Peer Review File

Stabilized Cu0 -Cu1+ Dual Sites in a Cyanamide Framework for Selective CO2 Electroreduction to Ethylene

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript proposes the design of stable Cu0-Cu1+ dual sites as electrocatalysts for efficient CO2 electroreduction to ethylene. Owing to the cyanamide-coordinated isolated Cu framework (Cuδ+NCN) with balanced metallic Cu (Cu0) and delocalized Cu (Cu1+) sites, the obtained materials exhibited outstanding CO2-to-C2H4 selectivity of 77.7 % at a partial current density of 400 mA cm-2, as well as long-term CO2-to-C2H4 electrolysis capability for almost 80 h in home-made MEA electrolysers. Both operando electrochemical experimental and theoretical calculations proved that important role of Cu0 atoms in activating CO2 and delocalized Cu1+ for boosting of C-C coupling together with reaction route of CO2-to-C2H4. This study provides instructive guidance and comprehensive insights for the rational design of stable, low-cost, and high-performance CO2-to-C2 catalysts for the audience in the field of CO2RR. Nevertheless, there still some issue needs to be addressed before the acceptance of the manuscript and a minor revision is recommenced.

1. Since the Cuδ+NCN samples were selected through varying reduction ratios, this has resulted in atomic ratios that no longer conform to those found in Cu2NCN. The authors need to employ Inductively Coupled Plasma (ICP) analysis to ascertain the mass fraction of Cu in the samples.
2. Regarding the stability tests of the flow cell, Cuδ+NCN demonstrated exceptional stability. The authors should provide the stability data for the CuNCN samples, as well as the changes in Faradaic efficiency for convincing comparison.
3. When evaluating the performance of samples with different reduction ratios, the authors should also conduct multiple test sets and indicate the margin of error.
4. For the post-reaction samples, the authors confirmed the morphology by SEM and bulk composition with XRD, how about the surface chemical composition and state, which should be important for the electrocatalytic CO2RR.
5. The article claims the unique structure of cyanamide-coordinated isolated Cu framework (Cuδ+NCN) with balanced metallic Cu (Cu0) and delocalized Cu (Cu1+) sites for the high selectivity of CO2-to C2H4, besides of experimental data, it is more reasonable to provide theoretical evidence on how the state of Cu affects the C-C coupling reaction.
6. The author calculated the free energy changes along the CHC and CHCHOH pathways, respectively. To gain deeper insights into the mechanism, additional reaction intermediates, such as *COCO, should be considered in the calculations.
7. Some minor issues should be well addressed, such as the language expression and format of the references, some entries appear to be incorrect.
8. The references in the manuscript are insufficient, especially the performance comparison. C2H4 from CO2 reduction using Cu-based catalysts is widely studied and there are some good catalysts those are not mentioned in this manuscript, such as Mg-CuxO (FEC2H4 70%, j C2H4 ~455 mA cm-1 for 48 h, Angew. Chem. Int. Ed. 2022, 61, e202213423.) and Cu-F (FEC2H4 80%, j C2H4 ~320 mA cm-1 for 40 h, Nat. Catal. 2020, 3, 478–487.). Apart from these, the CO2 reduction work using Indium cyanamide (J. Am. Chem. Soc. 2023, 145, 14101−14111.) firstly proposed the strong σ-donation effect and structure transformation from [NCN]2- to protect the metal oxidation state should be also cited. The obvious peak of C≡N at different potentials in ATR-SEIRA spectra in Figure

4i may come from the structure transformation of [NCN].

Reviewer #2 (Remarks to the Author):

The authors proposed a cyanamide-coordinated isolated Cu framework (Cuδ+NCN) with balanced metallic Cu (Cu0) and delocalized Cu (Cu1+) sites acting as an efficient electrocatalyst for CO2-to-C2H4 reduction. The as-proposed electrocatalyst delivers outstanding selectivity and activity. The authors claimed that Cu0 atoms in Cuδ+NCN enhanced the surface *CO by activating CO2, while the electron delocalized Cu1+ lead to boost of C-C coupling by offering a lower Gibbs free energy for *CHC formation and subsequent high selectivity for C2H4. Overall, the authors provide both experimental and theoretical evidence for supporting their conclusions. However, some important issues should be well addressed before publication.

1. The main concern about this work is the identification of co-existing Cu0 and Cu1+ in the as-proposed Cu2NCN sample. The authors mentioned that “The Cu-N coordination number (CN) of Cuδ+NCN was confirmed to be 1.6, smaller than that of Cu2NCN (CN=2) ... This observation further suggested the presence of atomic Cu0 in the Cuδ+NCN” (line 105), it should be noted that EXAFS spectra cannot distinguish Cu0 and Cu1+.
2. The authors should provide more experimental evidence on the co-existing Cu0 and Cu1+. The XAS just provide average information on the Cu valence state. The current results did not provide convincing evidence.
3. In addition to the [N–C≡N]2- and [N=C=N]2-, the Cu-O can be also observed in FTIR curve of Cuδ+NCN in Fig. 2f, however, the Cu-O path (only Cu-N path included for the first shell) was not considered in the EXAFS fitting and discussed in this work. A recent work might provide insightful information about it [Nat. Commun., 2023, 14, 5245; J. Am. Chem. Soc., 2020, 142, 12119-12132].
4. The authors claimed that “The stability of Cu-N coordination has been proved during electrochemical CO2RR” (line 193), but they didn’t provide any evidence. In line 195, they further claimed that the isolated Cu0 would aggregate to form few-atom Cu clusters, such result evidenced the unstable Cu-N bonds. These results are contradictory.
5. The authors should provide more physical characterizations of Cuδ+NCN during Co2rr at various potentials and after stability testing, and give corresponding discussions.
6. The authors highlighted the in situ formation of Cu clusters during CO2RR. Another concern of this work is the actually active sites for the C2 production, Cu clusters or co-existing Cu0 and Cu1+?
7. The authors mentioned that “Linear sweep voltammetry (LSV) curves (Fig. 3a) indicated that the activity of Cuδ+NCN was much better than the CuNCN and CuO with lowest onset potential and higher current density, demonstrating the reaction priority to CO2RR”. According to the Figure 3a, the current density of CuO seems better than that of Cuδ+NCN at the potential between -0.6~-1.4 V, the authors should explain it.
8. Recent researches might provide the authors with useful insights [Nat. Commun., 2023, 14, 6576; Angew. Chem. Int. Ed., 2021, 60, 17254-17267； ACS Appl. Mater. Interfaces, 2022, 14, 22681-22696； J. Am. Chem. Soc., 2023, 145， 27054-27066; Chem. Soc. Rev., 2023, 52, 5013-5050].

Reviewer #3 (Remarks to the Author):

Yue et al. report the catalytic activity of a cyanamide catalyst with isolated copped dimer sites within electrochemical CO_2 reduction. The catalyst show remarkable selectivity towards the desired C2+ products with ethylene faradaic efficiencies (FE) up to 70%, combined with H_2 FE of only 10%. A series of spectroscopic analyses has been conducted to study the oxidation state of the doped Cu-sites, suggesting a combination of neutral and oxidized Cu sites on the surface. Theoretical calculations have been conducted to rationalize the improvements in activity and selectivity. However, I am afraid they do not add significant value to the insights of the paper. Given my theoretical expertise, I based my assessment mostly on that part of the paper and, thus have to recommend rejection of it.
My detailed assessment is given below:

In figure 4i, the authors assign peaks appearing at 1530 cm-1 and 1440cm-1 to *COCO and *COCHO. On which basis was this assignment made. No reference or computational result was given to justify it. In fact, given that *CO dimerization is generally considered as the rate-limiting step towards C2+ products, no coverage *COCO should be expected.
In a previous publication (Ref. 27; https://doi.org/10.1038/s41929-022-00887-z), the authors suggested that Cu_2NCN is paramagnetic, the same may not automatically be true for the surface Cu0 atoms. Assessing an inappropriate spin state for single atom additive can lead to erroneous assessment of reaction energetics.

The choice of the computationally studied reaction step has not been justfied by the authors. They argue that *CHCOH is formed out of the (also not explicitly justfied) protonated *CO dimer *COCHO. Reference 37 is used as a justification for the choice. However, the reference does not mention the chosen *CHCOH, in their proposed mechanism.

In Fig. 3b, the selectivity of CuNCN towards H_2 is significantly lower than the values found in the analogous result in Fig. S22 of Ref. 27. Is there an explanation for this improvement in selectivity?

The calculated reaction energetics in figure 5d, bear little information. As the chosen step is quite likely not rate limiting it does not give information on the activity of the catalyst. Further, since the thermodynamics are exergonic and no kinetic information there is no way to estimate relative reaction rates to ethylene or ethanol from this result.

The definition of cavity formation energy is not specific enough. In the supporting material, the authors write that the chemical potential of Cu after desorption is the energy of a single Cu atom, but it is not specified whether they refer to an atom in vacuum or an atom in Cu-metal.

Dear Reviewers,

Thank you for your letter and for the opportunity to revise our manuscript "*Stabilized Cu*^{0}*-Cu*$^{1+}$ *Dual Sites in Cyanamide Framework for Highly Selective* CO_2 *Electroreduction to Ethylene*." We sincerely appreciate the time and effort the reviewers have put into evaluating our work, and we are grateful for their insightful comments and suggestions.

We understand the concerns raised by the reviewers and acknowledge that addressing these issues is crucial to strengthen the impact and scientific robustness of our study. We are prepared to undertake a thorough revision of the manuscript and perform the additional experiments and analyses as suggested. We will provide a detailed point-by-point response to each of the reviewers' comments, explaining how we have addressed each concern in the revised manuscript.

We aim to provide comprehensive data and discussion to directly address each point raised by the reviewers. All changes will be clearly marked in the revised manuscript using track changes or color highlighting for ease of review. We are confident that we can meet the reviewers' expectations and significantly improve our manuscript, ensuring that our resubmission meets the high standards of *Nature Communications*.

Note: In the response manuscript, comments suggested by reviews are in blue font, our responses are in **black font**, and revised parts in the text and SI are highlighted in yellow. The figures in our Manuscript, Supplementary Information and Response documents are displayed in the form of Fig. XX, Supplementary Fig. XX.

Reviewer #1 The manuscript proposes the design of stable Cu^0-Cu^{1+} dual sites as electrocatalysts for efficient CO_2 electroreduction to ethylene. Owing to the cyanamide-coordinated isolated Cu framework ($Cu^{\delta+}NCN$) with balanced metallic Cu (Cu^0) and delocalized Cu (Cu^{1+}) sites, the obtained materials exhibited outstanding CO_2-to-C_2H_4 selectivity of 77.7 % at a partial current density of 400 mA cm^{-2}, as well as long-term CO_2-to-C_2H_4 electrolysis capability for almost 80 h in home-made MEA electrolysers. Both operando electrochemical experimental and theoretical calculations proved that important role of Cu^0 atoms in activating CO_2 and delocalized Cu^{1+} for boosting of C-C coupling together with reaction route of CO_2-to-C_2H_4. This study provides instructive guidance and comprehensive insights for the rational design of stable, low-cost, and high-performance CO_2-to-C_2 catalysts for the audience in the field of CO_2RR. Nevertheless, there still some issue needs to be addressed before the acceptance of the manuscript and a minor revision is recommenced.

Response: Thank you for recognizing the merits of our work on the novel Cu^0-Cu^{1+} dual-site electrocatalysts for CO2 electroreduction to ethylene and for acknowledging the potential impact of our findings in the field of CO_2RR. We are pleased to hear that our study offers instructive guidance and comprehensive insights into the design of effective catalysts for this purpose.

We understand that despite the strengths of our manuscript, there are issues that need to be addressed to meet the publication standards. We are fully committed to making the necessary revisions to enhance the quality of our manuscript. To this end, we will address each point raised by you and provide additional data to ensure that our findings are robust, reproducible, and transparent.

Comment 1: Since the $Cu^{\delta+}NCN$ samples were selected through varying reduction ratios, this has resulted in atomic ratios that no longer conform to those found in Cu_2NCN. The authors need to employ Inductively Coupled Plasma (ICP) analysis to ascertain the mass fraction of Cu in the samples.

Response: Thank you for your insightful suggestion regarding the characterization of our $Cu^{\delta+}NCN$ samples. We agree that employing ICP analysis is essential for accurately determining the mass fraction of copper in the samples, especially since the atomic ratios have deviated from those in the original Cu_2NCN due to the varying reduction ratios used during sample preparation.

In response to your recommendation, we have conducted ICP analysis on all our $Cu^{\delta+}NCN$ samples. The ICP results have confirmed that the copper mass fractions are consistent with the expected values based on the reduction ratios employed. Specifically, we observed that the mass fraction of Cu in the CuNCN samples was 60.45%, which is close to the theoretical value of 61.36%. The $Cu^{\delta+}NCN$ sample, on the other hand, has a high mass fraction of Cu due to partial Cu reduction, with an actual test value of 67.23%, which is consistent with our expectations.

Revised part in manuscript:

In page 5:

The elemental content of Cu was confirmed to be 67.23% by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), in comparison to the 60.45% in CuNCN, this can be attributed to the reduction by hydrazine hydrate leading to a decrease in the $[NCN]^{2-}$ group ratio. (**Supplementary Table 1**)

Revised part in supplementary:

In page 3:

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was performed on an Agilent 5110 ICP spectrometer.

In page 38:

Supplementary Table 1. ICP-MS of the atom ratio in Cu_2NCN and $Cu^{\delta+}NCN$.

Samples	Cu (%)
Cu_2NCN	60.45%
$Cu^{\delta+}NCN$	67.23%

Comment 2: Regarding the stability tests of the flow cell, $Cu^{\delta+}NCN$ demonstrated exceptional stability. The authors should provide the stability data for the CuNCN samples, as well as the changes in Faradaic efficiency for convincing comparison.

Response: Thank you for your valuable feedback regarding the stability tests of our electrocatalysts in the flow cell setup. Your suggestion to provide stability data for the CuNCN samples, along with changes in Faradaic efficiency, is well-received and acknowledged as an essential aspect of presenting a comprehensive comparison. In response to your comment, we have performed additional stability tests on the CuNCN samples under the same conditions as those used for the $Cu^{\delta+}NCN$ samples.

We observed that compared to Cu$^{\delta+}$NCN, which can maintain ~70% ethylene selectivity in the flow cell for 15 h, CuNCN showed a significant decrease in Faraday efficiency after only 2 h, due to the ongoing reduction of the CuNCN sites. These results provide a clear comparison between the CuNCN and Cu$^{\delta+}$NCN samples, underscoring the enhanced stability and efficiency of the Cu$^{\delta+}$NCN framework for CO_2 electroreduction to ethylene.

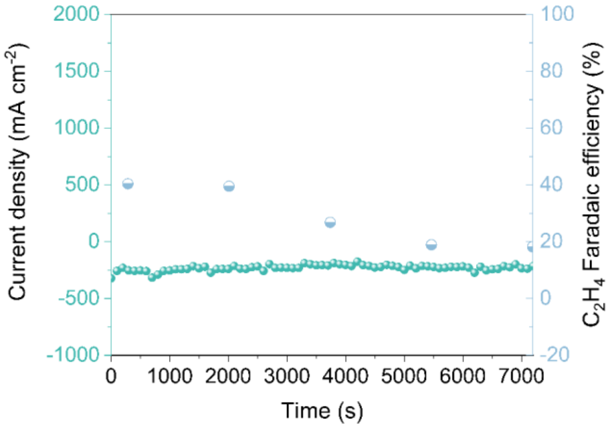
We have incorporated this additional data into the manuscript. We believe these additions significantly strengthen our findings and provide a more convincing comparison between the two types of samples, as suggested.

Revised part in manuscript:

In page 8: In contrast, the FE$_{C2H4}$ of CuNCN decreased from ~40% to ~18% after only 2 h under the same conditions (**Supplementary Fig. 7**).

Revised part in supplementary:

In page 17:



Supplementary Fig. 7. Performance of CuNCN in a three-electrode flow cell to produce ethylene.

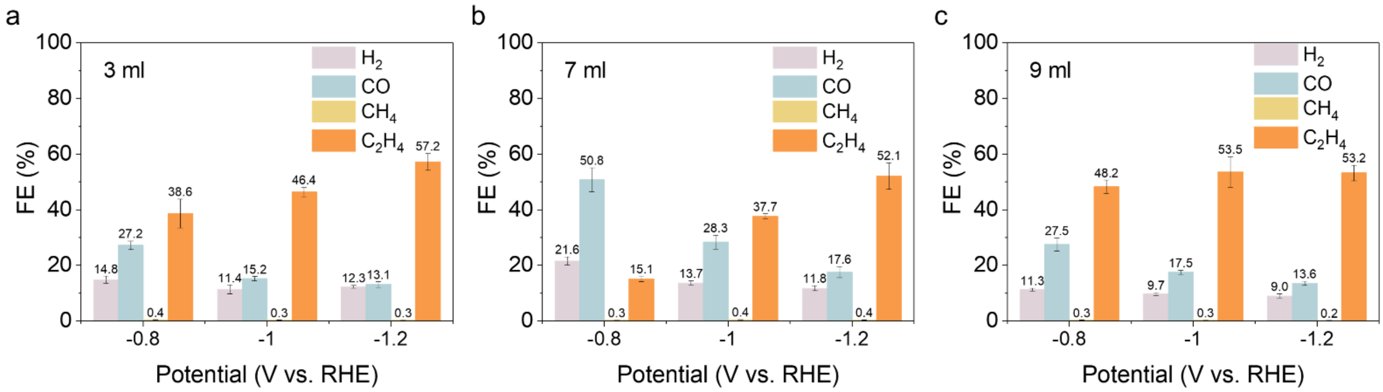
Comment 3: When evaluating the performance of samples with different reduction ratios, the authors should also conduct multiple test sets and indicate the margin of error.

Response: We appreciate your attention to detail and the emphasis on the robustness of our data through the suggestion to conduct multiple test sets and report the margin of error for the performance evaluation of our samples with different reduction ratios. We have taken your recommendation into consideration and have performed additional test sets to ensure the reproducibility and reliability of our results.

The performance metrics of each sample were consistent across the multiple test sets, and we have calculated the Faradaic efficiency of error. You will find this additional data presented in the **Supplementary Fig. 8** of the revised manuscript. We believe that including this information will allow for a clear comparison of the performance of the samples, which will greatly enhance our study.

Revised part in supplementary:

In page 18:



Supplementary Fig. 8. FE of various products of Cu$^{\delta+}$NCN with different levels of reduction at different potentials.

Comment 4: For the post-reaction samples, the authors confirmed the morphology by SEM and bulk composition with XRD, how about the surface chemical composition and state, which should be important for the electrocatalytic CO_2RR.

Response: We appreciate your insightful comment on the necessity to characterize the surface chemical composition and state of the post-reaction samples, recognizing their potential impact on the catalytic activity and selectivity during the CO_2RR. Understanding that the surface properties of catalysts can undergo significant changes during the reaction, which can, in turn, influence their catalytic performance, we have now conducted additional surface-sensitive analyses to complement our initial findings from SEM and XRD.

