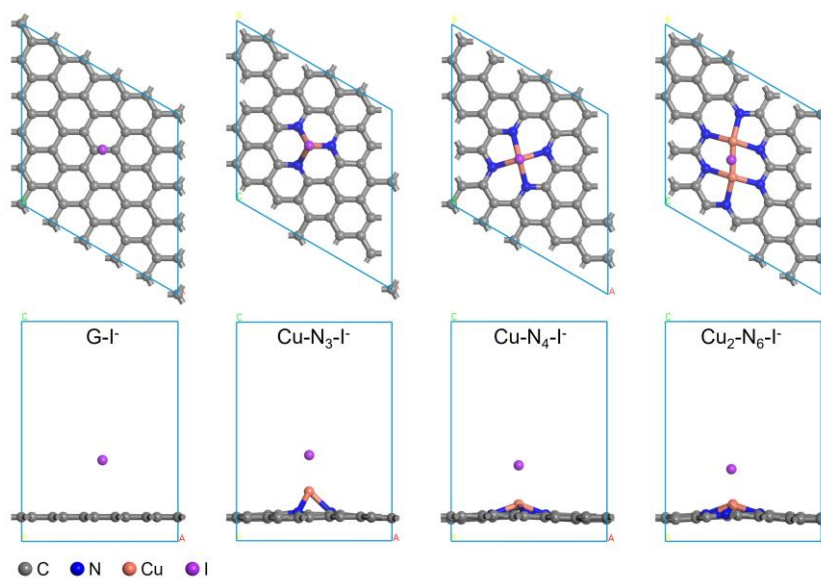


Supplementary Figure 20. Theoretical calculation models of Ac (G) and various Cu-N_x configurations in Cu-N/PC.

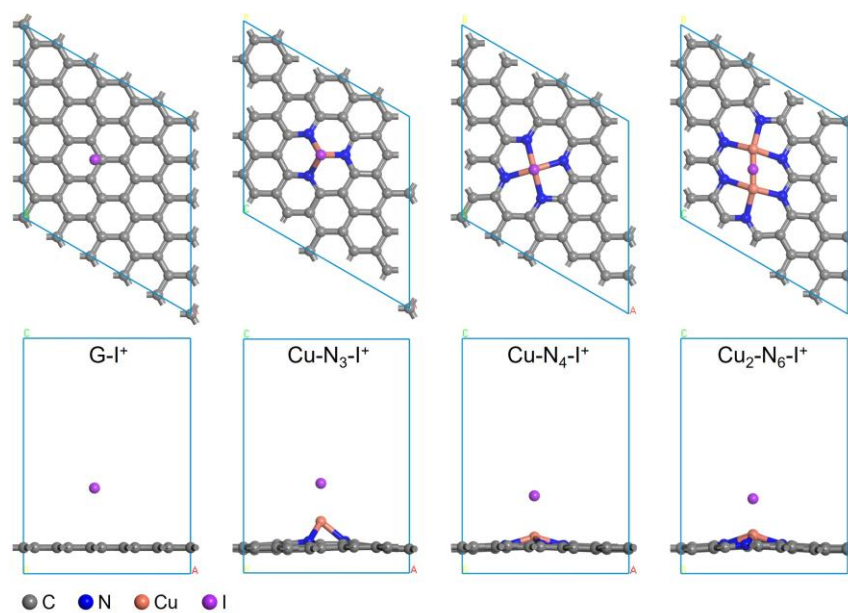


Supplementary Figure 21. Electron density difference patterns of various Cu-N_x configurations in Cu-N/PC.

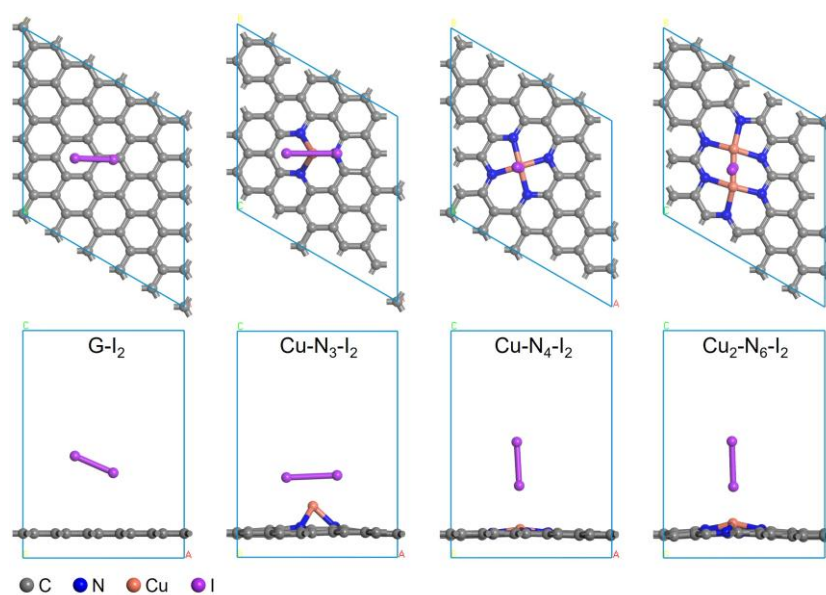
Owing to the strong electron-withdrawing character of Cu, π -electron density is partially shifted from the carbon skeleton toward the Cu center. In the Cu-N_x coordination structure, the higher electronegativity of N withdraws partial electron density from the Cu atom. Overall, these interactions drive a net electron transfer from the carbon matrix to the Cu-N_x sites, resulting in localized electron enrichment around the Cu center and concurrent electron depletion in the neighboring carbon skeleton. This charge redistribution effectively generates positively charged hole-like regions within the carbon host, which can enhance the adsorption and activation of iodine species.



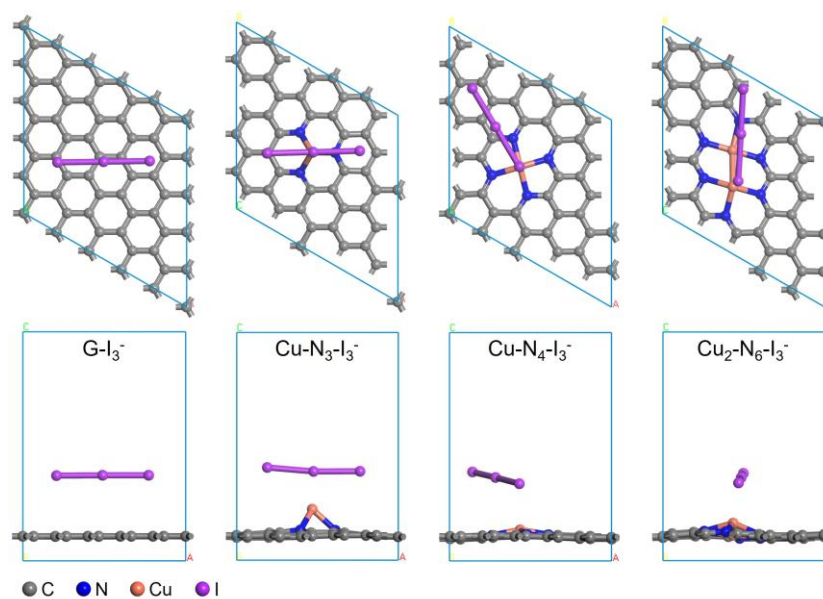
Supplementary Figure 22. The adsorption models of Ac (G) and various Cu-N_x configurations with I⁻.



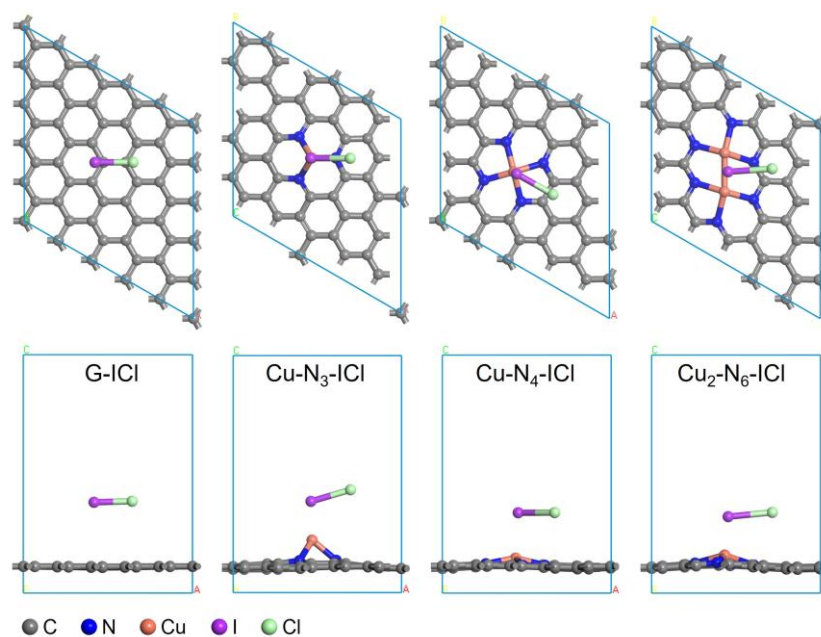
Supplementary Figure 23. The adsorption models of Ac (G) and various Cu-N_x configurations with I⁺.



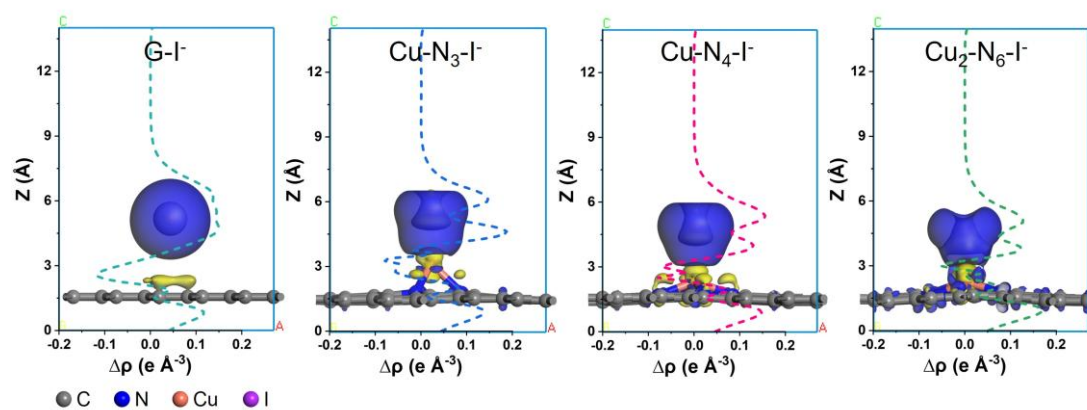
Supplementary Figure 24. The adsorption models of Ac (G) and various Cu-N_x configurations with I₂.



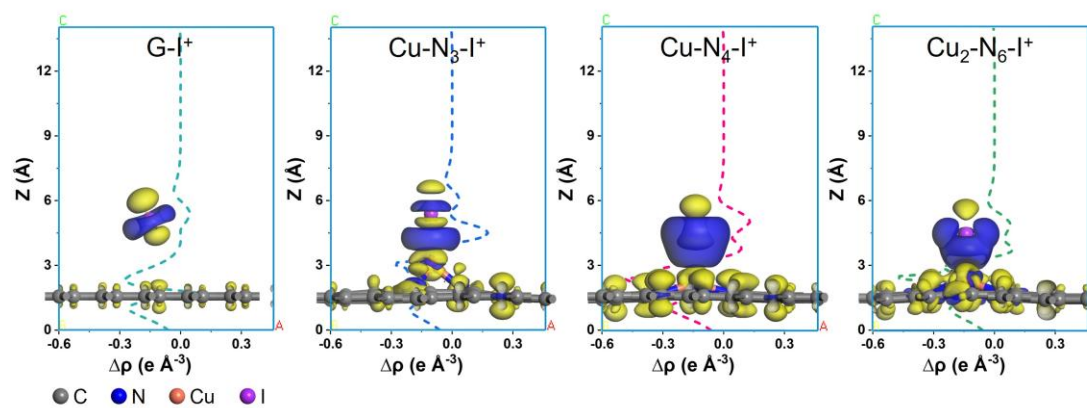
Supplementary Figure 25. The adsorption models of Ac (G) and various Cu-N_x configurations with I₃⁻.



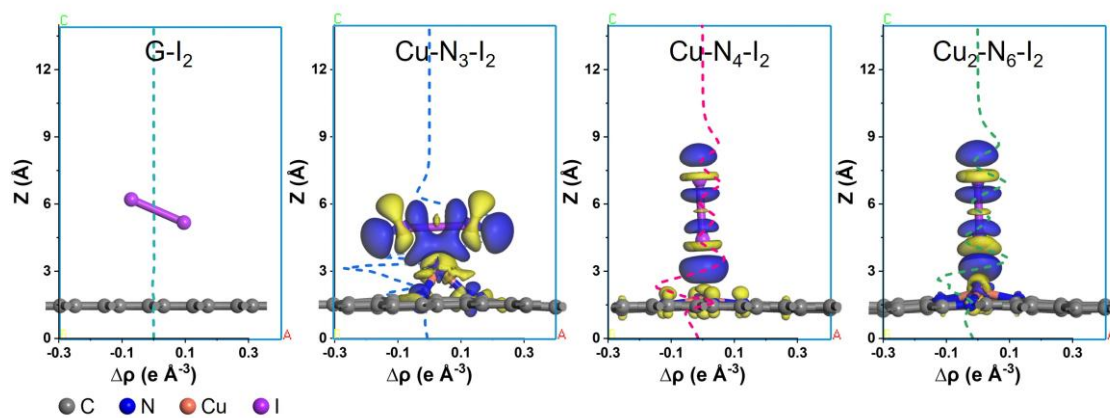
Supplementary Figure 26. The adsorption models of Ac (G) and various Cu-N_x configurations with ICl.



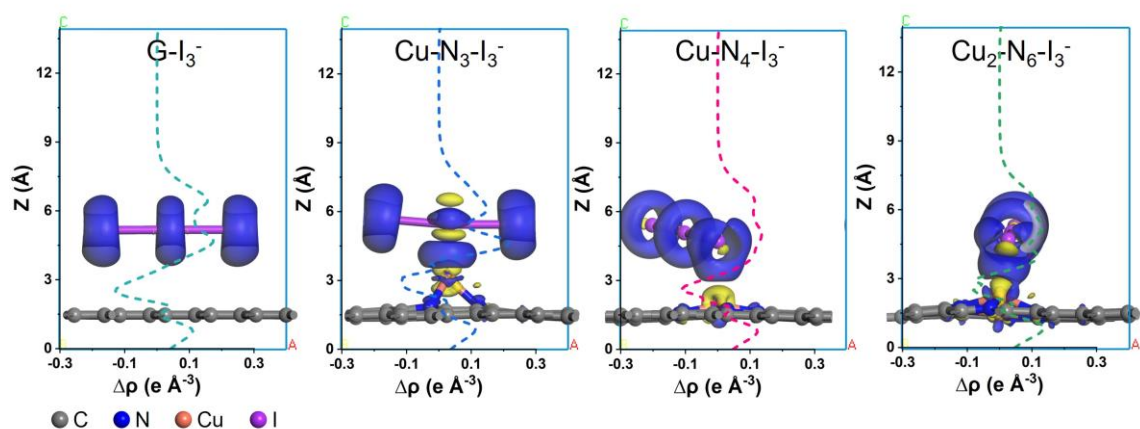
Supplementary Figure 27. Electron density difference patterns of Ac (G) and various Cu-N_x configurations with I⁻.



