

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

Corresponding Author: Professor Bingang Xu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors report the use of a copper single-atom embedded nitrogen-doped carbon host (Cu-N/PC) to facilitate I⁻/I₀/I⁺ redox chemistry in aqueous Zn||I₂ cells, employing a relatively low concentration of chloride ions (0.1 M) in the electrolyte. An initial capacity of 251 mAh/g at 10 A/g is demonstrated. However, the strategy of utilizing single-atom embedded nitrogen-doped carbon hosts to promote iodine conversion has already been widely reported. Furthermore, aqueous Zn||I₂ cells operating in Cl⁻-free electrolytes have also been extensively documented. As a result, the novelty and potential impact of this work appear limited. In conclusion, this study does not meet the high standards required for publication in Nature Communications.

Some detailed comments are shown below:

- 1) It is recommended to include XANES/EXAFS measurements and corresponding discussions to validate the Cu-N/PC single-atom catalyst.
- 2) A more detailed discussion of the results presented in Figure 3h-i and Supporting Information Figures 31-33 should be provided.
- 3) In addition to the theoretical calculations shown in Figure 3, experimental verification of the strong adsorption capacity of the Cu-N/PC single-atom catalyst for ICl₂ should be conducted.
- 4) Tafel plots for the oxidation process of the iodine cathode should be added to Figure 4b.
- 5) In situ characterization techniques, such as Raman spectroscopy and UV-vis tests, should be employed to monitor the conversion of iodine species in the iodine cathode during the charge/discharge process.
- 6) As shown in Figure 4k, the fitted line for the Cu-N/PC-2 XPS results within the range of 623–620 eV is not convincing.
- 7) Why was CHCl₃ chosen as the Cl⁻ source? Additionally, what is the performance of the Zn||I₂ cell when the CHCl₃ concentration is below 0.1 M?
- 8) How does the Zn||I₂ cell perform during long-term cycling at a low current density (e.g., 0.2 A/g)?
- 9) Characterization methods such as TEM, SEM, and XPS should be performed to evaluate the structural and morphological stability of the single-atom catalyst after long-term cycling.
- 10) Self-discharge tests of the Zn||I₂ cell should also be included.

Reviewer #2

(Remarks to the Author)

This manuscript reports the design and synthesis of a copper single-atom embedded nitrogen-doped porous carbon (Cu-N/PC) host for four-electron zinc-iodine batteries. The authors demonstrate that the Cu-N_x sites synergistically couple d-p hybridization with localized Cl⁻ microenvironment to stabilize reactive I⁺ intermediates, lower the energy barrier for I₀/I⁺ conversion, and suppress polyiodide shuttling. The resulting battery achieves a high discharge capacity of 408 mAh g⁻¹, an extended cycling stability over 50,000 cycles with a low decay rate of 0.0062% per cycle, and excellent rate capability. More importantly, the experimental and theoretical analyses provided sufficiently support the conclusions drawn in this paper. This manuscript presents a significant advance in the field of aqueous zinc-iodine batteries through a well-conceived single-atom catalyst strategy. Therefore, I believe the manuscript is suitable for publication in Nature Communications after minor revisions. Nevertheless, here are some comments to be addressed:

1. While XPS and HAADF-STEM confirm atomic dispersion, the exact Cu loading (at.%) in Cu-N/PC-x is not provided. This information is essential for correlating structure with activity and for reproducibility.
2. The manuscript emphasizes synergy between Cu-N_x sites and Cl⁻, but it is unclear whether Cl⁻ is essential only for I⁺ stabilization or also participates in the catalytic cycle. A control experiment with a Cl⁻-free electrolyte on Cu-N/PC would help delineate the contribution of Cl⁻.
3. The difference in electrical conductivity between Ac and Cu-N/PC-2 should be addressed, as this may explain the larger ohmic polarization.
4. Why was a graphene model chosen to represent the carbon host instead of an amorphous carbon structure?
5. The projected density of states (PDOS) and d-band center analysis are used to rationalize the interaction between Cu-N_x sites and iodine species. However, the spin polarization is not explicitly mentioned, and the charge transfer analysis is limited to Mulliken charges. Given that iodine species can exhibit spin-orbit coupling and relativistic effects, how robust are the calculated electronic properties? More advanced charge analysis methods (e.g., electron localization function) should be provided to confirm this conclusion.
6. The ball-and-stick models in Fig. 2a need to be labeled with atomic types (such as C, H, O, N, Cu, and Zn etc.). In addition, it should be noted that the periodic boundary condition assumption in DFT.
7. It is recommended to provide morphological and compositional analysis (such as SEM/XPS, etc.) of cathodes after cycling to verify the stability of the material structure.
8. The authors should provide the key parameters of the soft-packaged zinc-iodine battery and the calculation process for energy density and N:P ratio.

Reviewer #3

(Remarks to the Author)

This manuscript reports a novel electrode material based on a copper single-atom-embedded nitrogen-doped carbon host to improve the redox chemistry of I⁻/I⁰/I⁺ species. The key features include enhanced iodine-species adsorption, accelerated redox kinetics, and suppressed I⁺ hydrolysis, enabled by Cu d-I p orbital hybridization. As a result, the zinc-iodine battery exhibits impressive and stable four-electron redox performance at high current densities. To further strengthen the manuscript, the following points should be addressed.

- Based on Figures 1b and 1c, the authors justify the selection of Cu by suggesting that both Cu and Ni exhibit moderate I⁺ adsorption energies—neither too strong nor too weak. However, the criterion for defining “optimal” adsorption strength remains unclear and should be explicitly clarified. In addition, it is not clear why the d-orbital analysis in Figure 1c is performed for neutral I₂ rather than for I⁺ species, which are more directly relevant to the proposed mechanism.
- Further clarification on the characterization of Cu in the Cu-N/PC electrode is required: (1) According to the XRD results in Supplementary Figures 12 and 13, a substantial amount of Cu/CuO species appears to be removed after the acid-washing process. Why are no discernible peaks corresponding to Cu-N_x species observed in the XRD patterns? (2) Providing the approximate atomic composition of Cu, N, and C in the final Cu-N/PC material (e.g., via TGA or elemental analysis) would greatly aid readers in understanding the material. (3) The EDS mapping results for Cu in Figure k4 and Supplementary Figures 14 and 15 do not appear to be consistent with the corresponding morphological images. This discrepancy should be clarified.
- Figure 4g presents the impedance evolution during the charge-discharge process. However, a more detailed discussion is needed to explain the origin of the observed cyclic variation. The subsequent DRT analysis does not provide a sufficiently clear interpretation of this behavior.
- While DRT is a useful tool for probing interfacial electrochemical processes, reliable peak assignment generally requires support from complementary in situ or operando techniques. In this study, the assignments of key features—particularly t₁, t₂, and t₃—remain ambiguous. Specifically, the physical meaning of the charge-transfer process (t₂) and the Faradaic process (t₃) is not clearly defined. Additional justification and evidence for these peak assignments are therefore necessary.
- The authors propose suppression of I⁺ hydrolysis as a key function of the Cu-N/PC electrode. However, the main electrochemical results primarily focus on rate performance. To substantiate the claimed stabilization of I⁺ species, additional evaluation is necessary. In particular, Coulombic efficiency measured at low current densities would provide more direct insight into I⁺ stability. Furthermore, rest (open-circuit) tests assessing capacity retention would be valuable for comparing the stability of iodine species under practical conditions.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed most of the concerns, and this work can be accepted.

Reviewer #2

(Remarks to the Author)

The authors have fully and satisfactorily addressed all of my previous comments and concerns. The manuscript has been significantly improved after revision. I have no further questions and recommend it for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The authors have adequately addressed the comments by this reviewer and significantly improved the manuscript. I recommend to accept this work at its present form.

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Response to Reviewers' Comments

Manuscript ID: NCOMMS-26-012461

Title: "Orbital coupling effect synergizes low-concentration chloride ions for iodine conversion chemistry"

We thank all the reviewers for their in-depth review of our manuscript and for enriching us with their valuable comments, which have helped us further improve the quality of the manuscript. The reviewers' comments and emphasis are listed in *blue font color*, and the authors' responses are listed in black font color. All the changes in the revised manuscript are marked in *red font color*.

Reviewer #1

The authors report the use of a copper single-atom embedded nitrogen-doped carbon host (Cu-N/PC) to facilitate $I^-/I^0/I^+$ redox chemistry in aqueous $Zn||I_2$ cells, employing a relatively low concentration of chloride ions (0.1 M) in the electrolyte. An initial capacity of 251 mAh g^{-1} at 10 A g^{-1} is demonstrated. However, the strategy of utilizing single-atom embedded nitrogen-doped carbon hosts to promote iodine conversion has already been widely reported. Furthermore, aqueous $Zn||I_2$ cells operating in Cl^- -free electrolytes have also been extensively documented. As a result, the novelty and potential impact of this work appear limited. In conclusion, this study does not meet the high standards required for publication in Nature Communications. Some detailed comments are shown below:

Response:

We sincerely thank the reviewer for this important comment and the opportunity to clarify the novelty and significance of our work. We agree that metal single-atom embedded nitrogen-doped carbon hosts have been previously reported for iodine conversion. We also acknowledge that aqueous zinc-iodine batteries operated in Cl^- -free electrolytes have already been reported in previous studies. We wish to clarify that the main contribution of our work is not limited to the use of a single-atom embedded nitrogen-doped carbon host to promote iodine conversion. More importantly, our work demonstrates the synergistic coupling between d - p orbital hybridization with a localized low-concentration Cl^- microenvironment, which stabilizes the electrophilic I^+ intermediate and enables highly reversible four-electron $I^-/I^0/I^+$ conversion under dilute chloride conditions. Following the reviewer's suggestion, we have revised the Abstract, Introduction, Results, and Discussion sections

to more clearly distinguish our work from previous studies based on single-atom embedded nitrogen-doped carbon hosts and chloride-free electrolyte strategies. The main distinctions are summarized as follows:

***d-p* orbital hybridization for I^+ stabilization:** The novelty of this work is not merely associated with the use of a single-atom carbon host. Our study is centered on the activation and stabilization of high-valence I^+ intermediates by a distinct interfacial strategy that employs $Cu-N_x$ sites, which synergistically couple *d-p* orbital hybridization with a localized low-concentration Cl^- microenvironment to stabilize the electrophilic I^+ intermediate. This synergistic interfacial regulation stabilizes the electrophilic I^+ species and enables highly reversible four-electron iodine chemistry. In contrast to previously reported single-atom hosts that primarily aim to enhance I^-/I^0 conversion kinetics and suppress polyiodide shuttling, our work systematically evaluates different metal single-atom sites according to their adsorption behavior toward I^+ species. Among these sites, $Cu-N_x$ sites are identified as suitable active centers because their moderate adsorption strength follows a Sabatier principle, thereby balancing the stabilization of iodine intermediates with their reversible conversion.^{1,2} Furthermore, *d*-band center analysis indicates more effective *d-p* orbital coupling between Cu *d* orbitals and I *p* orbitals (Fig. 1c), accompanied by electron transfer from iodine to the Cu center. This orbital interaction not only stabilizes I^+ but also facilitates the I^0/I^+ conversion, which is corroborated by subsequent theoretical and experimental evidence. PDOS and Gibbs free-energy analyses confirm the Cu *d*-I *p* orbital hybridization and the reduced barrier energy for I^+ generation on $Cu-N_x$ sites (Fig. 4h-j, and Supplementary Figs. 34-36), while the calculated hydrolysis pathway indicates improved stabilization of ICl against hydrolysis (Fig. 4k and Supplementary Figs. 41 and 42). Therefore, the role of $Cu-N_x$ sites in this work goes beyond the conventional iodine adsorption; it provides an electronic-level regulation pathway for stabilizing high-valence iodine species.

Localized low-concentration Cl^- microenvironment enabled by the single-atom host: Although Cl^- -containing electrolytes have been reported for zinc-iodine batteries, most previous systems require relatively high halide concentrations (typically exceeding 1M) to stabilize high-valence I^+ species, which may inevitably aggravate zinc anode corrosion and parasitic interfacial reactions. Meanwhile, while chloride-free zinc-iodine batteries have also recently emerged, they are mainly based on electrolyte-centered coordination or complexation strategies. Distinct from these

electrolyte-centered strategies, our work focuses on regulating high-valence iodine chemistry at the interface through Cu-N_x active sites under a low-concentration Cl⁻ electrolyte environment. Specifically, the Cu-N_x sites not only promote iodine species adsorption and interfacial charge redistribution, but also facilitate the formation of a localized I-Cl microenvironment at the cathode interface. This localized chemical confinement allows efficient I⁰/I⁺ conversion even with only a low Cl⁻ concentration in the electrolyte. Therefore, the dilute Cl⁻ in our system does not function as a conventional supporting salt or a highly concentrated halide medium; rather, it acts as an interfacial chemical mediator that cooperates with Cu-N_x catalytic sites to stabilize high-valence iodine species. This cathode-electrolyte interfacial synergy allows reversible I⁰/I⁺ conversion without relying on super-concentrated or eutectic electrolytes, thereby distinguishing our work from previously reported Cl⁻-free electrolyte strategies. Control experiments further confirm that a well-defined high-voltage plateau and the corresponding I⁰/I⁺ redox peaks appear only when the Cu-N/PC host is combined with the Cl⁻-containing electrolyte, whereas they are absent in the control systems without Cu-N_x sites or without Cl⁻ (Supplementary Figs. 47-49). These results demonstrate that the indispensable synergy between Cu-N_x sites and localized chloride coordination.

Achieving stable four-electron conversion in dilute electrolytes: Benefiting from the above synergistic interfacial regulation, the Cu-N/PC-2 cathode exhibits clear I⁻/I⁰/I⁺ dual-voltage plateaus, delivering a high specific capacity of approximately 408 mAh g⁻¹ at 1 A g⁻¹ and stable cycling over 50,000 cycles at 10 A g⁻¹ with a low-capacity decay rate of only 0.0062% per cycle. In addition, the use of a dilute Cl⁻ electrolyte effectively mitigates zinc anode corrosion. After cycling, the zinc anode maintains a smooth and compact surface morphology (Fig. 6h, i), further confirming the good compatibility of this system with the zinc anode while achieving efficient four-electron iodine conversion. These results demonstrate that this system realizes four-electron iodine conversion with high capacity, long cycling life, and favorable zinc anode compatibility under low-concentration Cl⁻ electrolyte conditions.

Therefore, distinct from previously reported single-atom carbon hosts or Cl⁻-free zinc-iodine batteries, our work emphasizes the stabilization of electrophilic I⁺ intermediates through the synergy between *d-p* orbital hybridization and a localized Cl⁻ microenvironment, thereby enabling high-voltage four-electron iodine conversion. This point has been clarified in the revised manuscript to better highlight the contribution of our work.

1. It is recommended to include XANES/EXAFS measurements and corresponding discussions to validate the Cu-N/PC single-atom catalyst.

Response:

Thank you for this valuable suggestion. We fully agree that X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements are essential for definitively validating the local coordination environment and electronic structure of the Cu single-atom sites in the Cu-N/PC catalyst. These techniques provide direct experimental evidence of the Cu-N_x coordination geometry, which complements the indirect evidence from HAADF-STEM and XPS presented in the original manuscript. To explore the chemical states and coordination environment of Cu atoms in the Cu-N/PC-2, synchrotron-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were conducted. Figure R1a shows the Cu K-edge XANES spectra of the Cu-N/PC-2 and other references, revealing that the valence state of Cu species in Cu-N/PC-2 is located between 0 and +2, which is consistent with the XPS results. Fourier transform (FT) EXAFS spectra reveal that there is no Cu-Cu coordination within the Cu-N/PC-2 (Figure R1b), indicating the isolated feature of Cu atoms in Cu-N/PC-2. Moreover, Cu-N/PC-2 exhibits a similar Cu K-edge EXAFS magnitude to CuPc with a main peak at 1.5 Å, which is ascribed to the Cu-N coordination.³ The EXAFS fitting results of the Cu-N/PC-2 show that the Cu atom is coordinated by an average of 3.4 N atoms with a bond length of 1.87 Å (Figures R1c, R2, and Table R1). The detailed contour plot of Cu-N/PC-2 shows that the maximum intensity for the wavelet transform (WT) occurs at approximately 4.2 Å⁻¹, which corresponds to the Cu-N bond in CuPc (Figure R1d-f). This stands in clear contrast to the Cu-Cu bond observed in the reference Cu foil, further confirming the atomic monodispersity of the Cu species.

We sincerely thank you for this important recommendation. The addition of XANES/EXAFS data has substantially strengthened our characterization of the single-atom catalyst and provides direct experimental validation for the atomic dispersion of Cu sites that underlie the excellent catalytic performance reported in this work.

Revision in Manuscript:

The detailed information and discussion are added on page 8, Fig. 3 in the revised manuscript, Supplementary Fig. 16 and Table 3 in the revised Supplementary Information.

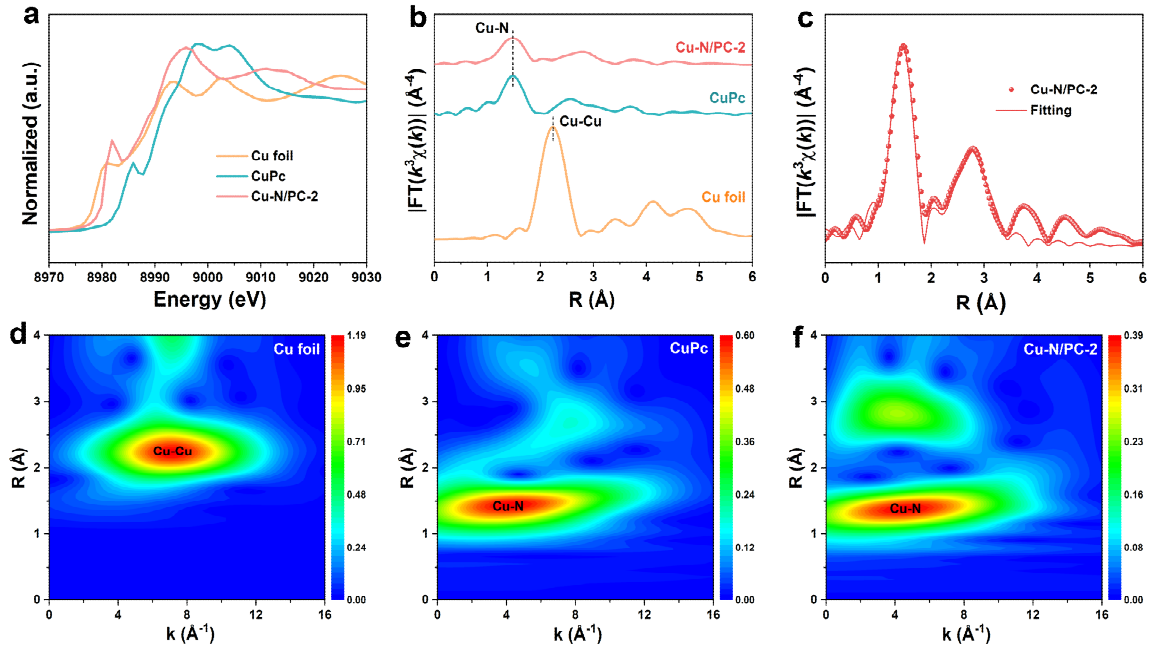


Figure R1. Spectral characterizations of various samples. (a) Cu K-edge XANES spectra of Cu-N/PC-2 and other control samples, and (b) the corresponding FT k^3 -weighted Cu K-edge EXAFS spectra. (c) FT-EXAFS fitting curves of Cu-N/PC-2 at the Cu K-edge in R -space. (d-f) Wavelet transformation (WT) of EXAFS plots of Cu foil, CuPc, and Cu-N/PC-2.

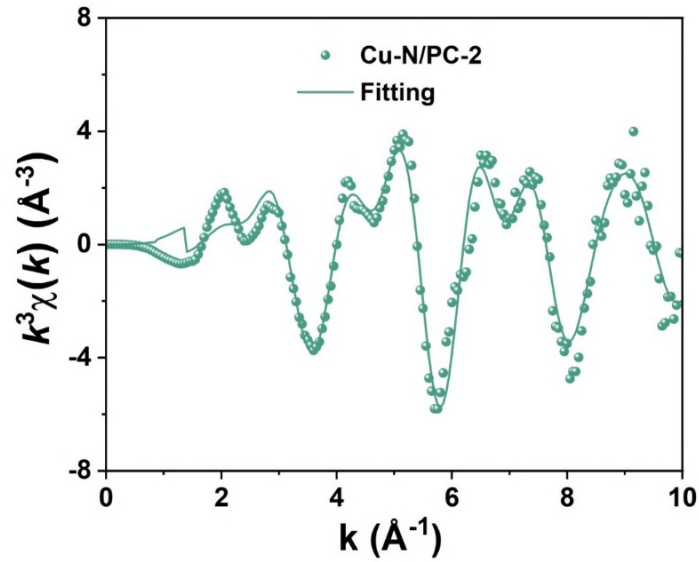


Figure R2. FT-EXAFS fitting curves of Cu-N/PC-2 at the Cu K-edge in k -space.

Table R1. 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: $0.70 < S_0^2 < 1.00$; $CN > 0$; $\sigma^2 > 0$ Å²; $|\Delta E_0| < 15$ 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.

2. A more detailed discussion of the results presented in Figure 4h-i and Supporting Information Figures 34-36 should be provided.