Specifically, we have analyzed the surface chemical state of the catalyst after the reaction using XPS. From the post-reaction XPS data, the Cu in CuNCN is significantly reduced, which is clearly observed in Cu LMM. This is matched by the fact that a clear aggregation of Cu was observed in the SEM. Thanks to the contribution of the $[NCN]^{2-}$ group, the valence state of the Cu sites in Cu$^{\delta+}$NCN is well maintained, which ensures that the

FE of the Cu^0-Cu^+ sites for the C_2 product is always kept at a high level. At the same time, these data will help us to discuss the activity and stability of the electrocatalysts under CO_2RR conditions.

We have incorporated the results and discussion of these surface analyses into the revised manuscript to ensure that the reader is fully aware of the potential impact of surface changes on catalytic behavior.

Revised part in manuscript:

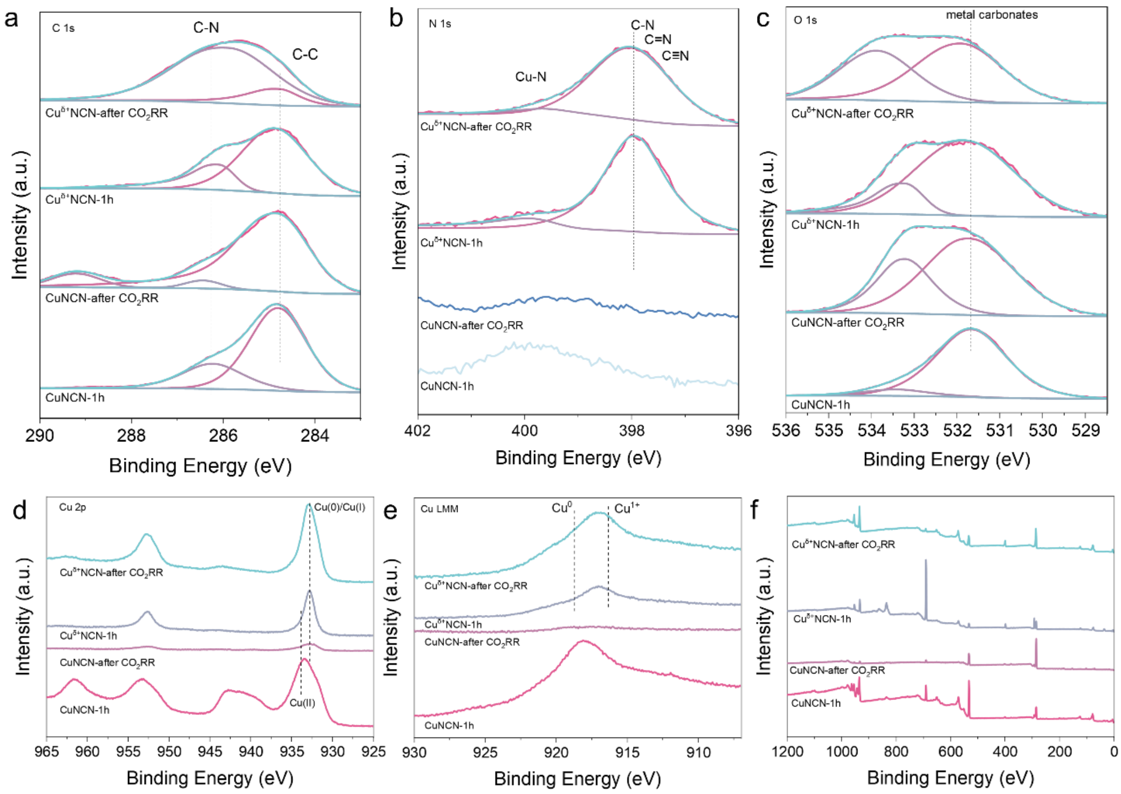
In page 11:

We also investigated the physical phases as well as the surface chemical states of $Cu^{\delta+}$NCN and CuNCN after undergoing CO_2RR by XRD, XPS, SEM and EDS spectroscopy.

The surface chemical states of $Cu^{\delta+}$NCN and CuNCN after undergoing CO_2RR for different times were further analyzed by XPS, as shown in **Supplementary Fig. S18a&b**. The C-N coordination can be clearly observed on the surface of $Cu^{\delta+}$NCN, whereas for CuNCN, C-N is almost not observed on the surface due to the loss of the NCN moiety, which agrees with the results of EDS. The valence changes of Cu observed from *operando* XAS are also confirmed in **Supplementary Fig. S18d&e**. When experiencing CO_2RR for different reaction times, Cu reduction in CuNCN is clearly detected, whereas $Cu^{\delta+}$NCN can maintain its surface chemical state even after a long time of reaction thanks to the protection of the oxidation state of strong σ-donation effect and structure transformation of $[NCN]^{2-}$.

Revised part in supplementary:

In page 28:



Supplementary Fig. 18. XPS spectra of Cu$^{\delta+}$NCN,and CuNCN after undergoing CO$_2$RR for 1h and 15h, respectively. **a,** C 1s high-resolution XPS. **b,** N 1s high-resolution XPS. **c,** O 1s high-resolution XPS. **d,** Cu 2p high-resolution XPS. **e,** Cu LMM spectra. **f,** XPS survey spectra.

Comment 5: The article claims the unique structure of cyanamide-coordinated isolated Cu framework (Cu$^{\delta+}$NCN) with balanced metallic Cu (Cu^0) and delocalized Cu (Cu^{1+}) sites for the high selectivity of CO$_2$-to C$_2$H$_4$, besides of experimental data, it is more reasonable to provide theoretical evidence on how the state of Cu affects the C-C coupling reaction.

Response: Thank you for your valuable feedback on our manuscript and for pointing out the importance of providing theoretical evidence to bolster our claims regarding the unique structure of the cyanamide-coordinated isolated Cu framework (Cu$^{\delta+}$NCN) and its role in the selectivity for CO$_2$-to-C$_2$H$_4$ conversion.

To address your concerns, we have now extended our study to include DFT calculations that provide insights into the electronic structure of the Cu$^{\delta+}$NCN sites and their influence on the C-C coupling reaction mechanism. The DFT results show that the presence of Cu^0 and Cu^{1+} states in the framework creates an optimal electronic environment as shown in **Fig 5a**. Furthermore, the activation energy of transition state 1(TS1) representing the C-C coupling is calculated to be 0.86 eV, providing theoretical insight into the catalytic process. These calculations allow us to theorize how the balance between metallic Cu (Cu^0) and delocalized Cu (Cu^{1+}) sites can facilitate the adsorption and activation of CO_2, and subsequently promote the C-C coupling steps necessary for ethylene formation. In the revised manuscript, we have updated the discussion to integrate these theoretical insights with our experimental observations, thus providing a comprehensive view of the catalytic mechanism of the Cu^0-Cu^{1+} dual sites.

Revised part in manuscript:

In page 24:

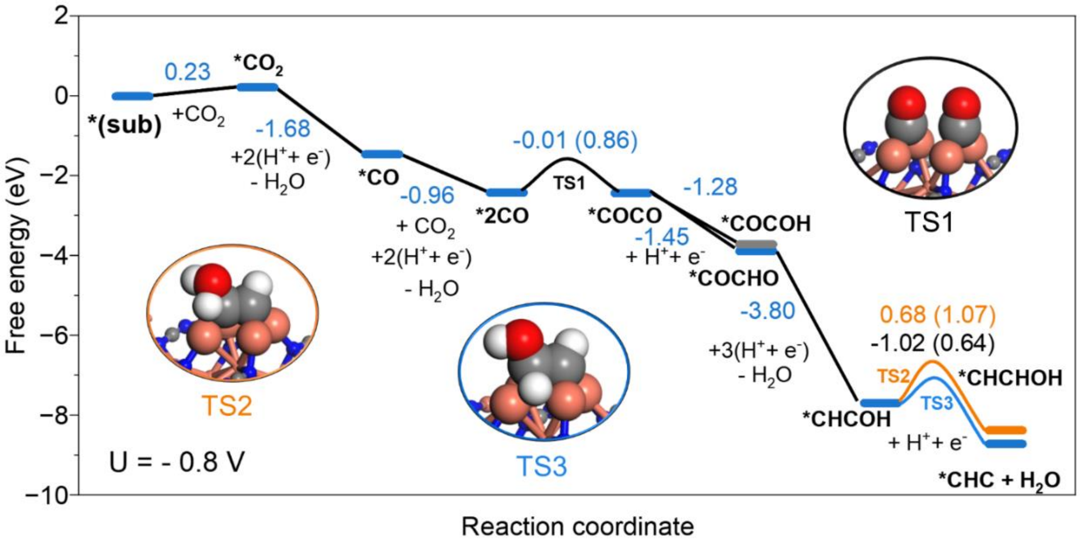


Fig. 5c Free energy profiles of the involved reaction intermediates under U = -0.8 V, the corresponding kinetic barriers of key reaction steps are provided in the brackets, the atomic structures of the transition states are shown in the insets.

Revised part in supplementary:

Comment 6: The author calculated the free energy changes along the CHC and CHCHOH pathways, respectively. To gain deeper insights into the mechanism, additional reaction intermediates, such as *COCO, should be considered in the calculations.

Response: We greatly appreciate your insightful suggestion to include additional reaction intermediates, such as *COCO, in our DFT calculations. Your recommendation highlights a critical aspect of understanding the detailed mechanism of the catalytic process, which indeed could provide a more comprehensive picture of the potential pathways and their energetics.

In response to your valuable feedback, we have expanded our theoretical investigation to consider the *COCO intermediate, which is pivotal for elucidating the full scope of the reaction mechanism, especially for pathways that may involve CO dimerization processes. By incorporating *COCO into our DFT calculations, we aim to explore not only the standard CHC (C-H coupling) and CHCHOH (hydroxylation followed by C-H coupling) pathways but also the potential for pathways that could lead to C-C coupling through CO dimerization. The results indicate the formation of ethylene via *CHC intermediate is more favorable than the formation of ethanol in both kinetics and thermodynamics, which agrees well with the experimental results.

Revised part in manuscript:

In page 14:

By combing the results of *operando* ATR-SEIRA analysis (**Fig. 4i**), the hydrogenated *CO dimer (*COCHO) formed a key C_2 intermediate *CHCOH after a sequence of proton and electron transfer steps.[46] As a later key stage of the C_2 pathway, the hydrogenation of *CHCOH can lead to branching pathways to either ethylene or ethanol. On the basis of reaction free energies (ΔG) calculated at constant potential of -0.8 V in **Fig 5c**, the *CHC pathway representing the formation of ethylene was proved to be more energetically favorable with a free energy change of -1.02 eV, much lower than that for *CHCHOH (ΔG = -0.68 eV), the typical pathway for ethanol. We further studied the kinetic barrier of this step, the barrier of *CHCOH → *CHCHOH is 1.07 eV, while the barrier of *CHCOH → *CHC is only 0.64 eV, indicating the formation of ethylene via *CHC intermediate is more favorable than the formation of ethanol in kinetics, consistent with our experimental results. Together, the reaction pathway of CO_2 to C_2H_4 on $Cu^{\delta+}$NCN was proposed as: CO_2 →*CO → *COCO→*COCHO→*CHCOH →*CHC → C_2H_4 based on the both operando characterization and theoretical calculations (**Fig 5c**).

In page 24:

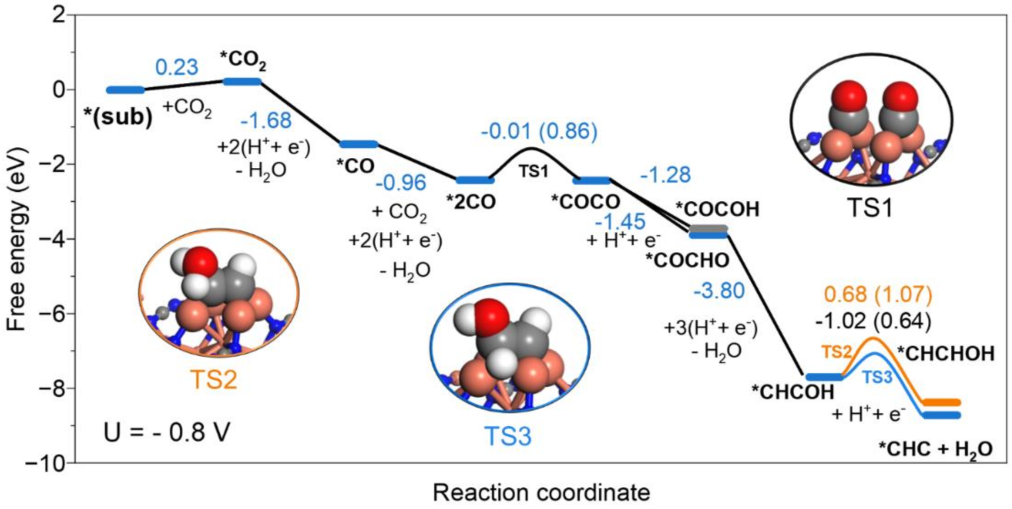


Fig. 5c Free energy profiles of the involved reaction intermediates under U = -0.8 V, the corresponding kinetic barriers of key reaction steps are provided in the brackets, the atomic structures of the transition states are shown in the insets.

Comment 7: Some minor issues should be well addressed, such as the language expression and format of the references, some entries appear to be incorrect.

Response: Thank you for bringing these minor issues to our attention. We apologize for the oversights. Regarding the reference formatting, we have meticulously gone through each citation to correct any inaccuracies and to ensure that all entries adhere strictly to the *Nature Communications*. We have also cross-checked each reference with the original sources to confirm that all details are accurate and complete.

The revised manuscript now includes a polished language presentation and a correctly formatted reference list. We have marked all changes in the text for easy identification and verification.

Revised part in supplementary:

Comment 8: The references in the manuscript are insufficient, especially the performance comparison. C_2H_4 from CO_2 reduction using Cu-based catalysts is widely studied and there are some good catalysts those are not mentioned in this manuscript, such as Mg-Cu_xO (FE_{C2H4} 70%, j_{C2H4} ~455 mA cm^{-2} for 48 h, Angew. Chem. Int. Ed. 2022, 61, e202213423.) and Cu-F (FE_{C2H4} 80%, j_{C2H4} ~320 mA cm^{-2} for 40 h, Nat. Catal. 2020, 3, 478–487.). Apart from these, the CO_2 reduction work using Indium cyanamide (J. Am. Chem. Soc. 2023, 145, 14101−14111.) firstly proposed the strong σ-donation effect and structure transformation from $[NCN]^{2-}$ to protect the metal oxidation state should be also cited. The obvious peak of C≡N at different potentials in

ATR-SEIRA spectra in Figure 4i may come from the structure transformation of [NCN].

Response: We express our sincere gratitude for your constructive comments regarding the need for a more comprehensive literature review, particularly in performance comparison with other Cu-based catalysts for CO_2-to-C_2H_4 conversion.

Upon reflection, we agree that the omission of recent significant advancements in this field was a gap in our manuscript. We acknowledge the importance of providing readers with a thorough context, which includes a comparison of our catalyst performance with other notable developments such as the Mg-Cu_xO and Cu-F catalysts in CO_2 reduction.

We have also considered the possibility that the peaks observed in the ATR-SEIRA spectra in Fig. 4i may indeed originate from the structural transition of [NCN] as you suggest, since in the ATR-SEIRA spectra only the [NCN] group of the $Cu^{\delta+}$NCN sample shows a pronounced peak intensification in conjunction with the XAS change of $Cu^{\delta+}$NCN during CO_2RR. It is reasonable to believe that the valence retention of Cu is related to the structural transformation of [NCN]. This finding prompted a more in-depth analysis, which is now included in our Discussion section, with a citation to the Indium cyanamide article in the relevant section.

Revised part in manuscript:

In page 8:

By comparing the FE of CO_2 to C_2H_4 and corresponding *j* of $Cu^{\delta+}$NCN with that for other reported excellent Cu-based electrocatalysts (**Fig. 3e** and **Supplementary Table 4**), the CO_2RR performance of $Cu^{\delta+}$NCN was found to locate in the best ranks of these Cu-based materials.[8,14,17-19,28-34]

In page 9:

Previous research also reported that the $[NCN]^{2-}$ group can safeguard the oxidation state of metals through a strong σ-donation effect and structural transformation, thereby maintaining the stability of the catalyst's average valence state.[25]

In page 17-18:

14 Ma, W. *et al.* Electrocatalytic reduction of CO_2 to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nat. Catal.* **3**, 478-487 (2020).

25 Jia, B. *et al.* Indium Cyanamide for Industrial-Grade CO_2 Electroreduction to Formic Acid. *J. Am. Chem. Soc.* **145**, 14101-14111 (2023).

34 Xie, M. *et al.* Fast Screening for Copper-Based Bimetallic Electrocatalysts: Efficient Electrocatalytic Reduction of CO_2 to C_{2+} Products on Magnesium-Modified Copper. *Angew. Chem., Int. Ed.* **61**, e202213423 (2022).

In page 20:

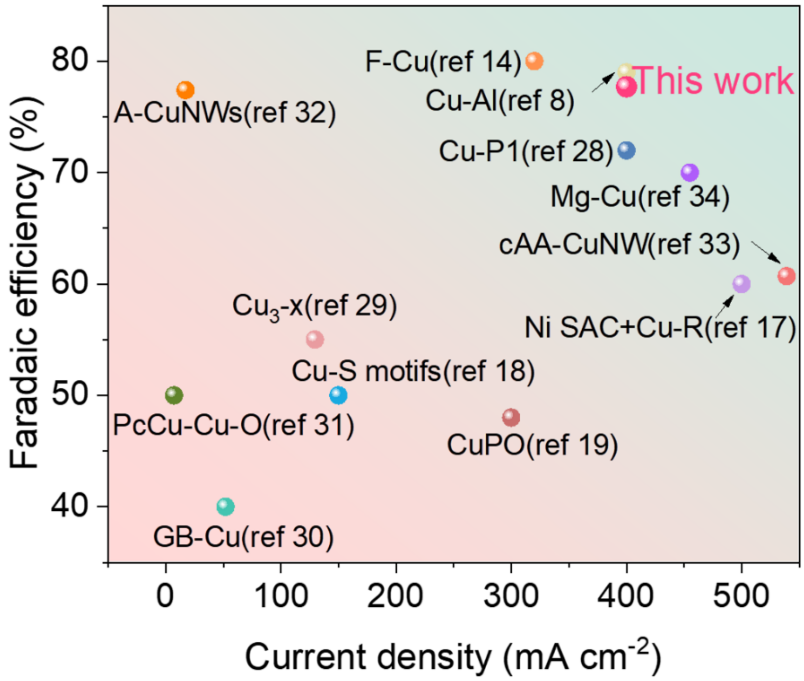


Fig. 3e Comparison of the $FE_{C_2H_4}$ and reduction current of $Cu^{\delta+}NCN$ with recently reported catalysts.