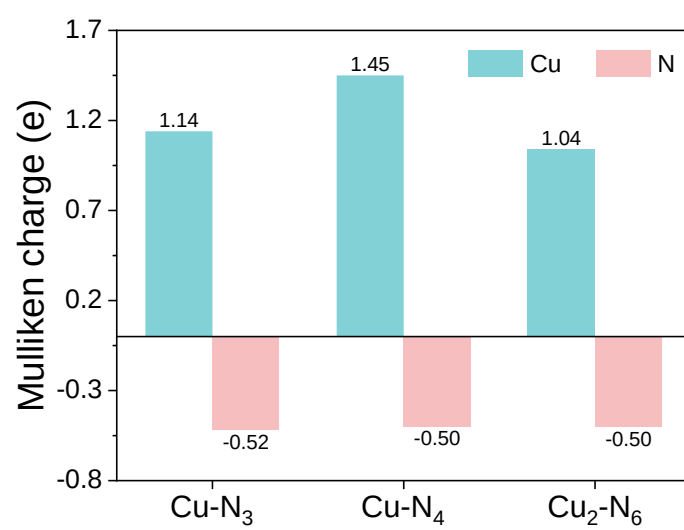
Supplementary Figure 28. Electron density difference patterns of Ac (G) and various Cu-N_x configurations with I⁺.



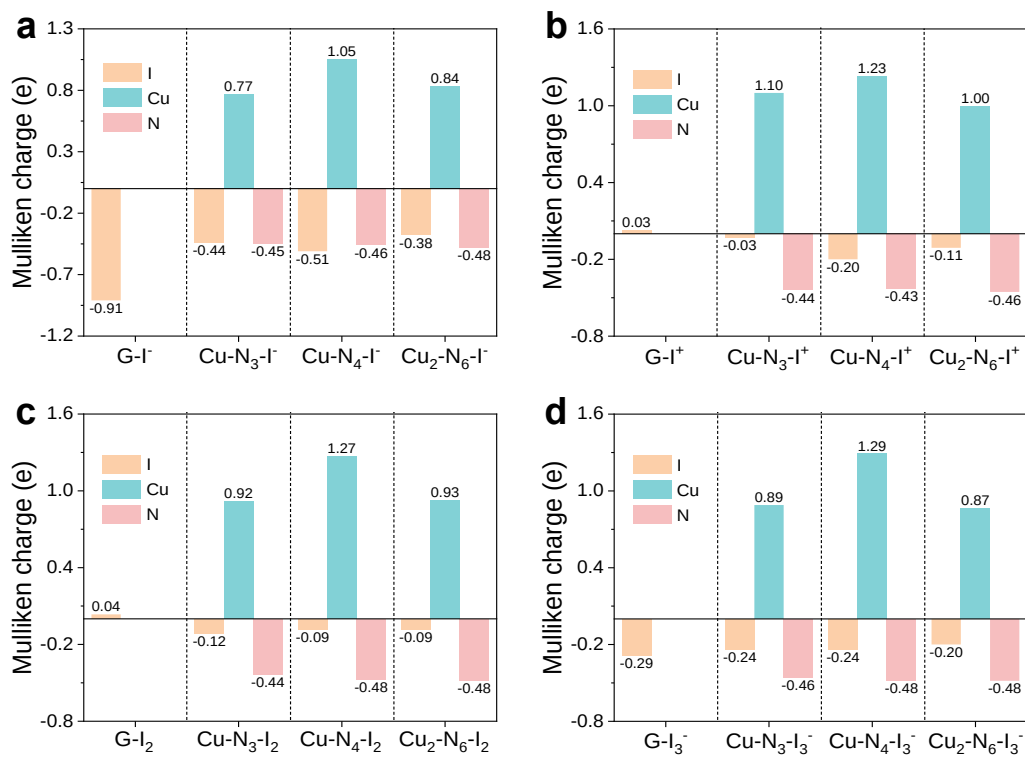
Supplementary Figure 29. Electron density difference patterns of Ac (G) and various $Cu-N_x$ configurations with I_2 .



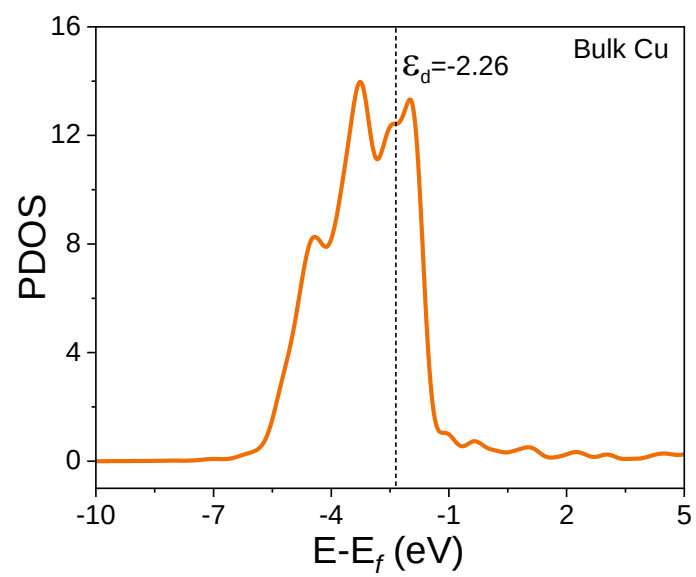
Supplementary Figure 30. Electron density difference patterns of Ac (G) and various Cu- N_x configurations with I_3^- .



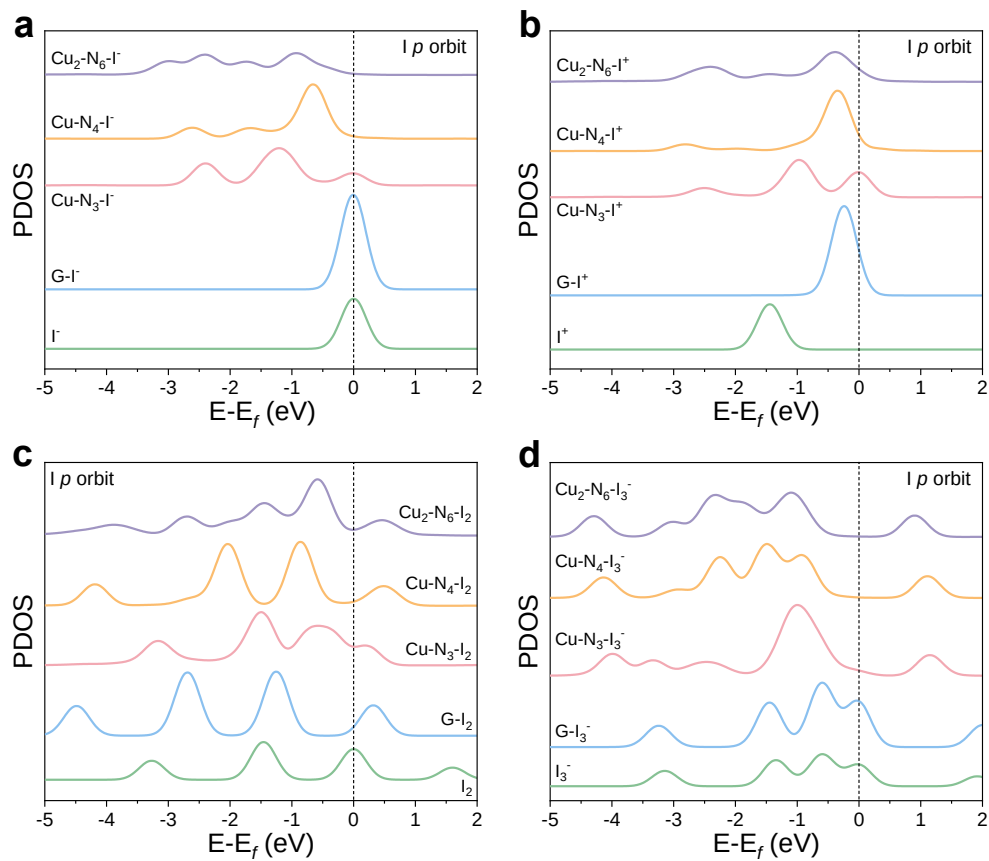
Supplementary Figure 31. Mulliken charge distributions of the various Cu-N_x configurations.



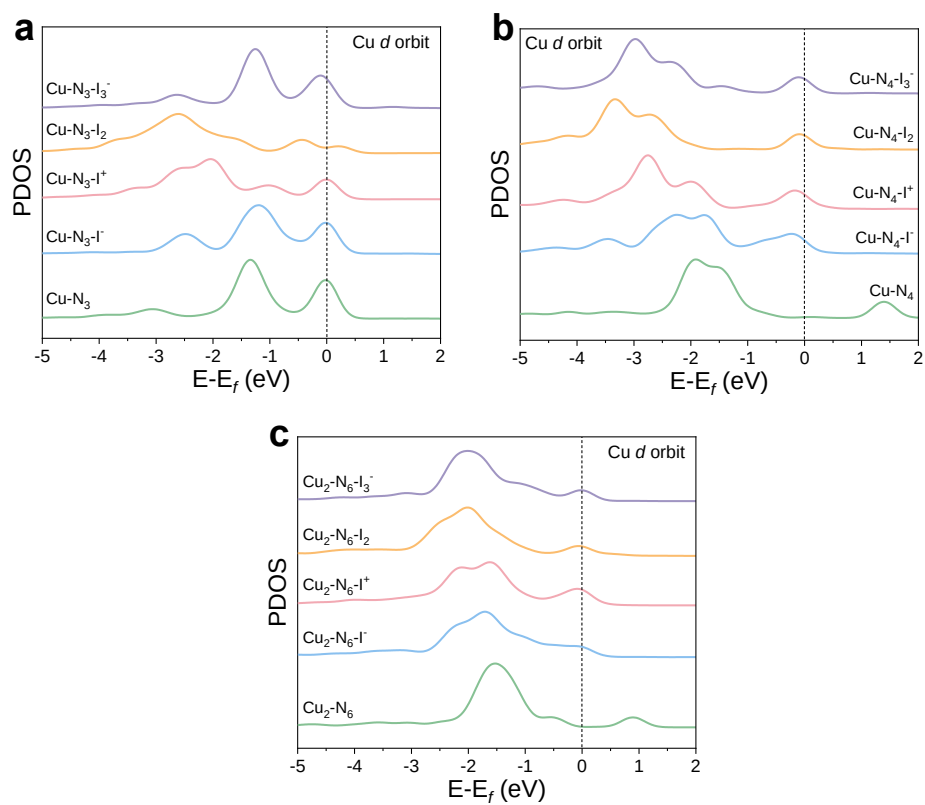
Supplementary Figure 32. Mulliken charge distributions of the various carriers with (a) Γ^- , (b) I^+ , (c) I_2 , and (d) I_3^- .



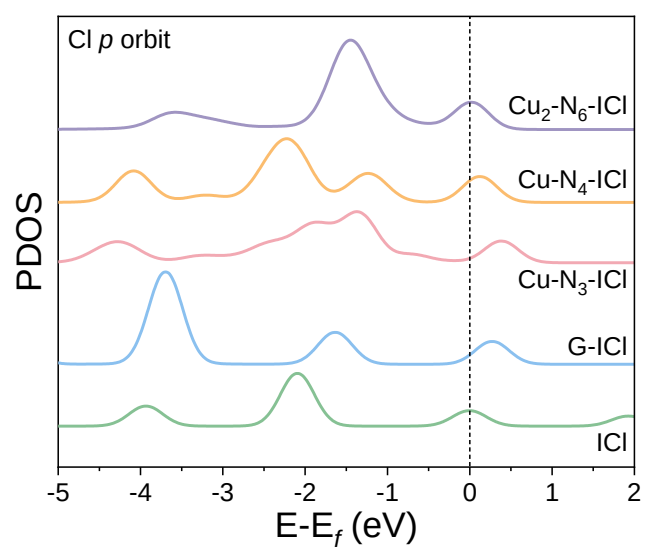
Supplementary Figure 33. The PDOS of Cu *d* orbital and the corresponding *d*-band center value of bulk Cu.



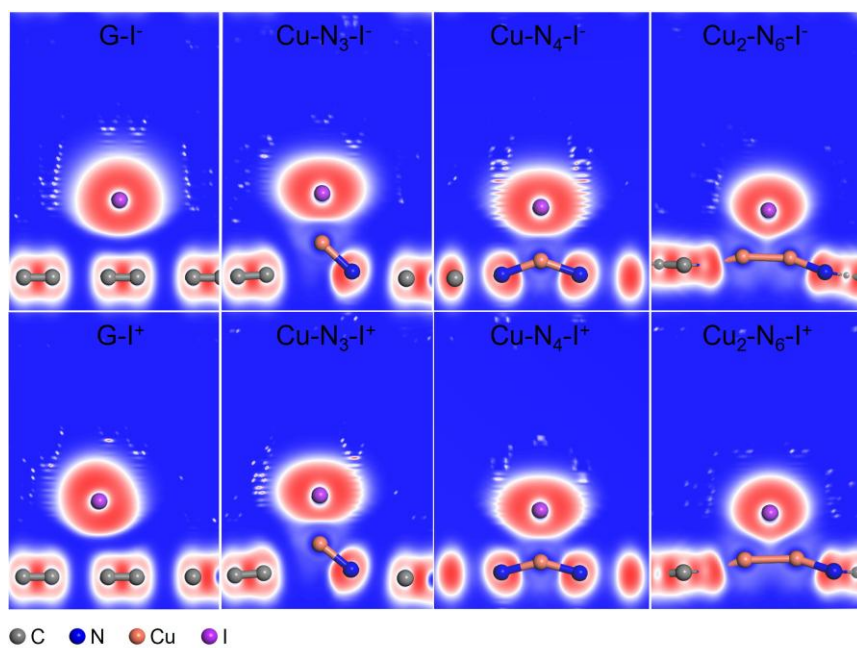
Supplementary Figure 34. The PDOS of the various carriers with (a) I^- , (b) I^+ , (c) I_2 , and (d) I_3^- for the $I p$ orbital.