Response:

Thank you for your constructive suggestion. We agree that a more detailed discussion of the projected density of states (PDOS) results presented in Fig. 4h-i and Supplementary Figs. 34-36 would enhance the reader's understanding of the electronic interaction mechanism between the Cu-N_x sites and various iodine species. Thus, we have expanded the discussion in the revised manuscript to provide a more thorough interpretation of these results. The PDOS calculations were performed to visualize the orbital-resolved electronic structure of iodine species (I, I⁺, I₂, I₃⁻, and ICl) adsorbed on the different substrates: the graphene (G) model (representing the Ac material) and various Cu-N_x configurations (Cu-N₃, Cu-N₄, and Cu₂-N₆). The key focus is on the hybridization between the Cu *d*-orbitals and the I *p*-orbitals near the Fermi level (E_f), which governs the strength of the electronic interaction and the degree of charge transfer. For iodine species adsorption on the graphene substrate, the I *p*-orbitals remain largely isolated with obvious overlap with the original iodine species near the Fermi level. This indicates weak physical adsorption with minimal electronic interaction, consistent with the physisorption mechanism dominant on Ac material. In contrast, the PDOS results reveal pronounced hybridization between the Cu *d*-orbitals and the I *p*-orbitals in the

energy range from approximately -3 eV to +1 eV relative to the Fermi level. Specifically: 1) The I *p*-orbitals in iodine species are significantly broadened and split, indicating strong orbital coupling with the Cu *d*-orbitals in Cu-N_x sites. 2) A clear hybridization peak appears near the Fermi level, suggesting the adsorbed iodine species gains additional electronic states that facilitate charge transfer. 3) The Cu *d*-orbitals exhibit a noticeable shift and redistribution of electronic density upon iodine species adsorption, further confirming the strong electronic coupling. 4) A particularly notable feature is the emergence of a new hybridized state just below the Fermi level, which corresponds to the formation of a Cu-I bonding orbital. This indicates that the Cu-N_x sites form direct chemical bonds with the I atom of iodine species, consistent with the charge redistribution observed in the electron density difference analysis (Fig. 4e and Supplementary Fig. 32) and the elongated I-Cl and I-I bonds (Fig. 5e and Supplementary Fig. 59). We have added the following expanded discussion to the Results section on page 10 in the revised manuscript: *“The projected density of states (PDOS) of various Cu-N_x sites with iodine species provides direct evidence for the d-p orbital hybridization mechanism near the Fermi level (Fig. 4h, i, and Supplementary Figs. 34-36). For iodine species adsorption on the graphene substrate (G), the I p-orbitals remain largely isolated with obvious overlap with the original iodine species near the Fermi level, indicating weak physical adsorption with minimal electronic interaction. In contrast, on the Cu-N_x substrates, the I p-orbitals in iodine species exhibit significant broadening and splitting, with clear hybridization with the Cu d-orbitals in Cu-N_x sites near the Fermi level, indicating strong chemisorption and effective charge transfer. Similarly, the Cu d-orbitals exhibit a noticeable shift and redistribution of electronic density upon iodine species adsorption, further confirming the strong electronic coupling. More importantly, for ICl adsorption, a pronounced Cu d-I p hybridization is observed, accompanied by the emergence of new hybridized states that correspond to Cu-I bond formation. This electronic interaction weakens the I-Cl bond and stabilizes the ICl intermediate against hydrolysis. These results collectively confirm that the Cu-N_x sites serve as bifunctional centers that simultaneously activate iodine species through catalytic d-p coupling and stabilize the reactive I⁺ intermediate through strong chemisorption.”*

3. In addition to the theoretical calculations shown in Figure 4, experimental verification of the strong adsorption capacity of the Cu-N/PC single-atom catalyst for ICl should be conducted.

Response:

Thank you very much for your valuable comment and suggestion. According to your suggestion, 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 (Figure R3), indicating their strong adsorption capacity for ICl due to their high specific surface area (Supplementary Figs. 6-7 and Table 1). 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 (Fig. 4b-d). Additionally, the UV-vis spectra were utilized to confirm the ICl adsorption capacity (Figure R4). These results experimentally confirm that the Cu-N/PC-2 single-atom catalyst possesses a strong adsorption capacity for ICl, consistent with our DFT calculations.

Revision in Manuscript:

The detailed information and discussion are added on page 8 in the revised manuscript and Supplementary Figs. 18 and 19 in the revised Supplementary Information.

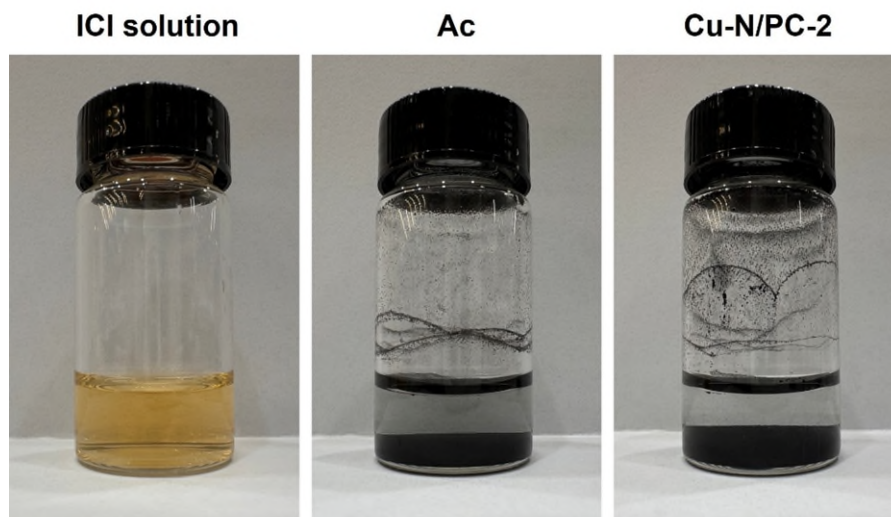


Figure R3. Digital photos for the adsorption tests of the different samples in the ICl solution after resting for 2 h (solution: 2M ZS + 0.1M ChCl).

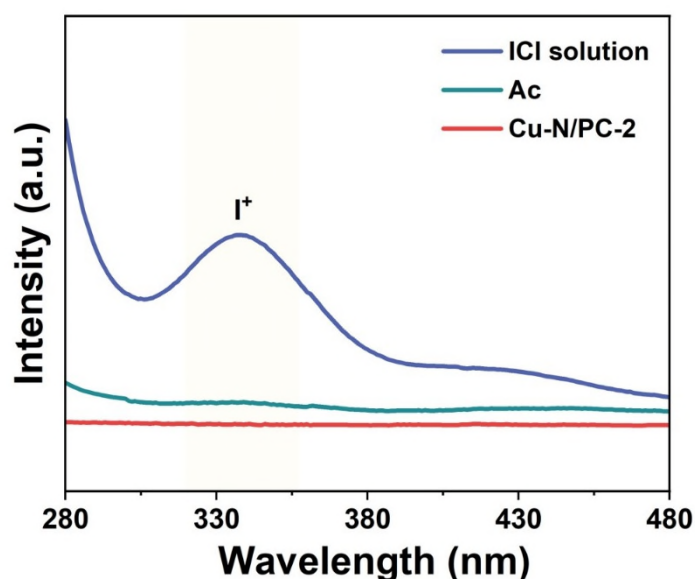


Figure R4. UV-vis spectra of Ac and Cu-N/PC-2 after being immersed in ICl solution for 2 h.

4. Tafel plots for the oxidation process of the iodine cathode should be added to Figure 5b.

Response:

Thank you for your constructive suggestion. We agree that including Tafel plots for the oxidation process of the iodine cathode would provide a more complete catalytic kinetics process. In the revised manuscript, we have now added the Tafel plots for the I^-/I^0 and I^0/I^+ oxidation processes. As shown in Figure R5, both the I^-/I^0 and I^0/I^+ reactions in the zinc-iodine battery with Cu-N/PC-2 host material exhibit smaller Tafel slopes compared to those with Ac host material, affirming that the Cu-N_x sites effectively accelerate the oxidation kinetics of iodine species.^{4,5} This result is consistent with the previously presented cathodic Tafel data and reinforces our conclusion that Cu single-atom sites facilitate reversible and efficient four-electron iodine conversion.

Revision in Manuscript:

The detailed information and discussion are added on page 13 in the revised manuscript and Supplementary Fig. 55 in the revised Supplementary Information.

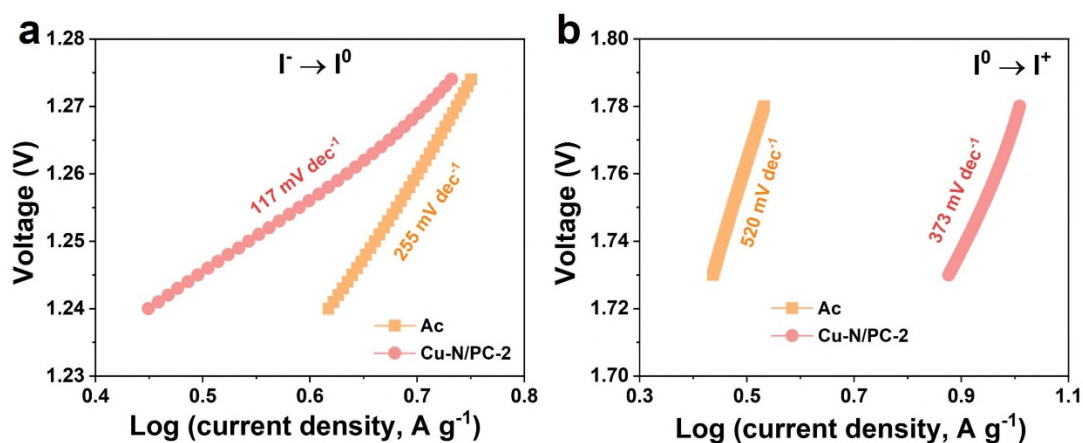


Figure R5. Tafel plots for the oxidation process of the iodine with Ac and Cu-N/PC-2 cathodes.

5. *In situ* characterization techniques, such as Raman spectroscopy and UV-vis tests, should be employed to monitor the conversion of iodine species in the iodine cathode during the charge/discharge process.

Response:

Thank you for this constructive suggestion. We agree that *in-situ* characterization techniques are essential for directly monitoring the dynamic evolution of iodine species during the charging/discharging process, providing real-time evidence for the proposed four-electron conversion mechanism. To address your comment, we have now performed *in-situ* UV-vis and Raman spectroscopy to monitor the evolution of iodine species in the Ac and Cu-N/PC-2 cathodes during the charging/discharging process. The results are summarized below and have been added to the revised manuscript. For the Cu-N/PC-2 cathode, *in-situ* UV-vis spectroscopy during cycling was performed as shown in Figure R6. The peaks at ~288 and 354 nm corresponding to I^- and I_x^- are observed in the low-voltage region. When charged to ~1.3 V, the peak at 447 nm appears and gradually enhances, suggesting the conversion from I^-/I_x^- to I_2 , accompanied by the disappearance of I^- and I_x^- peaks. As the voltage is gradually increased to ~1.7 V, the I_2 peak gradually decreases and the I^+ peak centered at ~340 nm becomes prominent.⁶ The peak of I^+ is at its maximum intensity at 1.8 V, implying a complete transition from I^- to I^+ during the charging process. The discharging process exhibits the opposite conversion, demonstrating the high reversibility of $I^-/I^0/I^+$ conversion.⁵ In contrast, the I^+ peak at ~340 nm is not observed even at the high-voltage plateau. Only I^- , I_x^- , and I_2 species are detected throughout the entire charge/discharge process (Figure R7). This confirms that without Cu-N_x sites, the I^0/I^+ conversion cannot be activated despite the presence of low-

concentration Cl^- in the electrolyte. The formation and stability of I^+ are further verified by XPS and Raman analyses (Figures R8-R10 and Fig. 5k). For example, we constructed a specially designed electrochemical cell with a quartz window to allow Raman signal collection during battery operation (Figure R8). The *in-situ* Raman spectra were recorded at various charging/discharging voltages. As shown in Figure R9, a distinct characteristic peak appears at around 200 cm^{-1} , corresponding to the formation of ICl .^{7,8} Then, this signal is observed to diminish during the subsequent discharging process, ultimately disappearing entirely, illustrating a high reversible I^0/I^+ conversion.

Revision in Manuscript:

The detailed information and discussion are added on pages 16-17 and Fig. 5j in the revised manuscript and Supplementary Figs. 62-66 in the revised Supplementary Information.

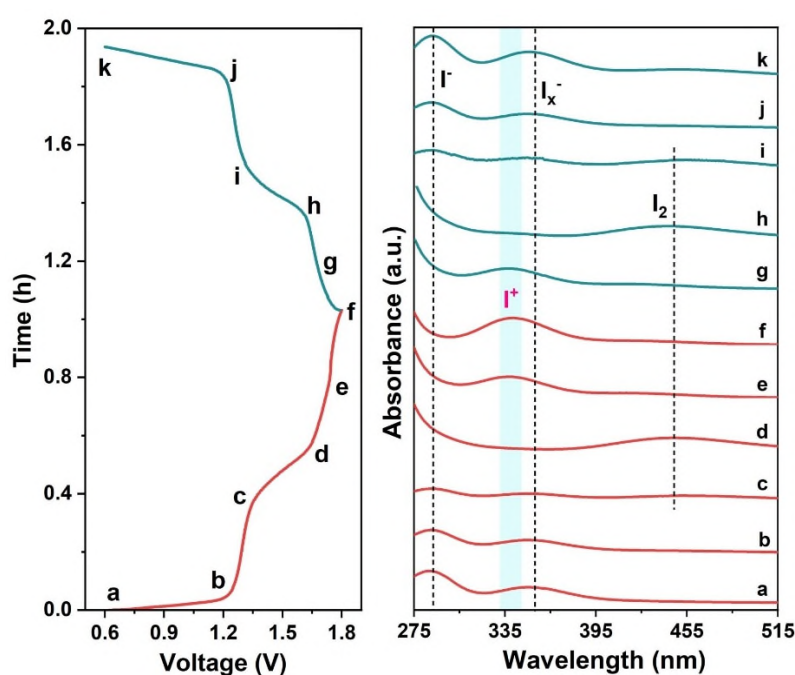


Figure R6. GCD curve and *in-situ* UV-vis spectra of zinc-iodine battery with Cu-N/PC-2 cathode.

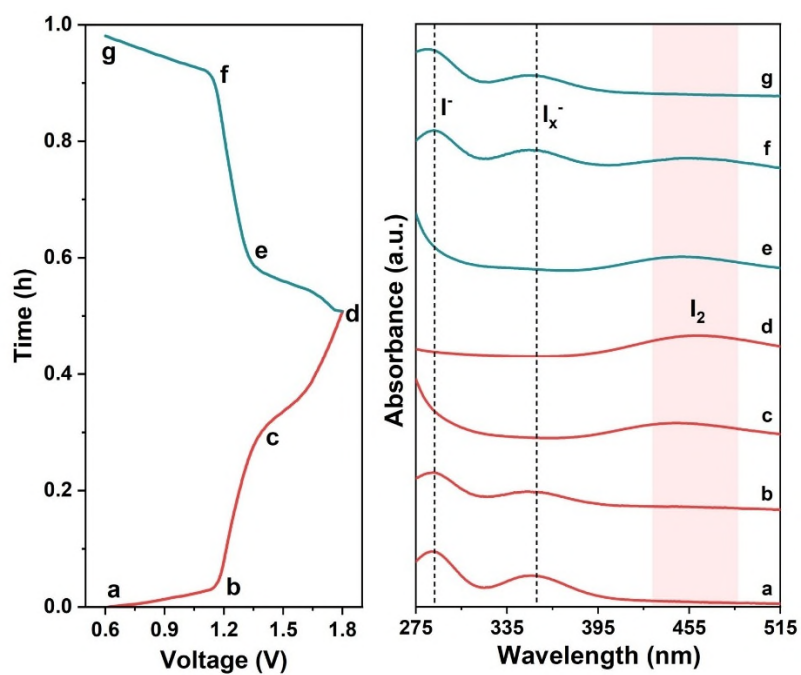


Figure R7. GCD curve and *in-situ* UV-vis spectra of zinc-iodine battery with Ac cathode.



Figure R8. Photographs of the customized battery device for *in-situ* Raman measurement.

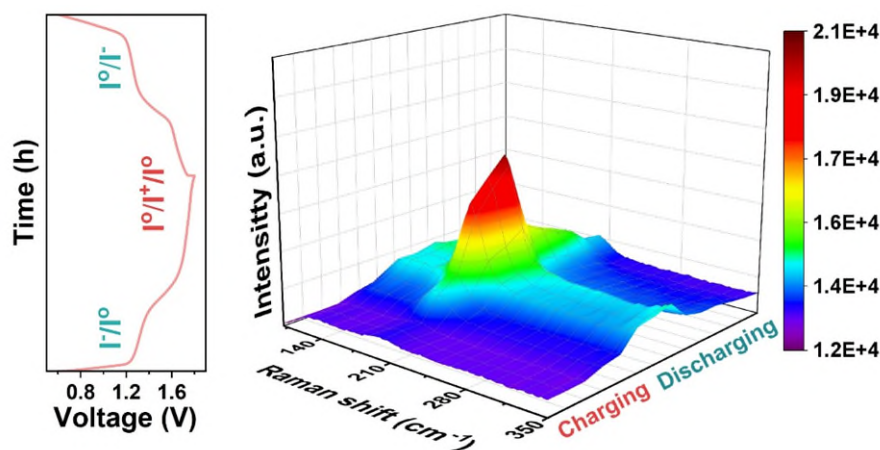


Figure R9. GCD curve and *in-situ* Raman spectra of zinc-iodine battery with Cu-N/PC-2 cathode.

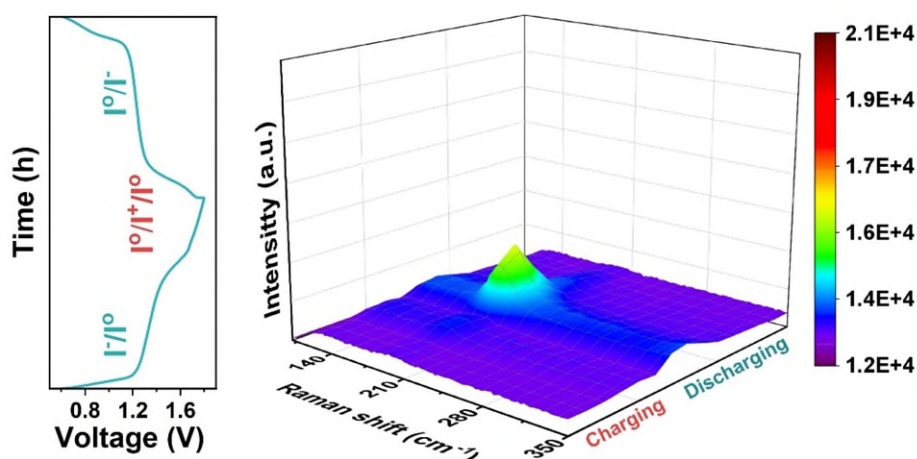


Figure R10. GCD curve and *in-situ* Raman spectra of zinc-iodine battery with Ac cathode.

6. As shown in Figure 5k, the fitted line for the Cu-N/PC-2 XPS results within the range of 623–620 eV is not convincing.

Response:

Thank you for your careful and critical observation regarding the XPS fitting shown in Fig. 5k. You are correct that the fitted line for the Cu-N/PC-2 XPS results within the range of 623–620 eV was not convincingly presented in the original figure. We have re-examined our original XPS data and the fitting procedures for the I 3d spectra of the Cu-N/PC-2 cathode. Upon careful inspection, we identified the following issues with the original fitting shown in Fig. 5k: 1) The baseline correction was not optimally applied in the entire I 3d spectral range, leading to a poor fitting quality. 2) The position of the fitted peak and spin-orbit splitting are unreasonable, resulting in an unconvincing fitting result in the low binding energy region. To address these issues, we have re-processed the

XPS spectra following more rigorous fitting protocols: 1) A Shirley-type background was applied consistently across the entire I 3d spectral range. 2) The I 3d doublets were fitted with the spin-orbit splitting of about 11.5 eV for iodine. The revised fitting results for the Cu-N/PC-2 cathode now show excellent agreement between the fitting curves and the experimental data across the entire binding energy range, including the previously problematic region of 623-620 eV (Figure R11). More importantly, the relative proportions of the various iodine species derived from the revised fitting curves remain consistent with our original conclusions. Furthermore, we have provided the full width at half maximum (FWHM) values for all XPS I 3d peaks to enable a more comprehensive assessment of the fitting quality. All the XPS spectra were fitted with a reasonable FWHM restriction ($0.5 < \text{FWHM} < 2.8 \text{ eV}$),^{9,10} as summarized in Table R2. At the fully discharged state (0.6 V), two prominent peaks centered at 631.60/620.06 and 630.45/618.96 eV were assigned to I^0 and I^- species, with corresponding FWHM values of 1.72/1.43 and 1.20/1.19 eV, respectively. Upon charging to 1.8 V, new peaks appear at $\sim 632.80/621.60 \text{ eV}$, indicating the oxidation to a higher valence state of I^+ with FWHM values of 2.66/1.69 eV, while the adjacent I^0 species show FWHM of 1.37/1.50 eV.

Revision in Manuscript:

The detailed information and discussion are added on page 17 and Fig. 5k in the revised manuscript.

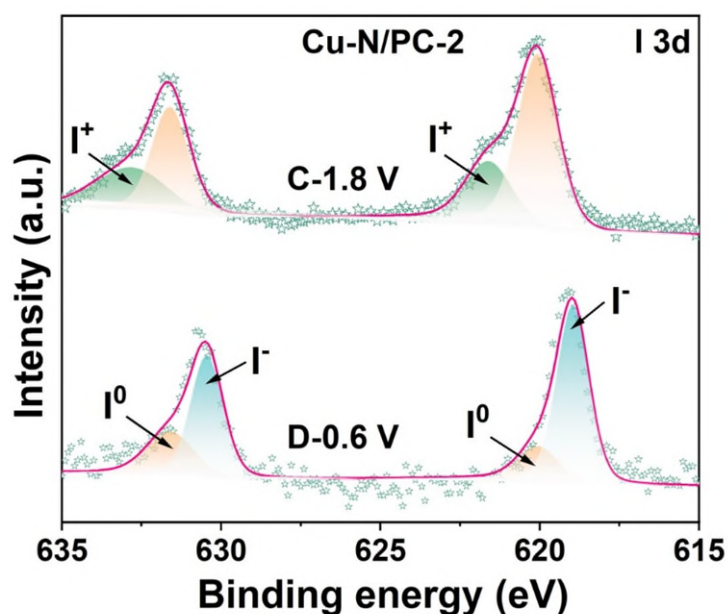


Figure R11. XPS I 3d spectra of the fully discharged and charged Cu-N/PC-2 cathodes.