Reviewer #2 The authors proposed a cyanamide-coordinated isolated Cu framework ($Cu^{\delta+}NCN$) with balanced metallic Cu (Cu^0) and delocalized Cu (Cu^{1+}) sites acting as an efficient electrocatalyst for CO_2-to-C_2H_4 reduction. The as-proposed electrocatalyst delivers outstanding selectivity and activity. The authors claimed that Cu^0 atoms in $Cu^{\delta+}NCN$ enhanced the surface *CO by activating CO_2, while the electron delocalized Cu^{1+} lead to boost of C-C coupling by offering a lower Gibbs free energy for *CHC formation and subsequent high selectivity for C_2H_4. Overall, the authors provide both experimental and theoretical evidence for supporting their conclusions. However, some important issues should be well addressed before publication.

Response: Thank you for your appraisal of the electrocatalyst design presented in our study and for acknowledging the experimental and theoretical evidence supporting our conclusions. We appreciate the opportunity to address the concerns and improve the quality and clarity of our manuscript.

Comment 1: The main concern about this work is the identification of co-existing Cu^0 and Cu^{1+} in the as-proposed Cu_2NCN sample. The authors mentioned that "The Cu-N coordination number (CN) of $Cu^{\delta+}NCN$ was confirmed to be 1.6, smaller than that of Cu_2NCN (CN=2). This observation further suggested the presence of atomic Cu^0 in the $Cu^{\delta+}NCN$" (line 105), it should be noted that EXAFS spectra cannot distinguish Cu^0 and Cu^{1+}.

Response: We thank you for your critical analysis of our work, particularly regarding the identification of the oxidation states of copper in the $Cu^{\delta+}NCN$ sample. Your point about the limitations of EXAFS spectroscopy in distinguishing between Cu^0 and Cu^{1+} is well-taken and indeed is a crucial detail that warrants further clarification in our manuscript.

Considering your comment, we have revisited our analysis and agree that the coordination number (CN) obtained from EXAFS alone is not sufficient to conclusively determine the presence of Cu^0 in the $Cu^{\delta+}NCN$ sample. We recognize that the CN could be influenced by other factors such as structural distortions or the presence of different ligand environments.

To address this issue, we have carefully judged the valence states of Cu using different characterization techniques that can provide supportive evidence for the presence of multiple copper oxidation states. Specifically, we distinguished the contribution of copper species with different valence states through Cu

LMM spectroscopy, which is more sensitive to the different oxidation states of copper and showed that the Cu0 peak is clearly visible in the $Cu^{\delta+}$NCN sample. At the same time, combined with the extent of the Cu *K*-egde shift, we can conclude that the average Cu valence state of the $Cu^{\delta+}$NCN sample is lower than 1. These complementary techniques confirm our initial hypothesis that both Cu^0 and Cu^{1+} species are present in the $Cu^{\delta+}$NCN sample.

We have amended the manuscript to include these additional results and revised the discussion to reflect a more cautious interpretation of the EXAFS data. The revised sections now clearly indicate that while EXAFS provided the initial hint of multiple copper species, it was the combination of XPS analyses that enabled us to make a more confident assertion regarding the co-existence of Cu^0 and Cu^{1+}.

Revised part in manuscript:

In page 6:

By integrating the structural information observed from $Cu^{\delta+}$NCN: the Cu-N coordination number in EXAFS being less than the theoretical value, the average valence state residing between 0 and +1 in the XAS *K*-edge, and the presence of both Cu^0 and Cu^{1+} atoms indicated by the Cu LMM Auger spectrum, we can deduce that both Cu^0 and Cu^{1+} coexist on the surface of $Cu^{\delta+}$NCN.

Comment 2: The authors should provide more experimental evidence on the co-existing Cu^0 and Cu^{1+}. The XAS just provide average information on the Cu valence state. The current results did not provide convincing evidence.

Response: We appreciate your insistence on a robust and rigorous demonstration of the co-existing Cu^0 and Cu^{1+} states in our $Cu^{\delta+}$NCN sample. We understand that the XAS provides averaged valence state information and agree that additional, more localized evidence would substantiate our claims more convincingly.

In response to your valuable feedback, we tested additional XPS data to strengthen our argument, and we performed high-resolution scans of the Cu 2p region while acquiring Cu LMM spectra to distinguish peaks in the Cu^0 and Cu^{1+} states. The results show that the characteristic peaks of Cu^0/Cu^{1+} can be clearly seen in the Cu 2p spectra of $Cu^{\delta+}$NCN samples, which suggests that it is possible for Cu sites in both Cu^0 and Cu^{1+} valence states to exist in $Cu^{\delta+}$NCN samples individually or simultaneously. Further Cu LMM spectroscopic data can provide further pointers to both, as shown in Supplementary Fig. 18, the Cu LMM binding energy in $Cu^{\delta+}$NCN is located between Cu^0 and Cu^{1+}. Combined with the fact that the average valence state of $Cu^{\delta+}NCN$ shown in XAS is also located between 0-1 valence, and the fact that the coordination number of Cu-N in EXAFS is less than the expected value of 2, it is reasonable to believe that both Cu^0 and Cu^{1+} sites exist in $Cu^{\delta+}NCN$.

We believe these additional experiments and analyses provide the compelling evidence required to support our claims. We hope that our revised manuscript now satisfies the concerns raised and contributes valuable information to the field.

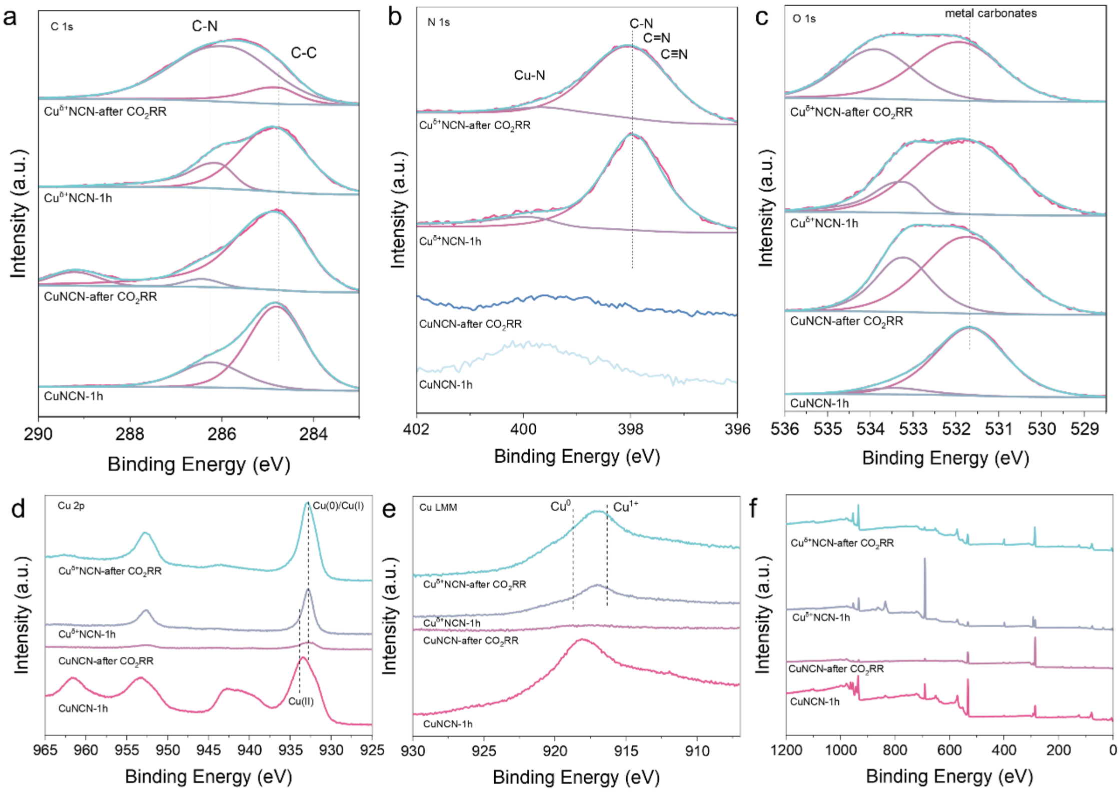
Revised part in manuscript:、

In page 11:

The surface chemical states of $Cu^{\delta+}NCN$ and CuNCN after undergoing CO_2RR for different times were further analyzed by XPS (**Supplementary Fig. 18**). The C-N coordination can be clearly observed on the surface of $Cu^{\delta+}NCN$, whereas for CuNCN, C-N is almost not observed on the surface due to the loss of the NCN moiety (**Supplementary Fig. 18a&b**), which agrees with the results of EDS. The valence changes of Cu observed from *operando* XAS are also confirmed from Cu 2p high-resolution XPS and Cu LMM spectra (**Supplementary Fig. 18d&e**). When experiencing CO_2RR for different reaction times, Cu reduction in CuNCN is clearly detected, whereas $Cu^{\delta+}NCN$ can maintain its surface chemical state even after a long time of reaction thanks to the protection of the oxidation state of strong σ-donation effect and structure transformation of $[NCN]^{2-}$.[25]

Revised part in supplementary:

In page 28:



Supplementary Fig. 18. XPS spectra of Cu$^{\delta+}$NCN,and CuNCN after undergoing CO$_2$RR for 1h and 15h, respectively. **a,** C 1s high-resolution XPS. **b,** N 1s high-resolution XPS. **c,** O 1s high-resolution XPS. **d,** Cu 2p high-resolution XPS. **e,** Cu LMM spectra. **f,** XPS survey spectra.

Comment 3: In addition to the [N–C≡N]$^{2-}$ and [N=C=N]$^{2-}$, the Cu-O can be also observed in FTIR curve of Cu$^{\delta+}$NCN in Fig. 2f, however, the Cu-O path (only Cu-N path included for the first shell) was not considered in the EXAFS fitting and discussed in this work. A recent work might provide insightful information about it [Nat. Commun., 2023, 14, 5245; J. Am. Chem. Soc., 2020, 142, 12119-12132].

Response: Thank you for pointing out the observation of the Cu-O species in the FTIR spectrum of our Cu$^{\delta+}$NCN sample, as evidenced in Fig. 2f, and for directing our attention to the recent publications that discuss similar systems and their characterization. We acknowledge the importance of considering all relevant paths, including Cu-O, when performing EXAFS fitting to ensure that the structural model reflects the actual coordination environment of the copper centers.

In response to your comments, we have undertaken the following steps:

We have expanded the discussion in our manuscript to include considerations about the possible origins and implications of the Cu-O interactions observed in the FTIR curve. This includes a review of the potential roles these interactions may play in the structure and reactivity of the $Cu^{\delta+}NCN$ catalyst, drawing parallels to findings presented in the referenced articles.

We have carefully reviewed the two articles mentioned from *Nature Communications (2023, 14, 5245)* and the *Journal of the American Chemical Society (2020, 142, 12119-12132)*. These studies provide insightful context and methodology for considering Cu-O interactions within similar compounds and have guided our approach to revisiting our EXAFS analysis.

Our revisions to the manuscript, including updating the EXAFS analysis with reference to the above two papers and adding a discussion of Cu-O interactions, are intended to provide a more accurate and complete description of the structure of the $Cu^{\delta+}NCN$ sample. We hope these revisions address the questions you have raised.

Revised part in manuscript:

In page 10:

Considering that the coordination of N, C, and O with Cu is difficult to be distinguished in EXAFS, for the sake of $Cu^{\delta+}NCN$ structural determinism, we performed the fitting with these two peaks corresponding to the typical scattering features of the Cu-N and Cu-Cu coordination, respectively, and the fitted data match the experimental data very well **(Supplementary Fig. 24&25).**

In page 18:

36 Chang, C. J. *et al.* Dynamic Reoxidation/Reduction-Driven Atomic Interdiffusion for Highly Selective CO_2 Reduction toward Methane. *J. Am. Chem. Soc.* **142**, 12119-12132 (2020).

37 Hsu, C.-S. *et al.* Activating dynamic atomic-configuration for single-site electrocatalyst in electrochemical CO_2 reduction. *Nat. Commun.* **14**, 5245 (2023).

Comment 4: The authors claimed that “The stability of Cu-N coordination has been proved during electrochemical CO_2RR” (line 193), but they didn’t provide any evidence. In line 195, they further claimed that the isolated Cu^0 would aggregate to form few-atom Cu clusters, such result evidenced the unstable Cu-N bonds. These results are contradictory.

Response: Thank you for your careful reading of our manuscript and for highlighting the apparent contradiction concerning the stability of the Cu-N coordination during the electrochemical CO_2RR and the subsequent discussion of Cu^0 aggregation.

Upon reviewing the manuscript with your comments in mind, it becomes clear that our language was not precise enough to convey the nuanced observations we intended to report. We acknowledge the need for clarity for our claims, especially those related to the stability of Cu-N bonds and the behavior of isolated Cu^0 atoms.

Experimental evidence for Cu-N stability: We can clearly see the increasing frequency contribution of $[NCN]^{2-}$ groups at 2250 cm^{-1} in the Operando ATR-SEIRA results, and in previous studies it has been shown that $[NCN]^{2-}$ groups can protect the metal oxidation state by strong σ-donation effects and structural transformations, which can indicate that Cu-N is stable during CO_2RR. (*J. Am. Chem. Soc.* **145**, 14101-14111 (2023))

Clarification of Cu^0 Aggregation: The mention of Cu^0 aggregation to form few-atom clusters was meant to describe a potential process that could occur if Cu-N bonds were to break under certain conditions, not an observed outcome of our experiments. We realize that our original phrasing was misleading. We have now reformulated this section to clarify that although, theoretically, isolated Cu^0 could aggregate, our experimental evidence indicates that the Cu-N coordination in $Cu^{\delta+}$NCN is stable within the voltage range where optimum CO_2RR activity is observed. As the voltage increases further, Cu^0 begins to aggregate into Cu clusters. Our theoretical calculations also support this, demonstrating that the aggregation of Cu clusters is merely a thermodynamic effect on the surface and is not directly related to the stability of the Cu-N coordination.

We have carefully reviewed the entire manuscript to ensure consistency in our claims and to provide proper context for our statements. Changes have been made throughout the document to ensure that our observations, results, and claims are accurately represented and fully supported by the experimental data we have.

We appreciate the opportunity to clarify these points and believe that the revisions made to our manuscript now present a coherent and evidence-backed narrative.

Revised part in manuscript:

In page 10-11:

Combined with the optimal activity intervals and the excellent stability of Cu$^{\delta+}$NCN in **Fig.3b&3d**, it can be judged that the coordination stability of Cu-N is crucial for Cu$^{\delta+}$NCN to maintain its catalytic stability.[37] And when the voltage is further increased to -1.6 V or even higher, the Cu^0 on the surface of Cu$^{\delta+}$NCN will aggregate into few-atom Cu clusters in a thermodynamically favorable way, and at the same time, the Cu-N will re-coordinate and stabilize these formed Cu clusters by keeping the bond length at around 2.58 Å, thus ensuring that the Cu^0 and Cu^{1+} on the surface will be maintained. The coexistence of Cu^0 and Cu^{1+} on the surface is very consistent with the excellent stability of Cu$^{\delta+}$NCN during the CO_2RR process.

Comment 5: The authors should provide more physical characterizations of Cu$^{\delta+}$NCN during CO_2RR at various potentials and after stability testing and give corresponding discussions.

Response: Thank you for your constructive feedback regarding the necessity for additional physical characterizations of the Cu$^{\delta+}$NCN catalyst during the CO_2RR at various potentials and following stability testing.

Based on your suggestion, we have supplemented and analyzed the XPS data of Cu$^{\delta+}$NCN in several different states. The results show that the Cu sites of Cu$^{\delta+}$NCN at different potentials as well as after stability tests have been performed are only partially reduced, which is consistent with the observed decrease in the average valence state of Cu in *operando* XAS, thus ensuring the co-existence of Cu^0 and Cu^{1+} sites, which facilitates the C-C coupling and maintains the Faraday efficiency of the C_2 product.

In addition to this, we have paid particularly attention on the structural evolution by analysis the *operando* ATR-SEIRA spectral of Cu$^{\delta+}$NCN at higher potentials (-1.6 V vs. RHE) with continues CO_2RR, as shown in Supplementary Fig. 20f, where $[NCN]^{2-}$ groups on the surface of Cu$^{\delta+}$NCN can be consistently observed for the time tested, which is key to the fact that Cu$^+$ can be stabilized during the CO_2RR process.

We have expanded the discussion section of our manuscript to incorporate the results of these additional characterizations. The discussion now includes a comprehensive analysis of how the catalyst's physical properties evolve with varying operational potentials and after extended periods of CO_2RR. These additions to our manuscript significantly enhance our understanding of the Cu$^{\delta+}$NCN catalysts performance during CO_2RR and its stability over time. By providing a more detailed characterization at various operational stages, we are better positioned to discuss the implications of these findings for the design and optimization of efficient and durable CO_2 reduction catalysts.

Revised part in manuscript:

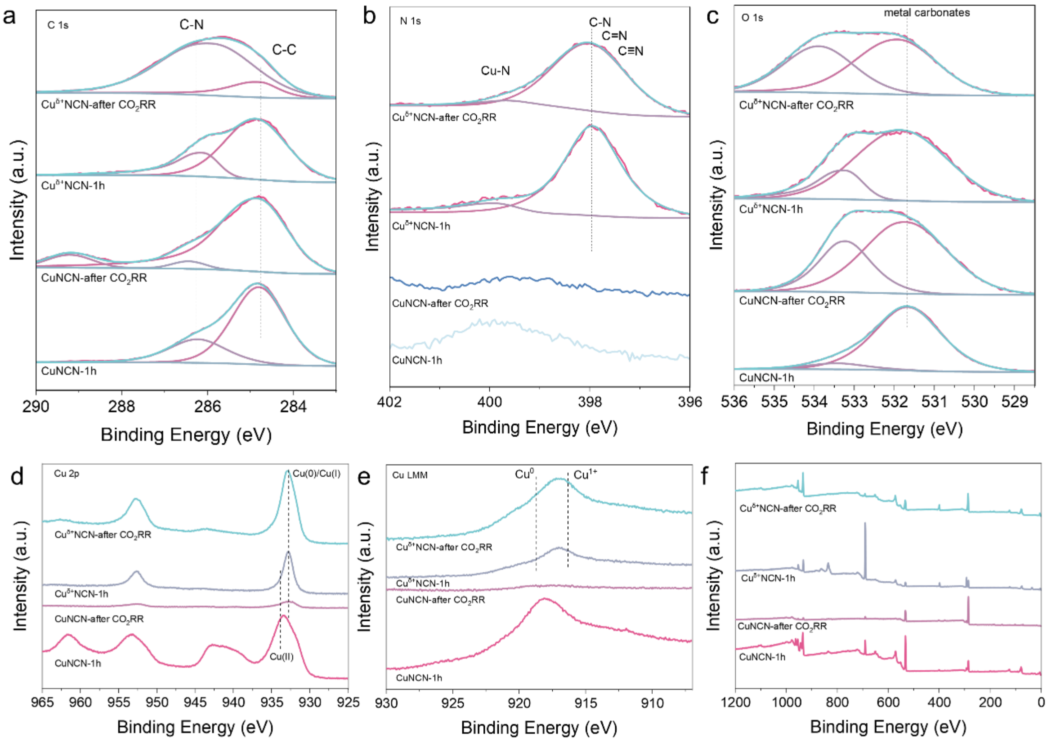
In page 11-12:

We also investigated the physical phases as well as the surface chemical states of $Cu^{\delta+}$NCN and CuNCN after undergoing CO_2RR by XRD, XPS, SEM and EDS spectroscopy.