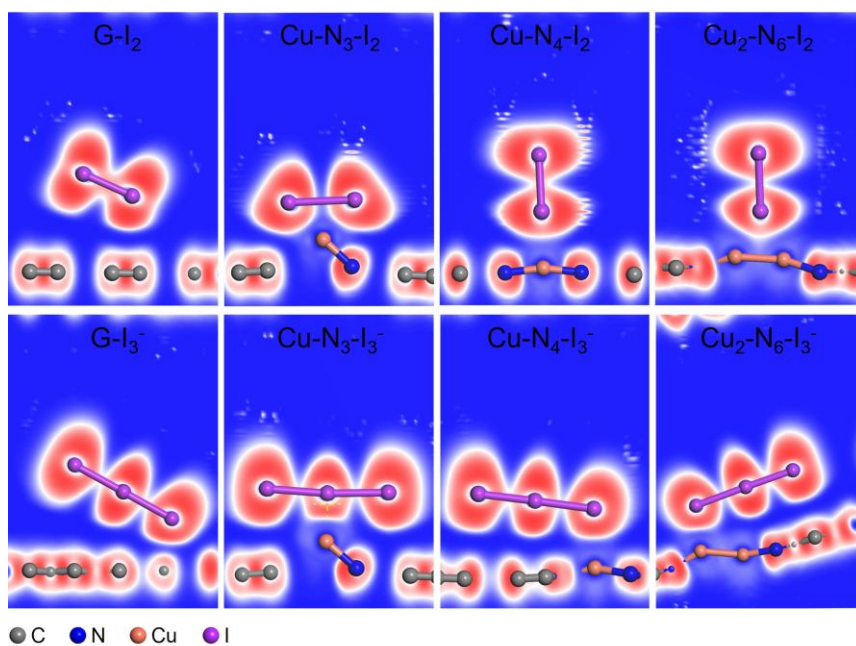
Supplementary Figure 35. The PDOS of the various carriers with iodine species for the Cu *d* orbital. (a) Cu-N₃, (b) Cu-N₄, and (c) Cu₂-N₆.



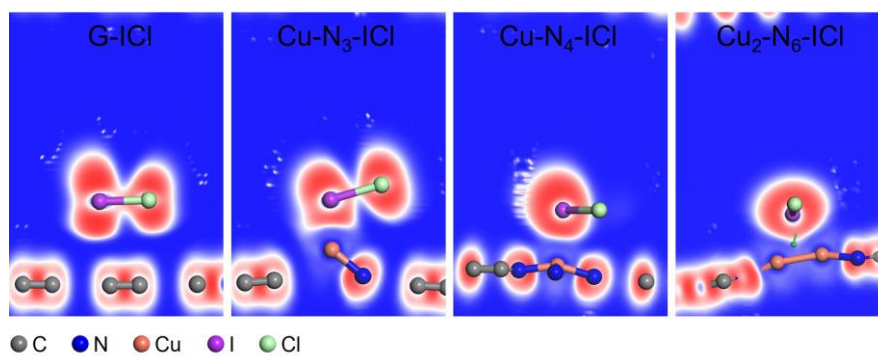
Supplementary Figure 36. The PDOS of the various carriers with ICl for the Cl p orbital.



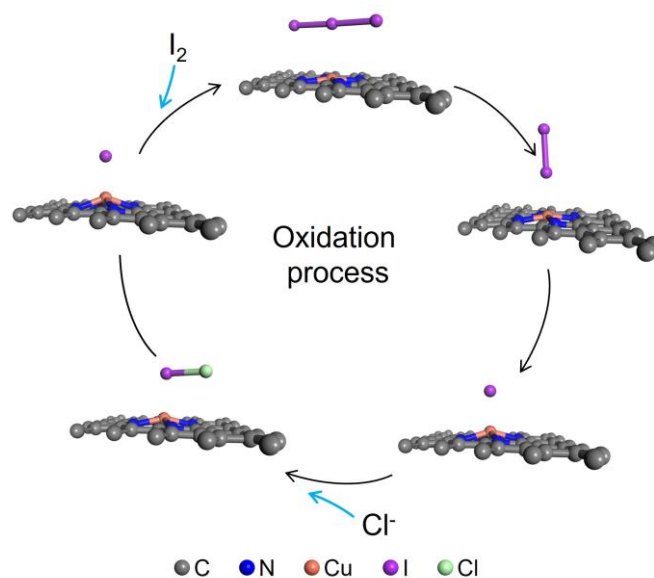
Supplementary Figure 37. ELF patterns of Ac (G) and various $Cu-N_x$ configurations with I^- and I^+ .



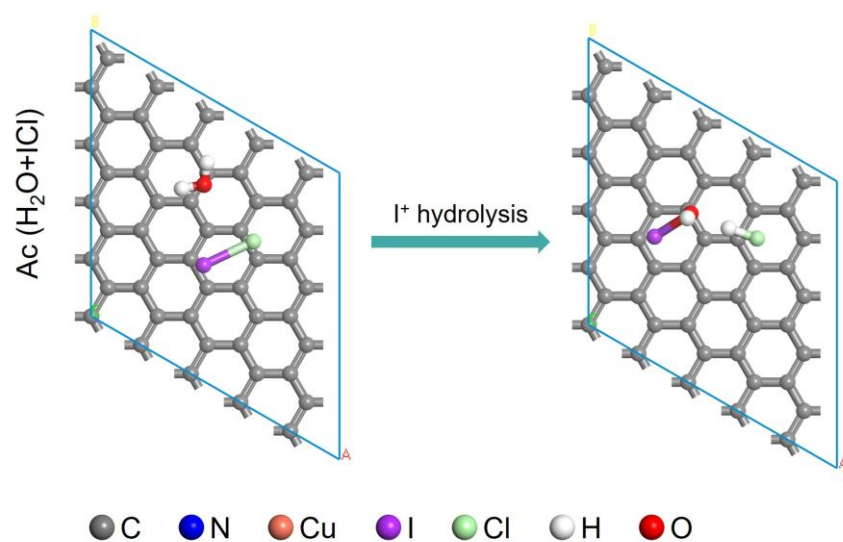
Supplementary Figure 38. ELF patterns of Ac (G) and various $Cu-N_x$ configurations with I_2 and I_3^- .



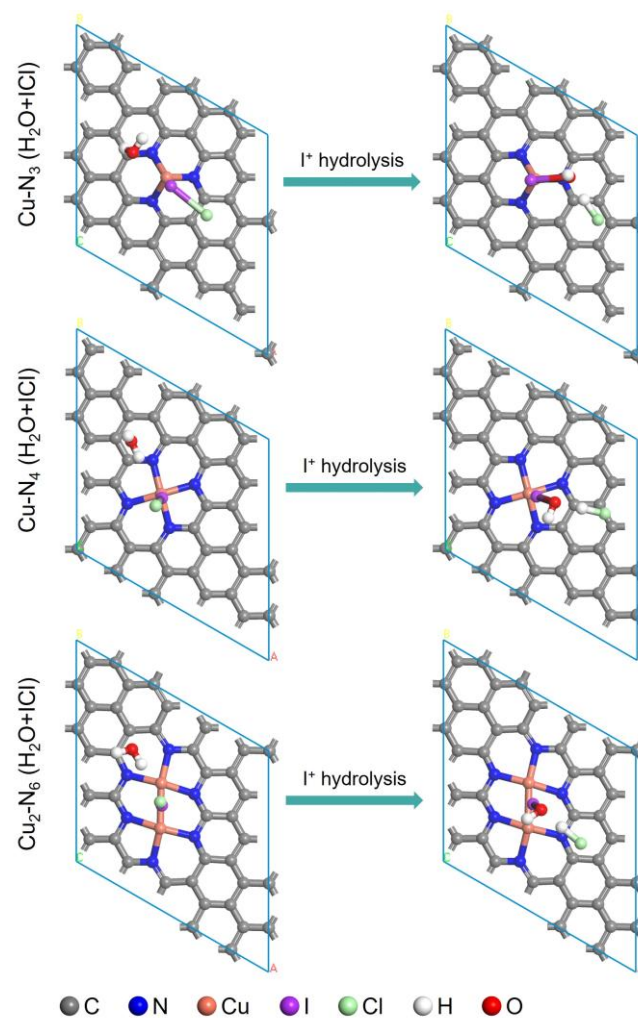
Supplementary Figure 39. ELF patterns of Ac (G) and various Cu-N_x configurations with ICl.



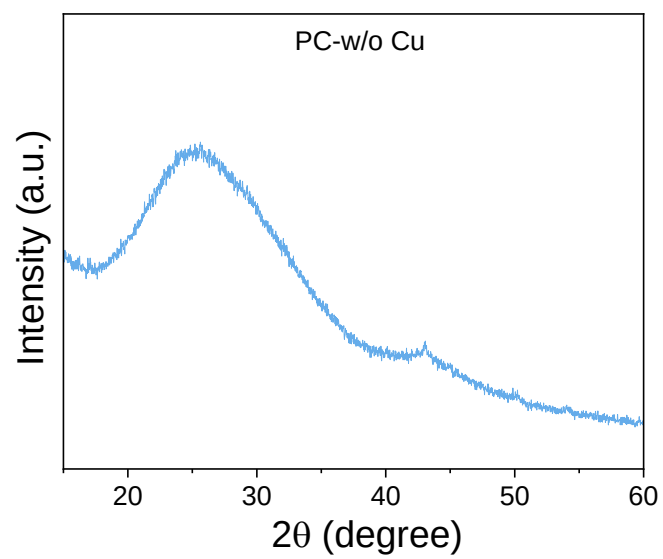
Supplementary Figure 40. Schematic diagram of the oxidation process of I^- (Take Cu-N_4 -containing carbon carrier as an example).



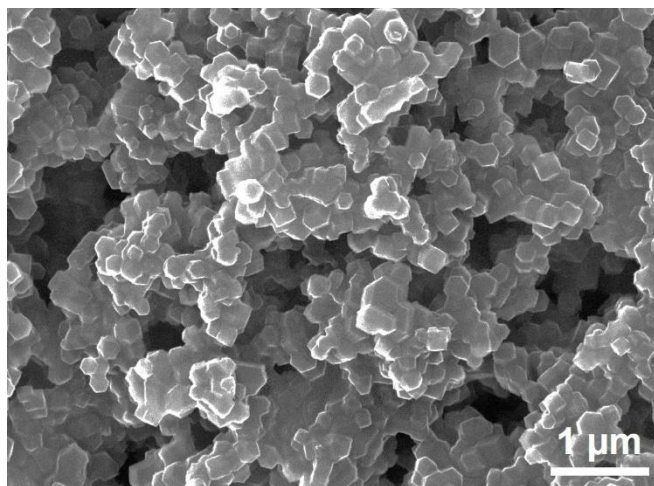
Supplementary Figure 41. The structure models of the ICl hydrolysis reaction with Ac.



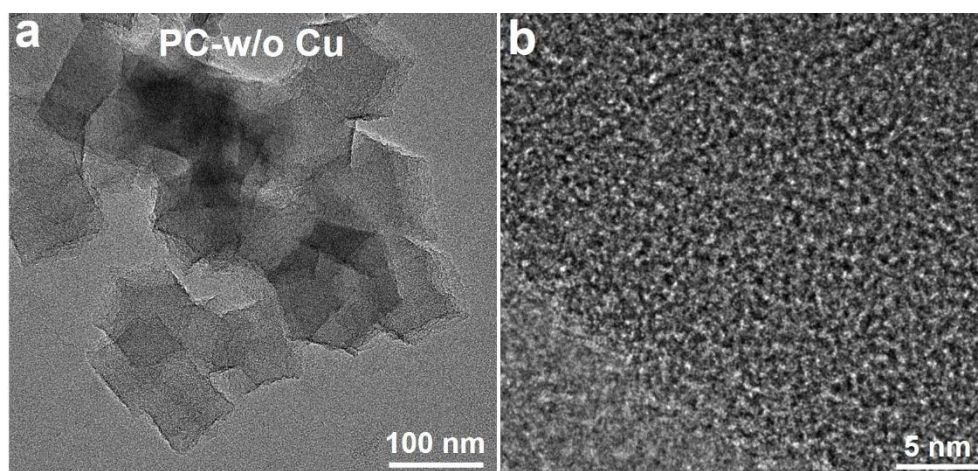
Supplementary Figure 42. The structure models of the ICl hydrolysis reaction with various Cu-N_x configuration carriers.



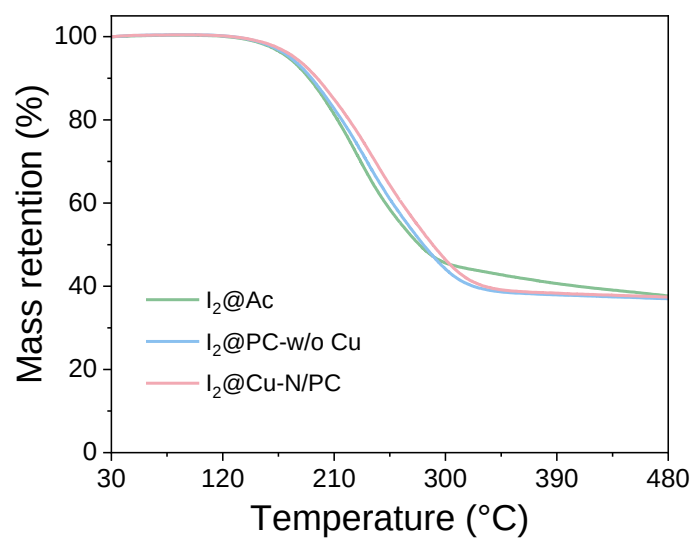
Supplementary Figure 43. XRD pattern of PC-w/o Cu.



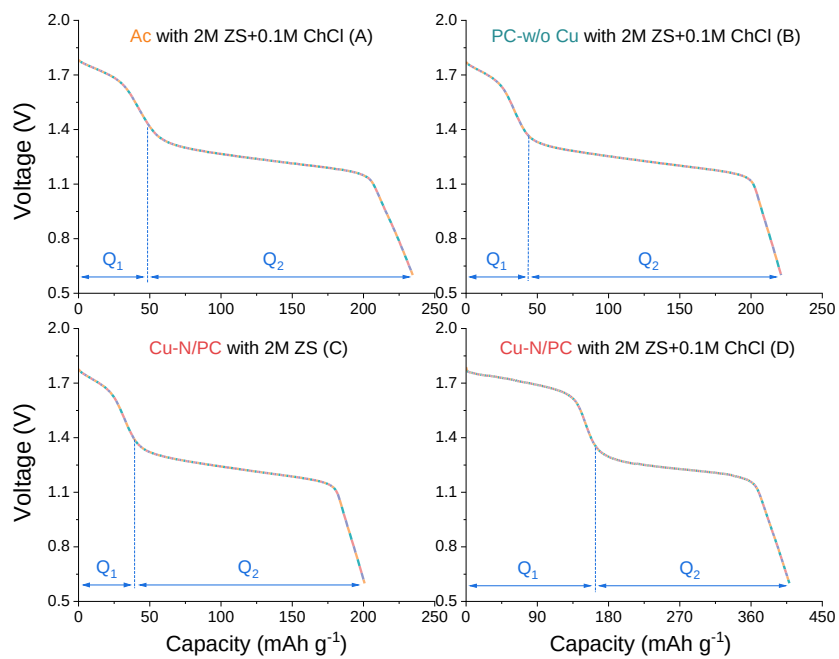
Supplementary Figure 44. SEM image of PC-w/o Cu.