Table R2. FWHM of the XPS I 3d peaks at different charge/discharge states.

State (Voltage)	Species	Binding Energy (eV)	FWHM (eV)	Binding Energy (eV)	FWHM (eV)
Discharged	I ⁰	~631.60	1.72	~620.06	1.43
Discharged	I ⁻	~630.45	1.20	~618.96	1.19
Charged	I ⁺	~632.80	2.66	~621.60	1.69
Charged	I ⁰	631.60	1.37	~620.06	1.50

7. Why was ChCl chosen as the Cl⁻ source? Additionally, what is the performance of the Zn||I₂ cell when the ChCl concentration is below 0.1 M?

Response:

Thank you for these two important and insightful questions regarding the choice of ChCl as the Cl⁻ source and the effect of its concentration on the cell performance. In addition to the advantages outlined in our original manuscript, we would like to provide a more comprehensive analysis of the dual functionality of the choline cation (Ch⁺), specifically its adsorption behavior on the Zn anode surface and the resulting electric double layer (EDL) effects. These effects further justify the selection of ChCl and contribute to the overall performance of our four-electron zinc-iodine battery.

Why was ChCl chosen as the Cl⁻ source: The choice of ChCl is justified by the synergistic role of the Ch⁺ at the zinc anode/electrolyte interface. Recent studies have demonstrated that choline-based additives actively participate in interface engineering to suppress dendrite growth and side reactions.¹¹⁻¹⁶ Ch⁺ ions exhibit a strong tendency to preferentially adsorb onto the surface of the zinc anode (Figures R12 and R13). Owing to their positive charge and hydrophobic/hydrophilic amphiphilic structure, Ch⁺ ions are electrostatically attracted to the negatively charged regions of the zinc anode surface during the plating/stripping process,¹⁷ then forming a dynamic “electrostatic shielding layer” on the zinc surface.¹² To evaluate the adsorption phenomenon of Ch⁺ ions on the zinc surface, the electric double layer (EDL) capacitance was investigated by the CV curves of the Zn||Zn cells. The Zn||Zn cell exhibits a lower EDL capacitance of 0.76 mF cm⁻² in the 2M ZS + ChCl electrolyte than the case (1.62 mF cm⁻²) of the 2M ZS electrolyte (Figures R14 and R15). The decrease of EDL capacitance is ascribed to the formation of an ion adsorption layer near zinc due to the strong adsorption ability between the additive ions and zinc plane, thus establishing a water-poor

EDL, which is beneficial to inhibit side reactions on the zinc surface.¹⁸ As a result, the Zn||Zn cell with the 2M ZS + ChCl electrolyte maintains a stable Coulombic efficiency of 99.88% at 3 mA cm⁻², 1 mAh cm⁻² over 2000 cycles (Figure R16). Furthermore, the cell with the 2M ZS + ChCl electrolyte exhibits a stable cycling life over 1600 h at 5 mA cm⁻², 1 mAh cm⁻² (Figure R17). Beyond physical adsorption, Ch⁺ plays a chemical role in modifying the electrolyte bulk and interface. The Ch⁺ is a well-known hydrogen bond acceptor, which can effectively disrupt the original hydrogen bond network of water molecules.¹¹ By breaking the original H-bond network, Ch⁺ reduces the number of free water molecules available to solvate Zn²⁺ or attack the I⁺ species. This complements the function of Cl⁻ in stabilizing the I⁺ intermediate against hydrolysis.

Comparison with other Cl⁻ sources: The dual functionality of Ch⁺ provides a distinct advantage over inorganic sources (e.g., ZnCl₂, NaCl, and KCl). While these inorganic salts provide Cl⁻ ions to stabilize I⁺, their cations often do not adsorb favorably on the zinc surface or may even participate in unwanted side reactions. For instance, high concentrations of ZnCl₂ can lead to acidic conditions or complex precipitation, while Na⁺/K⁺ ions do not provide the electrostatic shielding effect necessary for dendrite suppression in the same manner as choline-based cations.

The performance of zinc-iodine batteries when the ChCl concentration is below 0.1M: To systematically investigate the effect of ChCl concentration on the activation and stability of the I⁺/I⁰ conversion, we performed additional experiments with varying ChCl concentrations (0.01M, 0.05M, and 0.1M) in the 2M ZS electrolyte using the Cu-N/PC-2 cathode, as shown in Figures R18 and R19. When the ChCl concentration is reduced 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. 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 cathode interface. Consequently, I⁺ species become vulnerable to hydrolysis, leading to capacity decay. When the ChCl concentration is further reduced 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.

Revision in Manuscript:

The detailed information and discussion are added on page 13 in the revised manuscript and Supplementary Figs. 50 and 51 in the revised Supplementary Information.

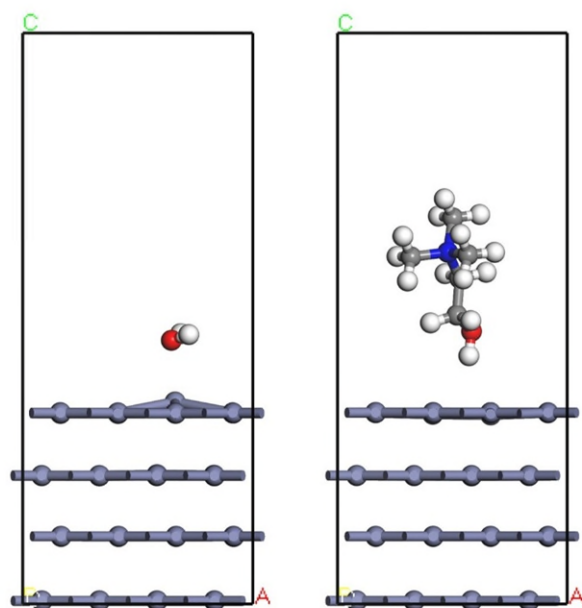


Figure R12. Surface adsorption structures of H_2O and Ch^+ on the $\text{Zn}_{[002]}$ plane.

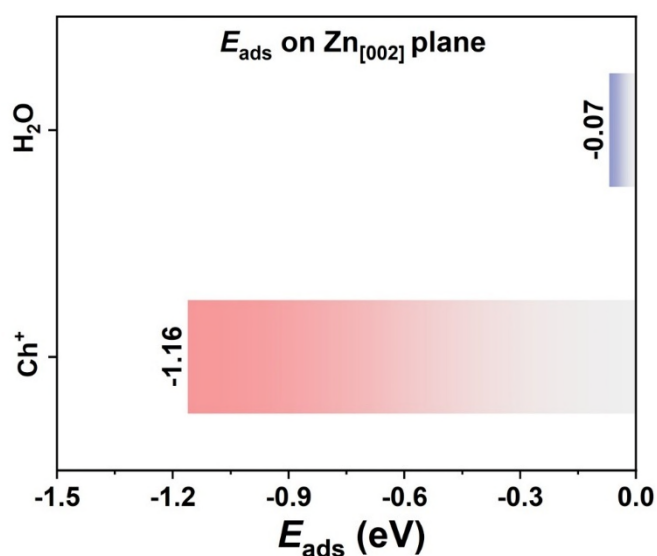


Figure R13. Values of surface adsorption energy of H₂O and Ch⁺ on the Zn_[002] plane.

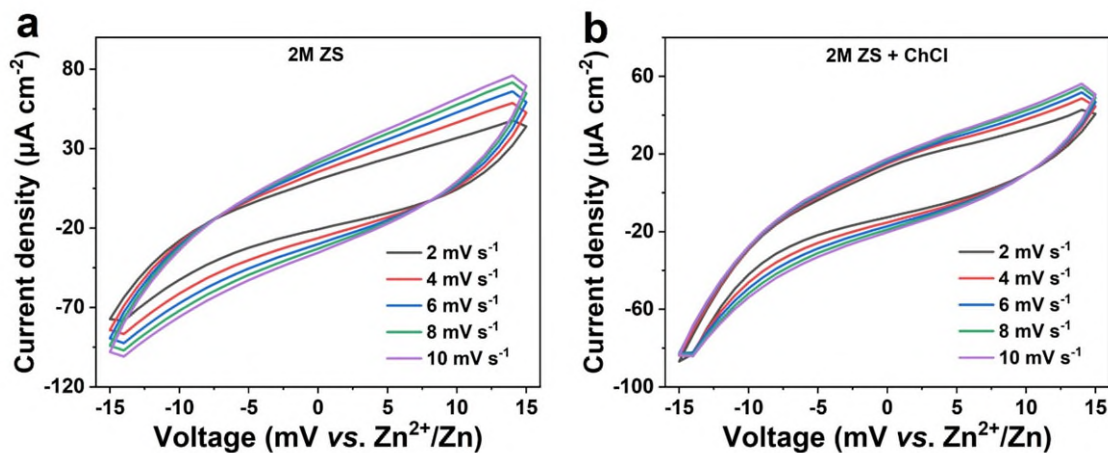


Figure R14. EDL measurements for Zn foils in the various electrolytes. (a) 2M ZS and (b) 2M ZS + ChCl.

The capacitance (C) is determined by the linear relationship between capacitive current (i_c) and scan rate (ν), which can be achieved from the slope of the current-voltage curves. Therefore, the C could be calculated by the following equation:

$$C = \frac{i_c}{\nu} \quad (R1)$$

where $i_c = (i_{0V+} - i_{0V-})/2$, meaning the half value of current difference during positive and negative scans at 0 V.

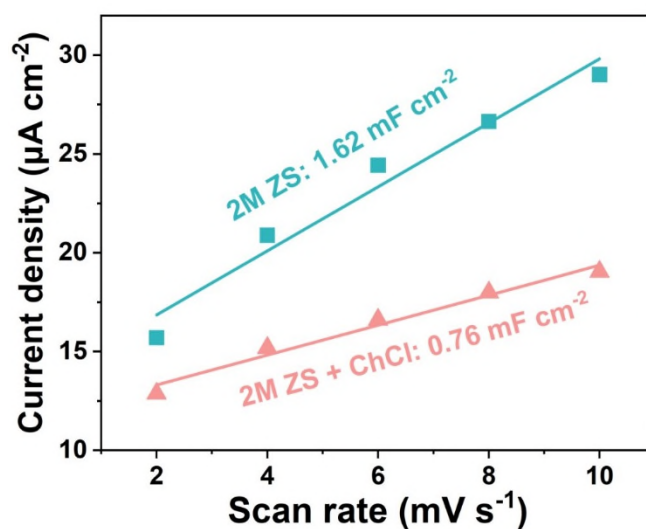


Figure R15. Plots of capacitive currents versus scan rates in the various electrolytes.

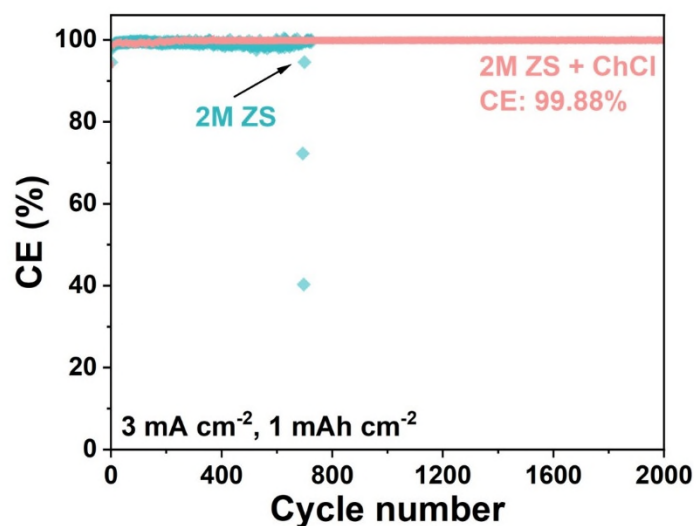


Figure R16. Coulombic efficiencies of Zn||Zn cells with the various electrolytes.

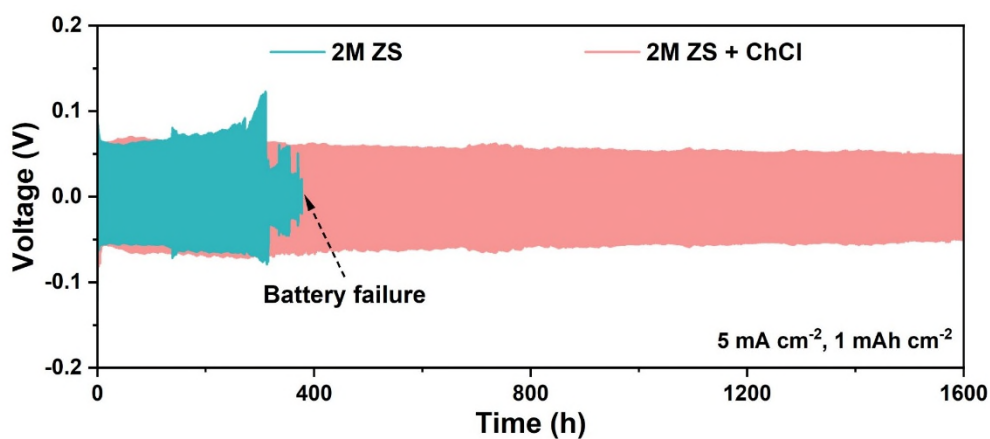


Figure R17. Cycling performance of Zn||Zn cells at 5 mA cm^{-2} , 1 mAh cm^{-2} with the various electrolytes.

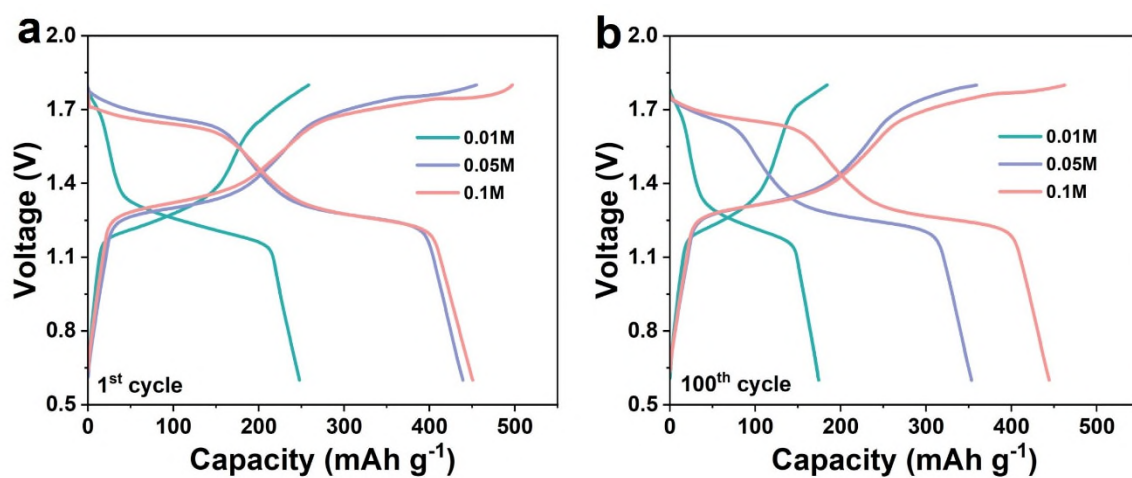


Figure R18. Galvanostatic discharge-charge curves of zinc-iodine batteries at 0.5 A g^{-1} with the

different ChCl concentrations. (a) The first cycle and (b) The 100th cycle.

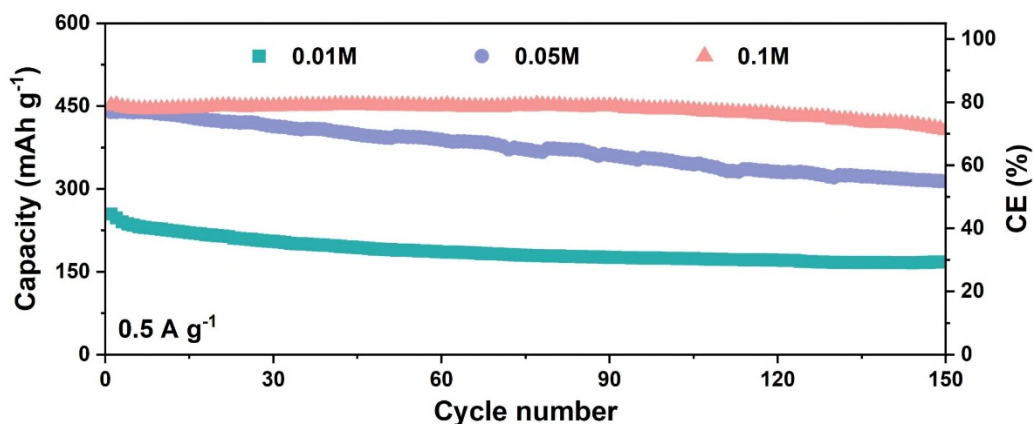


Figure R19. Cycling performance of zinc-iodine batteries at 0.5 A g⁻¹ with the different ChCl concentrations.

8. How does the Zn||I₂ cell perform during long-term cycling at a low current density (e.g., 0.2 A/g)?

Response:

Thank you for your helpful suggestion, and we think it's of great value. According to your suggestion, we have supplemented the electrochemical performance data and the complete charge-discharge voltage profiles at a low current density of 0.2 A g⁻¹ to reveal the polarization behavior and reversibility of the battery under low-rate conditions. As shown in Figure R20a, at a low current density of 0.2 A g⁻¹, the zinc-iodine battery with the Cu-N/PC-2 cathode exhibits two distinct voltage plateaus, corresponding to the I⁺/I⁰ and I⁰/I⁻ redox couples. In addition, the battery delivers an initial discharge capacity of approximately 463.2 mAh g⁻¹ and retains ~79.4% of its initial capacity after 100 cycles (Figure R20b), demonstrating excellent reversibility and cycling stability. Moreover, we also added the electrochemical performance data of the zinc-iodine battery with the various cathodes at 0.5 A g⁻¹ (Figures R21 and R22). The results show that the zinc-iodine battery with the Cu-N/PC-2 cathode delivers a higher discharge capacity than that with the Ac cathode. More importantly, the battery with the Cu-N/PC-2 cathode exhibits a long-term cycling life of over 160 cycles with a capacity retention of 87.1% at 0.5 A g⁻¹ (Coulombic efficiency close to 97.5%), surpassing the values of Ac cathode. These results confirm that the Cu-N_x sites in Cu-N/PC-2 cathode can stabilize the iodine species even under low-rate conditions, mitigating the polyiodide shuttling and I⁺ hydrolysis.

Revision in Manuscript:

The detailed information and discussion are added on page 18 in the revised manuscript and Supplementary Figs. 69 and 70 in the revised Supplementary Information.

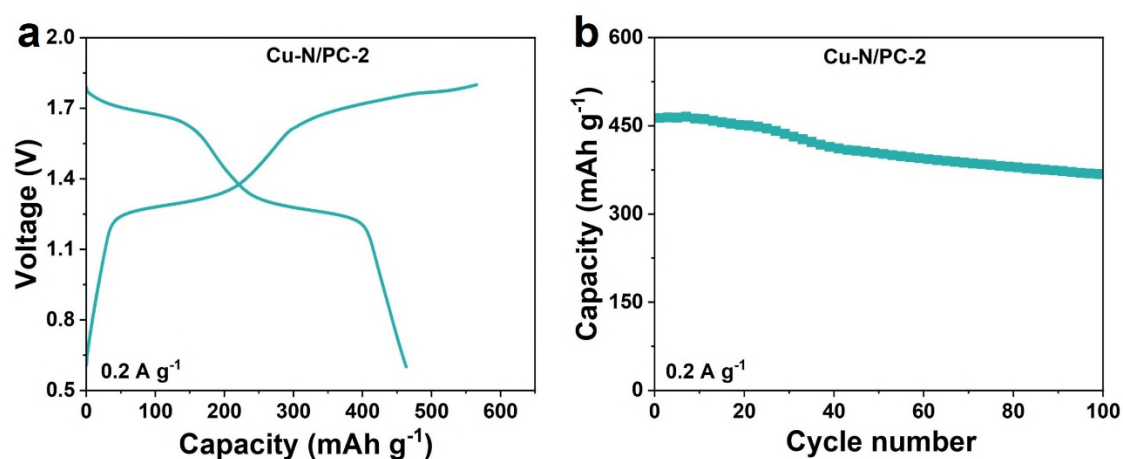


Figure R20. (a) Galvanostatic discharge-charge curves of zinc-iodine battery at 0.2 A g⁻¹ with Cu-N/PC-2 cathode, and (b) the corresponding cycling performance.

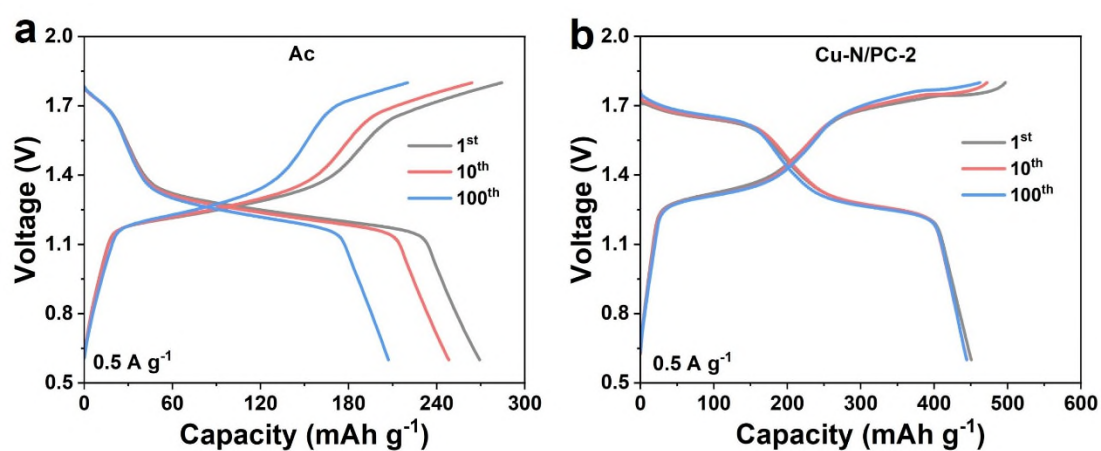


Figure R21. Galvanostatic discharge-charge curves of zinc-iodine batteries at 0.5 A g⁻¹ with the various cathodes. (a) Ac and (b) Cu-N/PC-2.