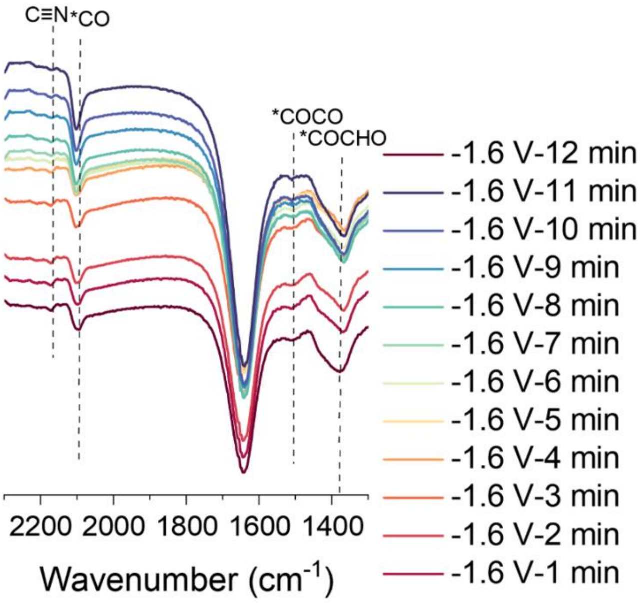
The surface chemical states of $Cu^{\delta+}$NCN and CuNCN after undergoing CO_2RR for different times were further analyzed by XPS (**Supplementary Fig. 18**). The C-N coordination can be clearly observed on the surface of $Cu^{\delta+}$NCN, whereas for CuNCN, C-N is almost not observed on the surface due to the loss of the NCN moiety (**Supplementary Fig. 18a&b**), which agrees with the results of EDS. The valence changes of Cu observed from *operando* XAS are also confirmed from Cu 2p high-resolution XPS and Cu LMM spectra (**Supplementary Fig. 18d&e**). When experiencing CO_2RR for different reaction times, Cu reduction in CuNCN is clearly detected, whereas $Cu^{\delta+}$NCN can maintain its surface chemical state even after a long time of reaction thanks to the protection of the oxidation state of strong σ-donation effect and structure transformation of $[NCN]^{2-}$.[25]

Revised part in supplementary:

In page 28:



Supplementary Fig. 18. XPS spectra of $Cu^{\delta+}$NCN,and CuNCN after undergoing CO_2RR for 1h and 15h, respectively. **a,** C 1s high-resolution XPS. **b,** N 1s high-resolution XPS. **c,** O 1s high-resolution XPS. **d,** Cu 2p high-resolution XPS. **e,** Cu LMM spectra. **f,** XPS survey spectra.



Supplementary Fig. 20 f. The 2D *operando* ATR-SEIRA spectra of $Cu^{\delta+}NCN$.

Comment 6: The authors highlighted the in situ formation of Cu clusters during CO_2RR. Another concern of this work is the actually active sites for the C_2 production, Cu clusters or co-existing Cu^0 and Cu^{1+}?

Response: Thank you for your continued engagement with our manuscript and for raising a critical question regarding the identity of the active sites responsible for C_2 product formation during CO_2RR on our $Cu^{\delta+}NCN$ catalyst. The nature of the active sites for electrocatalytic processes, particularly for CO_2RR, is indeed a fundamental aspect that requires clear elucidation.

Although we have focused on the in situ formation of Cu clusters in the CO_2RR process, this is in order to characterize the potential processes that may occur under specific conditions of Cu-N bond breaking, rather than what we have observed experimentally.

Our experimental evidence suggests that Cu-N coordination in $Cu^{\delta+}NCN$ is stable over the range of voltages at which optimal CO_2RR activity is observed. With further voltage increase, Cu^0 starts to aggregate into Cu clusters. This is supported by our theoretical calculations, which demonstrate that the aggregation of Cu clusters is only a surface thermodynamic effect.

We are more interested in whether Cu-N is stably present than in the production of Cu clusters, and we would like to emphasize the contribution of $[NCN]^{2-}$ to Cu^{1+}. The coexisting Cu^0 and Cu^{1+} are true active sites, facilitating the C-C coupling process and thus the efficient production of ethylene products.

The manuscript's revised version includes these analyses, which we believe significantly bolster our understanding of the active sites within the $Cu^{\delta+}$NCN catalyst system for CO_2RR. We appreciate the opportunity to refine our conclusions based on solid experimental evidence and theoretical backing.

Revised part in manuscript:

In page 10-11:

Combined with the optimal activity intervals and the excellent stability of $Cu^{\delta+}$NCN in **Fig.3b&3d**, it can be judged that the coordination stability of Cu-N is crucial for $Cu^{\delta+}$NCN to maintain its catalytic stability.[39] And when the voltage is further increased to -1.6 V or even higher, the Cu^0 on the surface of $Cu^{\delta+}$NCN will aggregate into few-atom Cu clusters in a thermodynamically favorable way, and at the same time, the Cu-N will re-coordinate and stabilize these formed Cu clusters by keeping the bond length at around 2.58 Å, thus ensuring that the Cu^0 and Cu^{1+} on the surface will be maintained. The coexistence of Cu^0 and Cu^{1+} on the surface is very consistent with the excellent stability of $Cu^{\delta+}$NCN during the CO_2RR process.

Comment 7: The authors mentioned that "Linear sweep voltammetry (LSV) curves (Fig. 3a) indicated that the activity of $Cu^{\delta+}$NCN was much better than the CuNCN and CuO with lowest onset potential and higher current density, demonstrating the reaction priority to CO_2RR". According to the Figure 3a, the current density of CuO seems better than that of $Cu^{\delta+}$NCN at the potential between -0.6~-1.4 V, the authors should explain it.

Response: Thank you for pointing out the discrepancy between our described results and the data presented in Figure 3a. Your attention to detail is appreciated, as it helps us ensure the accuracy and clarity of the information presented in our findings.

Upon revisiting Figure 3a and the corresponding text, we realize that our statement regarding the superior activity of $Cu^{\delta+}$NCN compared to CuNCN and CuO was not appropriately nuanced to account for the entire potential range examined. Specifically, the oversight concerning the current density of CuO outperforming $Cu^{\delta+}$NCN between -0.6 to -1.4 V requires clarification.

To address this, we have undertaken a thorough re-analysis of our results and offer the following explanation:

The claim about the activity of $Cu^{\delta+}$NCN being superior was primarily based on its lower onset potential for CO_2RR compared to the other catalysts. The onset potential is a crucial metric for evaluating electrocatalyst performance, as it indicates the potential at which the reaction begins to occur significantly. While CuO exhibits higher current densities at more negative potentials, the onset potential for CO_2 reduction is higher than that of $Cu^{\delta+}NCN$. Besides, the overall activity for CO_2RR cannot be assessed solely by current density, as it doesn't distinguish between the various possible reduction products. In the revised manuscript, we now provide a more comprehensive analysis that includes Faradaic efficiency measurements for the targeted C_2 products at various potentials. These measurements demonstrate that while CuO may produce a higher total current, $Cu^{\delta+}NCN$ exhibits a higher selectivity towards C_2 products, thus reaffirming its superior catalytic performance for the desired reaction.

We have revised the discussion in the manuscript to explicitly address this issue. The revised text acknowledges that CuO exhibits a higher total current density over a range of potentials but emphasizes the selectivity of the high-value C_2 product and the importance of partial currents as an indicator of comparative catalyst performance.

We hope that these revisions and explanations address the concerns raised and accurately reflect the performance characteristics of the $Cu^{\delta+}NCN$ catalyst. We are grateful for the opportunity to clarify these points and ensure that our conclusions are supported by a comprehensive analysis of the data.

Revised part in manuscript:

In page 7-8:

Linear scanning voltammetry (LSV) curves (**Fig. 3a**) showed that $Cu^{\delta+}NCN$ exhibited the lowest onset potentials as well as better reaction kinetics, especially in the presence of CO_2, compared to CuNCN and CuO.

It is important to note that although the total catalytic current density of $Cu^{\delta+}NCN$ is lower than that of CuO in the range of -1.0 V to -1.3 V vs RHE, the j_{C2H4} on $Cu^{\delta+}NCN$ is significantly more advantageous due to its high FE_{C2H4}, and this advantage becomes even more pronounced as the potential increases (**Fig. 3c**).

Comment 8: Recent research might provide the authors with useful insights [Nat. Commun., 2023, 14, 6576; Angew. Chem. Int. Ed., 2021, 60, 17254-17267； ACS Appl. Mater. Interfaces, 2022, 14, 22681-22696； J. Am. Chem. Soc., 2023, 145， 27054-27066; Chem. Soc. Rev., 2023, 52, 5013-5050].

Response: Thank you for bringing to our attention the recent publications that could offer valuable insights pertinent to our research. We are indeed vigilant in keeping abreast of the latest developments in our field and are grateful for the specific literature you have pointed out.

We have revised the manuscript to include discussions and citations of these articles where appropriate. These changes have enriched the context of our work.

Revised part in manuscript:

In page 17-18:

2 Spatially and temporally understanding dynamic solid-electrolyte interfaces in carbon dioxide electroreduction. *Chem. Soc. Rev.* **52**, 5013-5050 (2023).

13 Strong Correlation between the Dynamic Chemical State and Product Profile of Carbon Dioxide Electroreduction. *ACS Appl. Mater. Interfaces* **14**, 22681−22696 (2022).

16 Linking the Dynamic Chemical State of Catalysts with the Product Profile of Electrocatalytic CO_2 Reduction. *Angew. Chem., Int. Ed.* **60**, 17254-17267 (2021).

26 In situ X-ray spectroscopies beyond conventional X-ray absorption spectroscopy on deciphering dynamic configuration of electrocatalysts. *Nat. Commun.* **14**, 6576 (2023).

38 Reversibly Adapting Configuration in Atomic Catalysts Enables Efficient Oxygen Electroreduction. *J. Am. Chem. Soc.* **145**, 27054-27066 (2023).

Reviewer #3 Yue et al. report the catalytic activity of a cyanamide catalyst with isolated copped dimer sites within electrochemical CO_2 reduction. The catalyst show remarkable selectivity towards the desired C_{2+} products with ethylene faradaic efficiencies (FE) up to 70%, combined with H_2 FE of only 10%. A series of spectroscopic analyses has been conducted to study the oxidation state of the doped Cu-sites, suggesting a combination of neutral and oxidized Cu sites on the surface.

Theoretical calculations have been conducted to rationalize the improvements in activity and selectivity. However, I am afraid they do not add significant value to the insights of the paper.

Given my theoretical expertise, I based my assessment mostly on that part of the paper and, thus have to recommend rejection of it.

Response: I understand the concerns raised regarding the perceived value of the theoretical calculations in our manuscript on the catalytic activity of the cyanamide catalyst featuring isolated copper dimer sites for electrochemical CO_2 reduction. Your expert insight, especially from a theoretical standpoint, is invaluable for us to revise and improve the work. In the revised manuscript, we have fully addressed all the raised specific concerns regarding the theoretical component. We have expanded the calculation and theoretical analysis to articulate the significance of the theoretical findings more explicitly. This includes a more detailed explanation of how the combination of neutral and oxidized Cu sites influences the binding energy of key intermediates, thereby facilitating improved selectivity for ethylene formation. We believe these added DFT data and enhanced discussion will make it clearer how the theoretical calculations add substantial value for the understanding of the excellent activity and selectivity for the CO_2RR mechanism.

Considering these enhancements, we kindly appreciate your reconsideration of the manuscript for publication. We believe that the revised manuscript now more clearly articulates the integral role of theoretical calculations in supporting the experimental observations and advancing our understanding of the catalytic system under study. The synergistic relationship between the theoretical and experimental aspects of our work is pivotal to the insights presented, and we hope that the revisions adequately address the concerns raised.

Comment 1: In figure 4i, the authors assign peaks appearing at 1530 cm^{-1} and 1440cm^{-1} to *COCO and *COCHO. On which basis was this assignment made. No reference or computational result was given to justify it. In fact, given that *CO dimerization is generally considered as the rate-limiting step towards C_{2+}

products, no coverage *COCO should be expected.

Response: Thank you for your astute observation regarding Figure 4i in our manuscript. The assignment of the peaks at 1530 cm^{-1} and 1440 cm^{-1} to the *COCO and *COCHO intermediates, respectively, was based on experimental results together with the published literature as reported in *J. Am. Chem. Soc.* 2024, 146, 1935: *Energy Environ. Sci.* 2020, **13**, 4301-4311; *Proc. Natl. Acad. Sci. U.S.A.*, 2022, 119(29): e2118166119, where the *COCO and *COCHO assignments have been observed and decided under similar catalytic conditions. In the revised manuscript, these references have been properly cited to prove such results.

Regarding the discussion of CO dimerization, if the dimerization of CO is the slowest step in the whole reduction process, then a higher concentration of CO intermediates will accumulate on the catalyst surface until they are able to interact with each other to form COCO. Therefore, in this case, the CO intermediates on the surface of the catalyst will not be converted immediately to COCO or other C_{2+} products, resulting in a lower coverage of COCO for a certain period.

However, whether this conclusion is correct depends on the experimental conditions and the specific nature of the catalyst. Under certain conditions, although the dimerization of CO is the rate-limiting step, once a CO intermediate is formed at one of the sites, it may rapidly react with CO intermediates at neighboring sites to form *COCO, due to the possibility of multiple active sites on the electrode surface. In addition, this is also dependent on the rate of diffusion of CO intermediates, the structure of the electrode, and electrochemical operating conditions (*e.g.*, potential, pH, temperature etc.) are relevant. Moreover, many published work (*Angew.Chem.*2021,133,25689–25696; *Energy Environ. Sci.*, 2022, 15, 2397–2409; *J. Am. Chem. Soc.* 2024, 146, 1, 289–297) have also reported such phenomenon and further prove it.

We hope that these updates and justifications provide the necessary clarity and validation for the peak assignments made in our study. We thank you for bringing this matter to our attention, as it has undoubtedly helped to strengthen the manuscript. Enclosed with our resubmission, you will find the updated sections of the manuscript that now include the additional references.

Revised part in manuscript:

In page 12:

In parallel, a distinctive peak shoulder around 1530 cm^{-1}corresponding to the *COCO intermediate via *CO dimerization was observed in Cu$^{\delta+}$NCN and increased accordingly with scanning to more negative potentials.[42,43].

In page 19:

42 Kim, Y. *et al.* Time-resolved observation of C–C coupling intermediates on Cu electrodes for selective electrochemical CO_2 reduction. *Energy Environ. Sci.* **13**, 4301-4311 (2020).

43 Delmo, E. P. *et al.* In Situ Infrared Spectroscopic Evidence of Enhanced Electrochemical CO_2 Reduction and C-C Coupling on Oxide-Derived Copper. *J. Am. Chem. Soc.* **146**, 1935-1945 (2024).

Comment 2: In a previous publication (Ref. 27; https://doi.org/10.1038/s41929-022-00887-z), the authors suggested that Cu_2NCN is paramagnetic, the same may not automatically be true for the surface Cu^0 atoms. Assessing an inappropriate spin state for single atom additive can lead to erroneous assessment of reaction energetics.

Response: You have raised a critical point regarding the assessment of the spin state of copper atoms in our catalyst system. The reference you mentioned (https://doi.org/10.1038/s41929-022-00887-z) indeed suggests that Cu_2NCN is paramagnetic, which may not be directly applicable to the surface Cu^0 atoms in our study. The spin state of copper centers, particularly when they are in a heterogeneous catalytic environment, can significantly influence the reaction energetics and, consequently, the interpretation of catalytic activity and selectivity.

We understand the potential implications of an incorrect spin state assignment and therefore would like to address this concern with the following actions:

Theoretical Reassessment: In parallel, we have performed additional theoretical calculations on different spin states of the single Cu^0 atoms. This will allow us to compare the resulting reaction energetics and identify the most stable spin state based on the computed energies. In this work, the spin state for the surface Cu^0 atoms has been theoretically tested. As shown below, the total energies of the CuNCN calculated with different magnetic moments of Cu^0 atoms (M_{Cu} = 0, 1, 2, and 3 μ_B) show that, in comparison with M_{Cu} = 0, higher spin of the Cu^0 atoms such as M_{Cu} = 1, 2, and 3 μ_B can significantly increase the total energies by 1.12 ~ 12.23 eV, indicating the M_{Cu} = 0 is the rational magnetic moment for Cu^0 atoms.

Following these theoretical investigations, we have amended the manuscript to include the findings and their implications for our reaction energetics assessment. We believe this will not only strengthen the validity of our current work but will also provide valuable insights into the influence of spin states on the catalysis by single atom additives.

We appreciate the opportunity to enhance the rigor of our analysis with these additional studies. We are committed to ensuring that our manuscript reflects an accurate and comprehensive understanding of the system under investigation and believe that these efforts will significantly improve the quality and impact of our findings.

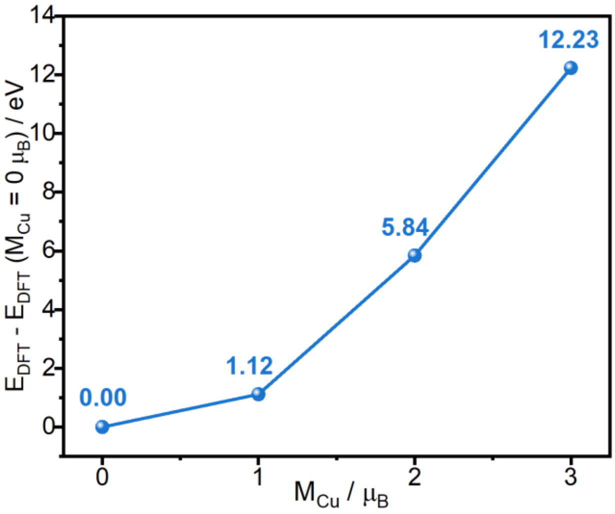
Revised part in manuscript:

In page 13:

Considering that the Cu^0 atoms on the surface of Cu_2NCN might be influenced by the paramagnetic of Cu_2NCN, we also studied the effects of different spin states on the energy calculations prior to computing the energy of the Cu^0 sites. The results show that, in comparison with $M_{Cu} = 0$, higher spin of the Cu^0 atoms such as $M_{Cu} = 1$, 2, and 3 μB can significantly increase the total energies by 1.12 ~ 12.23 eV, indicating the $M_{Cu} = 0$ is the rational magnetic moment for Cu^0 atoms (**Supplementary Fig. 22**).

Revised part in supplementary:

In page 32:



Supplementary Fig. 22. The the total energies of the CuNCN calculated with different magnetic moments of the Cu^0 atoms (MCu = 0, 1, 2, and 3 μB).

Comment 3: The choice of the computationally studied reaction step has not been justfied by the authors. They argue that *CHCOH is formed out of the (also not explicitly justfied) protonated *CO dimer *COCHO. Reference 37 is used as a justification for the choice. However, the reference does not mention the chosen *CHCOH, in their proposed mechanism.