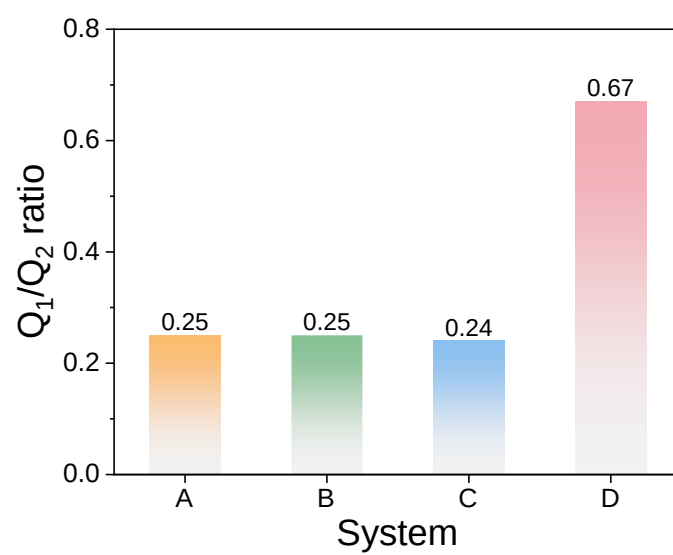
Supplementary Figure 45. (a) TEM and (b) HRTEM image of PC-w/o Cu.



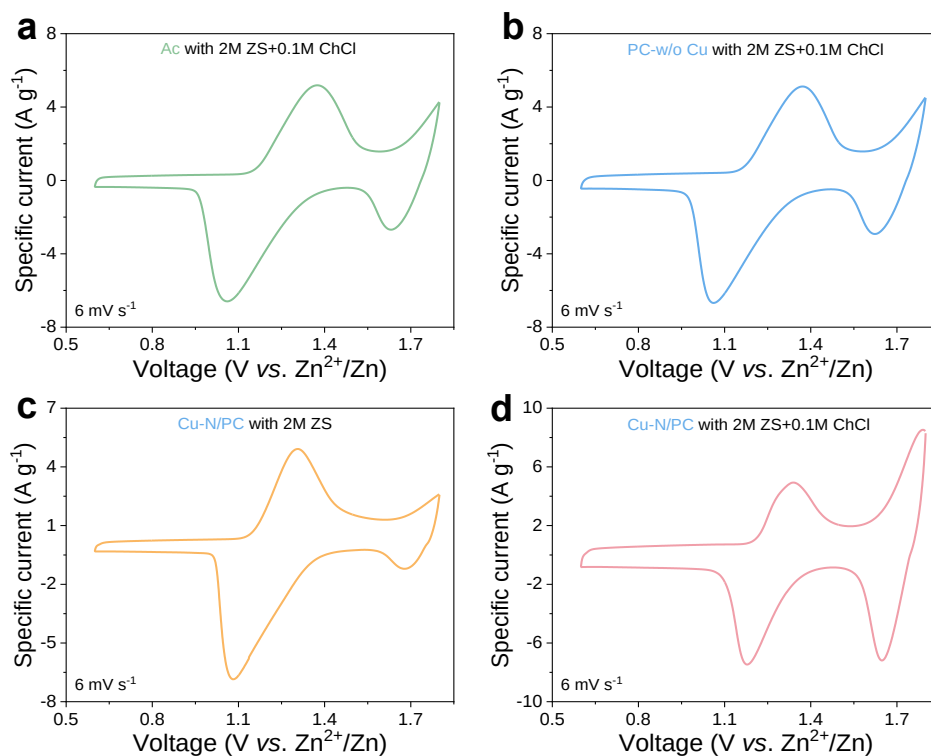
Supplementary Figure 46. Thermogravimetric analysis (TGA) of the different positive electrodes at 5.0 °C min⁻¹.



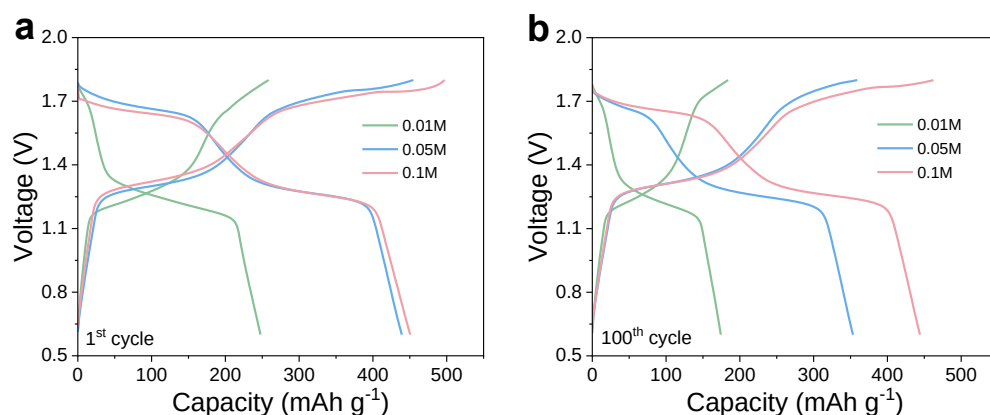
Supplementary Figure 47. Discharge curves of various positive electrodes with 2M ZS or 2M ZS+0.1M ChCl electrolytes at 1 A g⁻¹ (Test temperature: 25 ± 2 °C).



Supplementary Figure 48. Q_1/Q_2 values of different systems (Data from Supplementary Fig. 47).

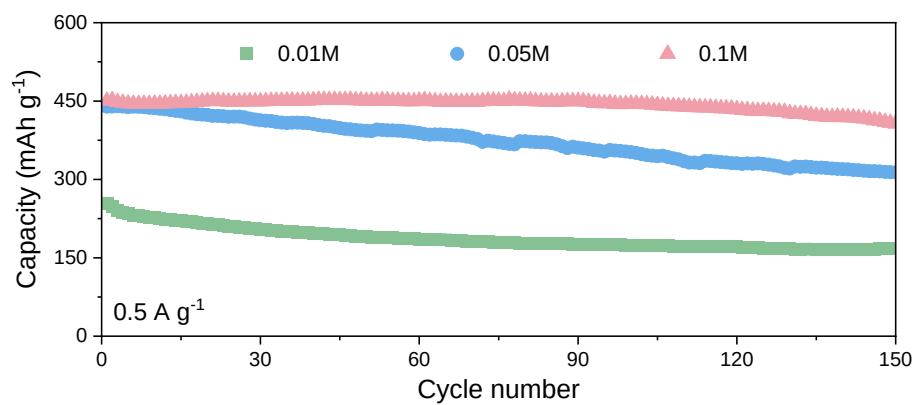


Supplementary Figure 49. CV curves of various positive electrodes with 2M ZS or 2M ZS+0.1M ChCl electrolytes (Test temperature: 25 ± 2 °C). (a) AC with 2M ZS + 0.1M ChCl, (b) PC-w/o Cu with 2M ZS + 0.1M ChCl, (c) Cu-N/PC with 2M ZS, and (d) Cu-N/PC with 2M ZS + 0.1M ChCl.

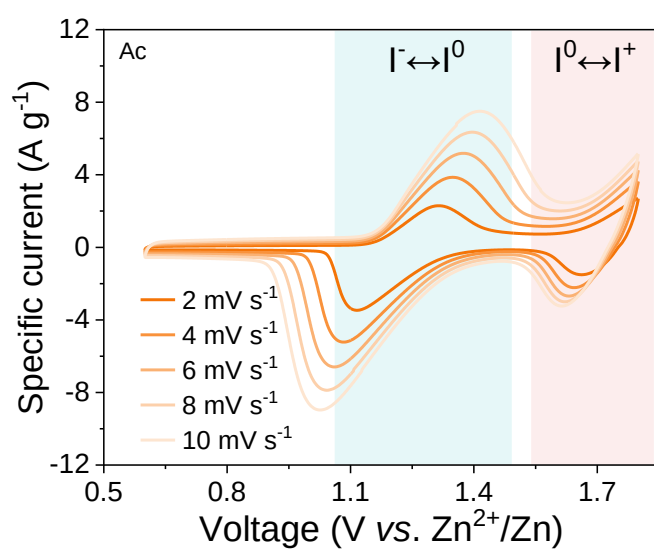


Supplementary Figure 50. Galvanostatic discharge-charge curves of zinc||iodine batteries at 0.5 A g⁻¹ with the different ChCl concentrations (Test temperature: 25 ± 2 °C). (a) The first cycle and (b) The 100th cycle.

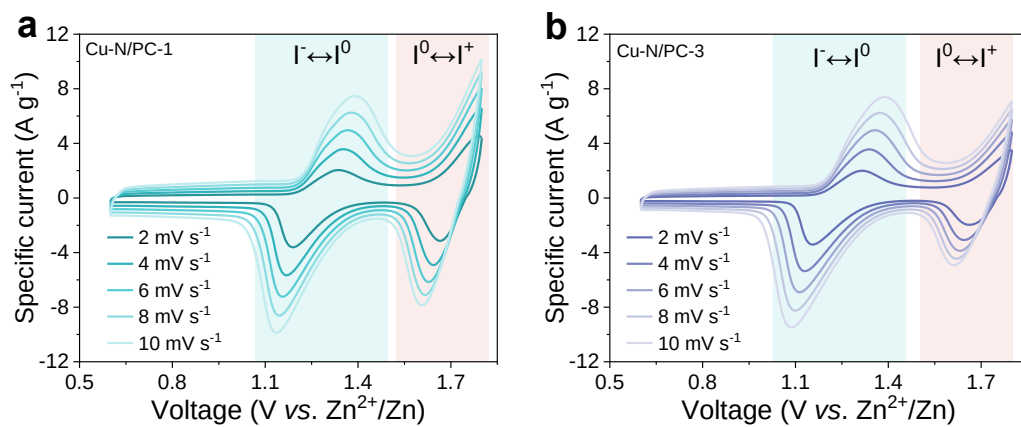
When the ChCl concentration reduces to 0.05M, the I⁺/I⁰ conversion is successfully activated, indicating that Cl⁻ concentration can activate the I⁺/I⁰ conversion through ICl complex formation. However, the cycling stability is significantly degraded compared to 0.1M ChCl. Specifically, the capacity retention after 150 cycles is only 71.4%, which is substantially lower than the 90.3% capacity retention observed for 0.1M ChCl (Supplementary Fig. 51). This degradation likely arises from insufficient Cl⁻ availability over extended cycling. During the cycling process, some Cl⁻ may be consumed or immobilized (e.g., through adsorption or irreversible side reactions), and a lower initial concentration becomes insufficient to maintain a stable I-Cl microenvironment at the positive electrode interface. Consequently, I⁺ species become vulnerable to hydrolysis, leading to capacity decay. When the ChCl concentration further reduces to 0.01M, the high-voltage plateau corresponding to the I⁺/I⁰ conversion is completely absent. Only the conventional two-electron I⁻/I⁰ conversion is observed, indicating that 0.01M ChCl provides an insufficient Cl⁻ concentration to effectively stabilize I⁺. The formation of ICl complexes is likely hindered by the low Cl⁻ activity, and any I⁺ generated at the Cu-N_x sites rapidly undergoes hydrolysis before it can be stabilized.



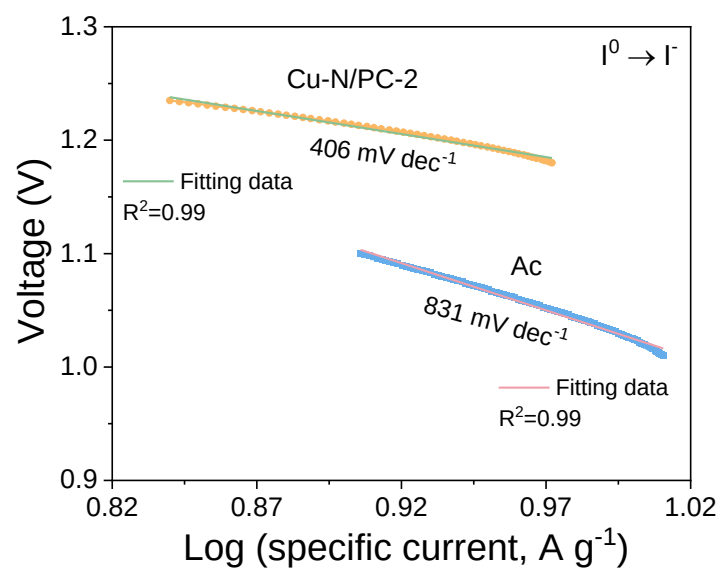
Supplementary Figure 51. Cycling performance of zinc||iodine batteries at 0.5 A g^{-1} with the different ChCl concentrations (Test temperature: $25 \pm 2 \text{ }^{\circ}\text{C}$).



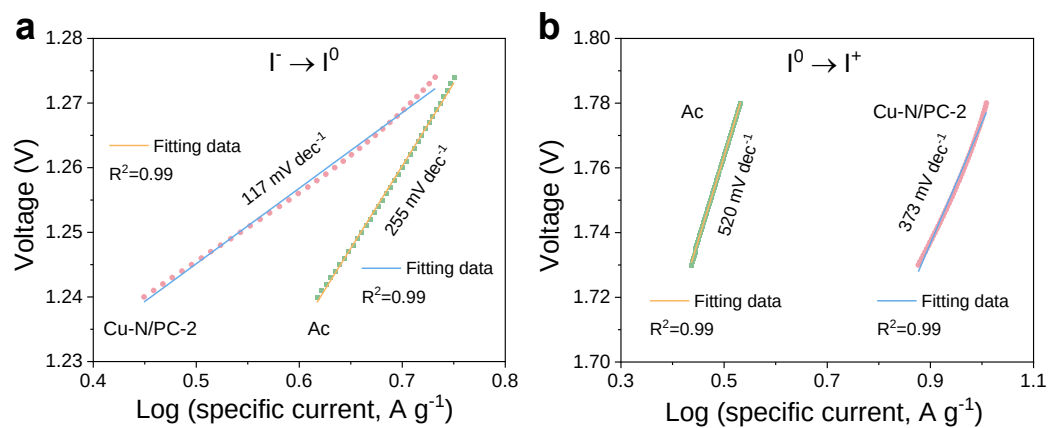
Supplementary Figure 52. CV curves of the zinc||iodine battery with Ac (Test temperature: 25 ± 2 °C).



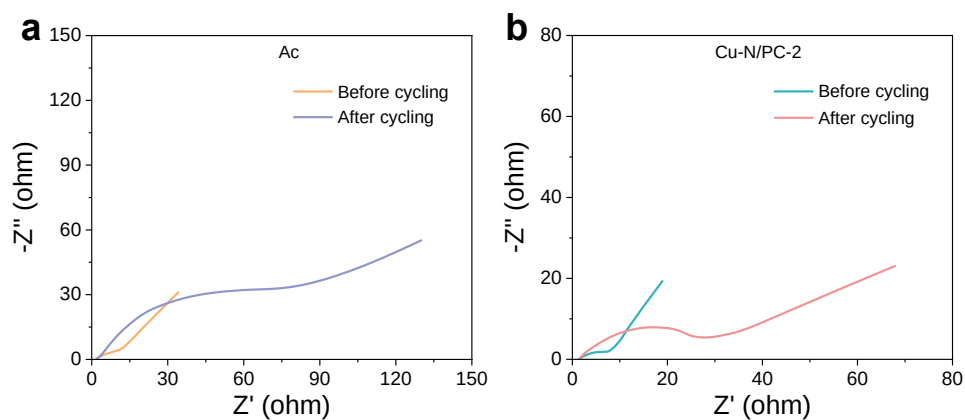
Supplementary Figure 53. CV curves of the zinc||iodine batteries with (a) Cu-N/PC-1, and (b) Cu-N/PC-3 (Test temperature: $25 \pm 2^\circ\text{C}$).