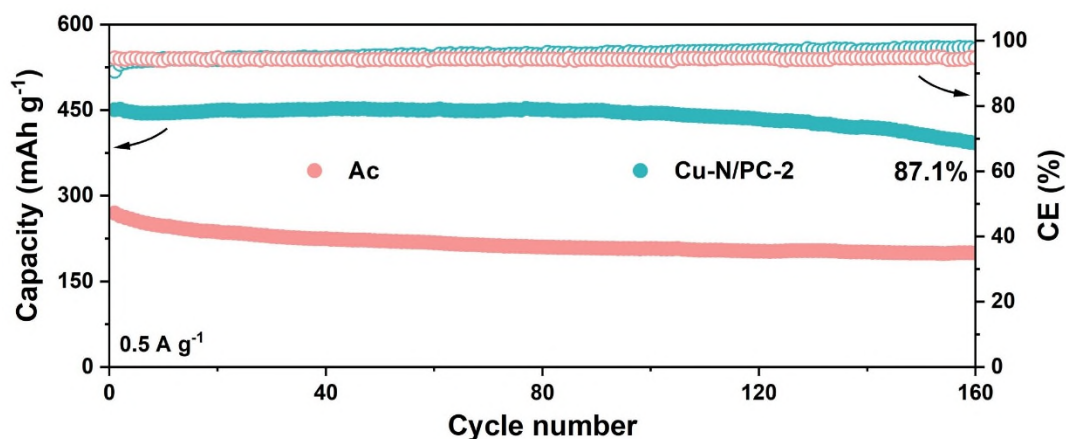


Figure R22. Cycling performance of zinc-iodine batteries at 0.5 A g^{-1} with the various cathodes.

9. Characterization methods such as TEM, SEM, and XPS should be performed to evaluate the structural and morphological stability of the single-atom catalyst after long-term cycling.

Response:

Thank you for your insightful and important suggestion. We agree that post-cycling characterization is essential to confirm that the Cu single-atom sites remain structurally and morphologically intact after prolonged electrochemical cycling. To address your concern, we have now performed some additional post-cycling characterizations on the Cu-N/PC-2 cathode after long-term cycling. Specifically, we conducted the following analyses:

Scanning electron microscopy (SEM): As shown in Figure R23, SEM and EDS mapping images of the post-cycled Cu-N/PC-2 cathode confirm that the overall porous structure of the cathode surface is well maintained, with no significant cracking, pulverization, or detachment from the carbon cloth current collector.

Transmission electron microscopy (TEM): To further examine the detailed morphologies and microstructures of the post-cycled Cu-N/PC-2 cathode, the post-cycled Cu-N/PC-2 material was carefully extracted from the disassembled cell, thoroughly washed, and dried. TEM and HRTEM images show that the polyhedral morphology of the carbon matrix is well preserved without visible collapse or aggregation (Figure R24a, b). The selected area electron diffraction (SAED) pattern of the post-cycled Cu-N/PC-2 cathode remains amorphous carbon without any highly crystallized phases (Figure R24c). More importantly, the HAADF-STEM image clearly reveals that isolated bright dots corresponding to Cu single atoms remain uniformly dispersed throughout the carbon matrix, with no evidence of nanoparticle formation or Cu clustering (Figure R24d, e). The EDS

elemental mapping images further verify the uniform dispersion of C, N, and Cu elements throughout the polyhedral framework (Figure R25). These results demonstrate the excellent atomic-level stability of the Cu-N_x sites under long-term cycling conditions.

X-ray photoelectron spectroscopy (XPS): XPS measurements were further performed to investigate the elemental compositions and N-bond configurations of the post-cycled Cu-N/PC-2 cathode. The XPS C 1s spectra of the sample can be deconvoluted into various peaks corresponding to C-C/C=C, C-O/C=N, and C=O/C-N functional groups (Figure R26).¹⁹ Moreover, the XPS N 1s and Cu 2p spectra show that the N 1s and Cu 2p configurations remain essentially unchanged compared to the pristine material (Figure R27). The Cu⁺/Cu²⁺ ratio and the Cu-N_x peak intensity exhibit no significant degradation, confirming that the chemical environment and coordination structure of the Cu single-atom sites are stable throughout long-term cycling.

These post-cycling characterization results collectively confirm that the Cu-N/PC-2 single-atom catalyst possesses outstanding structural and morphological robustness, which underlies the exceptional long-term cycling stability at a high current density of 10 A g⁻¹ (70% capacity retention over 50,000 cycles) reported in our manuscript.

Revision in Manuscript:

The detailed information and discussion are added on pages 18 and 19 in the revised manuscript and Supplementary Figs. 74-78 in the revised Supplementary Information.

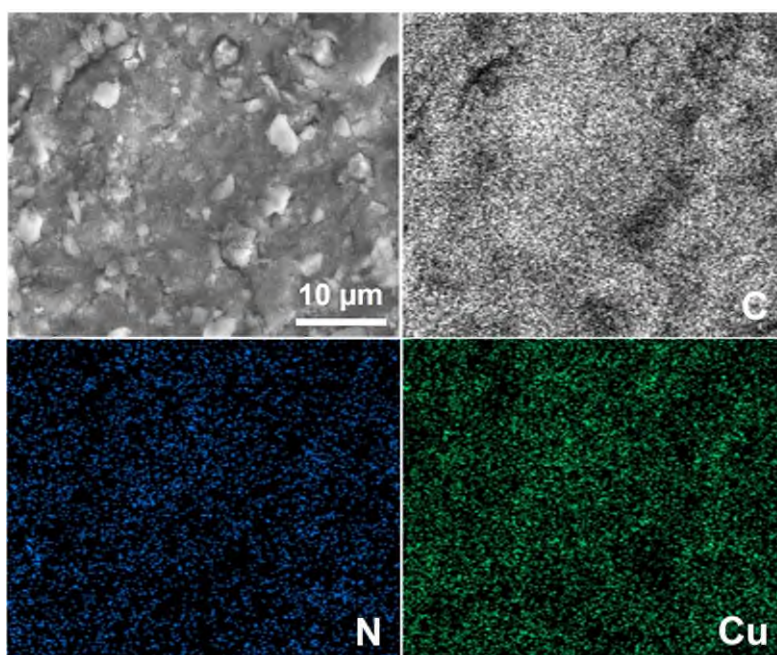


Figure R23. SEM and the corresponding element mapping images of Cu-N/PC-2 cathode after cycling.

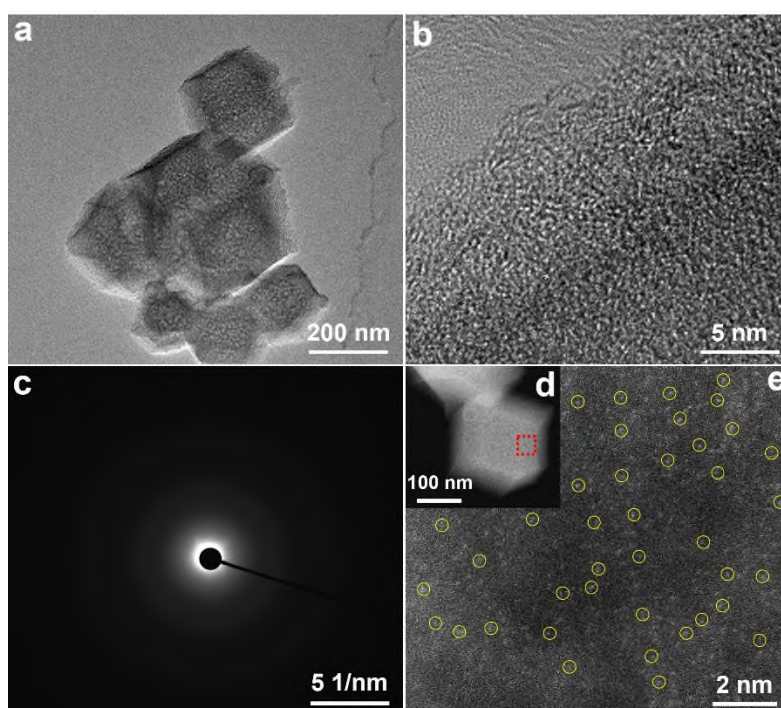


Figure R24. (a-c) TEM, HRTEM, and the corresponding SAED pattern of Cu-N/PC-2 cathode after cycling. (d, e) Aberration-corrected HAADF-STEM images of Cu-N/PC-2 cathode after cycling with the atomic dispersion of Cu highlighted by yellow circles.

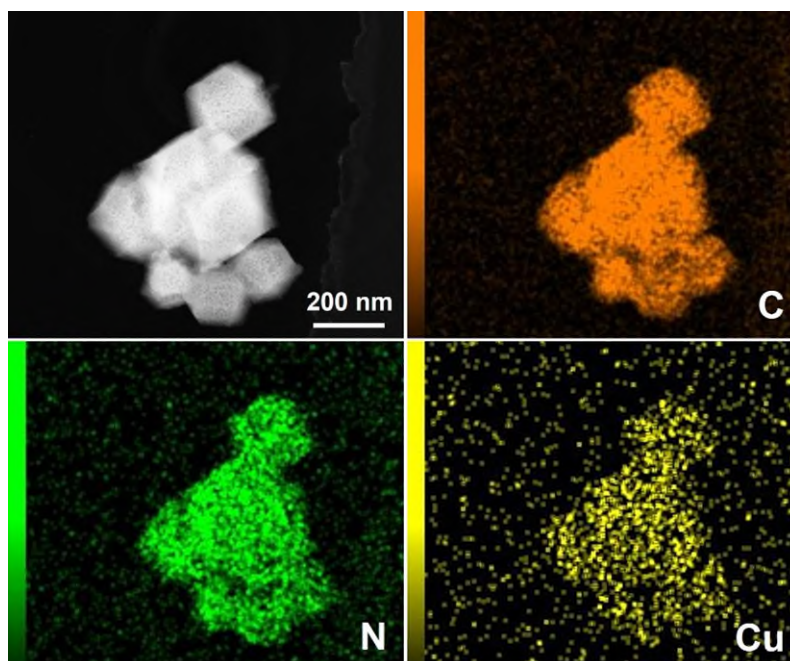


Figure R25. EDS mapping images of C, N, and Cu in the Cu-N/PC-2 cathode after cycling.

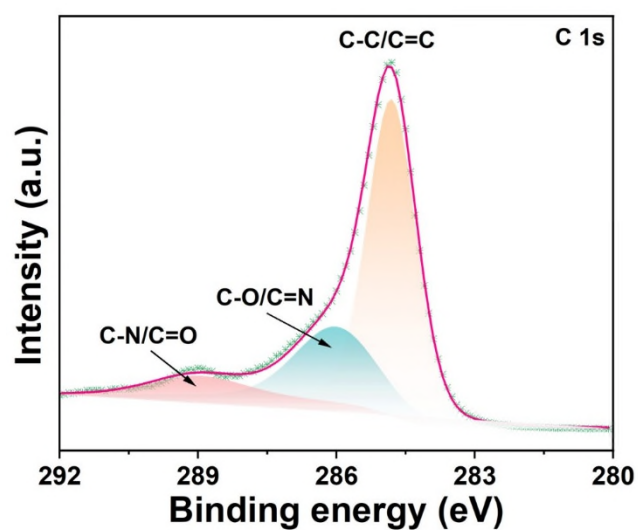


Figure R26. XPS C 1s spectra of Cu-N/PC-2 cathode after cycling.

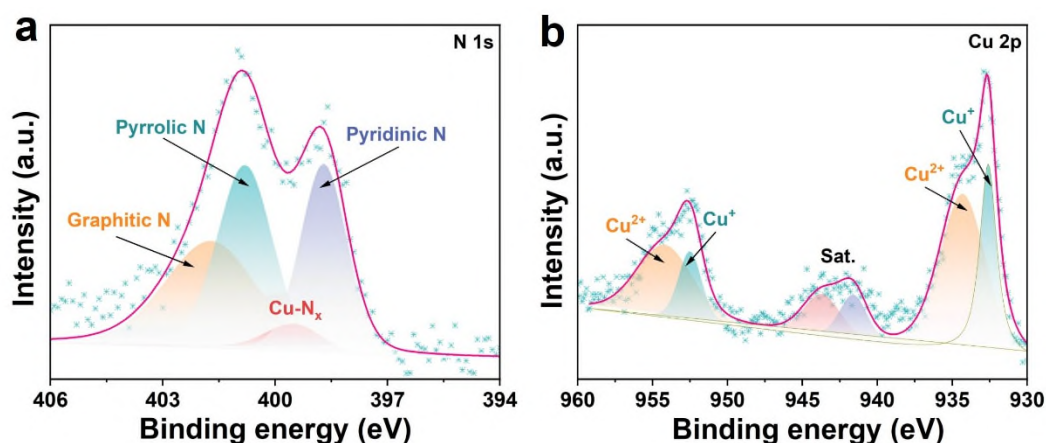


Figure R27. (a) XPS N 1s and (b) Cu 2p spectra of Cu-N/PC-2 cathode after cycling.

10. Self-discharge tests of the Zn||I₂ cell should also be included.

Response:

Thank you very much for your insightful comment. According to the reviewer's suggestion, the self-discharge performance of the Zn||I₂ cell was measured. As shown in Figure R28, the battery with the Cu-N/PC-2 cathode maintains a high open-circuit voltage of ~1.67 V after resting 6 hours, which is significantly higher than the low-voltage plateau of the I⁰/I⁺ redox couple. This clearly indicates that the I⁺ species formed during charging remain effectively stable, thereby enabling the high-voltage I⁰/I⁺ redox reaction. In contrast, the battery with the Ac cathode rapidly drops to ~1.43 V under the same conditions, confirming that only the I⁰/I⁺ reaction can be sustained, while the I⁺ species undergo severe hydrolysis or irreversible conversion. This conclusion is further corroborated by the discharged capacity after rest: the zinc-iodine battery with the Cu-N/PC-2 cathode delivers a high capacity of ~386.8 mAh g⁻¹, close to the theoretical four-electron capacity, whereas the zinc-iodine battery with the Ac host material only achieves a capacity of ~168.9 mAh g⁻¹, consistent with the limited two-electron transfer process. These results provide direct electrochemical evidence that our orbital coupling effect with low-concentration chloride ions effectively suppresses I⁺ hydrolysis and promotes highly reversible I⁰/I⁺ conversion.

Revision in Manuscript:

The detailed information and discussion are added on page 19 in the revised manuscript and Supplementary Fig. 79 in the revised Supplementary Information.

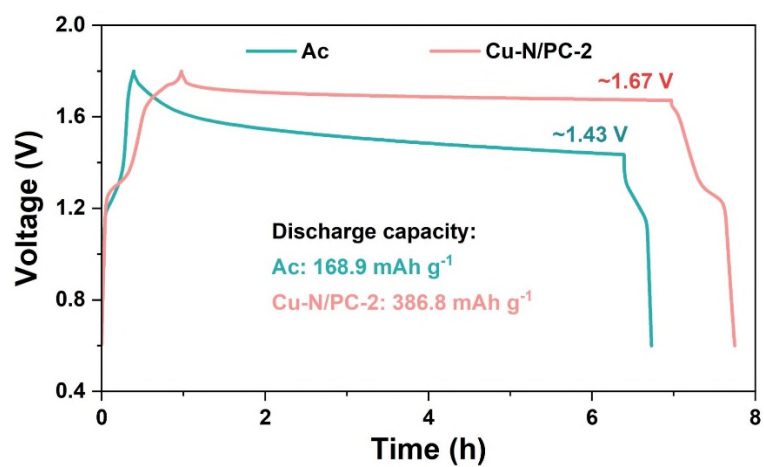


Figure R28. Self-discharge capability of the zinc-iodine batteries with the various cathodes.

Reviewer #2

This manuscript reports the design and synthesis of a copper single-atom embedded nitrogen-doped porous carbon (Cu-N/PC) host for four-electron zinc-iodine batteries. The authors demonstrate that the Cu-N_x sites synergistically couple d-p hybridization with localized Cl⁻ microenvironment to stabilize reactive I⁺ intermediates, lower the energy barrier for I⁰/I⁺ conversion, and suppress polyiodide shuttling. The resulting battery achieves a high discharge capacity of 408 mAh g⁻¹, an extended cycling stability over 50,000 cycles with a low decay rate of 0.0062% per cycle, and excellent rate capability. More importantly, the experimental and theoretical analyses provided sufficiently support the conclusions drawn in this paper. This manuscript presents a significant advance in the field of aqueous zinc-iodine batteries through a well-conceived single-atom catalyst strategy. Therefore, I believe the manuscript is suitable for publication in Nature Communications after minor revisions. Nevertheless, here are some comments to be addressed:

Response:

We really appreciate your deep and thorough review of our manuscript. According to your comments and suggestions, we have revised and improved our manuscript.

1. While XPS and HAADF-STEM confirm atomic dispersion, the exact Cu loading (at.%) in Cu-N/PC-x is not provided. This information is essential for correlating structure with activity and for reproducibility.

Response:

Thank you for your constructive comment. We agree that the exact Cu loading (at.%) in the Cu-N/PC-x samples is essential for correlating the structure with catalytic activity and for ensuring the reproducibility of our work. To address your concern, we have now determined the Cu loading in the Cu-N/PC-x samples using X-ray photoelectron spectroscopy (XPS). The results are summarized in the table below (Figure R29 and Table R3):

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 crystals 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.

Revision in Manuscript:

The detailed information and discussion are added on page 6 in the revised manuscript and Supplementary Fig. 10 and Table 2 in the revised Supplementary Information.

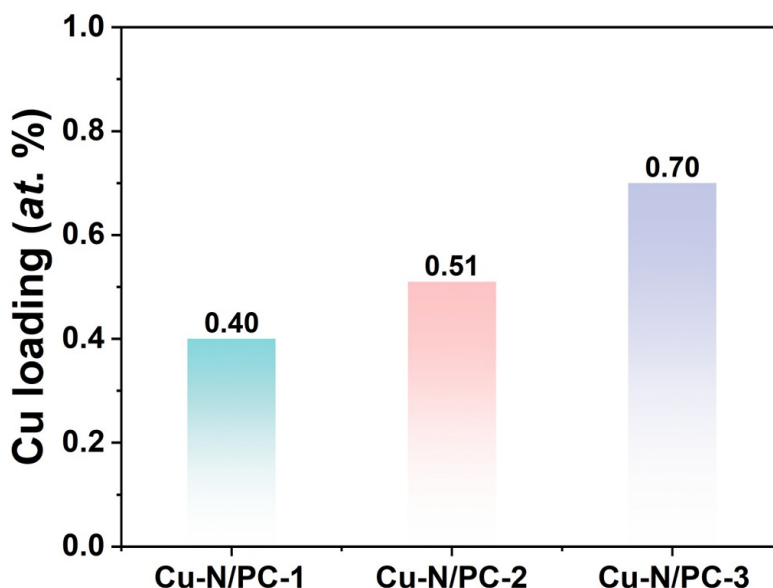


Figure R29. The Cu loading values (at.%) of the Cu-N/PC-x samples.

Table R3. The elemental composition information of Cu-N/PC-x samples.

Samples	C (at. %)	O (at. %)	N (at. %)	Cu (at. %)	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

2. The manuscript emphasizes synergy between Cu-N_x sites and Cl⁻, but it is unclear whether Cl⁻ is essential only for I⁺ stabilization or also participates in the catalytic cycle. A control experiment with a Cl⁻-free electrolyte on Cu-N/PC would help delineate the contribution of Cl⁻.

Response:

Thank you for this excellent and incisive comment. We agree that a control experiment with a Cl⁻-free electrolyte on Cu-N/PC is necessary to delineate the contribution of Cl⁻. To elucidate the distinct roles of Cu-N_x sites and Cl⁻ ions in activating the four-electron iodine redox chemistry, we evaluated the electrochemical performance using different host materials and electrolyte compositions. Specifically, a control host denoted as PC-w/o Cu was synthesized following the same Cu-N/PC preparation procedure but without adding any copper source (Figures R30-R32). The key experimental matrix includes (Figure R33): A) Ac + Cl⁻-containing electrolyte, B) PC-w/o Cu + Cl⁻-containing electrolyte, C) Cu-N/PC + Cl⁻-free electrolyte, and D) Cu-N/PC + Cl⁻-containing electrolyte. The results are summarized below:

A and B systems: A weak and poorly defined high-voltage plateau (1.7 V) emerges, indicating that Cl⁻ alone can partially activate the I⁰/I⁺ conversion. However, the plateau is not well-defined, and the capacity contribution from the I⁰/I⁺ conversion remains low. This suggests that while low-concentration Cl⁻ ions can stabilize I⁺ to some extent through ICl complex formation, the carbon and PC-w/o Cu hosts lack sufficient catalytic activity to drive the I⁰/I⁺ conversion efficiently.

C system: Despite the presence of catalytically active Cu-N_x sites, the high-voltage plateau is still absent. The Cu-N_x sites alone cannot stabilize the electrophilic I⁺ intermediate in the absence of Cl⁻, as I⁺ undergoes rapid hydrolysis or comproportionation with I₃⁻ in aqueous media. The Cu-N_x sites enhance the kinetics of the I⁰/I⁺ conversion, but the four-electron pathway is not activated.