Response: Thank you for pointing out the apparent discrepancy in the justification for our choice of the computationally studied reaction step, specifically the formation of *CHCOH from the protonated *CO dimer (*COCHO), and the reference provided for this choice. The clarification you seek is fundamental to ensuring the integrity and coherence of our study, and I appreciate the opportunity to address this concern.

Upon reviewing your comment and revisiting our manuscript, we recognize that the connection between our chosen reaction step and the justification provided was not adequately clarified. This lack of clarity inadvertently led to confusion regarding the basis of our computational analysis. Here is how we intend to address and resolve these concerns:

Clarification and Expanded Justification: We have revised the manuscript to include a more detailed justification for focusing on the *CHCOH formation step. This involves a deeper dive into existing literature and theoretical studies that suggest or support the viability and relevance of this step in similar catalytic systems. Our goal is to establish a stronger rationale for investigating this reaction step, even if it was not explicitly mentioned in Ref. 37. As the *CHCOH can proceed to ethanol through further carbon protonation, or to ethylene by leaving an oxygen atom, it is frequently recognized as a critical intermediate to differentiate the competing ethanol and ethylene formation during CO_2RR *(J. Am. Chem. Soc.* 2019, 141, 21, 8584–8591; *Proc. Natl. Acad. Sci.* 2023, 120, e221898712; *ACS Catal.* 2023, 13, 15448–15456). These relevant references have been cited in the revised manuscript.

Supplementary Computational Studies: Acknowledging the gap in direct literature support for our chosen reaction step, we carefully undertake supplement computational studies to address the reviewer's concern. For the calculation, we explored alternative intermediates and pathways that have been explicitly mentioned in the literature to ensure a comprehensive analysis of possible reaction mechanisms. This will not only fortify our manuscript but also provide valuable insights into the catalytic process under study. Specially, the free energy difference between *CHCOH and *COCHO were calculated and shown below, the exothermic free energy change of -3.80 eV suggests the formation of *CHCOH out of *COCHO is highly favorable in thermodynamics.

We are grateful for the opportunity to address this valuable suggestion from your comment. We believe that by implementing the above steps, our manuscript will offer a more compelling and scientifically sound contribution to the field.

Revised part in manuscript:

In page 14:

Mechanisms for the generation of C_2H_4 product have been widely explored and many different reaction pathways have been proposed.[44,45] The *CO mechanism was preferred for $Cu^{\delta+}$NCN than the *OCHO mechanisms due to the continuous generation of the CO product with the formation of C_2H_4 in the testing window as shown in **Fig. 3b**. By combing the results of *operando* ATR-SEIRA analysis (**Fig. 4i**), the hydrogenated *CO dimer (*COCHO) formed a key C_2 intermediate *CHCOH after a sequence of proton and electron transfer steps.[46] As a later key stage of the C_2 pathway, the hydrogenation of *CHCOH can lead to branching pathways to either ethylene or ethanol. On the basis of reaction free energies (ΔG) calculated at constant potential of -0.8 V in **Fig 5c**, the *CHC pathway representing the formation of ethylene was proved to be more energetically favorable with a free energy change of -1.02 eV, much lower than that for *CHCHOH (ΔG = -0.68 eV), the typical pathway for ethanol. We further studied the kinetic barrier of this step, the barrier of *CHCOH → *CHCHOH is 1.07 eV, while the barrier of *CHCOH → *CHC is only 0.64 eV, indicating the formation of ethylene via *CHC intermediate is more favorable than the formation of ethanol in kinetics, consistent with our experimental results. Together, the reaction pathway of CO_2 to C_2H_4 on $Cu^{\delta+}$NCN was proposed as: CO_2 →*CO → *COCO→*COCHO→*CHCOH →*CHC → C_2H_4 based on the both operando characterization and theoretical calculations (**Fig 5c**).

In page 19:

44 Kastlunger, G., Heenen, H. H. & Govindarajan, N. Combining First-Principles Kinetics and Experimental Data to Establish Guidelines for Product Selectivity in Electrochemical CO_2 Reduction. *ACS Catal.* **13**, 5062-5072 (2023).

45 Li, X., Wu, X., Lv, X., Wang, J. & Wu, H. B. Recent advances in metal-based electrocatalysts with hetero-interfaces for CO_2 reduction reaction. *Chem Catal.* **2**, 262-291 (2022).

46 Li, Y. C. *et al.* Binding Site Diversity Promotes CO_2 Electroreduction to Ethanol. *J. Am. Chem. Soc.* **141**, 8584-8591 (2019).

In page 24:

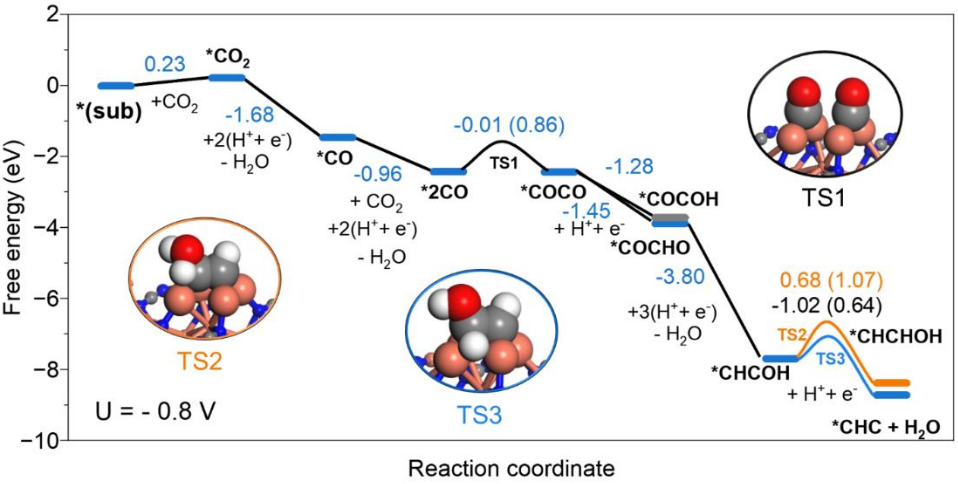


Fig. 5c Free energy profiles of the involved reaction intermediates under U = -0.8 V, the corresponding kinetic barriers of key reaction steps are provided in the brackets, the atomic structures of the transition states are shown in the insets.

Comment 4: In Fig. 3b, the selectivity of CuNCN towards H_2 is significantly lower than the values found in the analogous result in Fig. S22 of Ref. 27. Is there an explanation for this improvement in selectivity?

Response: Thank you for your attentive comparison of the selectivity data presented in Fig. 3b of our manuscript with the analogous results depicted in Fig. S22 of Ref. 27. The observed discrepancy in the selectivity towards H_2 arising from the use of CuNCN catalysts warrants a thorough explanation.

Here are several potential factors that could explain the improvement in selectivity in our study:

The main reason for the difference in selectivity is the fact that the test method we used during the CO_2RR test was a flow cell setup and the electrolyte of choice was 1 M KOH, whereas the test in ref you mentioned (https://doi.org/10.1038/s41929-022-00887-z) used MEA based electrolyzer, which is the main reason for the difference in selectivity. Specifically, in MEA, the catalyst is in direct contact with the proton membrane and the local pH is much lower than in the flow cell. In contrast, the flow cell employing 1 M KOH benefits from a higher pH value, which is more conducive to suppressing the Hydrogen Evolution Reaction process. The influence of pH on the selectivity of CO_2RR products is also proved by *Georg Kastlunger et.al.* (*ACS Catal.* **2023**, 13, 7, 5062–5072). They reported the major role played by the electrode potential and electrolyte pH in determining the selectivity toward ethylene, oxygenates, and methane from both the experimental and theoretical perspective.

On the other hand, due to the use of gas diffusion electrodes during the flow cell test, it is more difficult for water vapor to pass through the electrodes to reach the catalyst surface, and thus the Faraday efficiency of H_2 can be reduced. In addition, minor differences such as catalyst preparation and pretreatment, catalyst composition and structure, and measurement and analysis techniques can lead to incomplete reproducibility of test results.

Revised part in manuscript:

44 Kastlunger, G., Heenen, H. H. & Govindarajan, N. Combining First-Principles Kinetics and Experimental Data to Establish Guidelines for Product Selectivity in Electrochemical CO_2 Reduction. *ACS Catal.* **13**, 5062-5072 (2023).

Comment 5: The calculated reaction energetics in figure 5d, bear little information. As the chosen step is quite likely not rate limiting it does not give information on the activity of the catalyst. Further, since the thermodynamics are exergonic and no kinetic information there is no way to estimate relative reaction rates to ethylene or ethanol from this result.

Response: Thank you for your critical comments on the reaction energetics presented in Fig. 5d of our manuscript. Your analysis highlights an essential aspect of catalytic research, that is the identification and characterization of the rate-limiting step and its relationship to the overall catalytic activity and selectivity. Additionally, the absence of kinetic data alongside the thermodynamic information indeed limits the ability to predict relative reaction rates. We carefully reviewed and referred some impressive works in this filed to help us to revise the manuscript (*Nat. Commun.,***2024***,* **15**, 938; *ACS Catalysis* **2023,** *13*, 5062; Chem Catal. **2022**, 2, 262-291). These published works have provided detailed microkinetic simulations to study the CO_2RR mechanism and the understanding of the selectivity toward various products.

Considering this, we have undertaken the following steps to address these concerns and enhance the value of the information presented in our manuscript:

Kinetic Analysis: We complemented our thermodynamic analysis with kinetic modeling or microkinetic simulations that can provide insights into the expected reaction rates based on the calculated energy barriers. The kinetic barrier of the key step in the C_2 pathway were calculated and shown below, the kinetic barrier of *CHCOH hydrogenation to*CHCHOH is 1.07 eV, while the hydrogenation barrier of *CHCOH to *CHC is only 0.64 eV, indicating the formation of ethylene via *CHC intermediate is more favorable than the formation of ethanol in kinetics, consistent with our experimental results.

Mechanism of Selectivity: To provide a more complete picture of the catalyst's mechanism for the production of C_2H_4, we have implemented a comparison of the reactivity towards different products such as ethylene and ethanol from the view of both *operando* electrochemical process and the DFT calculations. Based on these supplement data and related analysis, we have carefully revised the manuscript, ensuring that both thermodynamic and kinetic aspects together with the experimental results are considered to provide a comprehensive understanding of the catalyst's behavior.

Revised part in manuscript:

In page 3:

Carbon conversion via electrochemical CO_2 reduction reaction (CO_2RR) provides a promising solution to mitigate rising CO_2 levels and simultaneously production of fuels and value-added feedstocks.[1-3]

In page 14:

Mechanisms for the generation of C_2H_4 product have been widely explored and many different reaction pathways have been proposed.[44,45] The *CO mechanism was preferred for $Cu^{\delta+}$NCN than the *OCHO mechanisms due to the continuous generation of the CO product with the formation of C_2H_4 in the testing window as shown in **Fig. 3b**. By combing the results of *operando* ATR-SEIRA analysis (**Fig. 4i**), the hydrogenated *CO dimer (*COCHO) formed a key C_2 intermediate *CHCOH after a sequence of proton and electron transfer steps.[46] As a later key stage of the C_2 pathway, the hydrogenation of *CHCOH can lead to branching pathways to either ethylene or ethanol. On the basis of reaction free energies (ΔG) calculated at constant potential of -0.8 V in **Fig 5c**, the *CHC pathway representing the formation of ethylene was proved to be more energetically favorable with a free energy change of -1.02 eV, much lower than that for *CHCHOH (ΔG = -0.68 eV), the typical pathway for ethanol. We further studied the kinetic barrier of this step, the barrier of *CHCOH → *CHCHOH is 1.07 eV, while the barrier of *CHCOH → *CHC is only 0.64 eV, indicating the formation of ethylene via *CHC intermediate is more favorable than the formation of ethanol in kinetics, consistent with our experimental results. Together, the reaction pathway of CO_2 to C_2H_4 on $Cu^{\delta+}$NCN was proposed as: $CO_2 \rightarrow {}^*CO \rightarrow {}^*COCO \rightarrow {}^*COCHO \rightarrow {}^*CHCOH \rightarrow {}^*CHC \rightarrow C_2H_4$ based on the both operando characterization and theoretical calculations (**Fig 5c**).

In page 19:

3 Abdellah, A. M. *et al.* Impact of palladium/palladium hydride conversion on electrochemical CO_2 reduction via in-situ transmission electron microscopy and diffraction. *Nat. Commun.* **15**, 938 (2024).

44 Kastlunger, G., Heenen, H. H. & Govindarajan, N. Combining First-Principles Kinetics and Experimental Data to Establish Guidelines for Product Selectivity in Electrochemical CO_2 Reduction. *ACS Catal.* **13**, 5062-5072 (2023).

45 Li, X., Wu, X., Lv, X., Wang, J. & Wu, H. B. Recent advances in metal-based electrocatalysts with hetero-interfaces for CO_2 reduction reaction. *Chem Catal.* **2**, 262-291 (2022).

In page 24:

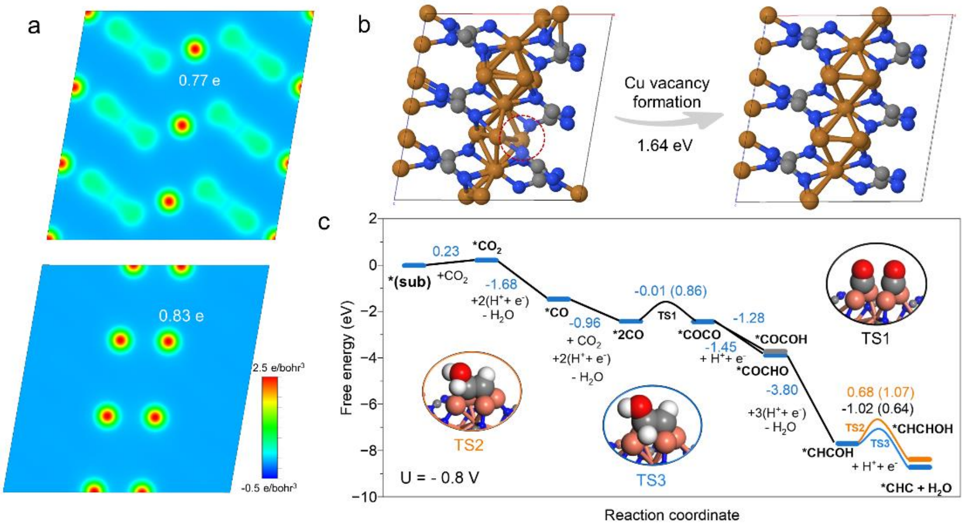


Fig. 5 DFT calculations. a Charge density section plots of surface Cu atoms and second layer Cu atoms of $Cu^{\delta+}$NCN. **b** The formation energy of surface Cu. **c** Free energy profiles of the involved reaction intermediates under U = -0.8 V, the corresponding kinetic barriers of key reaction steps are provided in the brackets, the atomic structures of the transition states are shown in the insets.

Comment 6: The definition of cavity formation energy is not specific enough. In the supporting material, the authors write that the chemical potential of Cu after desorption is the energy of a single Cu atom, but it is not specified whether they refer to an atom in vacuum or an atom in Cu-metal.

Response: Thank you for your attention to the details regarding the definition of cavity formation energy, specifically concerning the chemical potential of copper (Cu) after desorption. Your observation about the lack of specificity in our description is helpful to avoid any ambiguity in our computational methodology.

The chemical potential of Cu after desorption should indeed be specified in a context that is meaningful for the calculations. The two scenarios you mentioned is Cu as an isolated atom in vacuum and Cu as an atom in bulk Cu-metal, which represent very different reference states that can significantly impact the calculation of the cavity formation energy. In our work the energy of single Cu atom refers to an isolated Cu atom in vacuum.

We have updated the main manuscript and supporting material to clearly state the reference state used for the chemical potential of Cu. This carefully suggestion ensure that the reference state used for the chemical potential is consistent with standard computational practices for calculating cavity formation energies.

Revised part in manuscript:

In page 14:

Meanwhile, the formation energy of surface Cu (Cu^0) was calculated to investigate the stability such surface Cu^0 by assuming an isolated Cu atom in vacuum. As shown in **Fig. 5b**, in comparison with the cohesive energy of bulk Cu (Cu^{1+}) (-4.27 eV), the formation energy of surface Cu^0 is calculated to be 1.64 eV, suggesting that the surface Cu atoms was relatively unstable relative to bulk Cu^{1+}.

Revised part in supplementary:

In page 10:

The Cu vacancy formation energy was defined as:

$$E_{vf} = \mathrm{E}_{vac} + E_{Cu} - E_{tot} \tag{3}$$

where E_{vac} is total energy of the structure with a surface Cu vacancy, E_{Cu} is the energy of a single Cu atom, E_{tot} is the total energy of the pristine structure without any defects. In this work the energy of single Cu atom refers to an isolated Cu atom in vacuum.

Finally, we express our sincere gratitude to the editor and reviewers for dedicating their valuable time and providing insightful comments, which have significantly contributed to improving the quality of our paper and shaping our future research direction. We have carefully addressed all the comments and suggestions raised by the reviewers, we hope that the reviewer understand and support our efforts and our revised manuscript meets the standards of *Nature communication*. We appreciate your understanding and support and look forward to the opportunity to share our work with the scientific community. Thank you once again for your invaluable contribution.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

All the questions have been addressed. The manuscript is ready for publication.

Reviewer #2 (Remarks to the Author):

The authors have addressed most of the issues raised by the reviewer, however, the following questions still need to be addressed before publication.
1. In the response to comment 3, corresponding descriptions about EXAFS fitting are not appropriate. Considering the coordination of N, C, and O with Cu is difficult to be distinguished by EXAFS, it is suggested to describe the scattering paths using Cu-N/C/O and Cu-Cu, instead of the Cu-N and Cu-Cu.
2. In the response to comment 6, the authors claimed that the coexisting Cu0 and Cu+ are truly active sites and the coordination stability of Cu-N is crucial for Cuδ+NCN to maintain its catalytic stability. However, the reviewer found that Cu-Cu coordination began to appear before the potentials where the optimal FEC2H4 was obtained, indicating that Cu-Cu clusters might also play crucial roles in dominating product profile. The authors should clearly explicate this.
In addition, the authors emphasized that the aggregation of Cu clusters is only a surface thermodynamic effect according to their theoretical calculations, based on which they concluded that the formation of Cu clusters did not originate from Cu-N bond breaking. This is unreasonable because the newly formed Cu clusters originate from initial Cu-N/C/O species, the concern is how to realize the formation of newly formed phase without the breaking of initial bonds?

Reviewer #4 (Remarks to the Author):

It is well noted and appreciated that the Authors have taken *considerable measures to improve their work*, with reference to the comments received during the first round of review.
Notably, the computational results have been significantly bolstered, better suited to the purpose of the explanation and interpretation of and support for the experimental results.
However, there remain *issues which ought to be addressed* before I can recommend the paper for publication.

(Having aided the previous Referee #3 in their review of the manuscript, the following will mostly be a mix of my further assessments of the changes made in response to their comments.
However, there are also other points of note, pertaining to the rest of the manuscript and to other Referees' comments, particularly in regard to the theoretical parts of the paper.
It is also noted that this review is written with reference to and in brief consultation with the previous Referee #3.)