Supplementary Figure 54. Tafel plots in low discharge voltage regions with Ac and Cu-N/PC-2.

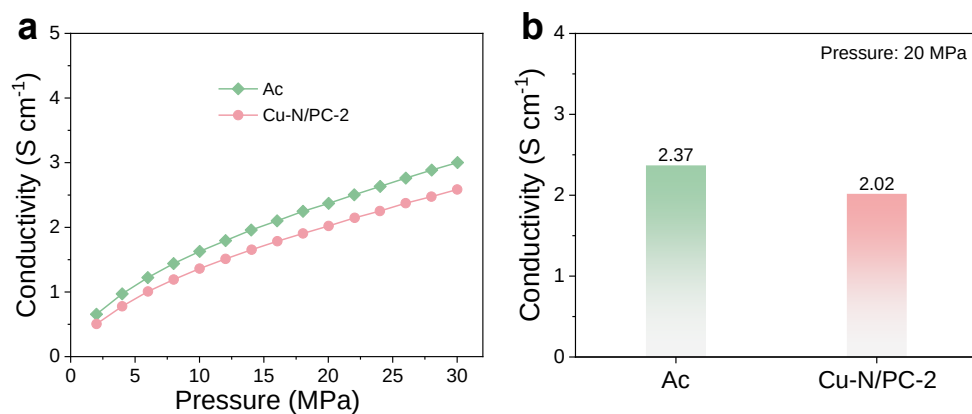


Supplementary Figure 55. Tafel plots for the oxidation process of iodine with Ac and Cu-N/PC-2.

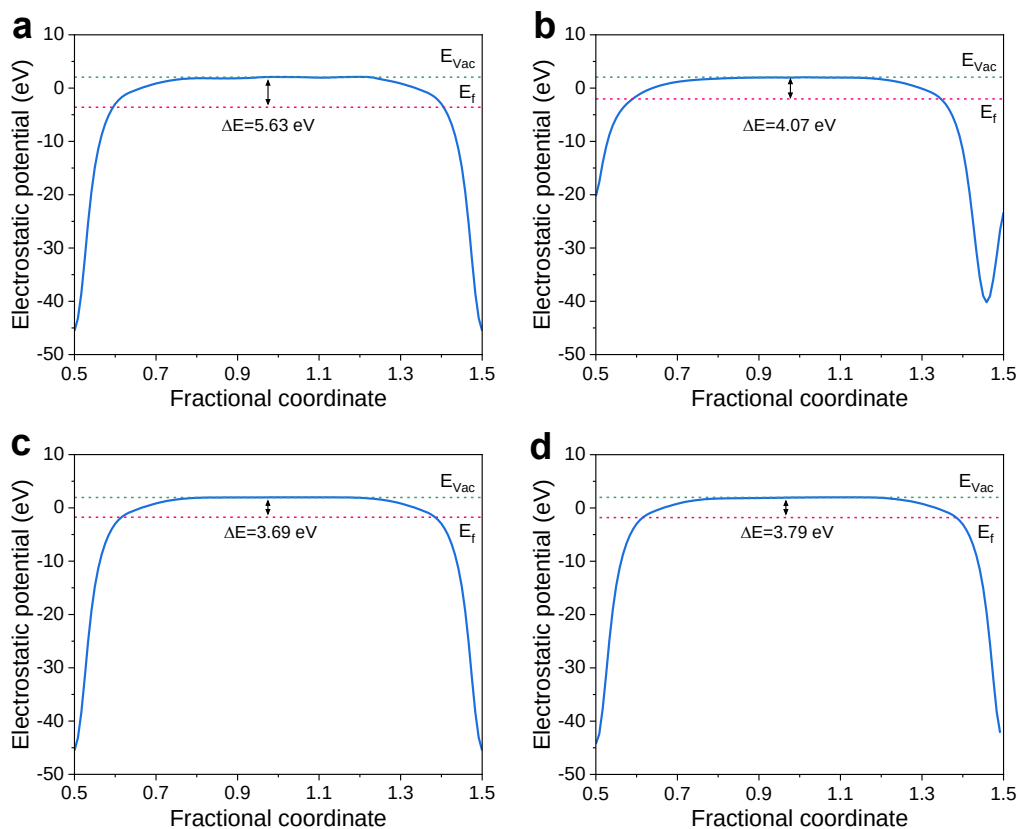


Supplementary Figure 56. The EIS curves of (a) Ac and (b) Cu-N/PC-2 before and after cycling.

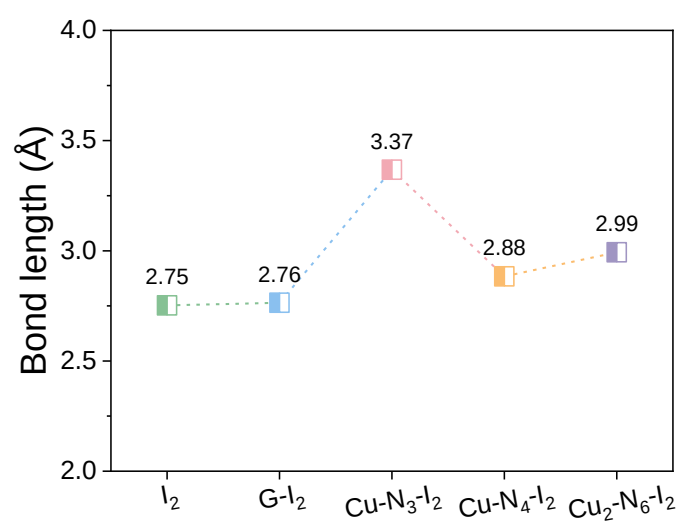
The measurements were performed at 25 ± 2 °C before and after 50 cycles at 1 A g^{-1} .



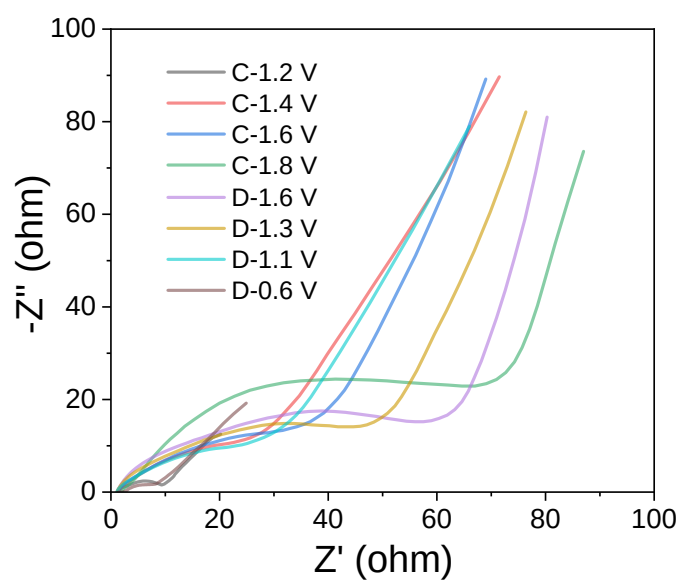
Supplementary Figure 57. (a) The electrical conductivity of Ac and Cu-N/PC-2 under different pressures. (b) The electrical conductivity of Ac and Cu-N/PC-2 at a pressure of 20 MPa.



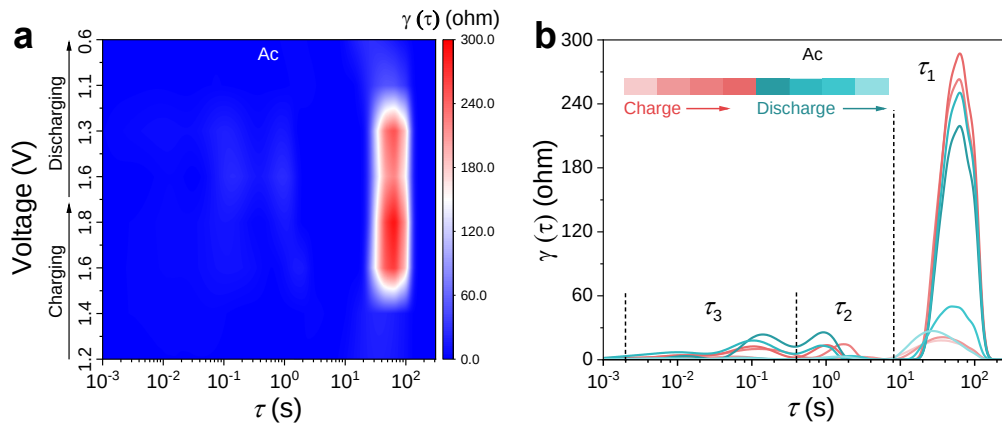
Supplementary Figure 58. The work function curves of the various carrier surfaces. (a) G, (b) Cu-N₃, (c) Cu-N₄, and (d) Cu₂-N₆.



Supplementary Figure 59. The bond lengths of the I-I bond on the various carrier surfaces.

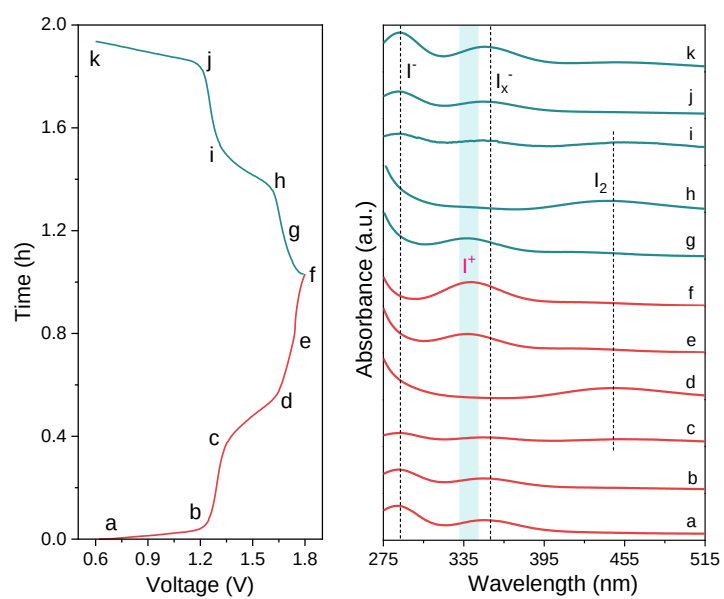


Supplementary Figure 60. EIS spectra of the zinc||iodine battery with Ac during the charge/discharge process (C: charge; D: discharge; Specific current: 1 A g^{-1} ; Rest time: 10 min; Test temperature: $25 \pm 2 \text{ }^{\circ}\text{C}$).

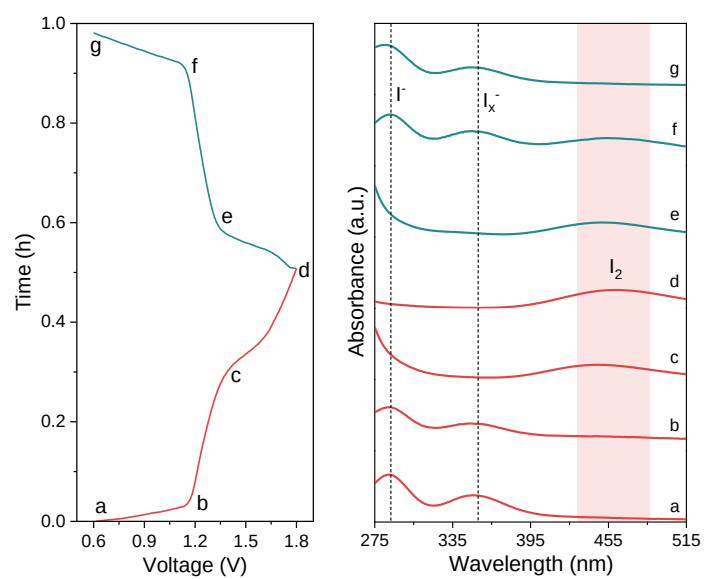


Supplementary Figure 61. (a) 2D DRT patterns, and (b) 2D DRT spectra of the zinc||iodine battery with Ac during the charge/discharge process.

In the DRT spectra, the x-axis corresponds to the relaxation time constant ($\tau = RC$, where R is the resistance and C is the capacitance). This parameter is independent of electrode surface area and reflects the intrinsic kinetics of each electrochemical process¹. The amplitude of each peak in the DRT spectra quantitatively represents the polarization resistance attributed to the associated relaxation step. Accordingly, the electrochemical process with distinct characteristic relaxation times appears as separate peaks in the DRT spectra, allowing their temporal resolution and unambiguous mechanistic interpretation.



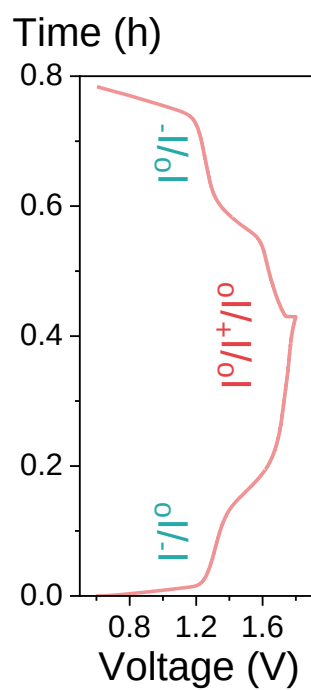
Supplementary Figure 62. GCD curve at 0.5 A g^{-1} and *in situ* UV-vis spectra of zinc||iodine battery with Cu-N/PC-2 (Test temperature: $25 \pm 2 \text{ }^\circ\text{C}$).



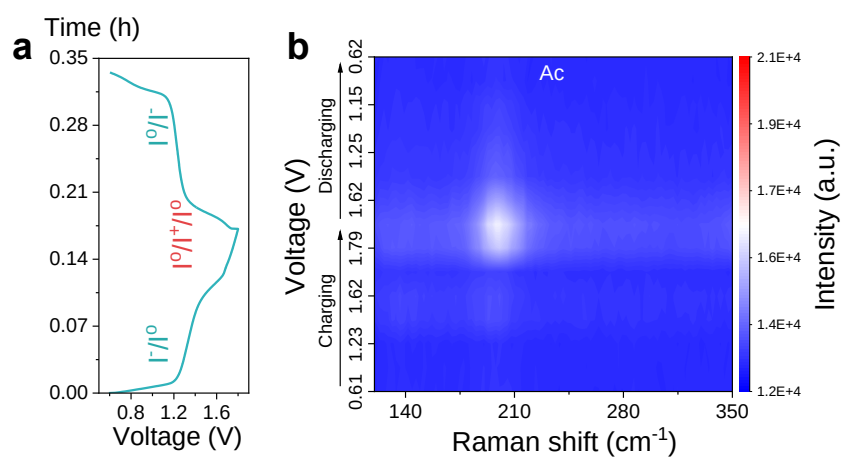
Supplementary Figure 63. GCD curve at 0.5 A g^{-1} and *in situ* UV-vis spectra of zinc||iodine battery with Ac (Test temperature: $25 \pm 2 \text{ }^\circ\text{C}$).