D system: Only when the Cu-N/PC host is used in conjunction with a Cl⁻-containing electrolyte does a well-defined high-voltage plateau emerge, corresponding to the I⁰/I⁺ redox couple, thereby achieving the full four-electron I⁻/I⁰/I⁺ conversion.

Figure R34 shows the Q₁/Q₂ values of different systems (Data from Figure R33), demonstrating the distinct and synergistic roles of Cu-N_x sites and Cl⁻ ions in the iodine conversion process. This observation is further corroborated by CV curves (Figure R35), which show distinct redox peaks for the I⁻/I⁰/I⁺ redox process solely under the combined Cu-N/PC host and Cl⁻-containing electrolyte. Based on these control experiments, we can now clearly delineate the respective roles: **1) Cl⁻ ions**

are essential for activating the I^0/I^+ conversion. Without Cl^- , the I^0/I^+ conversion efficiency is extremely low regardless of the host material, because the electrophilic I^+ cannot be stabilized in the aqueous media. **2) $Cu-N_x$ sites effectively lower the energy barrier for the I^0/I^+ conversion.** Even with Cl^- ions, the Ac or PC-w/o Cu host yields only a weak and inefficient I^0/I^+ conversion. The $Cu-N_x$ sites catalyze the oxidation step, as evidenced by DFT calculations showing reduced Gibbs free energy for the conversion from I^- to I^+ . This catalytic effect is essential for achieving a high-efficiency, low-polarization four-electron process. Therefore, Cl^- ions are not merely passive stabilizers but active participants in the catalytic process, enabling the reversible formation of I-Cl complexes. The $Cu-N_x$ sites provide the necessary catalytic activity to overcome the kinetic barrier of the I^0/I^+ conversion. The synergy between the two factors is indispensable: Cl^- ions are essential for the thermodynamic stabilization of I^+ , while $Cu-N_x$ sites are essential for the kinetic acceleration of I^+ formation.

Revision in Manuscript:

The detailed information and discussion are added on pages 12 and 13 in the revised manuscript and Supplementary Figs. 43-45, 47-49 in the revised Supplementary Information.

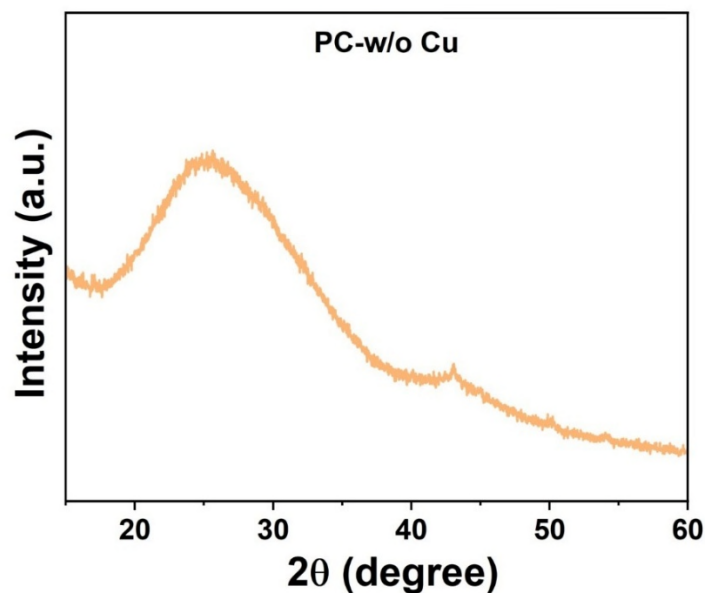


Figure R30. XRD pattern of PC-w/o Cu.

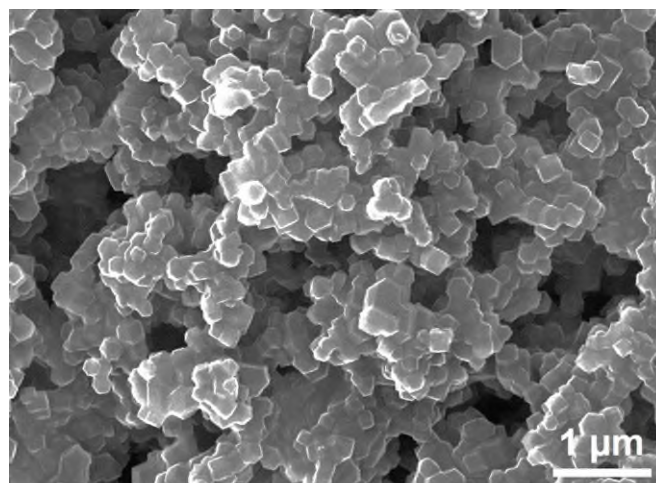


Figure R31. SEM image of PC-w/o Cu.

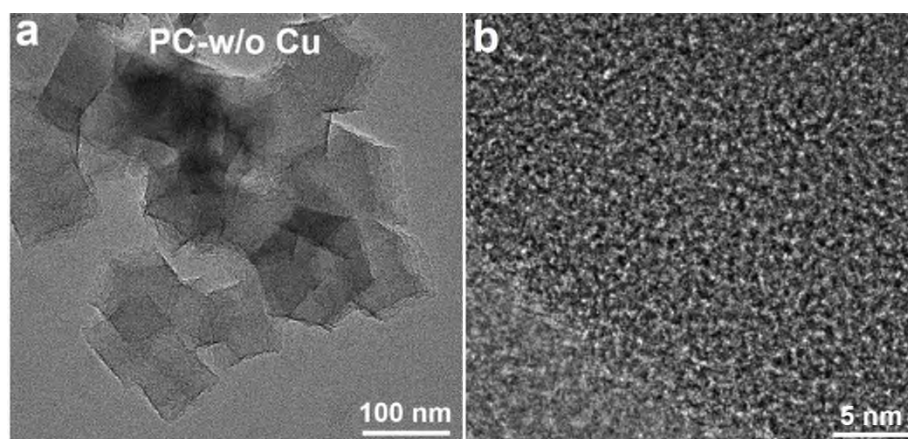


Figure R32. TEM and HRTEM image of PC-w/o Cu.

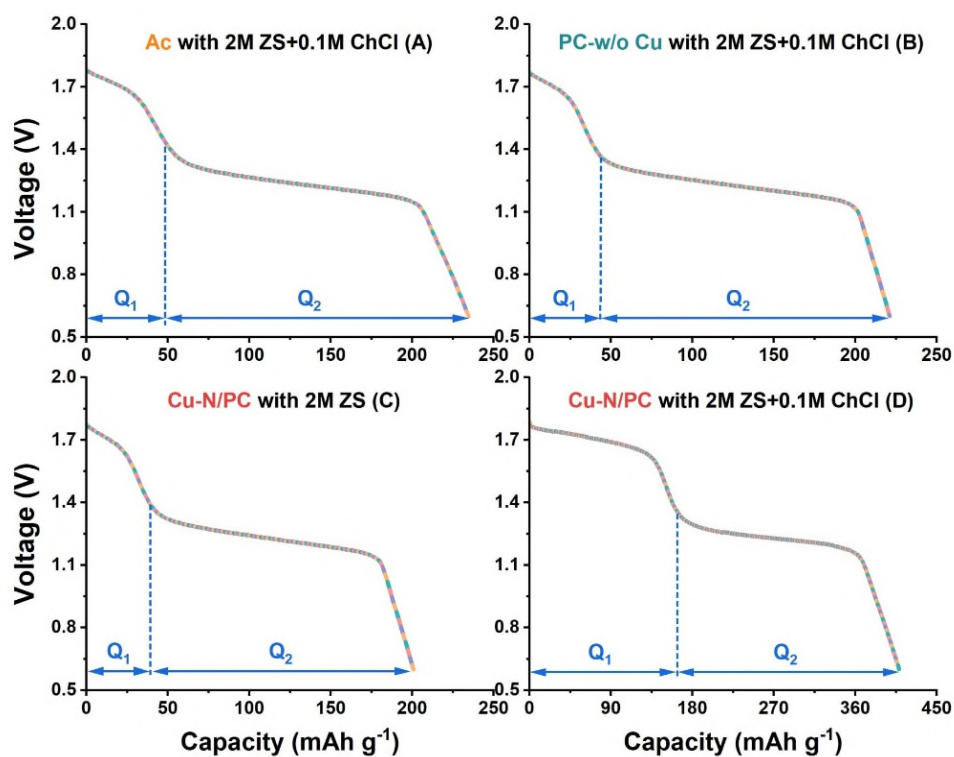


Figure R33. Discharge curves of various cathodes with 2M ZS or 2M ZS+0.1M ChCl electrolytes.

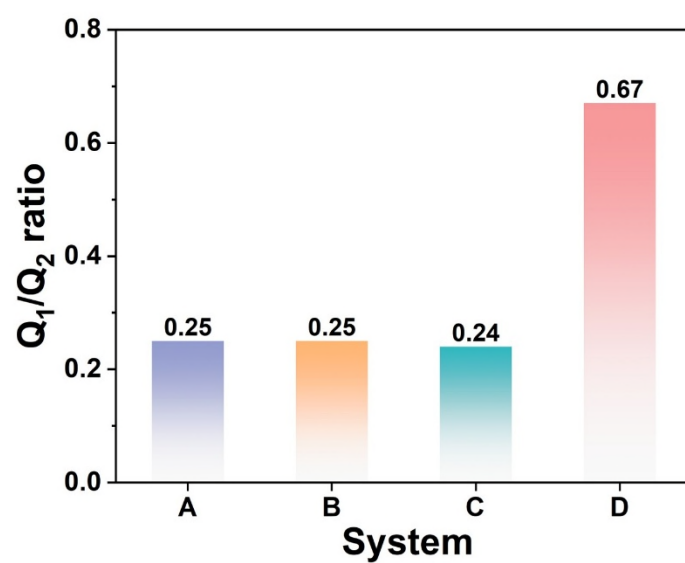


Figure R34. Q_1/Q_2 values of different systems (Data from Figure R33).

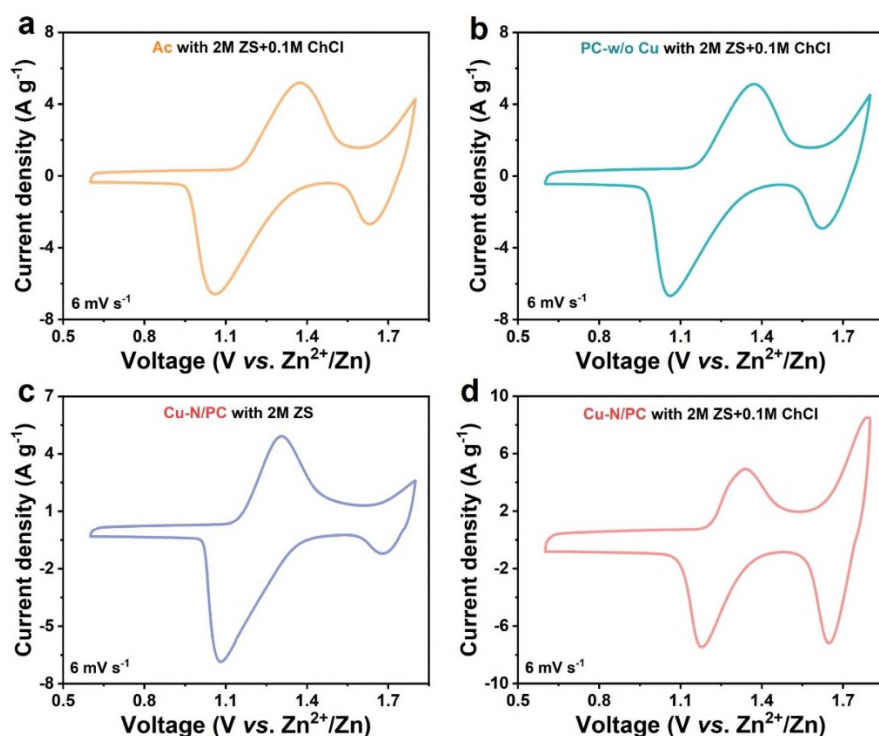


Figure R35. CV curves of various cathodes with 2M ZS or 2M ZS+0.1M ChCl electrolytes.

3. The difference in electrical conductivity between Ac and Cu-N/PC-2 should be addressed, as this may explain the larger ohmic polarization.

Response:

We sincerely appreciate the reviewer's insightful observation regarding the electrical conductivity differences between Ac and Cu-N/PC-2 materials. To directly address your concern, we have performed additional measurements to compare the electrical conductivity of the two host materials. Specifically, we measured the electronic conductivity of pressed pellets of Ac and Cu-N/PC-2 using a four-point probe method (Figure R36). The results show that Cu-N/PC-2 exhibits a high electronic conductivity of approximately $2.02 \text{ S cm}^{-1}@20 \text{ MPa}$, which is close to the case of Ac ($2.37 \text{ S cm}^{-1}@20 \text{ MPa}$). Such high electronic conductivity of Cu-N/PC-2 can be attributed to the following factors: 1) the high-temperature carbonization at 1000°C promotes a highly graphitized carbon structure with improved electron transport pathways, and 2) the incorporation of atomically dispersed Cu-N_x sites may modulate the local electronic structure of the carbon matrix, potentially increasing the carrier density.

The high electronic conductivity of Cu-N/PC-2 partially explains the smaller ohmic polarization observed in the electrochemical impedance measurements. However, we note that the

high conductivity alone cannot fully account for the superior catalytic activity of Cu-N/PC-2, particularly the activation of the I^0/I^+ redox couple and the stabilization of I^+ species. As demonstrated in our DFT calculations and experimental adsorption tests (Figs. 4b-i, Supplementary Figs. 17-20), the Cu single-atom sites play a unique and irreplaceable role in orbital hybridization, charge transfer, and I-Cl complex formation, which are not present in the Ac host. Thus, the enhanced performance of Cu-N/PC-2 arises from a synergistic combination of: 1) high electronic conductivity, 2) strong chemical adsorption of iodine species via Cu-N_x sites, 3) low energy barriers for iodine conversion, and 4) effective stabilization of I^+ through *d-p* orbital coupling and localized I-Cl microenvironments.

Revision in Manuscript:

The detailed information and discussion are added on page 14 in the revised manuscript and Supplementary Fig. 57 in the revised Supplementary Information.

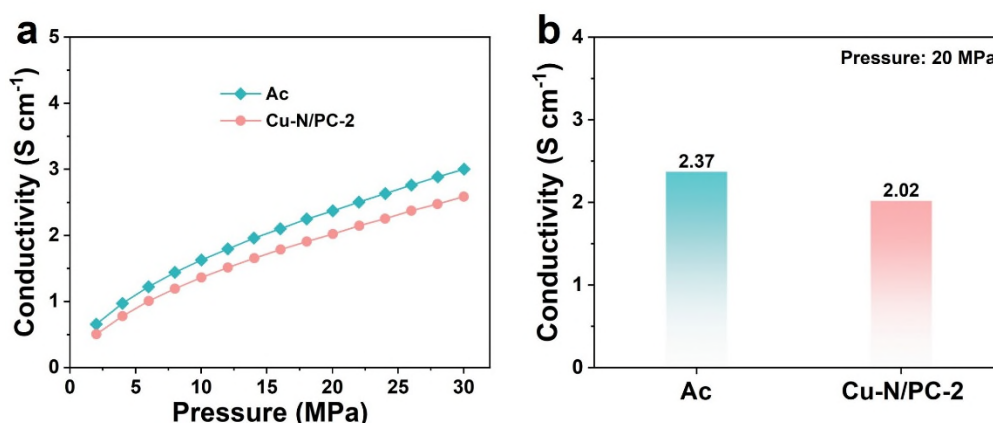


Figure R36. (a) The electrical conductivity of Ac and Cu-N/PC-2 under different pressures. (b) The electrical conductivity of Ac and Cu-N/PC-2 at a pressure of 20 MPa.

4. Why was a graphene model chosen to represent the carbon host instead of an amorphous carbon structure?

Response:

Thank you for this thoughtful and technically important question. You are absolutely correct that the actual carbon host in our experiment is primarily amorphous in nature, rather than crystalline graphene. We appreciate the opportunity to clarify our rationale for using a graphene model in the

DFT calculations. Our choice of a monolayer graphene model was based on the following considerations:

Computational feasibility and convergence: Amorphous carbon lacks long-range periodic order, making it extremely challenging to construct a representative and computationally tractable periodic model for DFT calculations. By contrast, graphene provides a well-defined, periodic, and computationally efficient platform to systematically investigate the fundamental electronic interactions between iodine species and carbon-based hosts, particularly the role of Cu-N_x active sites embedded within a carbon matrix.

Local structural similarity: Despite the overall amorphous nature of our Cu-N/PC material (as confirmed by the broad XRD peak around 24° and the SAED pattern showing amorphous carbon without highly crystallized phases, see Fig. 2h and Supplementary Figs. 12-13), the local coordination environment of the Cu single atoms embedded in N-doped carbon is dominated by short-range ordered Cu-N_x configurations. These Cu-N_x sites are anchored on locally graphitic or disordered carbon domains. The electronic structure and chemical bonding of such local sites can be effectively captured by a graphene-based model, as the Cu-N_x coordination geometry and its interaction with adsorbates are primarily determined by the local nearest-neighbor environment rather than the long-range amorphous structure.

Established precedent: Using graphene or graphitic models to represent the carbon matrix in DFT studies of single-atom catalysts on N-doped carbon supports is a widely accepted and standard practice in the literature.^{3,20-26} Many high-impact studies on M-N-C single atom catalysts employ graphene or graphitic models to investigate adsorption energies, reaction pathways, and electronic structures, because these models effectively isolate the role of the M-N_x active sites from the complexities of amorphous carbon.

We acknowledge that amorphous carbon may contain edge sites, topological defects, and other structural features that are not fully represented by the ideal graphene model. However, constructing a realistic amorphous carbon model with controlled defect distributions and then embedding Cu-N_x sites into such a structure remains a significant computational challenge. We have now added a clear statement in the revised manuscript acknowledging the use of the graphene model as a simplified yet effective representation of the carbon host, and we have included the rationale described above. We have also cited several key references where similar modeling approaches have been

successfully employed for M-N-C single-atom catalysts.

Revision in Manuscript:

The detailed information and discussion are added on pages 25 and 26 in the revised manuscript.

5. The projected density of states (PDOS) and d-band center analysis are used to rationalize the interaction between Cu-N_x sites and iodine species. However, the spin polarization is not explicitly mentioned, and the charge transfer analysis is limited to Mulliken charges. Given that iodine species can exhibit spin-orbit coupling and relativistic effects, how robust are the calculated electronic properties? More advanced charge analysis methods (e.g., electron localization function) should be provided to confirm this conclusion.

Response:

Thank you for your insightful comments. You have raised several important points regarding the electronic structure calculations, including spin polarization, relativistic effects of iodine, and the limitations of Mulliken charge analysis. We acknowledge that spin polarization was not explicitly mentioned in our original manuscript. In our DFT calculations, we did consider spin-unrestricted (spin-polarized) calculations for systems containing transition metals (Cu) and iodine species, as both can potentially have unpaired electrons under certain conditions. In addition, you raise an excellent point regarding the potential importance of relativistic effects and spin-orbit coupling for iodine species. In our original calculations, we employed all-electron core treatment rather than effective core potentials. DMol3 uses a numerical atomic orbital basis set and treats all electrons explicitly for elements, including iodine. Within this all-electron framework, scalar relativistic effects are naturally included through the relativistic DFT formulation implemented in DMol3, which accounts for the mass-velocity and Darwin terms (the dominant scalar relativistic corrections). However, we acknowledge that spin-orbit coupling was not explicitly included, as it is computationally demanding and not implemented in the standard DMol3. Moreover, you are correct that Mulliken charges are basis-set dependent and can be sensitive to the choice of basis functions. While our DMol3 calculations used a double-numeric quality basis set with polarization functions (DNP), which is reasonably robust, we agree that complementary charge analysis methods would strengthen our conclusions. To address your concern, we have performed electron localization

function (ELF) analysis for the iodine species on Ac (G) and various Cu-N_x configurations, as shown in Figures R37-R39. The ELF patterns provide a basis-independent visualization of electron localization/delocalization. Taking ICl adsorption on different substrates as an example:

On the graphene substrate: The ELF patterns clearly show that ICl and the graphene substrate are electronically isolated from each other. There is no discernible electron density redistribution or bonding interaction between ICl and the carbon surface, indicating a purely physical adsorption mechanism dominated by weak Van der Waals forces. The electron localization remains largely confined to the I-Cl bond region and the graphene π -system independently, with no mixing between them.

On the various Cu-N_x configurations: In contrast, the ELF patterns reveal pronounced electronic interactions between ICl and the Cu-N_x sites. Specifically: 1) A clear electron accumulation region is observed between the Cu center and the I atom of ICl, indicating the formation of a Cu-I chemical bond. 2) The electron density is redistributed away from the original I-Cl bond region, suggesting bond weakening and activation of the ICl molecule. 3) The electron density isosurfaces show continuous delocalization between the Cu-N_x site and the adsorbed ICl, confirming strong electronic coupling.

These ELF observations provide direct visual evidence that the Cu-N_x sites enable strong chemisorption of ICl through interfacial electronic interactions, whereas the pristine carbon surface (G) lacks such capability. This visual conclusion is fully consistent with our calculated adsorption energies, bond length elongations, and PDOS results, collectively confirming that the Cu single-atom sites are essential for activating iodine species and facilitating the I⁰/I⁺ conversion chemistry.

Revision in Manuscript:

The detailed information and discussion are added on pages 10, 11, 25 in the revised manuscript and Supplementary Figs. 37-39 in the revised Supplementary Information.