Referee #3, Comment #1

The *additional references* on P. 12 for the assignment of the *COCO and *COCHO peak wavenumbers are well received.
However, the positioning of the citations seem to indicate that they pertain only to the former surface species, but not the latter.
I would suggest moving the reference or rephrasing the text.

Referee #3, Comment #2

The Authors have addressed the concern of the sampling of magnetic states with the addition of Supp. Fig. 22, showing that *the choice of the non-magnetized Cu^0 site is justified*.
However:
- Where possible, I would like to suggest an additional data point of an antiferromagnetic arrangement of the surface Cu^0 sites, which many require an enlargement of the simulation cell though.
- Speaking of which, it is noticed that details on the construction of the simulation cell of Cu^{δ+}NCN is left scarce and scattered (Supp. Figs. 4, 21).

For clarity, *the structure should be more clearly shown* as with Supp. Figs. 1 and 2, which conveyed the structures of CuNCN and CuO well respectively.

Referee #3, Comments #3, 5

The Authors have supplied *references* (P. 14) supporting the importance of the *CHCOH state and acknowledging the complexity of the web of reactions, as well as having vastly improved the utility of the DFT calculations by supplying a *free-energy diagram with barriers esp. at the final step* (Fig. 5c), illustrating the reaction pathway while corroborating and explaining the experimentally-observed selectivity.
Still:
- *It is unclear as to how the addition of Abdellah et al. (Ref. 3) specifically relates to the comment at hand* (about the quality of the energetics, which the Authors have already immensely improved); nor does it, being a study focused on characterization and mechanisms, seem an apt citation for the "big-picture" point made in the opening sentence of the paper.
- The number 0.68 in Fig. 5c, which refers to the free-energy change for the *CHCOH–*CHCHOH step, seems to be *missing a negative sign* given that it is exergonic.

Referee #3, Comment #4

The Authors have *addressed the discrepancy* shown in the CuNCN Faradaic efficiency towards H_2 with that of Ref. 27 (now Ref. 24), attributing it to the differences in the electrochemical setup.
While it can be inferred from context in the running text of the manuscript (P. 7) that the results shown in Fig. 3b (and a, c, d, and e) are measured with a flow-cell setup, as opposed to the MEA setup illustrated in Fig. 3f and used for the results in Fig. 3g–h, such is unclear from the standalone Figure, which combines the two kinds of results and visually very prominently features the MEA cell

in Fig. 3f.
I would highly recommend *better qualifying the results in Figs. 3a–e* with their respective captions.

Referee #3, Comment #6

The Authors have *clarified their use of the atomic reference state* by the additions on P. 14 of the manuscript and P. 10 of the Supplementary Information on Methods.
Still, it is to be considered *whether it is physically sound* to directly compare the (per-Cu-atom) cohesion energy, a bulk quantity, with the vacancy formation energy of a single surface site.
Directly computing the energetic difference between single Cu vacancies [surface (Cu^0) and bulk (Cu^{1+})] would be in my opinion way more conducive to the comparison of the stabilities of the two Cu sites – while eliminating the need to choose a reference state for Cu altogether.

Referee #1, Comment #5

In the Authors' reply to the comment, which inquired about theoretical/computational support for the asserted roles of the variation of Cu oxidation states in C–C coupling, they point to the existing DFT calculations of the charge distribution (Fig. 5a), as well as the new free-energy diagram of the CO2–*CHC pathway (Fig. 5c).
While the calculation results do support the experimentally-observed variance in oxidation states, it would seem to me that the crux of the issue, that is, the mechanism through which this variation in Cu oxidation states "creates an optimal electronic environment [for C–C coupling]" as is written in the Rebuttal, has not been directly addressed.

It is suggested that either (1) the free-energetic analysis be repeated on surfaces without the mix of Cu oxidation states, *establishing the Cu^{0/1+} baselines with which Cu^{δ+}NCN can be compared*;
or (2) that additional references to the existing theoretical literature be added which covers the mechanistic issue.
In addition, there are also other points of note:
- On P. 13, Fig. 5a, and Supp. Fig. 23, the Authors produce the numbers 0.83 and 0.77 electrons for the "charge density" around the Cu^{1+} and Cu^0 sites respectively. However, *it is unclear how these site-localized numbers are obtained* from the continuous charge distribution.
Any method used (e.g. PAW-based projection, Bader/Mulliken analysis) should be specified in the text, figure captions, and/or the Supplementary Information on Methods.
- On P. 13–14, the Authors refer to Supp. Fig. 23 which illustrates a charge transfer from the substrate to the surface sites, and asserted that "such electron distribution [is] vital for the stabilization of oxidized Cu^{1+} and the preserv[ation] of surface neutral Cu^0".
However, to me *the strength of the statement would require additional support* as to how the charge transfer and the stabilization/preservation are related.

Dear Reviewers,

Thank you again for considering our manuscript "*Stabilized* Cu^0-Cu^{1+} *Dual Sites in Cyanamide Framework for Highly Selective* CO_2 *Electroreduction to Ethylene*" and for providing the opportunity to address the comments and concerns raised by the reviewers. We are grateful for the feedback which is instrumental in strengthening the quality and impact of our research.

We recognize the importance of the concerns regarding the X-ray characterization and the computational analysis as highlighted by *Referees #2* and *#4*. We are committed to performing the recommended experiments and additional analyses to address these technical concerns comprehensively.

We believe that the additional work and revisions will substantially improve the manuscript and address the critical points necessary for the advancement of our work in this field. We thank the reviewers for their constructive feedback and look forward to submitting a revised manuscript that meets the high standards of *Nature Communications*.

Note: In the response manuscript, comments suggested by reviews are in blue font, our responses are in **black font**, and revised parts in the text and SI are highlighted in yellow. The figures in our Manuscript, Supplementary Information and Response documents are displayed in the form of Fig. XX, Supplementary Fig. XX and Fig. R XX.

Reviewer #1 All the questions have been addressed. The manuscript is ready for publication.

Response: I am truly grateful for your time and effort put into the review process of my paper. I appreciate the thoroughness of your review and your affirmation of my work.

Reviewer #2 The authors have addressed most of the issues raised by the reviewer, however, the following questions still need to be addressed before publication.

Response: We would like to express our sincere gratitude for your thorough review and constructive feedback on our manuscript. We acknowledge that there are still questions that need to be addressed, and we are committed to providing the necessary clarifications and revisions to meet the high standards. Below, we address each of the remaining questions:

Comment 1: In the response to comment 3, corresponding descriptions about EXAFS fitting are not appropriate. Considering the coordination of N, C, and O with Cu is difficult to be distinguished by EXAFS, it is suggested to describe the scattering paths using Cu-N/C/O and Cu-Cu, instead of the Cu-N and Cu-Cu.

Response: Thank you for your thorough review and valuable comments on our manuscript, especially regarding the EXAFS fitting descriptions. Your insight has helped highlight an important aspect of our analysis that can be improved for clarity and accuracy.

In response to your comment on the difficulty of distinguishing between the coordination of N, C, and O with Cu using EXAFS, we agree with your suggestion to describe the scattering paths in a more generalized and accurate manner. The specificity of Cu-N, Cu-C, and Cu-O paths indeed presents a challenge in differentiation due to the similar scattering strengths and distances involved in these interactions.

To address this, we have revised the corresponding sections of our manuscript to use the more reasonable term "Cu-N/C/O and Cu-Cu" instead of specifically mentioning "Cu-N and Cu-Cu". This change reflects a more accurate representation of the EXAFS analysis, acknowledging the complexity and limitations in distinctly identifying the coordination of Cu with N, C, and O atoms. We believe this modification improves the manuscript by providing a clearer and more technically sound description of the EXAFS fitting results.

Revised part in manuscript:

In page 6: The Cu–N/C/O coordination number (CN) of Cu$^{\delta+}$NCN was confirmed to be 1.6, smaller than that of Cu$_2$NCN (CN=2) in the first coordination layer by fitting the EXAFS spectra (**Supplementary Table 2&3**). By integrating the structural information observed from Cu$^{\delta+}$NCN: the Cu–N/C/O coordination number in EXAFS being less than the theoretical value, the average valence state residing between 0 and +1 in the XAS

K-edge, and the presence of both Cu^0 and Cu^{1+} atoms indicated by the Cu LMM Auger spectrum, we can deduce that both Cu^0 and Cu^{1+} coexist on the surface of $Cu^{\delta+}NCN$.

In page 21:

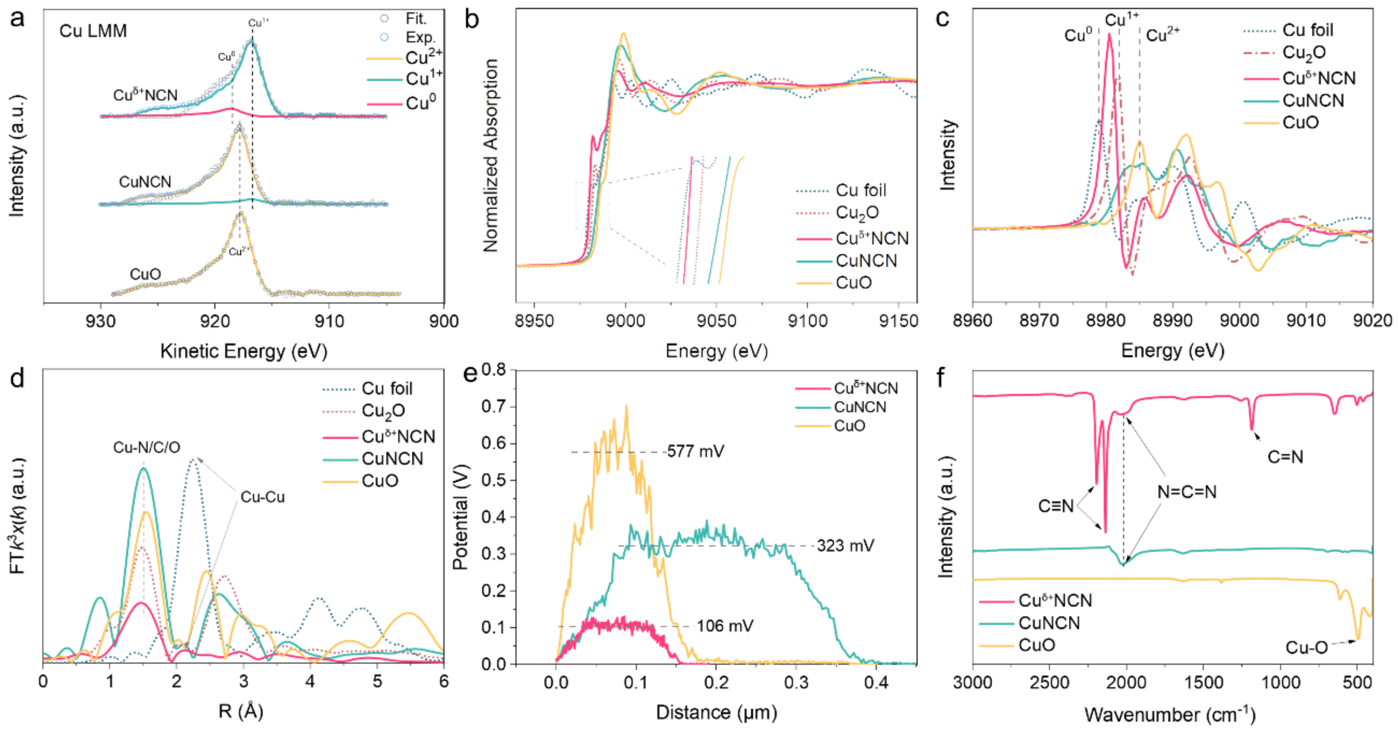


Fig. 2 Electronic and fine structural characterizations. a Cu LMM spectra of $Cu^{\delta+}NCN$, CuNCN and CuO. **b** Normalized Cu *K*-edge XANES spectra and **c** the derived normalized $\chi\mu(E)$ spectra of $Cu^{\delta+}NCN$, CuNCN, CuO, Cu foil and standard Cu_2O samples. **d** FT-EXAFS spectra of $Cu^{\delta+}NCN$, CuNCN, CuO, Cu foil and standard Cu_2O samples. **e** Surface potential profiles of $Cu^{\delta+}NCN$, CuNCN and CuO. **f** FT-IR spectra of $Cu^{\delta+}NCN$, CuNCN and CuO.

In page 23:

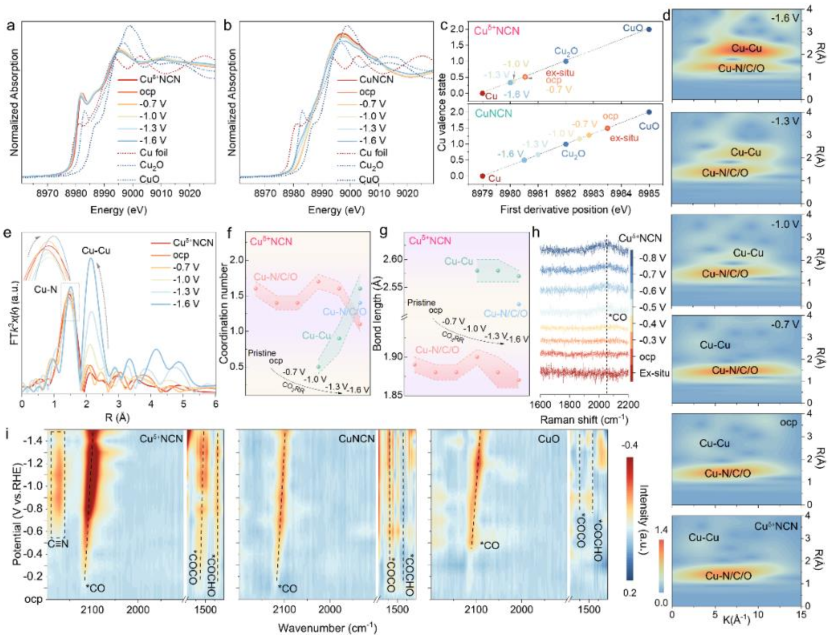
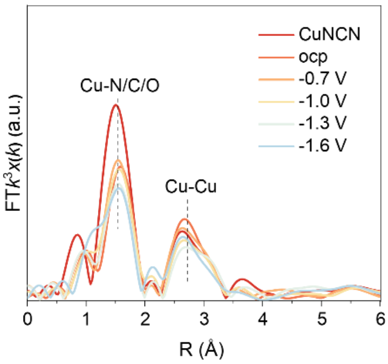


Fig.4. Mechanism investigations. *Operando* XANES spectra of **a** Cu$^{\delta+}$NCN and **b** CuNCN**. c** Fitted linear relationship between the energy position of the Cu *K*-edge in *operando* XANES spectra and the valence state of Cu. **d** Comparison of the EXAFS WTs of the Cu *K*-edge recorded during *operando* testing on Cu$^{\delta+}$NCN. **e** Fourier-transformed k^3-weighted EXAFS signals of the Cu *K*-edge recorded at different potentials on Cu$^{\delta+}$NCN. **f** Changes of coordination number for the Cu–N, Cu–Cu and Cu–N/C coordination shells. **g** Changes of bond length for the Cu–N, Cu–Cu and Cu–N/C coordination shells. **h** *Operando* Raman spectra of Cu$^{\delta+}$NCN. **i** *Operando* ATR-SEIRA spectra of Cu$^{\delta+}$NCN, CuNCN and CuO.

Revised part in supplementary:

In page 22:



Supplementary Fig. 12. Fourier-transformed k^3-weighted EXAFS signals of the Cu *K*-edge recorded at different potentials for the Cu$^{\delta+}$NCN.

Comment 2: In the response to comment 6, the authors claimed that the coexisting Cu^0 and Cu^+ are truly active sites and the coordination stability of Cu-N is crucial for $Cu^{\delta+}$NCN to maintain its catalytic stability. However, the reviewer found that Cu-Cu coordination began to appear before the potentials where the optimal FE_{C2H4} was obtained, indicating that Cu-Cu clusters might also play crucial roles in dominating product profile. The authors should clearly explicate this.

In addition, the authors emphasized that the aggregation of Cu clusters is only a surface thermodynamic effect according to their theoretical calculations, based on which they concluded that the formation of Cu clusters did not originate from Cu-N bond breaking. This is unreasonable because the newly formed Cu clusters originate from initial Cu-N/C/O species, the concern is how to realize the formation of newly formed phase without the breaking of initial bonds?

Response: Thank you once again for the thorough analysis and insightful comments regarding our manuscript. Your expertise has helped us critically evaluate our findings, and we acknowledge the points you have raised. We have re-examined our data and interpretations and provide the following detailed responses to your concerns:

Regarding the claim on Cu^0 and Cu^+ as active sites, we agree that our initial claim regarding the synergetic role of Cu^0 and Cu^+ as active sites may have overlooked the potential contribution of Cu-Cu clusters. The appearance of Cu-Cu coordination at reduction potentials preceding the optimal formation of FE_{C2H4} does suggest a possible influence of these clusters on the product profile.

To address this issue, we conducted additional analyses to further investigate the role of Cu clusters. Specifically, we consider that as the voltage is continuously applied, Cu^0 on the surface of $Cu^{\delta+}$NCN would aggregate due to thermodynamic reasons, and further formation of Cu clusters would occur due to partial breakage of Cu-N bonds. With the generation of Cu clusters, we observed the emergence of a new coordination, confirmed through EXAFS fitting as Cu-N/C/O, potentially suggesting that the presence of Cu-N can stabilize the Cu clusters generated during the reaction. The surface environment of the catalyst at this stage is characterized by the coexistence of Cu^0 and Cu^{1+}. In our previous analysis, the presence of Cu^0 was found to promote the adsorption of *CO, which is consistent with our in situ infrared test results shown in **Fig. 4i**, where $Cu^{\delta+}$NCN exhibited stronger *CO adsorption. Furthermore, theoretical calculations have confirmed that the lowest activation energy required for C-C coupling occurs under conditions where both Cu^0 and Cu^{1+}

coexist (**Fig. 5c**). In summary, in this round of revisions, we have taken into account the formation process of Cu clusters and their impact on the catalytic process. We also emphasize the synergetic role of the Cu^0-Cu^{1+} dual active sites in the formation of ethylene.

In response to the concerns about the formation of Cu clusters without Cu-N bond breaking, we initially concluded that Cu-N bond breaking was not a prerequisite for Cu cluster formation based on our theoretical calculations. However, we recognize that this viewpoint may have been too simplistic and did not fully account for the dynamic nature of the catalytic system. Your comment has prompted us to reconsider our interpretation of the thermodynamics of Cu cluster aggregation and bond stability.

To rectify this, we have revisited our theoretical framework. This is now elucidated in the revised sections, where we present a more detailed and theoretically substantiated explanation of how Cu clusters could originate from the initial Cu-N/C/O species, including potential pathways for bond rearrangement and cluster nucleation.