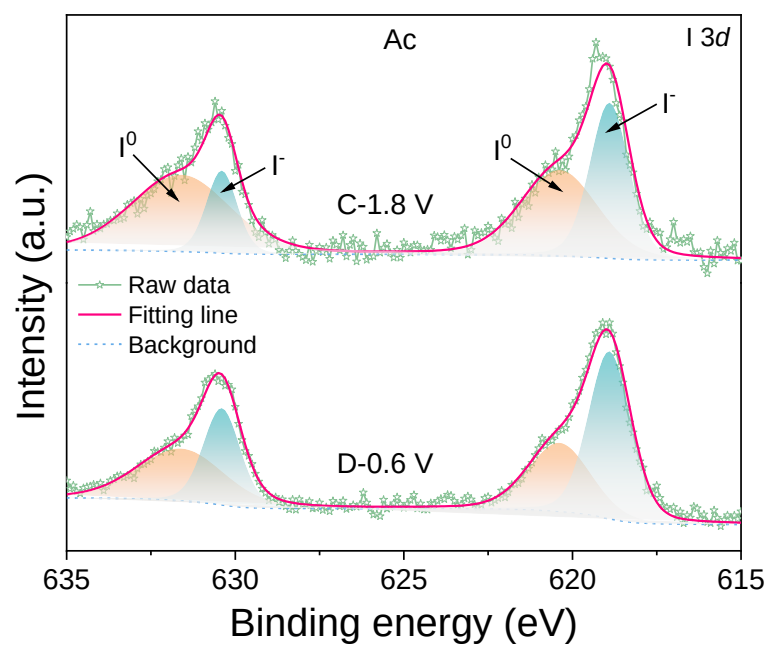
Supplementary Figure 64. Photographs of the customized battery device for *in situ* Raman measurement.



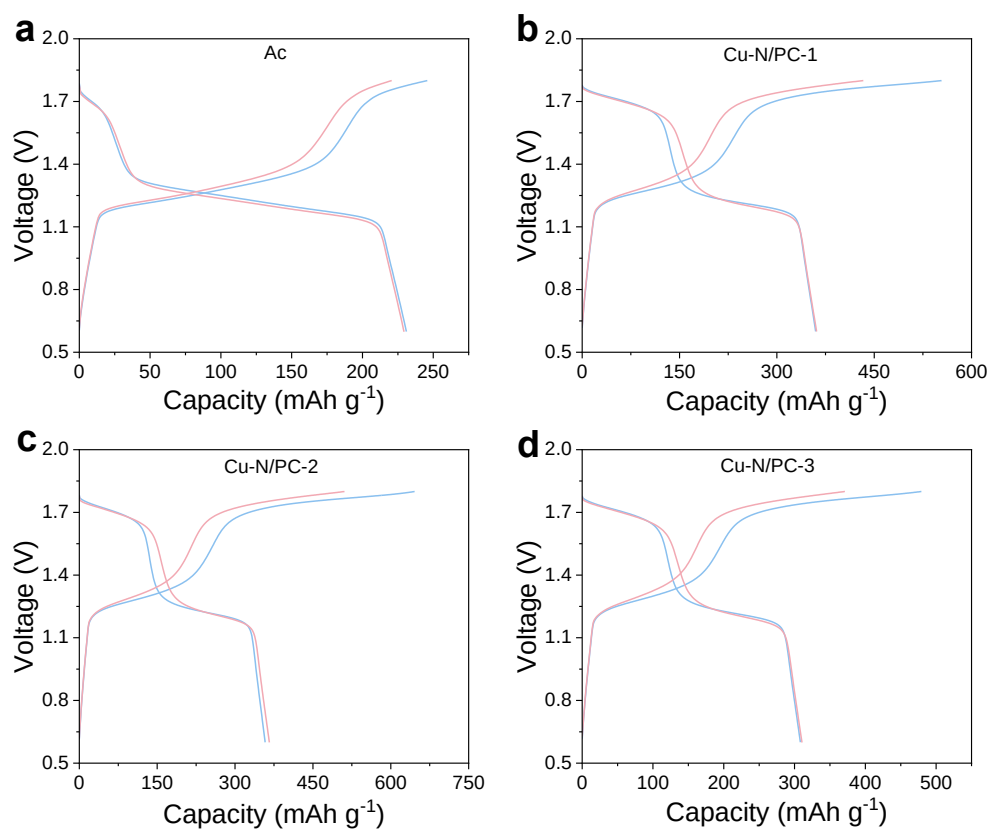
Supplementary Figure 65. GCD curve of zinc||iodine battery with Cu-N/PC-2.



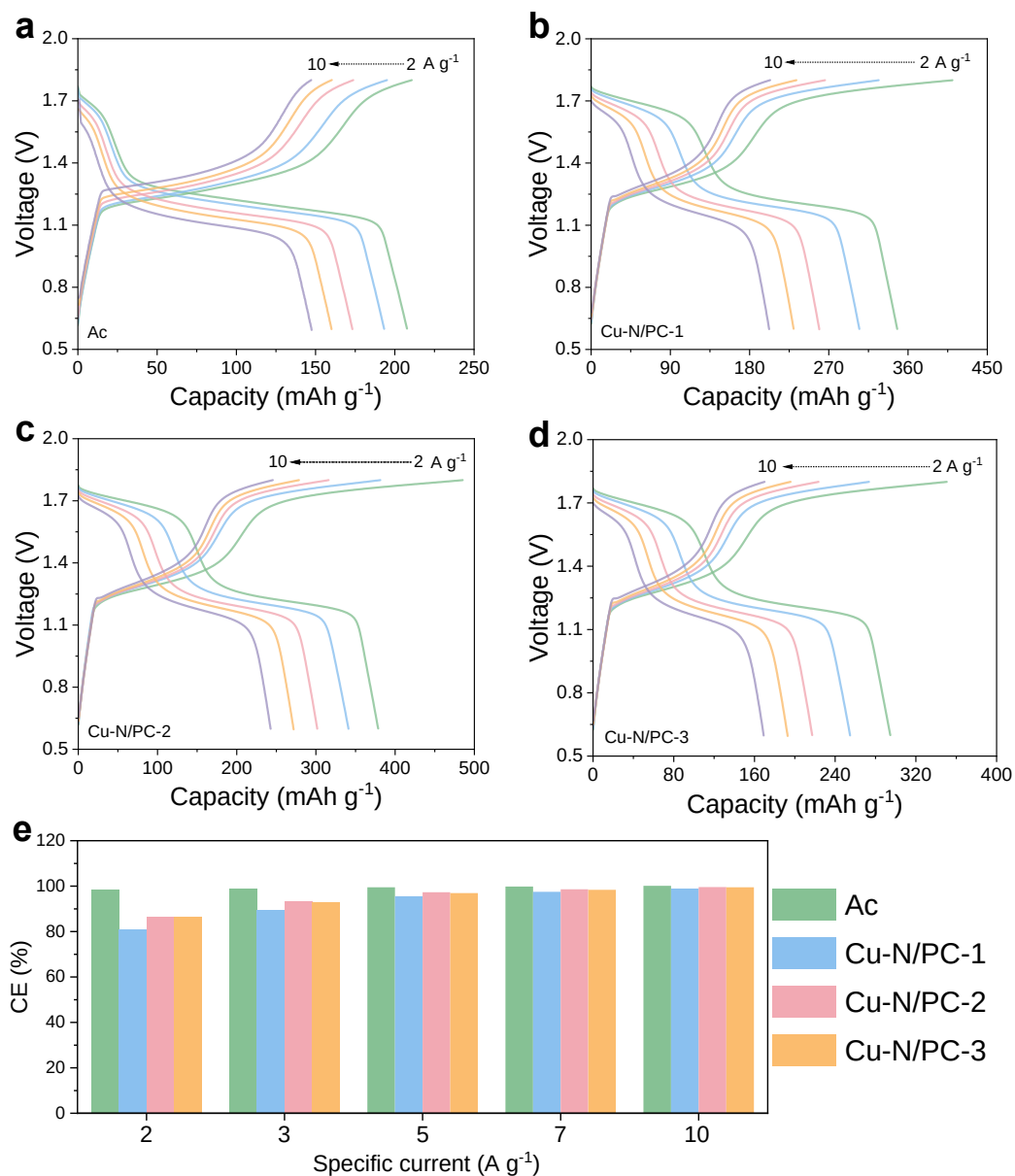
Supplementary Figure 66. (a) GCD curve and (b) *in situ* Raman spectra of zinc||iodine battery with Ac (Specific current: 1 A g^{-1} ; Test temperature: $25 \pm 2\text{ }^{\circ}\text{C}$).



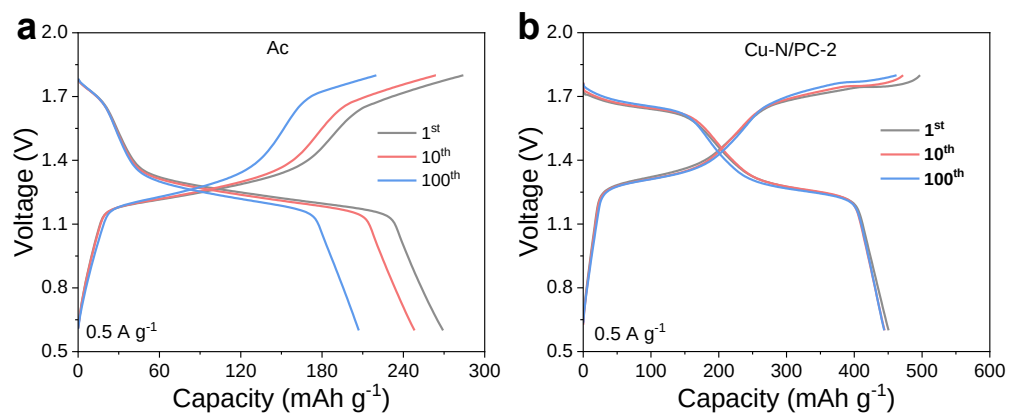
Supplementary Figure 67. XPS I 3d spectra of the fully discharged-0.6 V and charged-1.8 V Ac (Specific current: 1 A g^{-1} ; Cycle number: 3 cycles; Test temperature: $25 \pm 2 \text{ }^\circ\text{C}$).



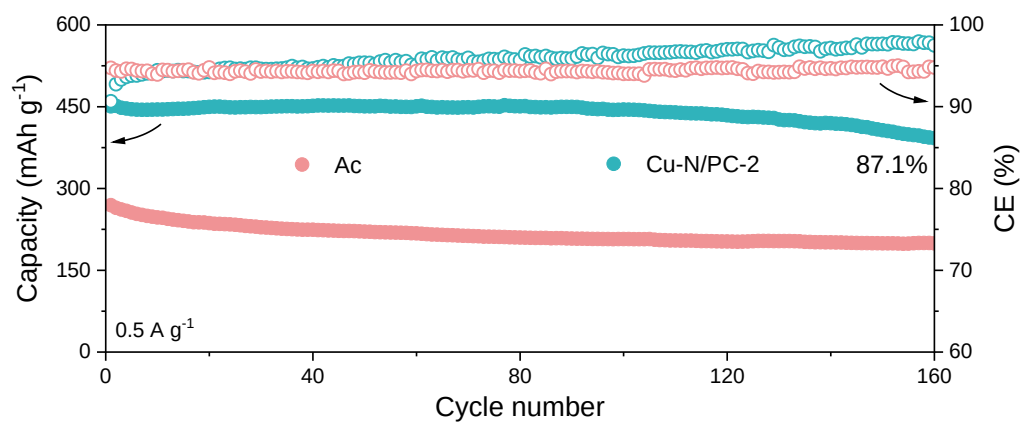
Supplementary Figure 68. The first two GCD cycles correspond to the activation process at 1 A g⁻¹ with various positive electrodes. (Test temperature: 25 ± 2 °C). (a) Ac, (b) Cu-N/PC-1, (c) Cu-N/PC-2, and (d) Cu-N/PC-3.



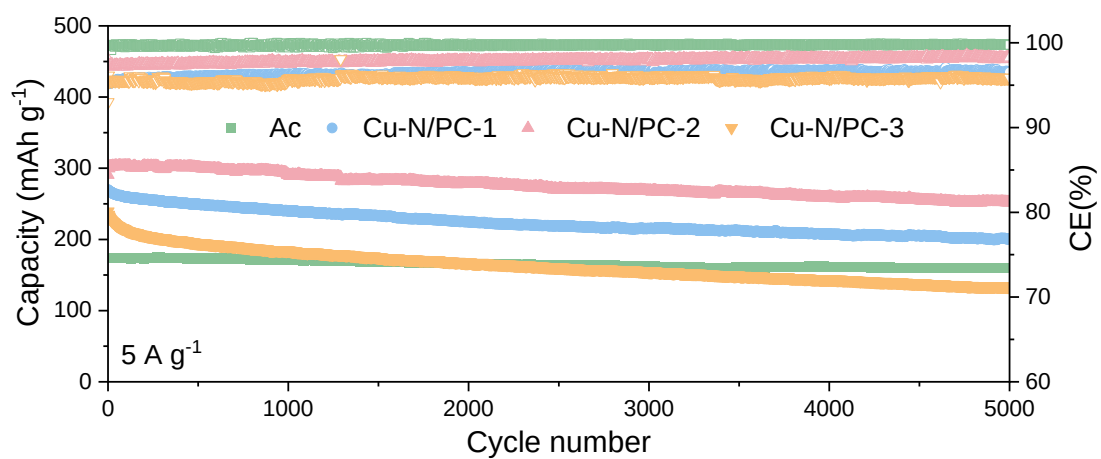
Supplementary Figure 69. Galvanostatic discharge/charge curves at different specific currents with the various positive electrodes (Test temperature: 25 ± 2 °C). (a) Ac, (b) Cu-N/PC-1, (c) Cu-N/PC-2, and (d) Cu-N/PC-3. (e) The average Coulombic efficiency (CE) of various positive electrodes at different specific currents.