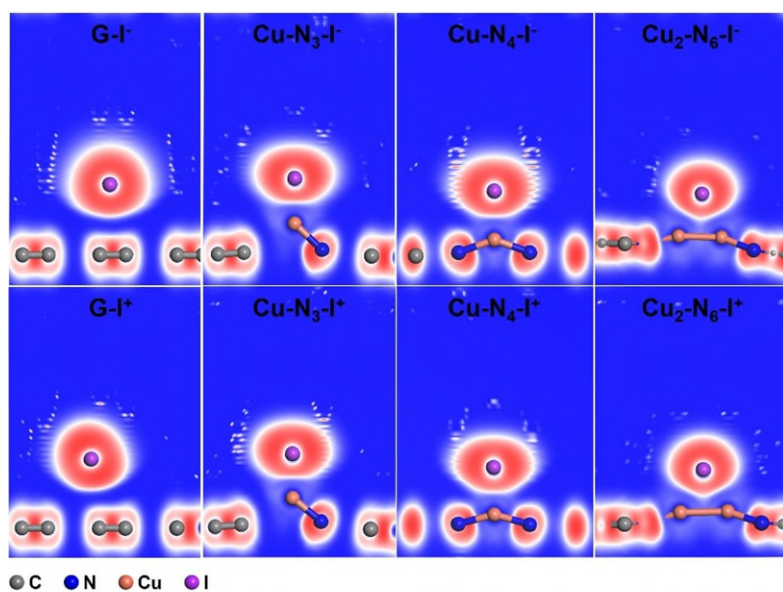


Figure R37. ELF patterns of Ac (G) and various $Cu-N_x$ configurations with I^- and I^+ .

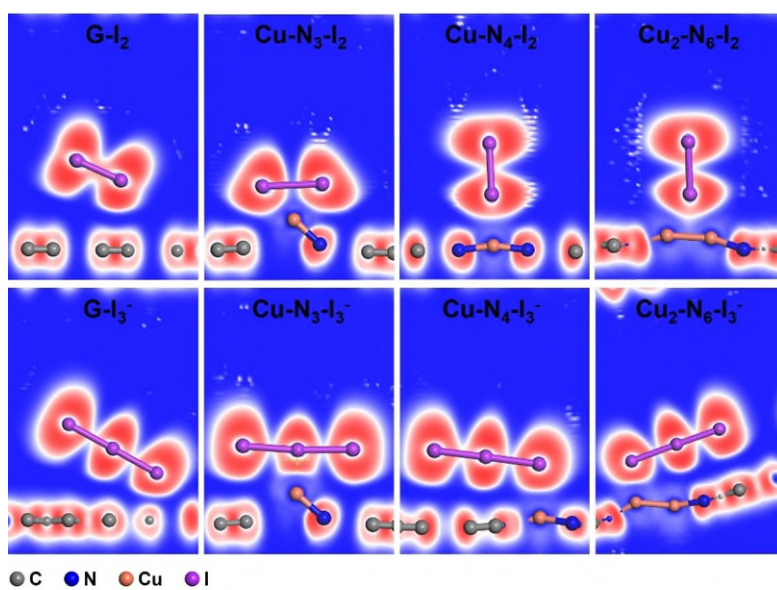


Figure R38. ELF patterns of Ac (G) and various $Cu-N_x$ configurations with I_2 and I_3^- .

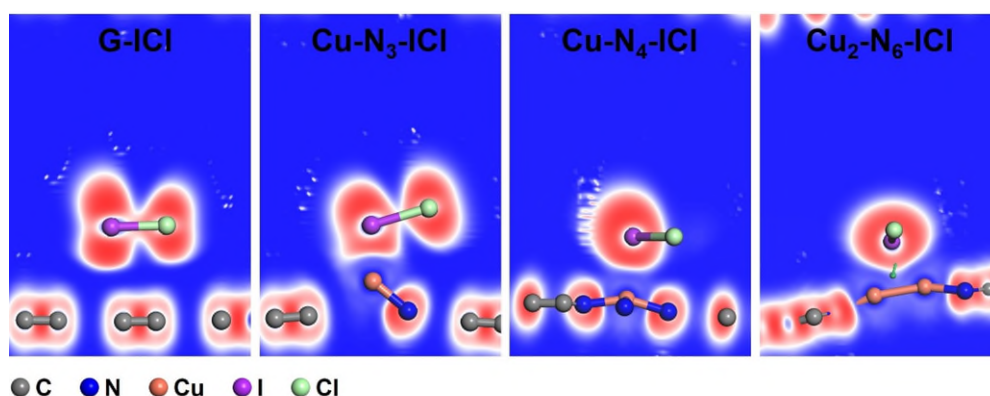


Figure R39. ELF patterns of Ac (G) and various Cu-N_x configurations with ICl.

6. The ball-and-stick models in Fig. 2a need to be labeled with atomic types (such as C, H, O, N, Cu, and Zn etc.). In addition, it should be noted that the periodic boundary condition assumption in DFT.

Response:

Thank you for your careful and constructive comments. According to your suggestion, all ball-and-stick models are now explicitly labeled with atomic symbols (C, H, O, N, Cu, and Zn) using distinct colors and legends, as shown in Figure R40. In addition, the DFT models employ periodic boundary conditions to approximate the extended monolayer structure of I species models on graphene and Cu-N_x-doped graphene models. The monolayer assumption aligns with prior DFT studies on analogous systems,^{27,28} which can effectively capture interfacial interactions without edge effects. In our original manuscript, we briefly mentioned in the Computational methods section that “The geometric models employ periodic boundary conditions to approximate the extended monolayer structure of iodine species on the carriers.” However, we agree that this statement could be made more prominent and clearer. In the revised manuscript, we have expanded the Computational methods section to provide a more detailed explanation: “All DFT calculations were performed using periodic boundary conditions (PBCs) to simulate an infinitely extended surface for the host materials (graphene and Cu-N_x-doped graphene models). PBCs eliminate edge effects and provide a realistic description of the electronic structure and adsorption properties of periodic solid surfaces. A vacuum layer of 15 Å was introduced along the z-direction (perpendicular to the monolayer plane) to avoid spurious interactions between periodically repeated slabs. The use of PBCs is standard in DFT studies of two-dimensional materials and surface adsorption phenomena, as it allows accurate

calculation of key properties such as adsorption energies, charge density differences, and density of states.”

Revision in Manuscript:

The detailed information and discussion are added on page 25 in the Computational methods section in the revised manuscript.

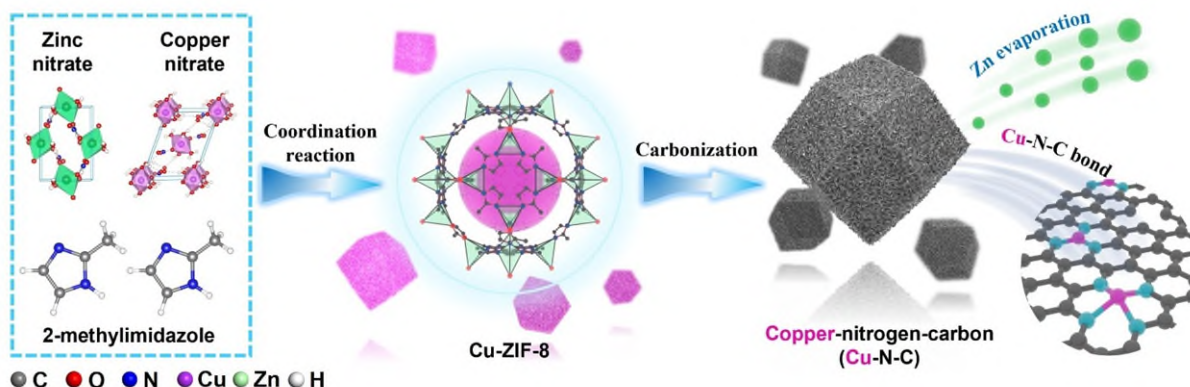


Figure R40. Scheme illustration for the synthetic procedure of Cu-N/PC.

7. It is recommended to provide morphological and compositional analysis (such as SEM/XPS, etc.) of cathodes after cycling to verify the stability of the material structure.

Response:

Thank you for your insightful and important suggestion. We agree that post-cycling characterization is essential to confirm that the Cu single-atom sites remain structurally and morphologically intact after prolonged electrochemical cycling. To address your concern, we have now performed some additional post-cycling characterizations on the Cu-N/PC-2 cathode after long-term cycling. Specifically, we conducted the following analyses:

Scanning electron microscopy (SEM): As shown in Figure R41, SEM and EDS mapping images of the post-cycled Cu-N/PC-2 cathode confirm that the overall porous structure of the cathode surface is well maintained, with no significant cracking, pulverization, or detachment from the carbon cloth current collector.

Transmission electron microscopy (TEM): To further examine the detailed morphologies and microstructures of the post-cycled Cu-N/PC-2 cathode, the post-cycled Cu-N/PC-2 material was

carefully extracted from the disassembled cell, thoroughly washed, and dried. TEM and HRTEM images show that the polyhedral morphology of the carbon matrix is well preserved without visible collapse or aggregation (Figure R42a, b). The selected area electron diffraction (SAED) pattern of the post-cycled Cu-N/PC-2 cathode remains amorphous carbon without any highly crystallized phases (Figure R42c). More importantly, the HAADF-STEM image clearly reveals that isolated bright dots corresponding to Cu single atoms remain uniformly dispersed throughout the carbon matrix, with no evidence of nanoparticle formation or Cu clustering (Figure R42d, e). The EDS elemental mapping images further verify the uniform dispersion of C, N, and Cu elements throughout the polyhedral framework (Figure R43). These results demonstrate the excellent atomic-level stability of the Cu-N_x sites under long-term cycling conditions.

X-ray photoelectron spectroscopy (XPS): XPS measurements were further performed to investigate the elemental compositions and N-bond configurations of the post-cycled Cu-N/PC-2 cathode. The XPS C 1s spectra of the sample can be deconvoluted into various peaks corresponding to C-C/C=C, C-O/C=N, and C=O/C-N functional groups (Figure R44).¹⁹ Moreover, the XPS N 1s and Cu 2p spectra show that the N 1s and Cu 2p configurations remain essentially unchanged compared to the pristine material (Figure R45 and Table R4). The Cu⁺/Cu²⁺ ratio and the Cu-N_x peak intensity exhibit no significant degradation, confirming that the chemical environment and coordination structure of the Cu single-atom sites are stable throughout long-term cycling.

These post-cycling characterization results collectively confirm that the Cu-N/PC-2 single-atom catalyst possesses outstanding structural and morphological robustness, which underlies the exceptional long-term cycling stability at a high current density of 10 A g⁻¹ (70% capacity retention over 50,000 cycles) reported in our manuscript.

Revision in Manuscript:

The detailed information and discussion are added on pages 18, 19 in the revised manuscript and Supplementary Figs. 74-78, and Table 5 in the revised Supplementary Information.

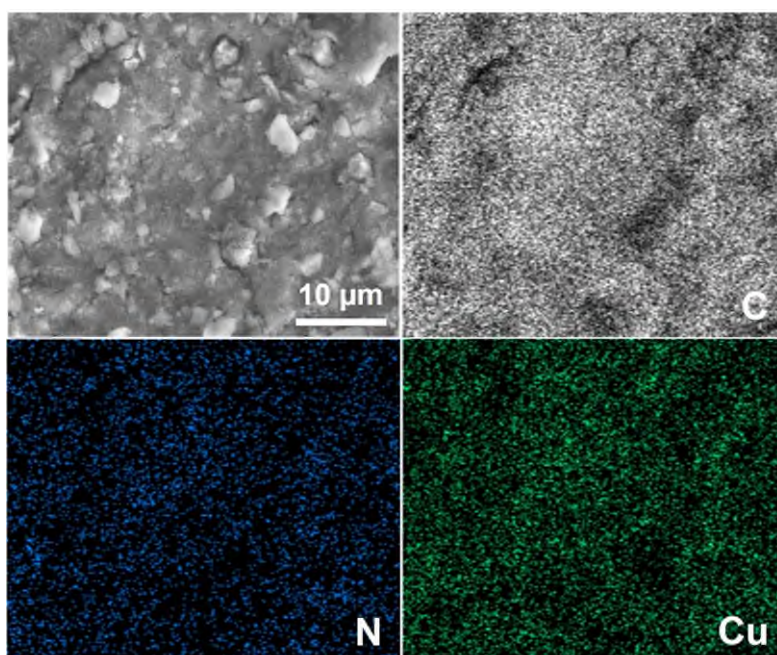


Figure R41. SEM and the corresponding element mapping images of Cu-N/PC-2 cathode after cycling.

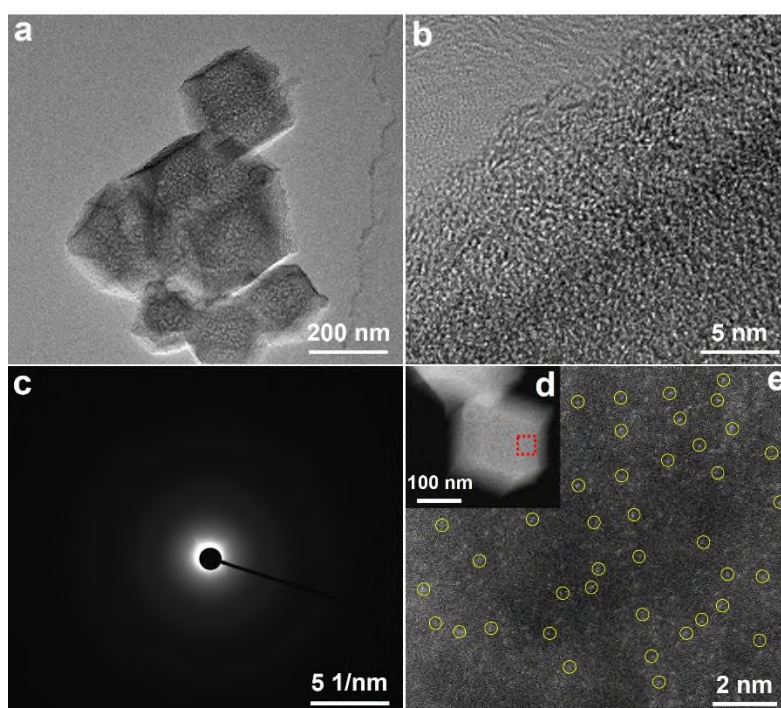


Figure R42. (a-c) TEM, HRTEM, and the corresponding SAED pattern of Cu-N/PC-2 cathode after cycling. (d, e) Aberration-corrected HAADF-STEM images of Cu-N/PC-2 cathode after cycling with the atomic dispersion of Cu highlighted by yellow circles.

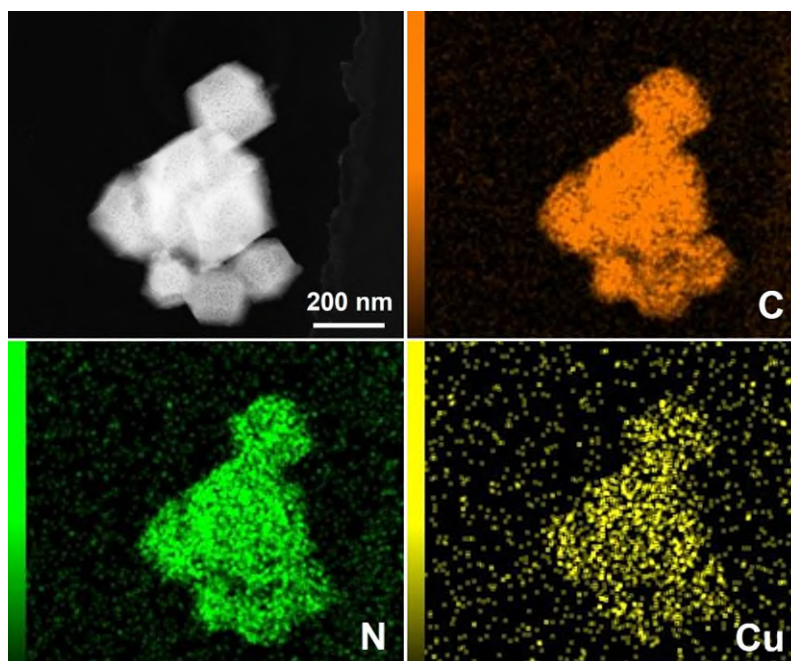


Figure R43. EDS mapping images of C, N, and Cu in the Cu-N/PC-2 cathode after cycling.

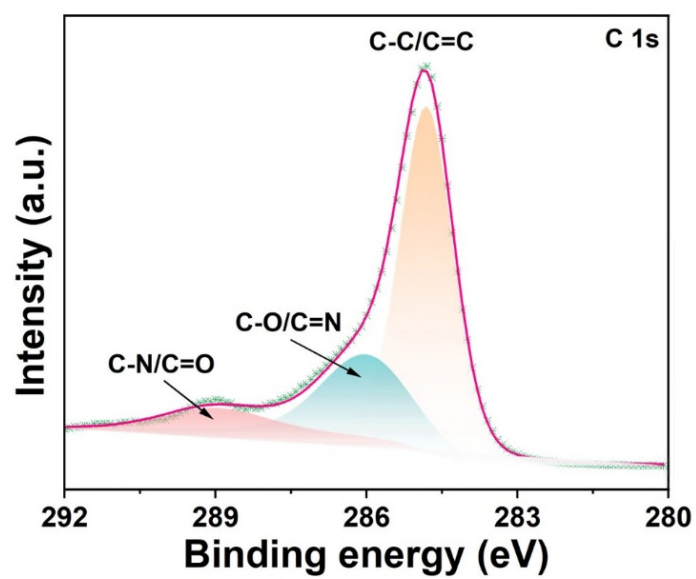


Figure R44. XPS C 1s spectra of Cu-N/PC-2 cathode after cycling.

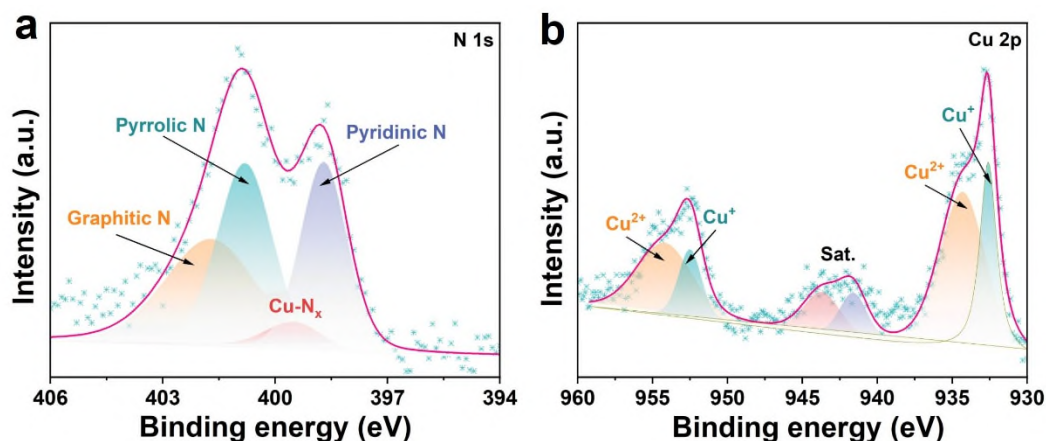


Figure R45. (a) XPS N 1s and (b) Cu 2p spectra of Cu-N/PC-2 cathode after cycling.

Table R4. The elemental composition information of Cu-N/PC-2 cathode after cycling (data from XPS analysis).

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

8. The authors should provide the key parameters of the soft-packaged zinc-iodine battery and the calculation process for energy density and N:P ratio.

Response:

Thank you for your valuable comment. We acknowledge the importance of these parameters for evaluating practical applicability. In the revised manuscript, we have included the following details for the soft-packaged battery (please see Table R5): 1) Electrode dimensions; 2) Areal loading; 3) Total capacity; 4) N:P ratio; 5) Full-cell energy density.

N:P ratio: The N:P ratio is defined as the ratio of the practical capacity of the anode (mAh) to that of the cathode. 1) Anode 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) Cathode 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:

$$N:P = \frac{\text{Practical capacity of anode (mAh)}}{\text{Practical capacity of cathode (mAh)}} = \frac{600 \times 80 / 1000}{313 \times 120 / 1000} = 1.28 \quad (\text{R2})$$

Full-cell energy density: The gravimetric energy density of the full cell was calculated according to the following equation:

$$\text{Energy density (Wh kg}^{-1}\text{)} = \frac{\text{Discharge capacity (Ah)} \times \text{Average discharge voltage (V)}}{\text{Total mass of active materials in both electrodes (kg)}} = \frac{37.56 / 1000 \times 1.5}{(80 + 120) / 1000000} \text{ (Wh kg}^{-1}\text{)} = 281.7 \text{ (Wh kg}^{-1}\text{)} \quad (\text{R3})$$

Revision in Manuscript:

The detailed information and discussion are added on pages 19, 20 in the revised manuscript, Supplementary Table 6, and the Supplementary Notes section in the revised Supplementary Information.

Table R5. Key parameters of the soft-packaged zinc-iodine battery.

Parameter	Value	Notes
Anode dimension	~80 mg (Length × Width × Thickness: 5 cm × 4 cm × 10 μm)	/
Cathode dimension	~120 mg (Length × Width: 5 cm × 4 cm)	/
Areal loading (cathode)	6 mg cm ⁻²	Active material mass per area
Areal loading (anode)	4 mg cm ⁻²	Active material mass per area
N:P ratio	1.28	Negative/positive capacity ratio
Total capacity	37.56 mAh	Measured at 0.25 A g ⁻¹
Full-cell energy density	281.7 Wh kg ⁻¹	Based on the total mass of active materials in both electrodes

Note: Please refer to the revised manuscript for detailed experimental conditions and calculation methods.

Reviewer #3

This manuscript reports a novel electrode material based on a copper single-atom-embedded nitrogen-doped carbon host to improve the redox chemistry of $I^-/I^0/I^+$ species. The key features include enhanced iodine-species adsorption, accelerated redox kinetics, and suppressed I^+ hydrolysis, enabled by Cu d-I p orbital hybridization. As a result, the zinc-iodine battery exhibits impressive and stable four-electron redox performance at high current densities. To further strengthen the manuscript, the following points should be addressed.