Specifically, on one hand, the formed $Cu^{\delta+}$NCN is featured with co-existence of Cu^0 and Cu^+, these formed Cu^0 atoms comes from the loss of $[NCN]^{2-}$ due to the addition of reductant during the synthesis process, which are analyzed thermodynamically to gather into clusters from the view of theoretical modelling. On the other hand, during the CO_2 catalytic process with gradually enhanced reduction potential, there will be a few loss of $[NCN]^{2-}$, thus resulting in a small decrease in the Cu-N/C/O coordination number as reflected from EXAFS, accompanied by a decrease in the average valence state of Cu. And these newly reduced Cu atoms will further polymerize into Cu clusters. Overall, we believe that the formation of Cu clusters undergoes both thermodynamic and kinetic effects.

The manuscript has been thoroughly updated to address these valuable concerns and these revisions made have fully strengthen our study and provide a clearer, more accurate representation of the catalytic processes in the $Cu^{\delta+}$NCN system. Finally, we once again appreciate the opportunity to refine our work and hope that these revisions meet your approval.

Revised part in manuscript：

In page 10-11： And when the voltage is further increased to -1.6 V or higher in a flow cell, a significant decrease in the coordination number of Cu-N/C/O on the surface of $Cu^{\delta+}$NCN is observed. This is accompanied by a rapid increase in the coordination number of Cu-Cu, indicating under the more negative voltages, in addition to the small amount of Cu clusters initially aggregated in a thermodynamically favorable manner, new Cu atoms emerged due to the breaking of some Cu-N/C/O bonds.

In page 12： These *CO signal bands were also detected in the *operando* ATR-SEIRA spectra around the 2100 cm^{-1} (**Fig. 4i**), and both the peak intensity and area for $Cu^{\delta+}NCN$ increased much more obviously with the altered potentials compared to that of CuNCN and CuO. This is accompanied by the formation of Cu-Cu cluster as evidenced by the FT-EXAFS results as shown in **Fig. 4f**, suggesting the existence of Cu^0 species have positive effect on the activation of CO_2.

In page 24：

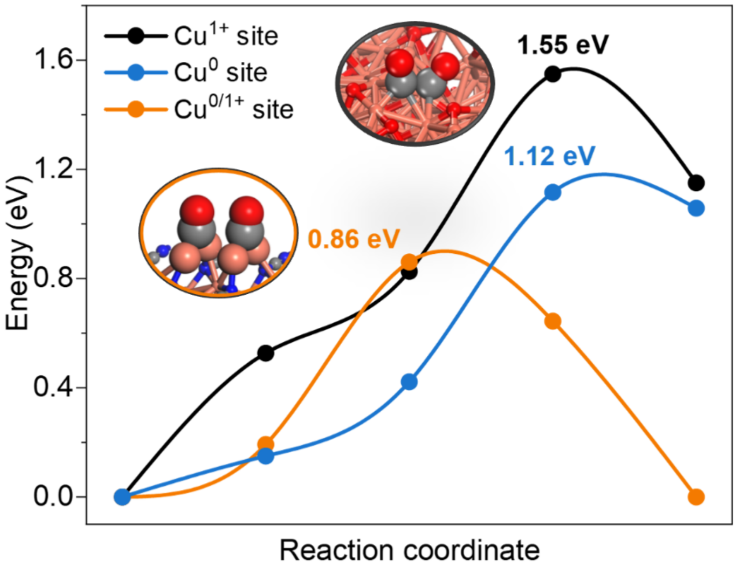


Fig. 5c Energy barriers of *CO-*CO coupling·on the $Cu^{\delta+}NCN$ surface, Cu (111) surface, and Cu_2O (110) surface at U = -0.8 V. The corresponding transition state structures are shown in the insets.

Reviewer #4 It is well noted and appreciated that the Authors have taken *considerable measures to improve their work*, with reference to the comments received during the first round of review.

Notably, the computational results have been significantly bolstered, better suited to the purpose of the explanation and interpretation of and support for the experimental results.

However, there remain *issues which ought to be addressed* before I can recommend the paper for publication.

(Having aided the previous Referee #3 in their review of the manuscript, the following will mostly be a mix of my further assessments of the changes made in response to their comments.

However, there are also other points of note, pertaining to the rest of the manuscript and to other Referees' comments, particularly in regard to the theoretical parts of the paper.

It is also noted that this review is written with reference to and in brief consultation with the previous Referee #3.)

Response: Thank you for your insightful feedback and the carefully assessment of our work along with interaction with the previous Referee #3. We are grateful for the recognition of the considerable efforts we have made to enhance our manuscript, particularly the computational aspects that now better support our experimental findings.

In the revised version, we have fully addressed the remaining issues you have concerned and raised. We are committed to the continuous improvement of our work and appreciate the opportunity to refine our manuscript further. We believe these changes strengthen our submission and hope they meet your approval for publication.

 # Referee #3, Comment #1

The *additional references* on P. 12 for the assignment of the *COCO and *COCHO peak wavenumbers are well received. However, the positioning of the citations seem to indicate that they pertain only to the former surface species, but not the latter. I would suggest moving the reference or rephrasing the text.

Response: Thanks for your attention to detail and for pointing out the ambiguity concerning the positioning of the citations related to the *COCO and *COCHO peak wavenumbers on Page 12 of our manuscript. We recognize the importance of clearly attributing references to ensure that readers can accurately discern which findings they support. To address this, we have carefully reviewed the text and agree that rephrasing would improve the clarity of the citation placement.

In the revised sentence, the references [42, 43] will now clearly pertain to both surface species, *COCO and *COCHO. We hope this change resolves the issue and thank you for your suggestion, which has undoubtedly improved the manuscript.

Revised part in manuscript:

In page 12-13: In parallel, a distinctive peak shoulder around 1530 cm^{-1}corresponding to the *COCO intermediate via *CO dimerization was observed in $Cu^{\delta+}$NCN and increased accordingly with scanning to more negative potentials.[42] Simultaneously, a relatively weak character peak line for *COCHO (1440 cm^{-1}), intermediate of hydrogenation of *CO dimer, was detected.[43]

Referee #3, Comment #2

The Authors have addressed the concern of the sampling of magnetic states with the addition of Supp. Fig. 22, showing that *the choice of the non-magnetized Cu^0 site is justified*.

However:

- Where possible, I would like to suggest an additional data point of an antiferromagnetic arrangement of the surface Cu^0 sites, which many require an enlargement of the simulation cell though.

- Speaking of which, it is noticed that details on the construction of the simulation cell of $Cu^{\delta+}$NCN is left scarce and scattered (Supp. Figs. 4, 21).

For clarity, *the structure should be more clearly shown* as with Supp. Figs. 1 and 2, which conveyed the structures of CuNCN and CuO well respectively.

Response: We greatly appreciate your recognition of our efforts to address the concerns regarding the sampling of magnetic states, as shown in Supplementary Fig. 22. We understand that establishing the justification for the choice of the non-magnetized Cu^0 site is crucial for the integrity of our computational analysis.

In response to your further suggestions:

Additional Antiferromagnetic Arrangement:

We acknowledge the value that adding data on an antiferromagnetic arrangement of the surface Cu^0 sites could bring to our study. Following the reviewer's suggestion, we have expanded the simulation cell by once and calculated the antiferromagnetic arrangement (M_{Cu} = 0 μB) of the surface Cu^0 sites. As shown below, with higher spin of the Cu^0 atoms such as M_{Cu} = 1 and 2 μB, the total energies are significantly higher than which with M_{Cu} = 0 μB by 1.64 and 12.5 eV, respectively, indicating the M_{Cu} = 0 μB is the rational magnetic moment for Cu^0 atoms. Furthermore, the density of states projected on the surface Cu^0 atoms (**Fig. R1b**) shows that the spin-up and the spin-down PDOS are symmetrical with respect to y = 0, indicating antiferromagnetic arrangement of Cu^0.

Simulation Cell Details:

We realize that the details provided on the construction of our simulation cell for the $Cu^{\delta+}NCN$ were insufficient and fragmented across the supplementary figures. To address this, we have consolidated the relevant information into a more coherent format.

These revisions have been incorporated into the supplementary materials as **Supplementary Fig. 21** and in the main manuscript. We believe that these changes not only improve the clarity of our presentation but also facilitate better understanding of our computational methodology.

We are grateful for your guidance and constructive feedback, which have been instrumental in refining and strengthening our manuscript. We hope that these revisions satisfactorily address your concerns and make the paper suitable for publication.

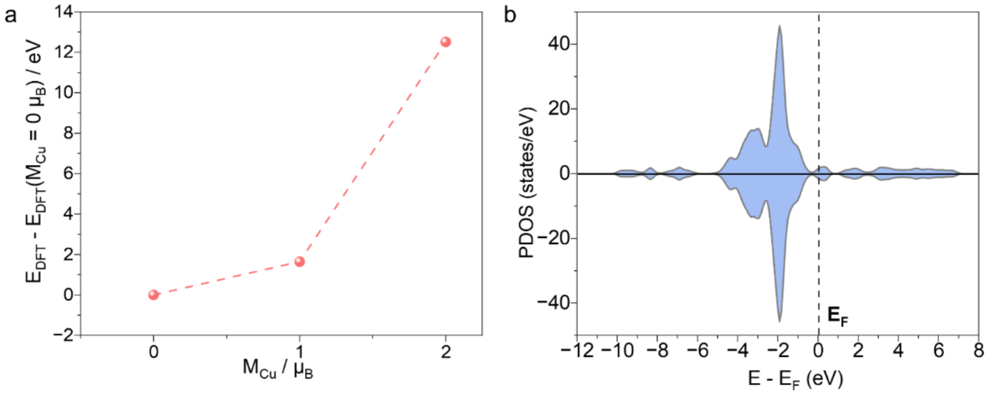
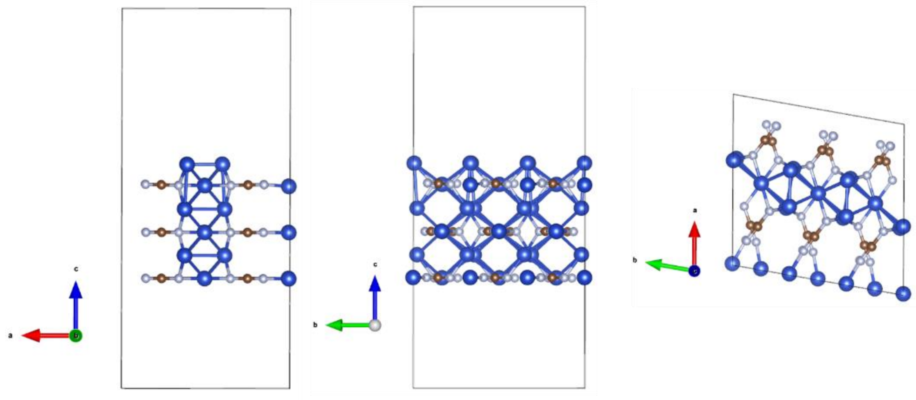


Fig. R1. a The total energies of the $Cu^{\delta+}NCN$ calculated with different magnetic moments of the Cu^0 atoms (M_{Cu} = 0, 1, and 2 μB). **b** The density of states projected on the surface Cu^0 atoms with M_{Cu} = 0 μB.

Revised part in supplementary:

In page 31:



Supplementary Fig. 21. Models of $Cu^{\delta+}NCN$ structure.

Referee #3, Comments #3, 5

The Authors have supplied *references* (P. 14) supporting the importance of the *CHCOH state and acknowledging the complexity of the web of reactions, as well as having vastly improved the utility of the DFT calculations by supplying a *free-energy diagram with barriers esp. at the final step* (Fig. 5c), illustrating the reaction pathway while corroborating and explaining the experimentally-observed selectivity.

Still:

- *It is unclear as to how the addition of Abdellah et al. (Ref. 3) specifically relates to the comment at hand* (about the quality of the energetics, which the Authors have already immensely improved);

nor does it, being a study focused on characterization and mechanisms, seem an apt citation for the “big-picture” point made in the opening sentence of the paper.

- The number 0.68 in Fig. 5c, which refers to the free-energy change for the *CHCOH–*CHCHOH step, seems to be *missing a negative sign* given that it is exergonic.

Response: We appreciate your acknowledgment of the improvements made to the free-energy diagram and the overall clarity of our reaction pathway explanation.

In response to your specific concerns:

Clarification of Reference to Abdellah et al. (Ref. 3):

We apologize for any confusion caused by the inclusion of Abdellah et al. (Ref. 3) on Page 14. Upon review, we agree that this reference, which primarily focuses on characterization and mechanisms, does not directly address the quality of the energetics discussed in our manuscript. To rectify this, we have removed the reference from the current context and another review-type reference related with electrochemical CO_2 reduction to multi-carbon products over copper-based catalysts is added.

We appreciate your attention to detail and your observation regarding the omission of the negative sign in the free-energy change value for the *CHCOH–*CHCHOH step in Fig. 5c (Fig. 5d in this version). We acknowledge that this reaction is exergonic, and the free-energy change should indeed be negative. To correct this oversight, we have updated Fig. 5d to include the appropriate negative sign, reflecting the true thermodynamic nature of the reaction. The revised Fig. 5d has been re-uploaded to ensure the accuracy and clarity of our work. We are committed to maintaining the highest standards of precision in our research and thank you for your valuable input.

Revised part in manuscript:

In page 24:

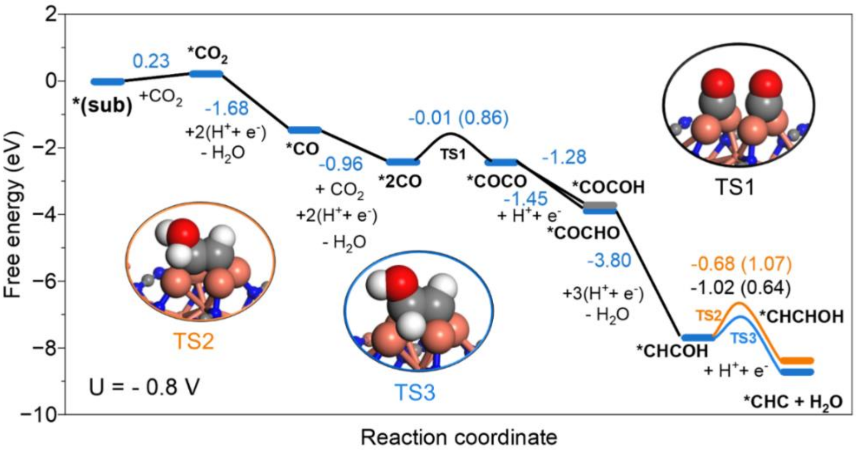


Fig. 5d Free energy profiles of the involved reaction intermediates under U = -0.8 V, the corresponding kinetic barriers of key reaction steps are provided in the brackets, the atomic structures of the transition states are shown in the insets.

In page 17:

3 Woldu, A. R., Huang, Z., Zhao, P., Hu, L. & Astruc, D. Electrochemical CO^2 reduction (CO_2RR) to multi-carbon products over copper-based catalysts. *Coord. Chem. Rev.* **454**, 214340 (2022).

Referee #3, Comment #4

The Authors have *addressed the discrepancy* shown in the CuNCN Faradaic efficiency towards H_2 with that of Ref. 27 (now Ref. 24), attributing it to the differences in the electrochemical setup.

While it can be inferred from context in the running text of the manuscript (P. 7) that the results shown in Fig. 3b (and a, c, d, and e) are measured with a flow-cell setup, as opposed to the MEA setup illustrated in Fig. 3f and used for the results in Fig. 3g–h, such is unclear from the standalone Figure, which combines the two kinds of results and visually very prominently features the MEA cell in Fig. 3f.

I would highly recommend *better qualifying the results in Figs. 3a–e* with their respective captions.

Response: Thank you for your continued attention to detail and valuable feedback on our manuscript. We appreciate the opportunity to further clarify the distinctions between the electrochemical setups used in our experiments, as represented in Fig 3.

In response to your recommendation, we have taken several steps to clarify and ensure consistency in the presentation of our electrochemical setup throughout the manuscript. Specifically, we have updated Fig. 3a–e to explicitly state that these results were obtained using a flow-cell setup, thereby eliminating any potential confusion. Additionally, we have thoroughly reviewed the running text to ensure that it consistently and clearly indicates the setup used for each set of results. Any ambiguity has been addressed, and we have revised the text to explicitly associate the flow-cell setup with the results in Fig. 3a–e and the MEA setup with the results in Fig. 3g–h. We appreciate your insightful comments and the opportunity to enhance the clarity and precision of our manuscript.

Revised part in manuscript:

In page 22:

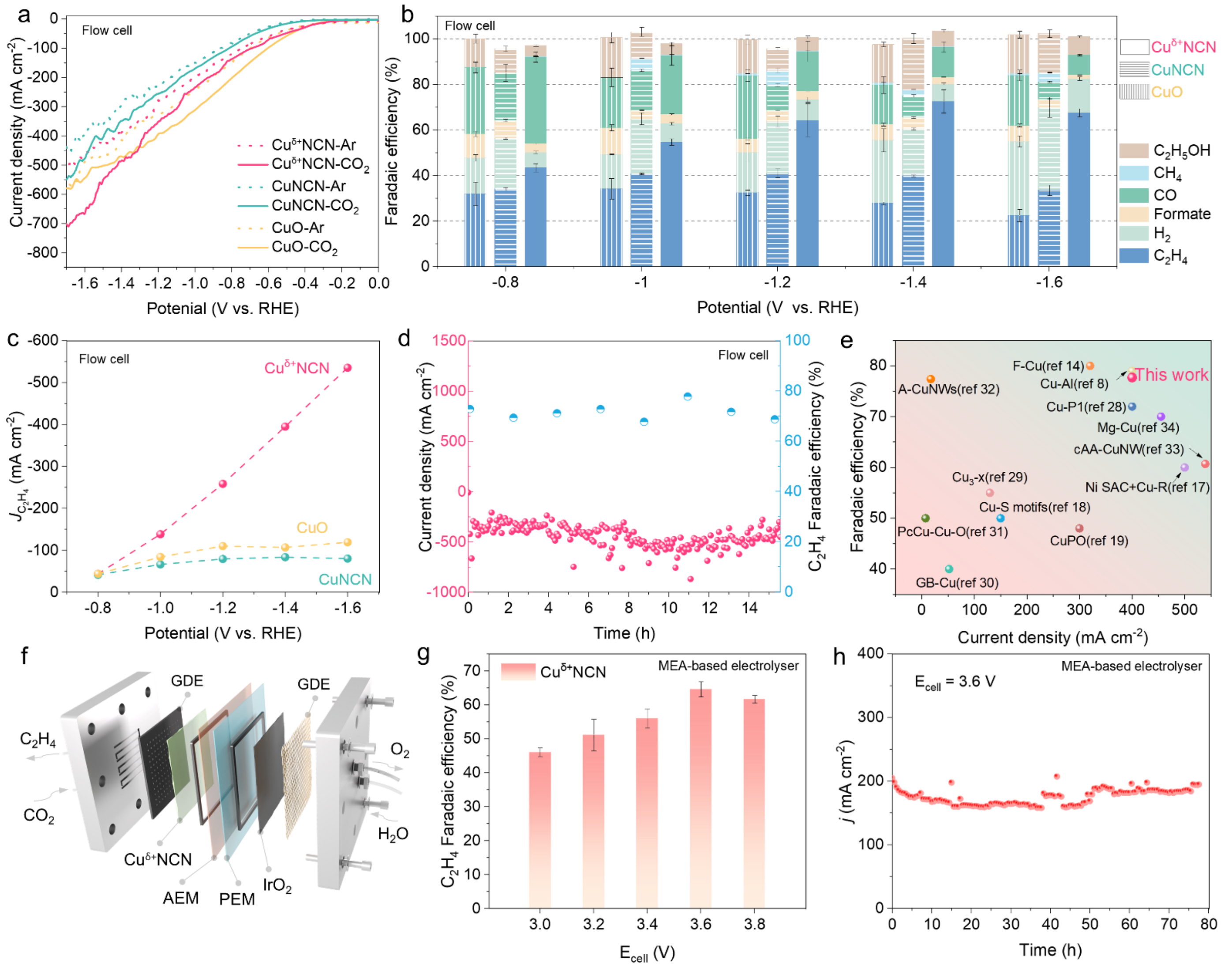


Fig. 3 CO_2 electroreduction performances. **a** LSV curves of $Cu^{\delta+}$NCN, CuNCN and CuO in a flow cell under CO_2 or Ar atmospheres. **b** FE of various products from $Cu^{\delta+}$NCN, CuNCN and CuO at different potentials in a flow cell. **c** Ethylene partial current densities of $Cu^{\delta+}$NCN, CuNCN and CuO at various potentials in a flow cell. **d** Performance of $Cu^{\delta+}$NCN in a three-electrode flow cell to produce ethylene. **e** Comparison of the $FE_{C_2H_4}$ and reduction current of $Cu^{\delta+}$NCN with recently reported catalysts. **f** Schematic illustration of the APMA-MEA biphasic electrode system apparatus. **g** $FE_{C_2H_4}$ of $Cu^{\delta+}$NCN at various potentials in a biphasic electrode MEA system. **h** Stability performance of $Cu^{\delta+}$NCN within the MEA to produce ethylene.