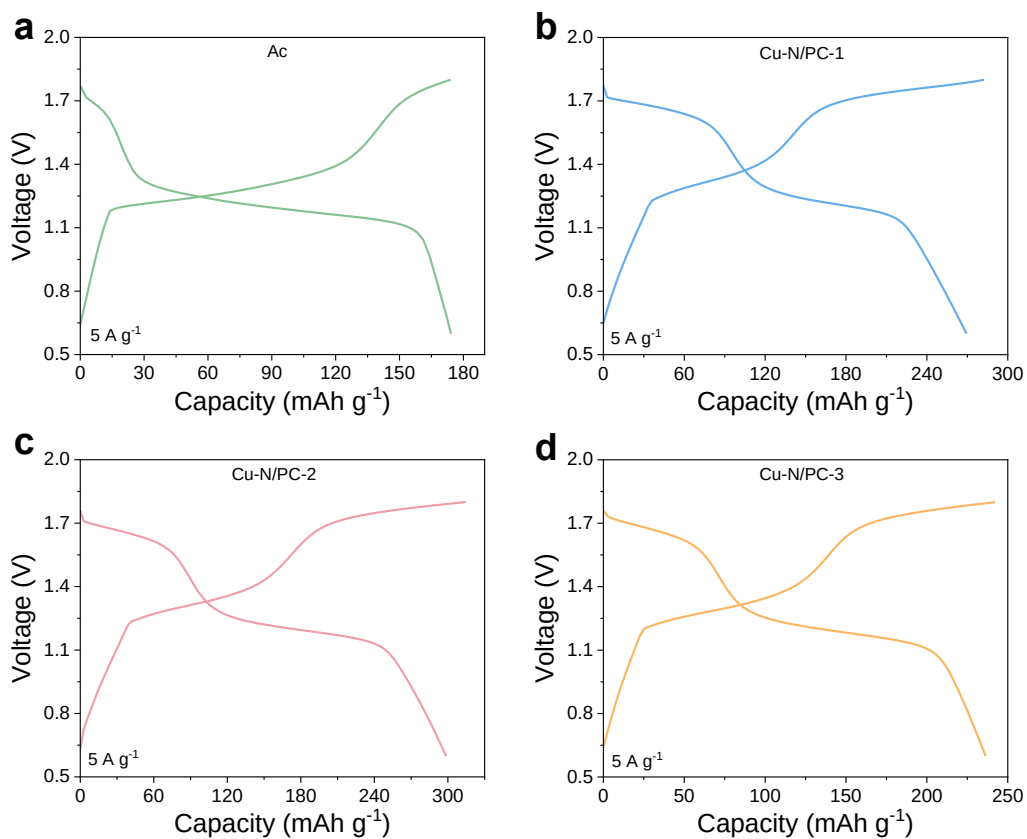
Supplementary Figure 70. Galvanostatic discharge-charge curves of zinc||iodine batteries at 0.5 A g⁻¹ with the various positive electrodes (Test temperature: 25 ± 2 °C). (a) Ac and (b) Cu-N/PC-2.



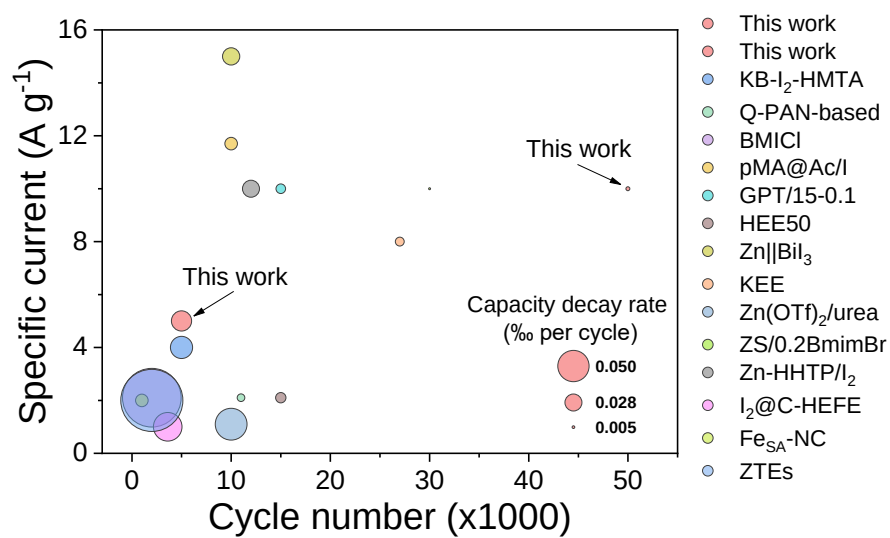
Supplementary Figure 71. Cycling performance of zinc||iodine batteries at 0.5 A g⁻¹ with the various positive electrodes (Test temperature: 25 ± 2 °C).



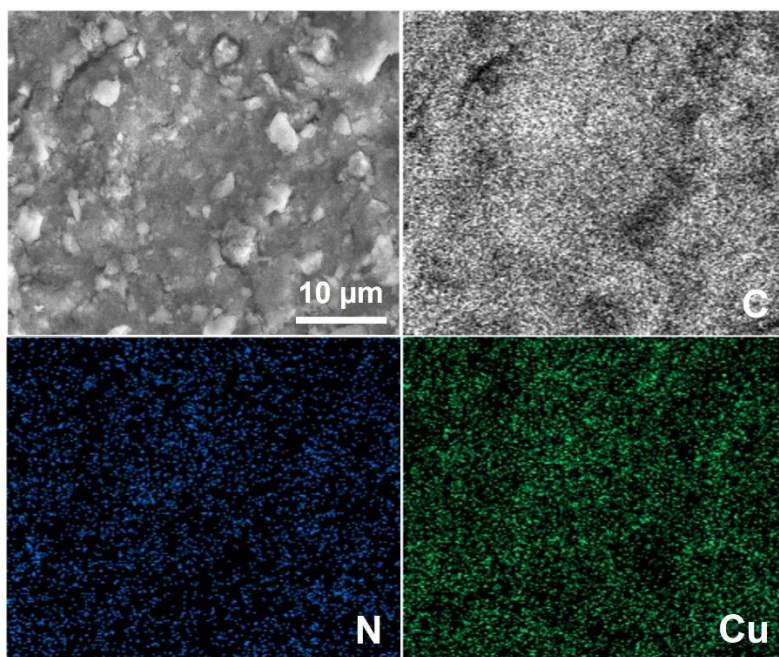
Supplementary Figure 72. Cycling performance of the different positive electrodes at 5 A g^{-1} (Test temperature: $25 \pm 2 \text{ }^{\circ}\text{C}$).



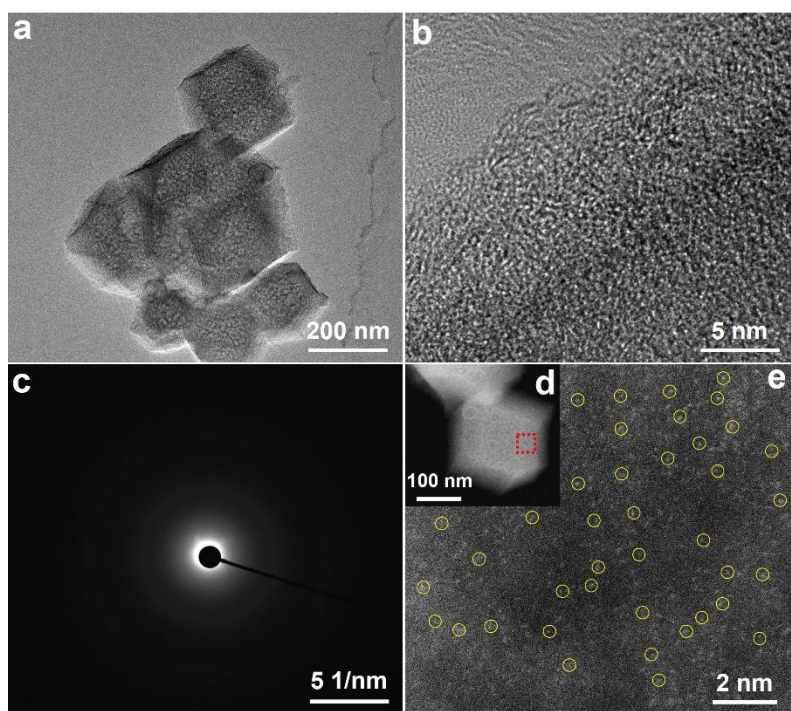
Supplementary Figure 73. Galvanostatic discharge/charge curves (the 3rd cycle) at 5 A g⁻¹ with the various positive electrodes (Test temperature: 25 ± 2 °C). (a) Ac, (b) Cu-N/PC-1, (c) Cu-N/PC-2, and (d) Cu-N/PC-3.



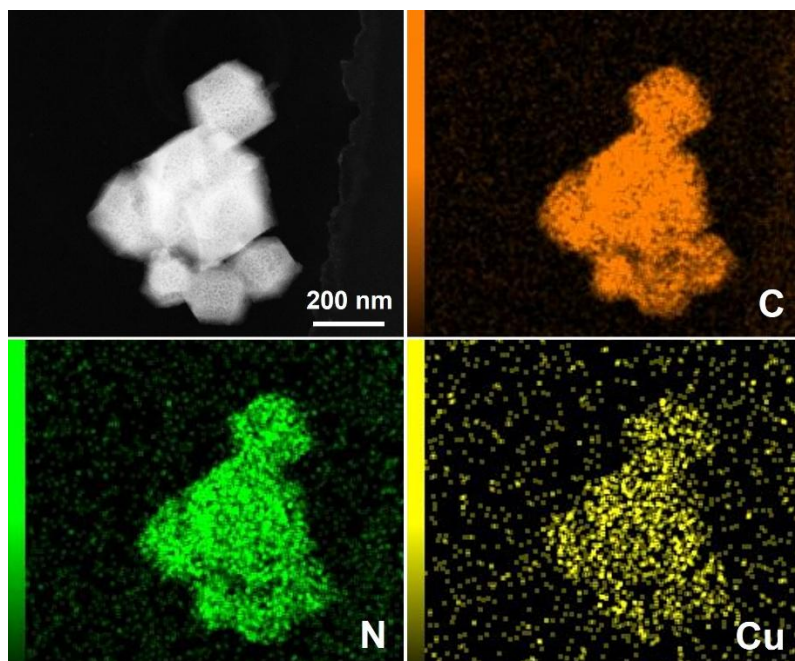
Supplementary Figure 74. Comparison of the cycling performance between the zinc||iodine battery with Cu-N/PC-2 and recent state-of-the-art zinc||iodine batteries²⁻¹⁵.



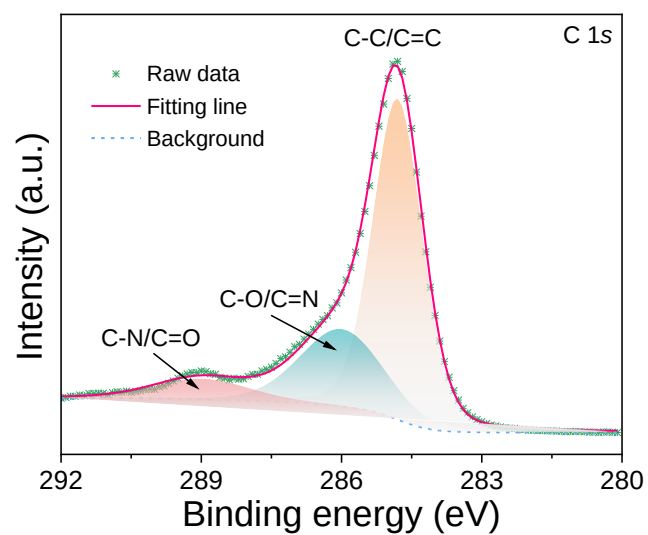
Supplementary Figure 75. SEM and the corresponding element mapping images of the Cu-N/PC-2 after cycling.



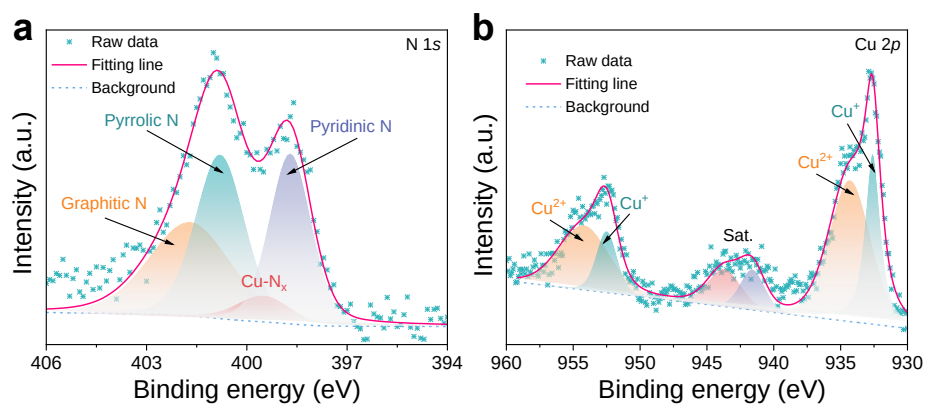
Supplementary Figure 76. (a-c) TEM, HRTEM, and the corresponding SAED pattern of Cu-N/PC-2 after cycling. (d, e) Aberration-corrected HAADF-STEM images of Cu-N/PC-2 after cycling with the atomic dispersion of Cu highlighted by yellow circles.



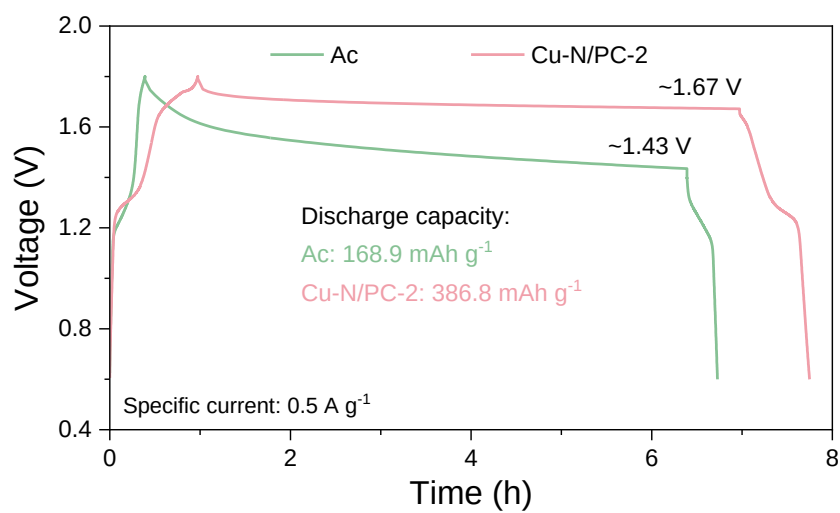
Supplementary Figure 77. EDS mapping images of C, N, and Cu in the Cu-N/PC-2 after cycling.



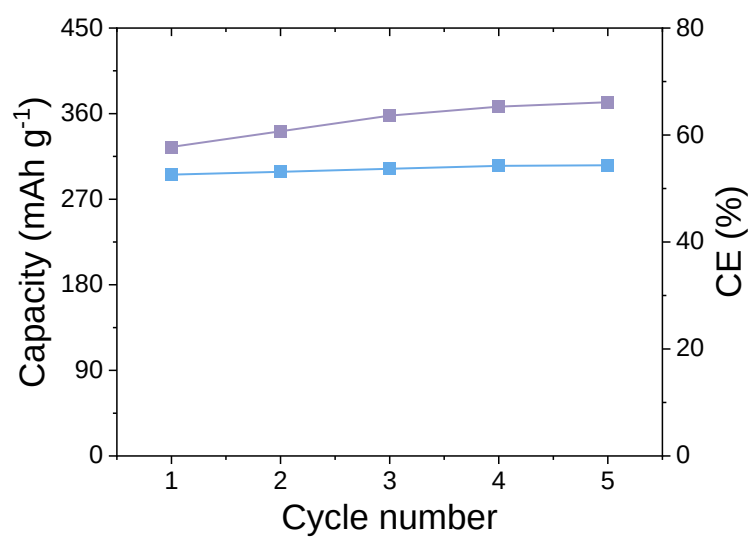
Supplementary Figure 78. XPS C 1s spectra of Cu-N/PC-2 after cycling.