Response:

We really appreciate your deep and thorough review of our manuscript. According to your comments and suggestions, we have revised and improved our manuscript.

1. Based on Figures 1b and 1c, the authors justify the selection of Cu by suggesting that both Cu and Ni exhibit moderate I^+ adsorption energies-neither too strong nor too weak. However, the criterion for defining “optimal” adsorption strength remains unclear and should be explicitly clarified. In addition, it is not clear why the d-orbital analysis in Figure 1c is performed for neutral I_2 rather than for I^+ species, which are more directly relevant to the proposed mechanism.

Response:

Thank you for your valuable comment. You have raised important points regarding the criterion for defining “optimal” adsorption strength and why the d-orbital analysis was performed for neutral iodine rather than for I^+ species. We appreciate the opportunity to provide a comprehensive and clear explanation.

Regarding the criterion for defining “optimal” adsorption strength: As the reviewer correctly pointed out, the criterion used to define the optimal adsorption strength should be explicitly clarified to better justify the selection of Cu as the research material. In our work, the optimal adsorption strength does not refer to the strongest adsorption toward I^+ species. Instead, it follows a Sabatier-type adsorption-conversion principle. According to this principle, the interaction between the catalyst and intermediates should reach a balance to avoid overly strong or weak interactions. Furthermore, it asserts that only moderate adsorption is necessary to achieve maximum catalytic activity.^{1,2,29} Therefore, enhanced adsorption energies do not necessarily correlate with increased catalytic activity. **1) *Balanced adsorption-conversion criterion for reversible four-electron iodine***

conversion. For reversible four-electron iodine conversion, the interaction between metal single-atom sites and I^+ should satisfy a balanced adsorption-conversion criterion. The adsorption should be strong enough to anchor and stabilize the electrophilic I^+ intermediate, promote interfacial charge redistribution, suppress polyiodide shuttling, and mitigate hydrolysis-induced loss of high-valence iodine species. However, excessively strong binding would over-stabilize adsorbed iodine species and impede their subsequent reduction/desorption during the discharge process, leading to sluggish iodine redox kinetics and poor reversibility of the I^0/I^+ conversion. **2) DFT screening and rationale for selecting Cu over Ni.** Based on this consideration, the adsorption strengths shown in Fig. 1b were used as a preliminary screening criterion to identify metal sites capable of balancing I^+ stabilization and reversible conversion. The DFT results show that metal single-atom sites exhibit excessively strong I^+ adsorption, which may favor the immobilization of iodine species but is unfavorable for the subsequent electrochemical conversion/desorption process. In contrast, Cu and Ni exhibit intermediate adsorption strengths, following a Sabatier-type principle, in which moderate adsorption favors a beneficial balance between iodine species stabilization and reversible conversion. **3) Theoretical and experimental validation.** Among Cu and Ni, Cu was further selected because the *d*-band center analysis indicates more effective *d-p* orbital coupling between Cu *d* orbitals and I *p* orbitals (Fig. 1c), accompanied by electron transfer from the iodine to the Cu center. This orbital interaction not only stabilizes I^+ but also facilitates the I^0/I^+ conversion (please see the second section (**Regarding the *d*-orbital of M-N₄-C alongside the *p*-orbital of iodine**) for details). This rationale is corroborated by subsequent theoretical and experimental evidence. PDOS and Gibbs free-energy analyses confirm the Cu *d*-I *p* orbital hybridization and the reduced barrier for I^+ generation on Cu-N_x sites (Figs. 4h-j and Supplementary Figs. 34-36), while the calculated hydrolysis pathway indicates improved stabilization of ICl against hydrolysis (Fig. 4k and Supplementary Figs. 41 and 42). Consistently, the Cu-N/PC-2 cathode delivers more well-defined I^0/I^+ redox peaks, smaller polarization, and lower Tafel slopes (Figs. 5a, b and Supplementary Figs. 53-55), together with decreased impedance and DRT relaxation amplitudes during the charge/discharge process (Figs. 5g-i and Supplementary Figs. 60 and 61), indicating accelerated iodine conversion kinetics. Moreover, *in-situ* UV-vis, *in-situ* Raman, and *ex-situ* XPS analyses further verify the formation and stabilization of I^+ species during the high-voltage charging (Figs. 5j-l and Supplementary Figs. 62-67). These results collectively demonstrate that Cu-N_x sites simultaneously provide moderate adsorption,

favorable *d-p* orbital hybridization, and catalytic activity for reversible four-electron iodine conversion.

Regarding the *d*-orbital of M-N₄-C alongside the *p*-orbital of iodine: We fully understand your concern. Indeed, I⁺ is the key intermediate in the proposed four-electron iodine conversion chemistry, and it would seem more direct to analyze the interaction between Cu-N_x sites and I⁺ species. However, our choice to use neutral iodine for the d-band center analysis in Fig. 1c was based on the following considerations: **1) The rate-determining step is the I⁰→I⁺ conversion.** In the four-electron iodine conversion pathway (I⁻→I⁰→I⁺), the conversion from I⁻ to I⁺ is the kinetically challenging and thermodynamically uphill step. This step needs a high energy barrier, as confirmed by our DFT calculations (Fig. 4j), where the Gibbs free energy for the conversion from I⁻ to I⁺ on the G substrate is as high as 5.22 eV. Therefore, the ability of the single-atom catalyst to facilitate the oxidation process is the key factor determining the overall kinetics of the four-electron process. Furthermore, it is important to emphasize that the I⁰→I⁺ conversion faces two distinct but interconnected challenges: a) Kinetic challenge: The I⁰→I⁺ oxidation requires a high activation voltage and involves electron transfer, which demands a material with catalytic activity to lower the energy barrier and accelerate the reaction kinetics. b) Thermodynamic challenge: I⁺ is highly electrophilic and extremely unstable in aqueous media, readily undergoing hydrolysis to form electrochemically inactive species (e.g., IO⁻) or comproportionation with I₃⁻ to revert to I₂. This demands a material with strong adsorption capability to trap and stabilize the reactive I⁺ intermediate at the electrode interface. Therefore, a bifunctional material combining both catalytic and adsorptive properties is essential for realizing the reversible and efficient I⁰/I⁺ conversion. **2) Rationale for comparing *d*-band centers with the *p*-band center of iodine:** In Fig. 1c, we plotted the *d*-band centers (ε_d) of various M-N₄-C configurations (M=Cu, Zn, Ni, Co, Mn, Fe, Nb, etc.) alongside the *p*-band center (ε_p) of the iodine molecule (-1.12 eV relative to the Fermi level). Among all the metal single-atom configurations, Zn, Ni, and Cu-based single-atom hosts have *d*-band centers that are more negative (further below the Fermi level) than the *p*-band center of iodine. This means that when iodine adsorbs onto these sites, iodine acts as an electron donor, transferring electrons to the metal *d*-orbitals, which can polarize the I-I bond and facilitate the I⁰→I⁺ conversion. More importantly, Cu-N_x-C configurations exhibit *d*-band centers that maintain an optimal energy separation from the *p*-band center of iodine, which are sufficiently below the I *p*-band to allow effective charge transfer and

bond activation. Therefore, the *d*-band center analysis using neutral iodine serves as a predictive descriptor for screening metal single-atom catalysts for their ability to activate and promote the $I^0 \rightarrow I^+$ oxidation.

Accordingly, Cu was selected as the active metal center because it simultaneously meets two critical requirements for reversible four-electron iodine chemistry: 1) moderate adsorption strength that follows the Sabatier principle, thereby balancing the stabilization of high-valence iodine intermediates with their reversible conversion; and 2) effective *d-p* orbital coupling between Cu *d* orbitals and I *p* orbitals, which promotes the I^0/I^+ conversion. This combined adsorption-activation capability differentiates Cu from other metal sites and provides a mechanistic foundation for the rational design of the Cu-N/PC host. Accordingly, we have revised the relevant discussion in the revised manuscript to explicitly define the criterion for “optimal” adsorption strength and to clarify the rationale for conducting the *d*-orbital analysis in Fig. 1c using neutral I_2 rather than I^+ species.

2. Further clarification on the characterization of Cu in the Cu-N/PC electrode is required: (1) According to the XRD results in Supplementary Figures 12 and 13, a substantial amount of Cu/CuO species appears to be removed after the acid-washing process. Why are no discernible peaks corresponding to Cu-N_x species observed in the XRD patterns? (2) Providing the approximate atomic composition of Cu, N, and C in the final Cu-N/PC material (e.g., via TGA or elemental analysis) would greatly aid readers in understanding the material. (3) The EDS mapping results for Cu in Figure 2k₄ and Supplementary Figures 14 and 15 do not appear to be consistent with the corresponding morphological images. This discrepancy should be clarified.

Response:

Thank you very much for your constructive comments. You have correctly noted that while a substantial amount of Cu/CuO species is removed after acid washing, no discernible peaks corresponding to Cu-N_x species are observed in the XRD patterns. We fully agree that further clarification is required. The absence of Cu-N_x-related diffraction peaks in the XRD patterns is not unexpected and can be explained by the fundamental limitations of XRD for probing single-atom structures. We have also performed Cu K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements to provide definitive evidence for the Cu-N_x coordination environment. The detailed explanation is as follows:

The limitation of XRD for single-atom structures: XRD relies on the presence of long-range periodic ordering to produce sharp diffraction peaks that satisfy Bragg's law ($n\lambda = 2d \sin\theta$). The Cu-N_x species in the Cu-N/PC catalyst are isolated single-atom coordination sites, where individual Cu atoms are anchored by nitrogen atoms at defect sites within the amorphous carbon matrix. Specifically, the Cu-N_x sites are randomly distributed across the carbon framework without forming an extended periodic array or a repeating unit cell. Moreover, each Cu atom is coordinated to a few N atoms locally, but there is no translational symmetry between adjacent Cu-N_x sites. Consequently, these isolated Cu-N_x sites cannot produce coherent scattering of X-rays, and therefore, no corresponding diffraction peaks appear in the XRD pattern.

XANES and EXAFS provide definitive evidence for Cu-N_x coordination: To explore the chemical states and coordination environment of Cu atoms in the Cu-N/PC-2, XANES and EXAFS measurements were conducted. These techniques provide direct experimental evidence of the Cu-N_x coordination geometry, which complements the indirect evidence from HAADF-STEM and XPS presented in the original manuscript. Figure R46a shows the Cu K-edge XANES spectra of the Cu-N/PC-2 and other references, revealing that the valence state of Cu species in Cu-N/PC-2 is located between 0 and +2, which is consistent with the XPS results. Fourier transform (FT) EXAFS spectra reveal that there is no Cu-Cu coordination within the Cu-N/PC-2 (Figure R46b), indicating the isolated feature of Cu atoms in Cu-N/PC-2. Moreover, Cu-N/PC-2 exhibits a similar Cu K-edge EXAFS magnitude to CuPc with a main peak at 1.5 Å, which is ascribed to the Cu-N coordination.³ The EXAFS fitting results of the Cu-N/PC-2 show that the Cu atom is coordinated by an average of 3.4 N atoms with a bond length of 1.87 Å (Figures R46c, R47, and Table R6). The detailed contour plot of Cu-N/PC-2 shows that the maximum intensity for the wavelet transform (WT) occurs at approximately 4.2 Å⁻¹, which corresponds to the Cu-N bond in CuPc (Figure R46d-f). This stands in clear contrast to the Cu-Cu bond observed in the reference Cu foil, further confirming the atomic monodispersity of the Cu species.

Revision in Manuscript:

The detailed information and discussion are added on page 8, Fig. 3 in the revised manuscript, Supplementary Fig. 16, and Table 3 in the revised Supplementary Information.

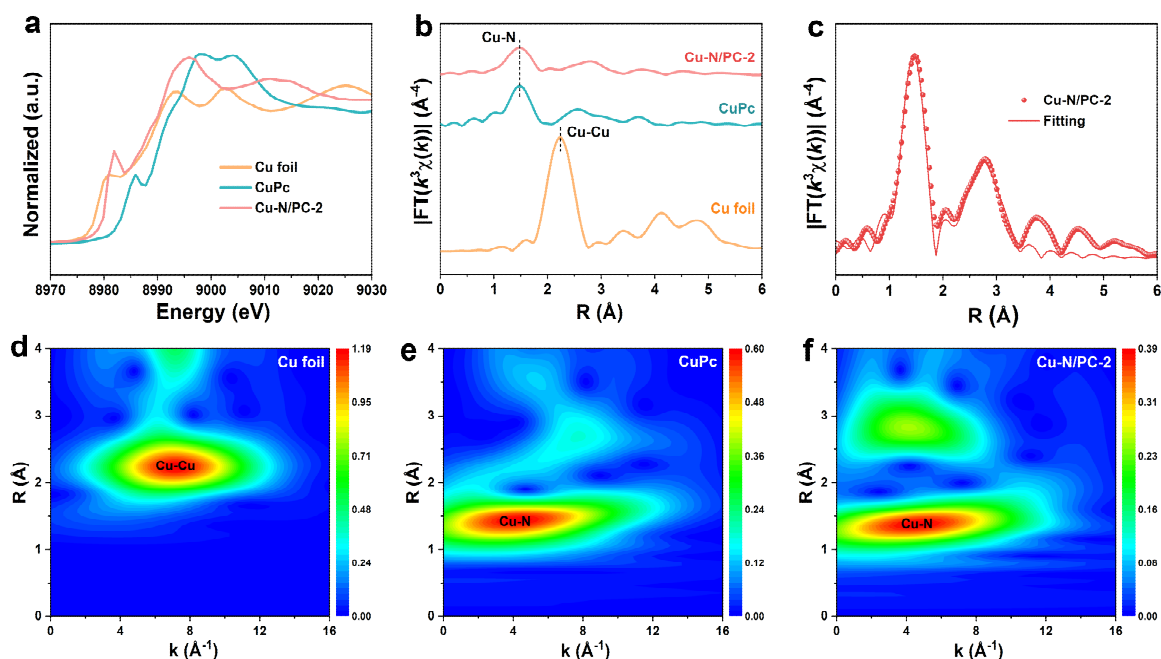


Figure R46. Spectral characterizations of various samples. (a) Cu K-edge XANES spectra of Cu-N/PC-2 and other control samples, and (b) the corresponding FT k^3 -weighted Cu K-edge EXAFS spectra. (c) FT-EXAFS fitting curves of Cu-N/PC-2 at the Cu K-edge in R -space. (d-f) Wavelet transformation (WT) of EXAFS plots of Cu foil, CuPc, and Cu-N/PC-2.

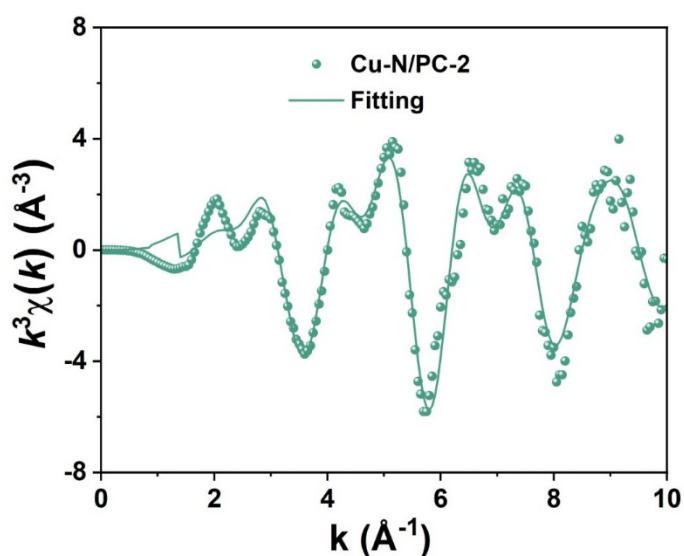


Figure R47. FT-EXAFS fitting curves of Cu-N/PC-2 at the Cu K-edge in k -space.

Table R6. 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: $0.70 < S_0^2 < 1.00$; $CN > 0$; $\sigma^2 > 0$ Å²; $|\Delta E_0| < 15$ eV; R factor < 0.02 .

The atomic composition in Cu-N/PC: You are correct that providing the approximate atomic composition of Cu, N, and C in the final Cu-N/PC materials would greatly aid readers in understanding the material and correlating its composition with performance. We apologize for this omission in our original manuscript. To address your concern, we have performed elemental analysis to determine the atomic composition of Cu, N, C, and O in the Cu-N/PC-2 material using X-ray photoelectron spectroscopy (XPS), as shown in Figure R48 and Table R7. 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. In addition, the Cu content measured is ~2.46 *wt.*% in the Cu-N/PC-2 according to the inductively coupled plasma atomic emission spectrometry (ICP-OES), consistent with the XPS results. Excessive Cu loading in Cu-N/PC-3 leads to partial aggregation of the precursor crystals 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. Nitrogen content ranges from 2.86-4.35 *at.*% across the three samples. The presence of N is essential for anchoring Cu single atoms, as the Cu-N_x coordination is the key active site structure. Carbon is the major component (~86 *at.*%), consistent with the material being a carbon-based host. These compositional data clarify the correlation between structure and activity: Cu-N/PC-2 has a moderate and dispersed Cu single-atom density, providing sufficient Cu-N_x active sites for iodine adsorption and catalysis, while

maintaining the structural integrity and high surface area of the carbon host.

Revision in Manuscript:

The detailed information and discussion are added on page 6 in the revised manuscript and Supplementary Fig. 10 and Table 2 in the revised Supplementary Information.

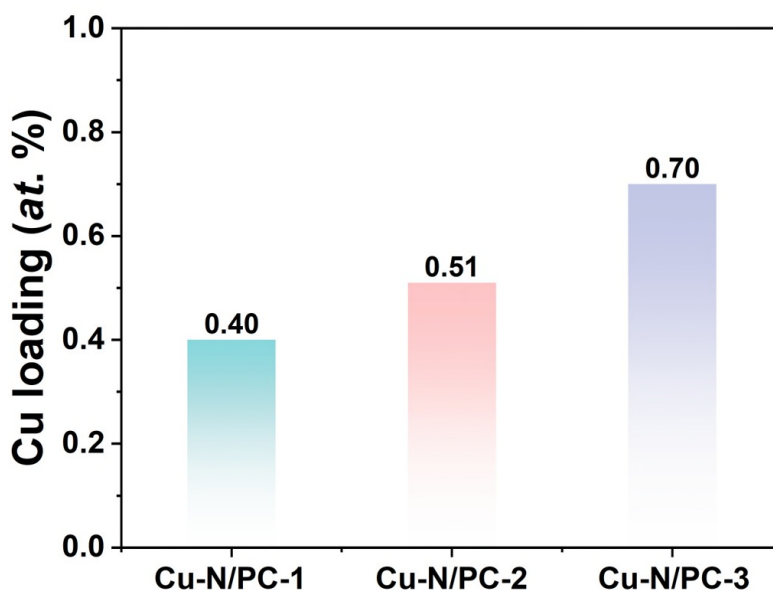


Figure R48. The Cu loading values (at.%) of the Cu-N/PC-x samples.

Table R7. The elemental composition information of Cu-N/PC-x samples.

Samples	C (at. %)	O (at. %)	N (at. %)	Cu (at. %)	Cu (wt. %)	Others
Cu-N/PC-1	86.62	10.04	2.86	0.40	~2.01	0.08
Cu-N/PC-2	86.28	9.95	3.14	0.51	~2.55	0.12
Cu-N/PC-3	85.63	9.22	4.35	0.70	~3.47	0.10

The discrepancy of EDS mapping images: The reviewer pointed out an important issue regarding the inconsistency between the Cu EDS mapping results and the corresponding morphological images in Fig. 2k and Supplementary Figs. 14 and 15. We fully acknowledge this discrepancy and appreciate your attention to detail. In our initial characterization, we used a copper grid as the support

for TEM and EDS mapping. Consequently, the Cu signal detected during EDS analysis was inevitably influenced by the copper grid itself, leading to a spatially distorted Cu distribution that did not accurately reflect the true location of Cu single atoms within the carbon skeletons. To address this issue, we have repeated the EDS mapping analysis using a gold grid instead of a copper grid. As demonstrated in the revised EDS mapping images (Figures R49-R51), the Cu signal is now uniformly distributed across the polyhedral carbon skeletons and is fully consistent with the morphology of the Cu-N/PC particles. This confirms that the Cu single atoms are indeed homogeneously dispersed throughout the nitrogen-doped porous carbon matrix, without any interference from the supporting grid.

Revision in Manuscript:

We have revised the EDS mapping images in Fig. 2k and Supplementary Figs. 14 and 15 in the revised manuscript and Supplementary Information.

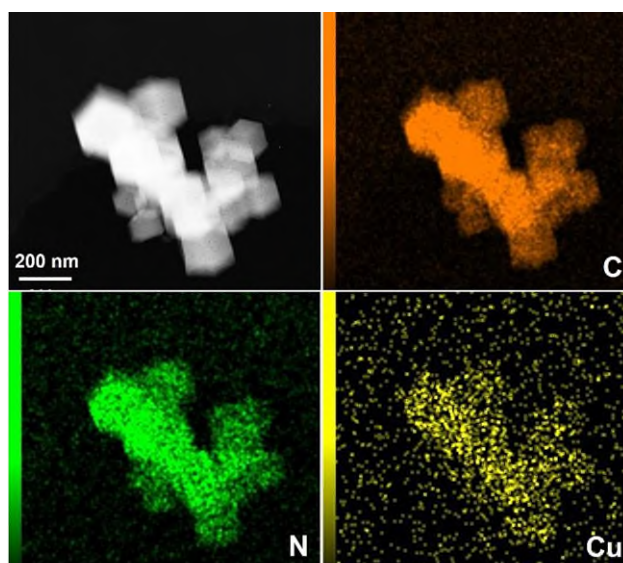


Figure R49. EDS mapping images of Cu-N/PC-1.