Referee #3, Comment #6

The Authors have *clarified their use of the atomic reference state* by the additions on P. 14 of the manuscript and P. 10 of the Supplementary Information on Methods.

Still, it is to be considered *whether it is physically sound* to directly compare the (per-Cu-atom) cohesion energy, a bulk quantity, with the vacancy formation energy of a single surface site.

Directly computing the energetic difference between single Cu vacancies [surface (Cu^0) and bulk (Cu^{1+})] would be in my opinion way more conducive to the comparison of the stabilities of the two Cu sites – while eliminating the need to choose a reference state for Cu altogether.

Response: We are grateful for your continued engagement with our manuscript and your insightful comments on the use of the atomic reference state in our analysis. Your suggestion to directly compare the energetic differences between single Cu vacancies on the surface and in the bulk presents a compelling alternative to our initial approach.

In response to your recommendation, we have re-calculated the vacancy formation energies for both the surface Cu^0 site and the bulk Cu^{1+} site. This direct computation allows for a more physically intuitive comparison of the stability between these two sites, thereby simplifying the analysis and eliminating potential misinterpretations that could arise from considering bulk cohesion energy. The vacancy formation energy of bulk Cu^{1+} in $Cu^{\delta+}NCN$ was calculated, which is 4.79 eV, significantly higher than which of the surface Cu^0 (1.64 eV), indicating the bulk Cu^{1+} is more stable than surface Cu^0. Besides, this new approach and the corresponding results have been included in the manuscript and in the Supplementary Information in the Methods section.

Thank you once again for your constructive critique, which has significantly contributed to the enhancement of our research presentation.

Revised part in manuscript:

In page 14: Meanwhile, for Cu^0 and Cu^{1+} in the surface and bulk phases, we calculated the vacancy formation energies of bulk Cu^{1+} and surface Cu^0 in $Cu^{\delta+}NCN$, respectively, and the results, as shown in **Fig. 5b**, show that the vacancy formation energy of Cu^{1+} (4.79 eV), is significantly higher than that of the surface Cu^0 (1.64 eV), which suggests that the bulk Cu^{1+} is more stable than the surface Cu^0.

In page 24:

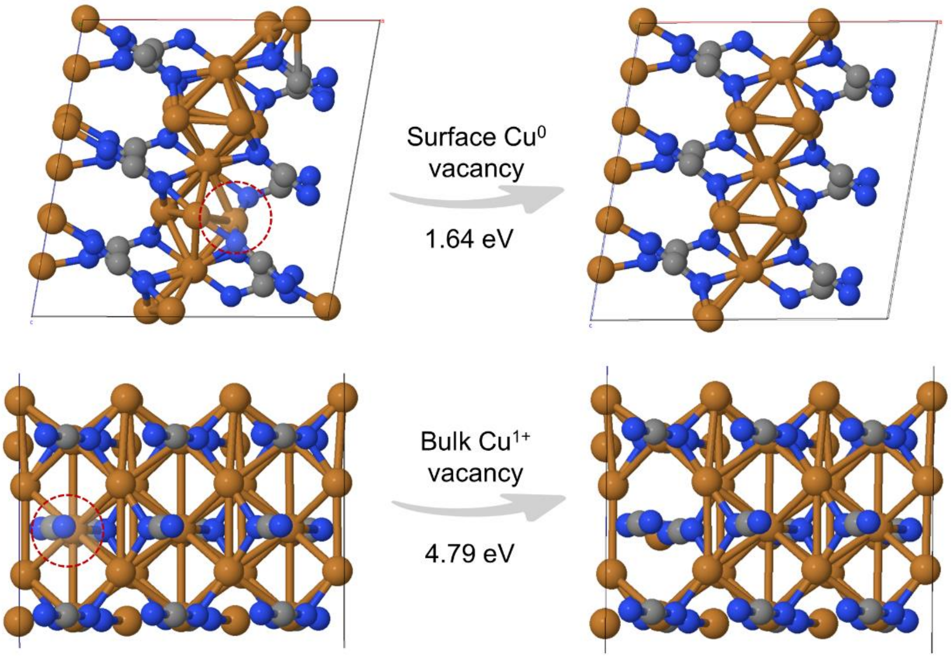


Fig. 5b Vacancy formation energy of surface Cu^0 and bulk phase Cu^{1+}.

Revised part in supplementary:

In page 10: Formation energy of a Cu vacancy.

The surface Cu^0 and bulk phase Cu^{1+} vacancy formation energies are defined as:

$$E_{vf} = \mathrm{E}_{vac} + E_{Cu} - E_{tot} \tag{3}$$

where E_{vac} is total energy of the structure with a Cu vacancy, E_{Cu} is the energy of a single Cu atom, E_{tot} is the total energy of the pristine structure without any defects. In this work the energy of single Cu atom refers to an isolated Cu atom in vacuum.

 # Referee #1, Comment #5

In the Authors' reply to the comment, which inquired about theoretical/computational support for the asserted roles of the variation of Cu oxidation states in C–C coupling, they point to the existing DFT calculations of the charge distribution (Fig. 5a), as well as the new free-energy diagram of the CO_2-*CHC pathway (Fig. 5c).

While the calculation results do support the experimentally-observed variance in oxidation states, it would seem to me that the crux of the issue, that is, the mechanism through which this variation in Cu oxidation states "creates an optimal electronic environment [for C–C coupling]" as is written in the Rebuttal, has not been directly addressed.

It is suggested that either (1) the free-energetic analysis be repeated on surfaces without the mix of Cu oxidation states, *establishing the $Cu^{0/1+}$ baselines with which $Cu^{\delta+}$NCN can be compared*; or (2) that additional references to the existing theoretical literature be added which covers the mechanistic issue.

Response: Thank you for your insightful feedback and the opportunity to further clarify the influence of variation in Cu oxidation states on C–C coupling mechanisms in our study. Your comments have highlighted an important aspect of our research and the need for a deeper analysis to solidify our findings.

In response to your suggestions, we have undertaken the following actions:

Free-Energetic Analysis on Varied Oxidation State Surfaces:

To directly address the role of Cu oxidation state variations in facilitating an optimal environment for C–C coupling, additional calculations was performed on surfaces characterized explicitly by uniform Cu oxidation states (namely Cu^0 and Cu^{1+}). Specifically, to establish the $Cu^{0/1+}$ baselines, the *CO-*CO coupling barriers were calculated over the Cu^{1+}-site-rich $Cu_2O(110)$ surface and the Cu^0-site-rich Cu(111) surface, and the results are 1.55 eV and 1.12 eV, respectively, both higher than the barrier over the $Cu^{\delta+}$NCN (0.86 eV). The results indicate the mix of Cu oxidation states can reduced C-C coupling barrier from the view of theoretical calculation. The results from these calculations have been added to our revised manuscript and provide a clearer understanding of how the variation in Cu oxidation states contributes to the energetics of C–C coupling.

Incorporation of Additional Theoretical References:

Recognizing the importance of grounding our findings within the broader context of existing literature, we have also supplemented our discussion with additional references that explore the mechanistic implications of Cu oxidation states in CO_2 electroreduction processes that similar to our work. These references provide theoretical support for the assertion that variations in Cu oxidation states can significantly impact the electronic environment conducive to C–C coupling, thereby offering a stronger theoretical foundation for our argument.

These additions and revisions have been meticulously integrated into both the main manuscript and the Supplementary Information. We believe these changes address the concerns raised and further strengthen the connection between our theoretical/computational findings and the experimentally observed variance in Cu oxidation states. Our revised analysis provides a more comprehensive understanding of the role these variations play in enhancing the efficiency of C–C coupling reactions. Once again it is grateful for your constructive critique, which has undoubtedly enriched our work. We hope that these adjustments will satisfy the concerns raised and make our manuscript suitable for publication.

Revised part in manuscript:

In page 14-15: As such, we firstly investigated the dimerization kinetics of *CO to *OCCO on Cu surfaces with different oxidation states. As shown in **Fig. 5c**, when the catalyst surface is entirely composed of Cu^{1+}, the dimerization of *CO on the surface requires overcoming a high activation energy barrier (1.55 eV) to form the transient state (TS1). When the catalyst surface is entirely composed of Cu^0, the barrier for TS1 is reduced to 1.12 eV. However, on the surface of $Cu^{\delta+}$NCN (coexistence of Cu^0/Cu^{1+}), the barrier for TS1 is further reduced to 0.86 eV. This clearly demonstrates the importance of the Cu^0/Cu^{1+} environment maintained by $Cu^{\delta+}$NCN for the efficient production of C_2 products.

In page 19:

46 Zhang, J. *et al.* Grain Boundary-Derived Cu^+ /Cu^0 Interfaces in CuO Nanosheets for Low Overpotential Carbon Dioxide Electroreduction to Ethylene. *Adv. Sci.* **9**, e2200454 (2022).

47 Yuan, X. *et al.* Controllable Cu^0 -Cu^+ Sites for Electrocatalytic Reduction of Carbon Dioxide. *Angew. Chem., Int. Ed.* **60**, 15344-15347 (2021).

In page 24:

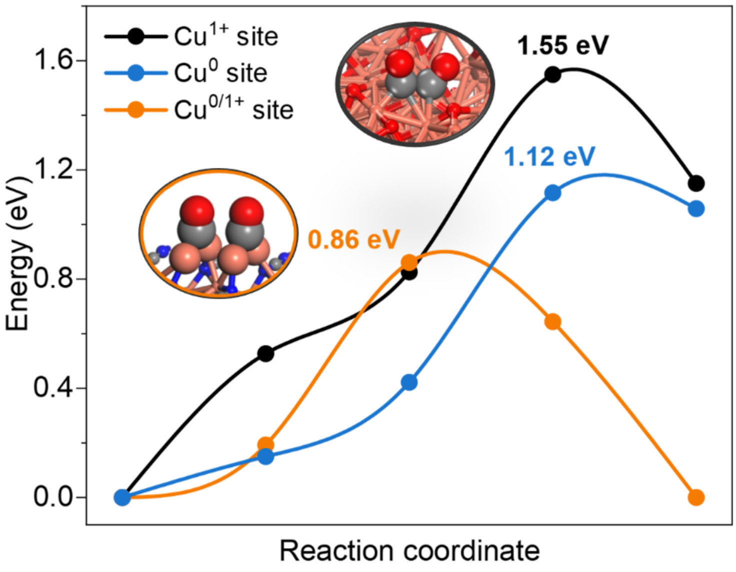


Fig. 5c Energy barriers of *CO-*CO coupling·on the $Cu^{\delta+}NCN$ surface, Cu (111) surface, and Cu_2O (110) surface at U = -0.8 V. The corresponding transition state structures are shown in the insets.

Additional comment #1: On P. 13, Fig. 5a, and Supp. Fig. 23, the Authors produce the numbers 0.83 and 0.77 electrons for the "charge density" around the Cu^{1+} and Cu^0 sites respectively. However, *it is unclear how these site-localized numbers are obtained* from the continuous charge distribution.

Any method used (*e.g.* PAW-based projection, Bader/Mulliken analysis) should be specified in the text, figure captions, and/or the Supplementary Information on Methods.

Response: We appreciate your attention to the details of our methodology and your suggestion to clarify the method used to obtain the site-localized charge densities around the Cu^{1+} and Cu^0 sites. Your feedback is crucial for ensuring transparency and reproducibility in our computational approach.

In response to your comment, we have revised the relevant sections of the manuscript to explicitly describe the method used to calculate the charge density around the Cu sites. Specifically, we obtained the charge values using the Bader charge analysis method, which is a well-established technique for partitioning charge in a localized region around atoms in a molecular system. To ensure consistency and clarity, we have also reviewed the entire manuscript to verify that all computational methods are appropriately described and referenced.

We hope that these revisions provide the necessary clarity regarding our computational methodology and that they meet the standards of rigor expected in scientific publications.

Revised part in manuscript:

In page 13: The charge density difference was calculated for the surface copper and the second layer of copper using the Bader charge analysis method.

Revised part in supplementary:

In page 9: The relative permittivity was set to 78.4, and a linearized Poisson−Boltzmann model with a Debye length of 3.0 Å was employed to mimic the compensating charge. In addition, we obtained the charge values using the Bader charge analysis method.

Additional comment #2: On P. 13–14, the Authors refer to Supp. Fig. 23 which illustrates a charge transfer from the substrate to the surface sites and asserted that "such electron distribution [is] vital for the stabilization of oxidized Cu^{1+} and the preserve[ation] of surface neutral Cu^0".

However, to me *the strength of the statement would require additional support* as to how the charge transfer and the stabilization/preservation are related.

Response: We appreciate your keen observation and the opportunity to further substantiate the relationship between charge transfer and the stabilization/preservation of Cu^{1+} and Cu^0 surface sites. Your feedback is crucial for ensuring that our claims are well-supported by both experimental and computational findings.

From the perspective of CO_2 electroreduction for producing C_2 products, the coexistence of Cu^0 and oxidized Cu is crucial. As discussed in our introduction, for general oxidized Cu such as CuO, Cu^+ can easily be reduced to metallic Cu if electrons continue to accumulate on the Cu^+ surface, thereby reducing the selectivity of catalysts. In contrast, for the as designed $Cu^{\delta+}NCN$, Fourier-transform infrared spectroscopy have clearly proved that coexisting of the characteristic vibration peaks of $[N–C≡N]^{2-}$ and $[N=C=N]^{2-}$ in $Cu^{\delta+}NCN$ (**Fig. 2f**). In particular, $[N–C≡N]^{2-}$ anions prefers to bind to softer cations (*e.g.* Cu^{1+}) to create an electron delocalization of the Cu atoms in the framework. Moreover, the differential charge analysis has demonstrated that the presence of $[NCN]^{2-}$can transfer electrons from Cu^+ to prevent further reduction, ensuring the stability and selectivity of the catalyst.

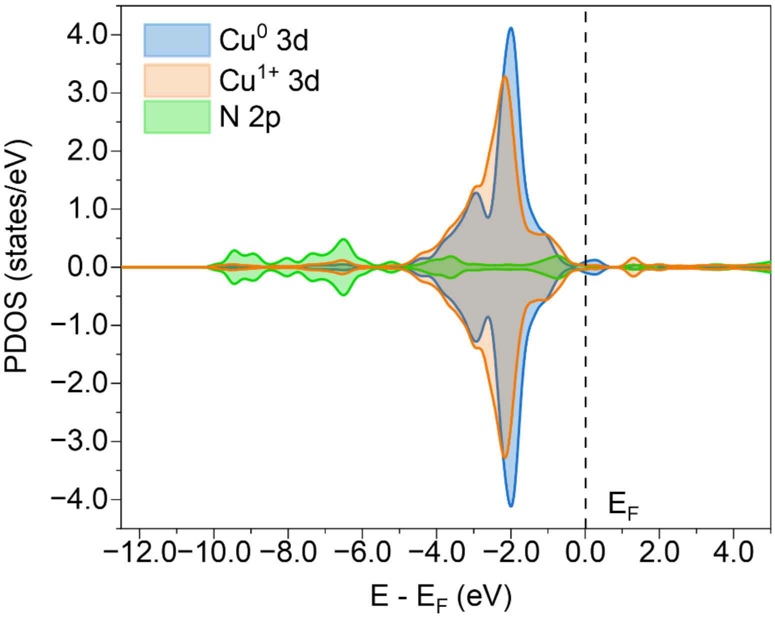
In response to your concern, we further calculated the density of states projected on Cu^0, Cu^{1+}, and the coordinating N atoms. The intense charge transfer implies strong orbital hybridization and overlaps between the involved atoms, as shown below, the results show obvious hybridization and overlap between the Cu^0 3d, Cu^{1+} 3d, and N 2p orbitals, which indicate strong bindings between Cu^0, Cu^{1+}, and the coordinating N atoms, and thus the structural stability of $Cu^{\delta+}NCN$. The relative stability of Cu^0 and Cu^+ can thus be achieved by the presence of $[NCN]^{2-}$.

Revised part in manuscript:

In page 14: We calculated the density of states projected on Cu^0, Cu^{1+}, and the coordinating N atoms. The intense charge transfer implies strong orbital hybridization and overlaps between the involved atoms (**Supplementary Fig. 24**), the results show obvious hybridization and overlap between the Cu^0 3d, Cu^{1+} 3d, and N 2p orbitals, which indicate strong bindings between Cu^0, Cu^{1+}, and the coordinating N atoms, leading to stabilized Cu^0 and Cu^{1+}.

Revised part in supplementary:

In page 34:



Supplementary Fig. 24. The calculated projected density of states results for Cu$^{\delta+}$NCN.

Finally, we hereby extend our profound appreciation to the editor and reviewers for the investment of their precious time and the provision of astute observations. Indeed, their contributions have been instrumental in enhancing the caliber of our manuscript. It is our earnest aspiration that the modifications implemented will resonate with their expectations and that our manuscript now aligns with the standards by *Nature Communications*. We reiterate our heartfelt thanks for your indispensable role in this scholarly endeavor.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have satisfied me with respect to the points I raised previously.

Reviewer #4 (Remarks to the Author):

It is noted that the authors have made immense improvements as to the scientific content, rigor, and clarity of the manuscript in response to the comments from the reviewers.
As such, I would like to recommend the manuscript for acceptance and publication.