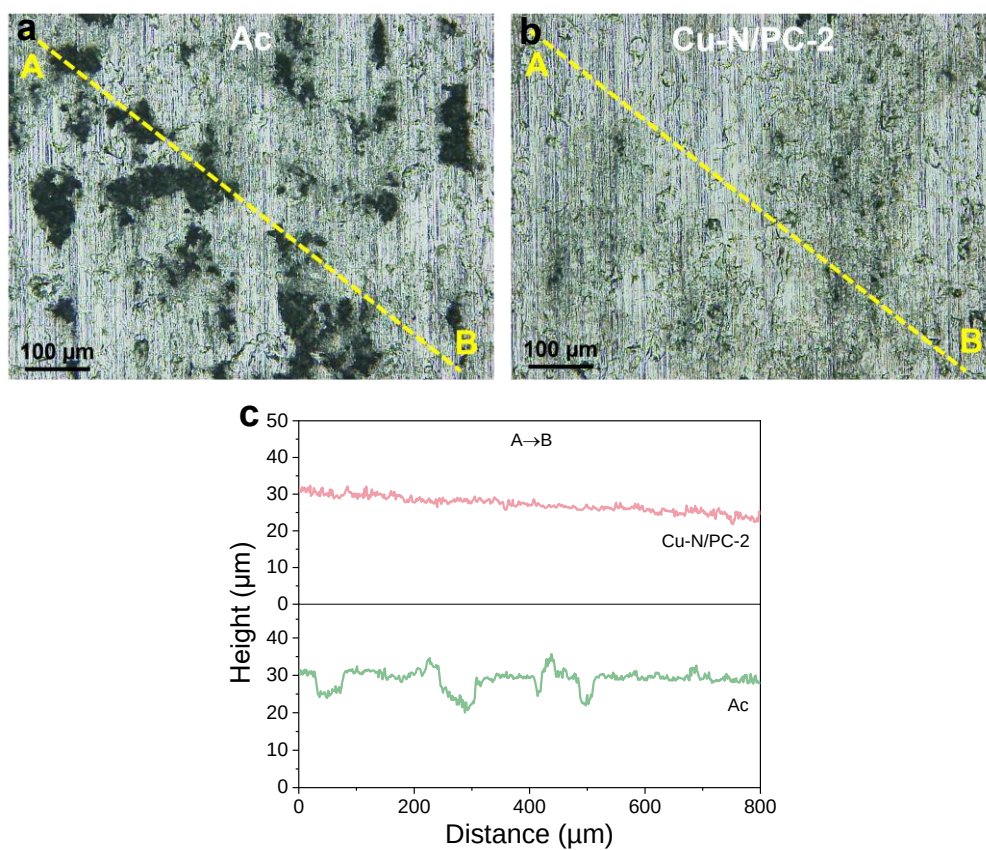
Supplementary Figure 79. (a) XPS N 1s and (b) Cu 2p spectra of Cu-N/PC-2 after cycling.



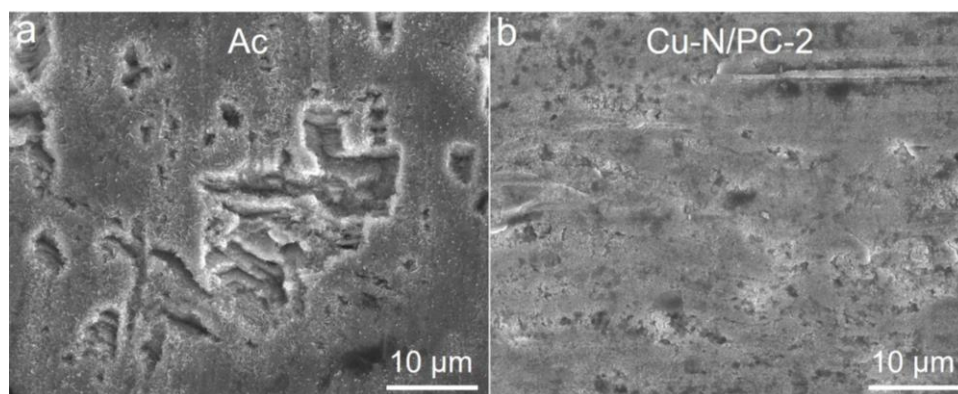
Supplementary Figure 80. Self-discharge capability of the zinc||iodine batteries with the various host materials (Test temperature: 25 ± 2 °C).



Supplementary Figure 81. The first five cycle performance correspond to the activation process at 0.25 A g^{-1} .



Supplementary Figure 82. 2D LSCM images and the corresponding surface roughness curves of the deposited Zn surface after 50 cycles. (a) Ac and (b) Cu-N/PC-2 positive electrodes, and (c) the corresponding surface roughness curves.



Supplementary Figure 83. SEM images of Zn negative electrodes after 50 cycles with (a) Ac and (b) Cu-N/PC-2.

Supplementary Table 1. The BET parameters of Ac and Cu-N/PC-x materials.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Micropore radius (nm)
Ac	2023.70	0.69
Cu-N/PC-1	1864.52	0.55
Cu-N/PC-2	1855.05	0.56
Cu-N/PC-3	1848.68	0.55

Supplementary Table 2. The elemental composition information of Cu-N/PC-x samples.

Samples	C (<i>at. %</i>)	O (<i>at. %</i>)	N (<i>at. %</i>)	Cu (<i>at. %</i>)	Others
Cu-N/PC-1	86.62	10.04	2.86	0.40	0.08
Cu-N/PC-2	86.28	9.95	3.14	0.51	0.12
Cu-N/PC-3	85.63	9.22	4.35	0.70	0.10

Supplementary Table 3. EXAFS fitting parameters at the Cu K-edge for various samples ($S_0^2 = 0.87$ from Cu foil).

Samples	Shell	CN ^a	R ^b (Å)	σ^2 ^c (Å ²)	ΔE_0 ^d (eV)	R factor
Cu foil	Cu-Cu	12	2.54±0.01	0.0087	4.3±0.6	0.0038
Cu-N/PC-2	Cu-N	3.4±0.7	1.87±0.01	0.0041	7.3±0.6	0.0154

^aCN: Coordination numbers; ^bR: Bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : Inner potential correction. R factor: goodness of fit. A reasonable range of EXAFS fitting parameters: $0.70 < S_0^2 < 1.00$; $CN > 0$; $\sigma^2 > 0 \text{ Å}^2$; $|\Delta E_0| < 15 \text{ eV}$; R factor < 0.02 . The obtained XAFS data were processed in Athena (version 0.9.26) for background, pre-edge line, and post-edge line calibrations. Then, the Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k^3 weighting, k-range of 3-12 Å⁻¹ and R range of 1-3 Å were used for the fitting of Cu-foil; k-range of 3-11 Å⁻¹ and R range of 1-3 Å were used for the fitting of samples.

Supplementary Table 4. Comparison of the electrochemical performance of several previously reported zinc||iodine batteries^{2,3,7,8,12,16-24}.

Positive electrodes	Electrolyte	Specific current/capacity (mAh g ⁻¹)	Cycle number/capacity retention (%)	Mass loading (mg cm ⁻²)	Ref.
KB-I ₂ -HMTA	ZS/NaCl-0.2HMTA	4 A g ⁻¹ /~276	5,000/82.1	5	2
Q-PAN-I ₂	3/5ZC electrolyte	10 C/210	11,000/87	1	3
I ₂ /AC	HEE50 electrolyte	10 C/~349	15,000/75.1	1	7
BiI ₃	2M ZnSO ₄ /0.3m KCl	1 A g ⁻¹ /~370	500/~81.1	/	8
Zn-HHTP/I ₂	ZnSO ₄ +KBr	10 A g ⁻¹ /~213.6	12,000/	1-1.5	12
I ₂ /AC	PVA/Urea/zinc ion hydrogel	1 A g ⁻¹ /80.3	8,000/73	2-3	16
KB-I ₂	2M ZnCl ₂ /1 wt.%SP	10 C/~160	6,000/91.1	2	17
M9	2M ZnSO ₄ 0.5M KOH/0.1M	2 A g ⁻¹ /162	10,000/NA	0.8-1.2	18
TBA-I ₃	ZnAc/saturated KCl	1 A g ⁻¹ /~280	350/70	1-1.2	19
I ₂ @AC	15m ZnCl ₂ -TEA ⁺	10 A g ⁻¹ /~138	35,000/47.5	/	20
I ₂ /AC	2M ZnSO ₄ /500mM TAH	2 A g ⁻¹ /~280	5,000/70	1	21
Ti ₃ C ₂ I ₂	2M ZnSO ₄ /1M KCl	3 A g ⁻¹ /~175	2,800/~71.4	1-1.5	22
C ₃ H ₉ IS/TZ-COFs	MPIBr-containing electrolyte	1 A g ⁻¹ /1296	1,200/86.3	1-2	23
I ₂ /HAC	1M ZnSO ₄ /0.1M H ₂ SO ₄ /0.1M KBr	2 A g ⁻¹ /~1050	150/76.2	1.5	24
I₂@Cu-N/PC-2	2M ZnSO₄/0.1M ChCl	5 A g⁻¹/~302.1	5,000/~86.8	1-2	This work
I₂@Cu-N/PC-2	2M ZnSO₄/0.1M ChCl	10 A g⁻¹/~251.4	50,000/~70	1-2	This work

Note: Measurements were performed at an average temperature of 25 ± 2 °C. The electrolyte volume of each 2032 cell was ~70-120 μL.

Supplementary Table 5. The elemental composition information of Cu-N/PC-2 after cycling (data from XPS analysis).

Samples	C (<i>at. %</i>)	O (<i>at. %</i>)	N (<i>at. %</i>)	Cu (<i>at. %</i>)	Others
Cycled Cu-N/PC-2	86.03	9.76	3.53	0.55	0.13

Supplementary Table 6. Key parameters of the 2032 zinc||iodine battery.

Parameter	Value	Notes
Negative electrode dimension	~24 mg (Diameter × Thickness: 12 mm × 30 μm)	/
Positive electrode dimension	~1.1 mg (Diameter: 12 mm)	/
Volumetric loading (negative electrode)	7.14 mg cm ⁻³	Active material mass per volume
Positive electrode current collector	Carbon cloth (CC, 0.35 mm)	/
Positive electrode thickness	~0.4 mm	Total thickness of the carbon cloth and the positive coating
N:P ratio	64.8 (Excessive zinc)	Negative/positive capacity ratio
Average capacity	0.22 mAh	Measured at 10 A g ⁻¹ , 50,000 cycles
Electrolyte	2M ZnSO ₄ and 0.1M CHCl ₃	/
Electrolyte total mass injected	~110 μL	/
Separator	Diameter: 16 mm	Whatman, GF/A
Package	SUS 304	2032

Supplementary Table 7. Key parameters of the soft-packaged zinc||iodine battery.

Parameter	Value	Notes
Negative electrode dimension	~142 mg (Length × Width × Thickness: 5 cm × 4 cm × 10 μm)	/
Positive electrode dimension	~120 mg (Length × Width: 5 cm × 4 cm)	/
Areal loading (positive electrode)	6 mg cm ⁻²	Active material mass per area
Volumetric loading (negative electrode)	7.14 mg cm ⁻³	Active material mass per volume
Positive electrode current collector	Carbon cloth (CC, 0.35 mm)	/
Composition ratio	8:1:1	I ₂ @Cu-N/PC-2, acetylene black, and PVDF binder
Positive electrode thickness	~0.4 mm	Total thickness of the carbon cloth and the positive coating
N:P ratio	2.32	Negative/positive capacity ratio
Total capacity	36.68 mAh	Measured at 0.25 A g ⁻¹
Full-cell specific energy	210 Wh kg ⁻¹	Based on the total mass of active materials in both electrodes
Electrolyte	2M ZnSO ₄ and 0.1M CHCl	/
Electrolyte amount injected	~54.5 g Ah ⁻¹	/
Electrolyte total mass injected	~2 g	/
Separator	Length × Width × Thickness: 5.5 cm × 4.5 cm × 260 μm; Total mass: ~130 mg	Whatman, GF/A
Package	Length × Width × Thickness: 6.2 cm × 4.6 cm × 4 mm; Total mass: ~11 mg	Aluminum-plastic film
External pressure	~12 kPa	/

Supplementary Note 1

Detailed information on soft-packaged cell: An external pressure of 12 kPa was applied to the soft-packaged cell during cycling using a constant-pressure clamp. The electrolyte injection and gas release procedures are follows: The soft-packaged cell was injected with 2 g of electrolyte in an dry room, followed by pre-sealing. After resting for 6 h, the cell was subjected to formation cycling, during which gas generated. The gas was then released by puncturing the gas bag under dry room, followed by final sealing.

N:P ratio for soft-packaged cell: The N:P ratio is defined as the ratio of the practical capacity of the negative electrode (mAh) to that of the positive electrode. 1) Negative electrode capacity: Zinc possesses a theoretical capacity of 820 mAh g⁻¹, corresponding to the $\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^-$ redox reaction. However, the practical capacity of zinc is typically lower due to factors such as polarization, dendrite formation, and side reactions. In our work, a practical capacity of ~600 mAh g⁻¹ was adopted; 2) Positive electrode capacity: Iodine has a theoretical capacity of 422 mAh g⁻¹, based on the four-electron $\text{I}^-/\text{I}^0/\text{I}^+$ redox process. The practical capacity of iodine, as determined from discharge curves, was measured to be 306 mAh g⁻¹, which reflects kinetic limitations and the dissolution of iodine during cycling. Therefore, the N:P ratio can be calculated through the following equation:

$$\text{N:P} = \frac{\text{Practical capacity of negative electrode (mAh)}}{\text{Practical capacity of positive electrode (mAh)}} = \frac{600 \times 142 / 1000}{306 \times 120 / 1000} = 2.32 \quad (1)$$

Full-cell specific energy: The specific energy was calculated using an average discharge voltage, because the discharge curve consists of two voltage regions (~1.7 and ~1.3 V) that contribute almost equally to the specific capacity. The gravimetric specific energy of the soft-packaged cell was calculated according to the following equation:

$$\text{Specific energy (Wh kg}^{-1}\text{)} = \frac{\text{Discharge capacity (Ah)} \times \text{Average discharge voltage (V)}}{\text{Total mass of active materials in both electrodes (kg)}} = \frac{36.68 / 1000 \times 1.5}{(80 + 120) / 1000000} \text{ (Wh kg}^{-1}\text{)} = 210 \text{ (Wh kg}^{-1}\text{)} \quad (2)$$

N:P ratio for 2032 coin cell: Taking Fig. 6d as an example. 1) Negative electrode capacity: The practical capacity of zinc is typically lower due to factors such as polarization, dendrite formation, and side reactions. In our work, a practical capacity of $\sim 600 \text{ mAh g}^{-1}$ was adopted; 2) Positive electrode capacity: Iodine has a theoretical capacity of 422 mAh g^{-1} , based on the four-electron $\text{I}^-/\text{I}^0/\text{I}^+$ redox process. The practical capacity of iodine, as determined from discharge curves, was measured to be 313 mAh g^{-1} , which reflects kinetic limitations and the dissolution of iodine during cycling. Therefore, the N:P ratio can be calculated through the following equation:

$$\text{N:P} = \frac{\text{Practical capacity of negative electrode (mAh)}}{\text{Practical capacity of positive electrode (mAh)}} = \frac{600 \times 24 / 1000}{202 \times 1.1 / 1000} = 64.8 \quad (3)$$

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