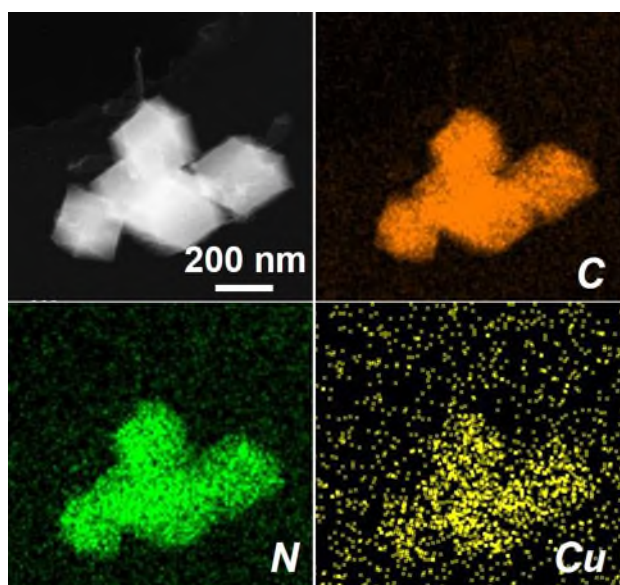


Figure R50. EDS mapping images of Cu-N/PC-2.

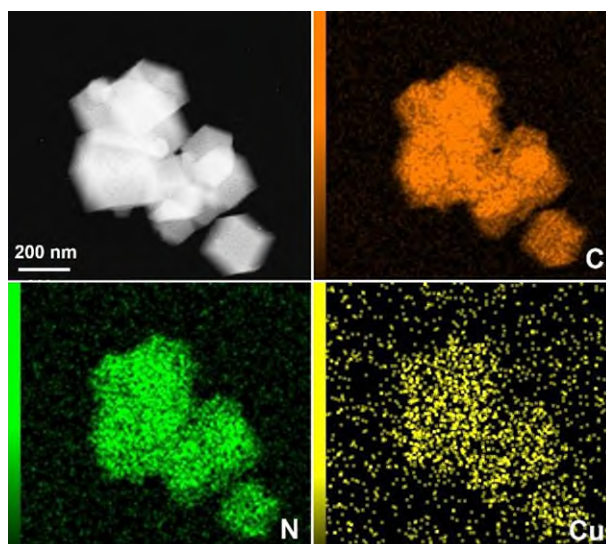


Figure R51. EDS mapping images of Cu-N/PC-3.

3. Figure 5g presents the impedance evolution during the charge-discharge process. However, a more detailed discussion is needed to explain the origin of the observed cyclic variation. The subsequent DRT analysis does not provide a sufficiently clear interpretation of this behavior.

Response:

We sincerely thank the reviewer for this insightful comment. We agree that the origin of the cyclic impedance evolution in Fig. 5g should be more clearly explained and better correlated with the DRT analysis. In the revised manuscript, we have added a concise discussion to clarify this point. **1) Regarding the origin of the cyclic impedance variation.** This behavior is mainly associated with

the reversible evolution of iodine species and the corresponding interfacial reaction kinetics during the charge/discharge process. The GCD and CV results show that the Cu-N/PC-2 cathode in the Cl^- -containing electrolyte exhibits a distinct high-voltage I^0/I^+ redox process (Fig. 6a and Supplementary Fig. 47). Consistently, the *in-situ* UV-vis spectra show that I^- and I_x^- species dominate in the low-voltage region, whereas the I^+ signal gradually appears in the high-voltage region (Figure R52), indicating the progressive oxidation from low-valence iodine species to high-valence I^+ during charging. The formation and stability of I^+ are further verified by *in-situ* Raman and *ex-situ* XPS analyses (Figure R53 and Fig. 5k). In addition, our DFT results demonstrate that the Cu-N_x sites lower the energy barrier for the oxidation of I^- to high-valence I^+ species and further stabilize the resulting I-Cl related intermediates through Cu-I interactions (Fig. 4j and Fig. 5e, f). Therefore, during the charging process, the accumulation, adsorption, and redistribution of high-valence iodine species and I-Cl related intermediates at the cathode/electrolyte interface increase interfacial polarization and mass-transport resistance, resulting in the gradual increase in impedance. During the subsequent discharge process, these high-valence iodine species are reversibly reduced back to I^0 , which relieves interfacial polarization and facilitates ion/electron transfer, thereby decreasing the impedance. **2) Regarding the DRT analysis.** We have further clarified that the three relaxation features correspond to the different kinetic contributions involved in the iodine redox process rather than isolated impedance responses. Specifically, τ_1 is mainly related to electrolyte/iodine-species mass transport and concentration polarization, τ_2 corresponds to interfacial charge-transfer relaxation, and τ_3 is associated with the adsorption-coupled faradaic conversion of iodine species. Therefore, the evolution of these DRT features reflects the dynamic changes in mass transport, charge transfer, and iodine conversion during the charge/discharge process. Compared with the Ac cathode, the Cu-N/PC-2 cathode exhibits lower $\gamma(\tau)$ amplitudes for these relaxation processes throughout the charge/discharge process. This result indicates that the Cu-N_x sites effectively reduce concentration polarization, facilitate interfacial charge transfer, and accelerate the reversible iodine conversion. These results further support the role of Cu-N_x sites in promoting the $\text{I}^-/\text{I}^0/\text{I}^+$ redox process and enhancing the charge/discharge kinetics. Accordingly, we have revised the related discussion in the revised manuscript to provide a clearer connection between the cyclic EIS evolution and the DRT analysis.

Revision in Manuscript:

The detailed information and discussion are added on pages 15-17 in the revised manuscript and Supplementary Figs. 62-66 in the revised Supplementary Information.

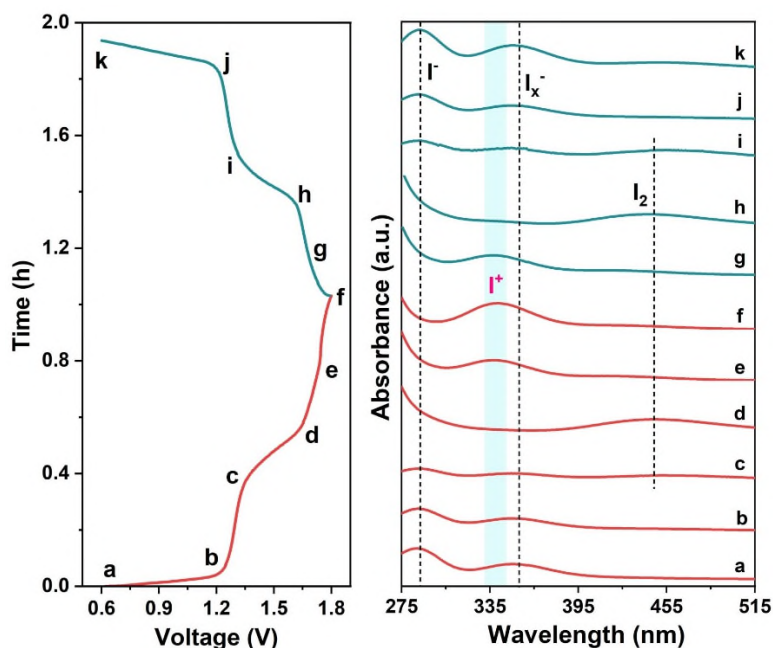


Figure R52. GCD curve and *in-situ* UV-vis spectra of zinc-iodine battery with Cu-N/PC-2 cathode.

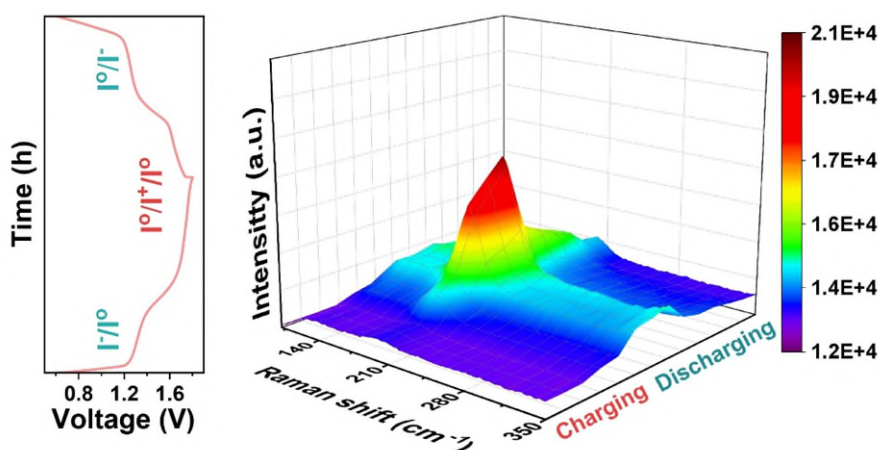


Figure R53. GCD curve and *in-situ* Raman spectra of zinc-iodine battery with Cu-N/PC-2 cathode.

4. While DRT is a useful tool for probing interfacial electrochemical processes, reliable peak assignment generally requires support from complementary in situ or operando techniques. In this study, the assignments of key features-particularly τ_1 , τ_2 , and τ_3 -remain ambiguous. Specifically, the physical meaning of the charge-transfer process (τ_2) and the Faradaic process (τ_3) is not clearly

defined. Additional justification and evidence for these peak assignments are therefore necessary.

Response:

We sincerely thank the reviewer for this insightful and constructive comment. We agree that DRT analysis alone cannot unambiguously determine the physical origin of each relaxation peak, especially in complex conversion-type zinc-iodine batteries. According to the timescale-identification framework of DRT analysis, different electrochemical processes can be distinguished by their characteristic relaxation times, whereas the physical meaning of a specific time constant should be assigned with the support of related theory, state-dependent electrochemical evolution, and chemical characterizations rather than DRT deconvolution alone.³⁰ Therefore, in the revised manuscript, we have clarified that the assignments of τ_1 , τ_2 , and τ_3 are not based solely on DRT analysis, but are supported by the combined evidence from in situ EIS evolution, CV/Tafel analysis, DFT calculations, Raman, XPS, and UV-vis results.

Specifically, τ_1 appears in the long-relaxation-time region and is therefore primarily associated with mass-transport-related processes, including electrolyte/iodine-species diffusion and concentration polarization within the porous cathode. This assignment is consistent with the low-frequency impedance response and the reversible evolution of the EIS spectra during the charge/discharge process. The lower $\gamma(\tau)$ intensity of τ_1 for the Cu-N/PC-2 cathode suggests reduced mass-transport polarization, which can be attributed to the porous conductive framework and the enhanced confinement/conversion of iodine intermediates by Cu-N_x sites. For τ_2 , we have defined it more clearly as an interfacial charge-transfer relaxation process. Here, charge transfer refers to the interfacial electron-exchange process between adsorbed iodine species and the conductive Cu-N/PC host at the electrode/electrolyte interface. This interpretation is supported by the electrochemical kinetic results: Cu-N/PC-2 cathode exhibits smaller Tafel slopes in both the low- and high-voltage regions (Fig. 5b, Supplementary Figs. 54 and 55), indicating faster iodine redox kinetics. In addition, the in situ EIS results show a lower and more reversible impedance response during the charge/discharge process (Fig. 5g and Supplementary Fig. 60), while the stable impedance evolution further confirms the improved interfacial charge-transfer behavior (Supplementary Fig. 56). The DFT results provide additional mechanistic support: Cu-N_x sites exhibit lower work functions (Fig. 5c, d and Supplementary Fig. 58), and PDOS analysis reveals obvious hybridization between the Cu *d* and I *p* orbitals of the adsorbed iodine species (Fig. 4h, i and Supplementary Figs. 34-36), which

promotes charge redistribution between the host and adsorbed iodine species. For τ_3 , we have revised the description to define it more clearly as an adsorption-coupled iodine-conversion relaxation process. This assignment is based on the short-relaxation-time feature observed in the DRT profiles and its charge/discharge-dependent evolution. Different from τ_2 , which mainly describes the interfacial electron-transfer step between adsorbed iodine species and the conductive host, τ_3 is related to the local relaxation process associated with the adsorption, bond activation, and conversion of iodine intermediates on catalytic Cu-N_x sites during the I⁻/I⁰ and I⁰/I⁺ redox reactions.

This interpretation is supported by the electrochemical and spectroscopic evidence.^{31,32} First, the CV curves show two distinct redox couples corresponding to the I⁻/I⁰ and I⁰/I⁺ conversions, and the Cu-N/PC-2 cathode exhibits more pronounced redox peaks and smaller Tafel slopes, indicating more favorable iodine-conversion kinetics (Fig. 5a, b and Supplementary Figs. 52-55). Second, *in-situ* UV-vis spectra reveal that I⁻/I_x⁻ species dominate in the low-voltage region, whereas the I⁺ signal gradually appears in the high-voltage region for the Cu-N/PC-2 cathode (Figure R52). In contrast, no obvious I⁺ signal is detected for the Ac cathode, suggesting that the high-voltage I⁰/I⁺ conversion is significantly suppressed without Cu-N_x sites (Supplementary Fig. 63). Third, XPS and *in-situ* Raman analyses further confirm the formation and stabilization of high-valence iodine species in the Cu-N/PC-2 cathode (Figure R53, Fig. 5k, l, and Supplementary Figs. 64-67). In addition, DFT calculations show that Cu-N_x sites lower the energy barrier for iodine oxidation (Fig. 4j, k and Supplementary Figs. 41-42) and activate the I-I/I-Cl bonds through charge redistribution (Fig. 5e, f and Supplementary Fig. 59), providing mechanistic support for the adsorption-coupled iodine-conversion process.

Overall, we have revised the DRT discussion to avoid overinterpretation and added *in-situ* UV-vis and Raman measurements. The three relaxation features are now more cautiously assigned to mass transport, interfacial charge transfer, and adsorption-coupled iodine conversion, respectively, based on their characteristic relaxation times and the combined support from EIS/DRT evolution, electrochemical kinetics, DFT calculations, and spectroscopic evidence.

5. The authors propose suppression of I⁺ hydrolysis as a key function of the Cu-N/PC electrode. However, the main electrochemical results primarily focus on rate performance. To substantiate the claimed stabilization of I⁺ species, additional evaluation is necessary. In particular, Coulombic

efficiency measured at low current densities would provide more direct insight into I^+ stability. Furthermore, rest (open-circuit) tests assessing capacity retention would be valuable for comparing the stability of iodine species under practical conditions.

Response:

Thank you very much for your constructive comment. The reviewer raised some critical points: while we propose that the Cu-N/PC cathode suppresses I^+ hydrolysis, our main electrochemical results primarily focus on the rate performance and cycling stability at high current densities. We agree that additional electrochemical evaluations are necessary to directly substantiate the claimed stabilization of I^+ species. To address your concern, we have performed the following additional experiments:

Coulombic efficiency at low current density: We measured the Coulombic efficiency of zinc-iodine batteries using Ac and Cu-N/PC-2 cathodes at a low current density of 0.5 A g^{-1} . As shown in Figure R54, the zinc-iodine battery with the Cu-N/PC-2 cathode exhibits two distinct voltage plateaus, corresponding to the I^+/I^0 and I^0/I^- redox couples. More importantly, the battery with the Cu-N/PC-2 cathode exhibits a high Coulombic efficiency of about 97.5% over 160 cycles with a capacity retention of 87.1%, surpassing the values of Ac cathode (Figure R55). Since low current density operation imposes longer residence times for iodine species in their oxidized states (such as I^+), the stable and high Coulombic efficiency of the zinc-iodine battery with the Cu-N/PC-2 cathode demonstrates that I^+ hydrolysis is effectively suppressed.

Self-discharge tests: We also conducted self-discharge tests by charging the batteries to 1.8 V (fully charged state, where iodine exists mainly as I^+ or ICl complexes) and then allowing them to rest under open-circuit conditions for 6 hours before discharging. As shown in Figure R56, the battery with the Cu-N/PC-2 cathode maintains a high open-circuit voltage of $\sim 1.67 \text{ V}$ after resting 6 hours, which is significantly higher than the low-voltage plateau of the I^0/I^- redox couple. This clearly indicates that the I^+ species formed during charging remain effectively stable, thereby enabling the high-voltage I^0/I^+ redox reaction. In contrast, the battery with the Ac cathode rapidly drops to $\sim 1.43 \text{ V}$ under the same conditions, confirming that only the I^0/I^- reaction can be sustained, while the I^+ species undergo severe hydrolysis or irreversible conversion. Furthermore, the battery with the Cu-N/PC-2 cathode delivers a high discharge capacity of $\sim 386.8 \text{ mAh g}^{-1}$, close to the theoretical four-electron capacity, whereas the zinc-iodine battery with the Ac host material only achieves a capacity

of $\sim 168.9 \text{ mAh g}^{-1}$, consistent with the limited two-electron transfer process. These results clearly indicate that the Cu-N/PC-2 with Cu-N_x sites effectively stabilizes the high-valence I⁺ species, preventing their hydrolysis and promoting highly reversible I⁰/I⁺ conversion.

Revision in Manuscript:

The detailed information and discussion are added on pages 18, 19 in the revised manuscript and Supplementary Figs. 69, 70, and 79 in the revised Supplementary Information.

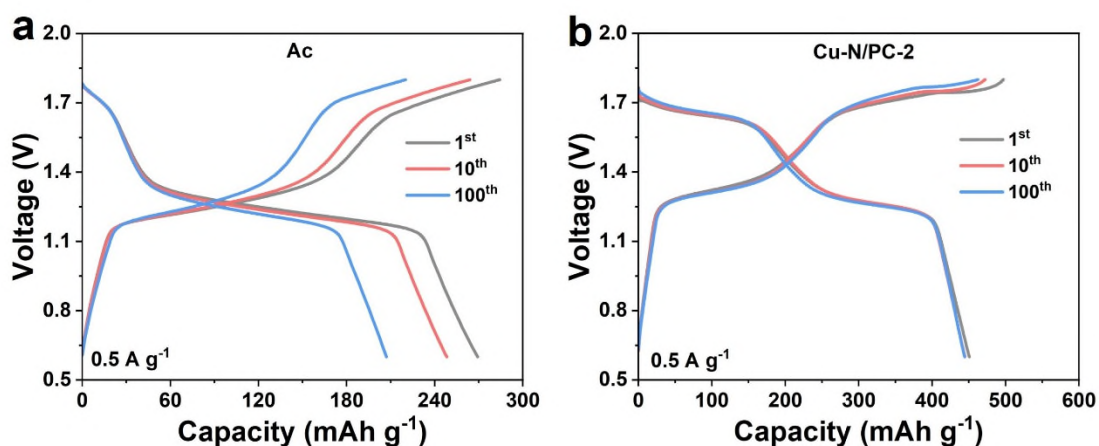


Figure R54. Galvanostatic discharge-charge curves of zinc-iodine batteries at 0.5 A g^{-1} with the various cathodes. (a) Ac and (b) Cu-N/PC-2.

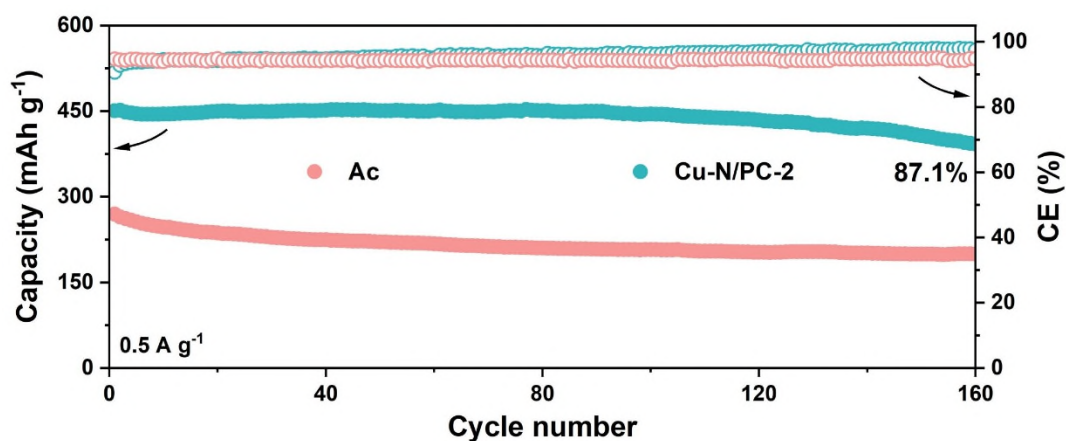


Figure R55. Cycling performance of zinc-iodine batteries at 0.5 A g^{-1} with the various cathodes.

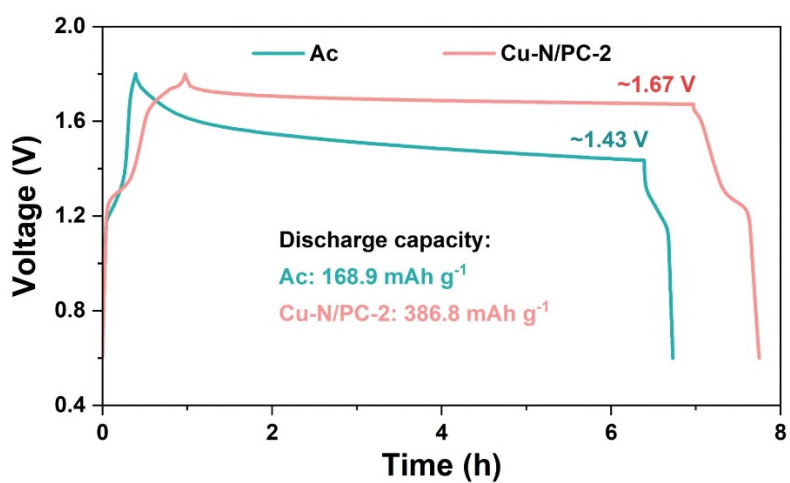


Figure R56. Self-discharge capability of the zinc-iodine batteries with the various cathodes.

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