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Peer Review File

Intermediate-regulated dynamic restructuring at Ag-Cu biphasic interface enables selective CO_2 electroreduction to C_{2+} fuels

Corresponding Author: Professor Liming Zhang

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript performed electrochemical CO2RR on a neat biphasic Ag/Cu interface, with a main focus on imaging the dynamic reconstruction of catalyst and deciphering the accurate structure-function correlation. This topic, is of high importance to the scientific community and general readers, given that electrocatalysts usually undergo surface reconstruction, which strongly impedes understanding the structure-performance correlation. In this paper, structural characterization is very impressive. Using highly-resolved HADDF-STEM imaging, the authors gained elegant insight into the atomic structural transformations of catalysts that were shown to influence the selectivity of C2+ fuels. Also, the *CO intermediate-regulated interfacial restructuring mechanism was thoroughly explained and supported by solid evidences. This work will contribute to the fundamental understanding of tandem CO2-to-C2+ conversion by highlighting the dynamic restructuring of bimetallic interface. Overall, I would support the acceptance of this manuscript in Nat. Commun. Prior to publication, I have a few questions that require further clarification:
1. Could the authors provide more explanations on the self-assembly process, e.g., why the bipy can successfully assemble Ag and Cu together? Will the bipy-function layer affect the performance evaluation of CO2RR?
2. In addition to the product selectivity, the current density on various Agx-Cux electrodes at different potentials should be provided.
3. As an important control experiment, the authors may need to consider comparing the activity difference of CORR on Cu and Ag0.5-Cu0.5 under multiple potentials.
4. The charge transfer between Ag and Cu is an interesting observation. It is better to provide detailed deconvolutions of the XPS signal in Figures 3d-f.
5. Ag seems to play an important role in the dynamic restructuring. How does the structure of Ag NPs change during CO2RR?
6. For the mechanism discussion, this paper illuminated different active sites for C2+ production: The Cu-rich interface favors ethylene production, while the in-situ formed CuAg interface favors alcohol production. Is it possible that the re-deposited Cu provides another independent pathway to directly convert CO2 to C2+ fuels, instead of the tandem process?

Reviewer #2

(Remarks to the Author)
Manuscript#: NCOMMS-24-24372-T

The manuscript presents a detailed study on CO2 electroreduction on bimetallic Ag-Cu substrate, providing insights onto the reconstruction of the Ag-Cu substrate, at different Ag:Cu ratios, after operation.

Despite the level of English used must be improved, the work is sound and all characterizations are well addressed.

Unfortunately, after a careful and thorough reading of the manuscript I found unsettling similarities with the following paper:

Wei, Daixing, et al. "Decrypting the controlled product selectivity over Ag–Cu bimetallic surface alloys for electrochemical

CO2 reduction." Angewandte Chemie 135.19 (2023): e202217369. https://doi.org/10.1002/ange.202217369

In particular, Figure 2c-d of the presented manuscript are by far too similar, almost identical, to the Figure 2 of the aforementioned paper, in terms of style, colors and way to present experimental data.

Stated that, I do not believe the presented material meets the required level of novelty needed to be accepted for publication on Nature Communications.

Reviewer #3

(Remarks to the Author)
The submitted manuscript entitled "Intermediate-regulated dynamic restructuring at Ag-Cu biphasic interface enables selective CO2 electroreduction to C2+ fuels" discusses the use of a bimetallic heterostructure, specifically an Ag-Cu biphasic interface, for the electroreduction of CO2 to produce multi-carbon (C2+) fuels. The authors investigate the interfacial structure and its role in determining the selectivity of the CO2 electroreduction pathway. The manuscript is interesting. However, there are numerous questions/issues to be discussed prior to acceptance.
1. The authors should provide more discussion about other Ag-Cu interfaces (ref 23-27) clarifying what has been done and what is missing. It will also help to clarify the novelty of this work.
2. It also remains a question of why Cu nanowires exhibit CO2R activity alike Bulk Cu.
3. Overall, the authors claim that the enhanced selectivity is due to the existence interface of Ag/Cu. Also, in Line 215, the authors claim that “The enrichment of Cu on Ag surface could already be observed after 0.5 h electrolysis. While the electrolysis time extended to 3 hours, more Cu species migrated onto Ag, resulting in a thicker Cu layer (~4 nm). The growing Cu layer is responsible for the decreased alcohol selectivity with prolonged time”. The migration of Cu on Ag is not justified. The authors should provide a valid explanation of why Cu is migrating on Ag surface. Additionally, the SI figure discussing time-dependent CO2R product distribution shows no alcohol products after 0.5 hours.
4. Moreover, stability remains an issue as deposition of Cu over Ag nanoparticle counited even after 4 hours. Why do cu atoms keep migrating and depositing on Ag nanoparticles?
5. Line 314: the author mentioned “Ag-Cu biphasic heterostructure for tandem electrochemical CO2R”. There is no evidence of tandem CO2R behavior.

Reviewer #4

(Remarks to the Author)
X. Gao, et al. reported the investigation about the restructuring of Cu-Ag bimetallic alloy during CO2 reduction reaction (CO2RR). Reconstruction (restructuring) in heterogeneous CO2RR catalysts is key issue because this impedes to understand the real catalytic active sites which steers the O2RR reaction pathway. Therefore, understanding the reconstruction especially for Cu alloy is essential for the selective C2+ chemicals production. Cu-Ag has received great attention because of spillover effect to tune the selectivity between ethylene and ethanol by increasing *CO intermediates. In this point of view, the topic of unveiling the reconstruction behavior of Cu-Ag can be of interest to catalysis society. This work provides an insight to understand the CO2RR selectivity trend (C2H4, C2H5OH, CO) with increasing Ag contents as the degree of Cu dissolution and redeposition on the Ag active sites. The topic of this work seems quite interesting, but this reviewer has several concerns about the novelty and explanation in this work. I can’t recommend the accept of this manuscript in its current form. This can be reconsidered after major revision. Details are as follows.

1. It seems that restructuring of Cu-Ag has been studied by investigating the HAADF-STEM images after CO2RR. However, in the manuscript, it is difficult to find the CO2RR condition (such as potential, current density, etc) for this post CO2RR characterization. In the CO2RR, -1.05 V (vs RHE) seems the potential where the dramatic CO2RR selectivity change occurs. Therefore, it is important to see the material study (after CO2RR) needs to be proceeded after CO2RR at -1.05 V (vs RHE).

2. Authors should provide more quantitative information about the Cu redeposition. Analysis of the Ag surface by HAADF-STEM does not represent the overall trend of restructuring because this only shows the narrow spot in whole catalysts. I think that there can be deviation in the Cu redeposition according to the Ag nanoparticle site. To generalize the behavior of Cu redeposition in the Ag nanoparticles-decoreated CuNWs, statistical results are essential.

3. It seems that CuNWs are coated with bipyridine functional group. In this condition, how does Cu dissolves to the electrolyte? Can authors investigate the coverage of bipyridine functional group?

4. As authors mentioned, it seems that CO2RR intermediates can affect the restructuring of Cu active sites. In the CO2RR of Cu-Ag catalysts, most representative products are H2 in general (Figure S8). I recommend authors to investigate the restructuring behavior of Cu-Ag catalysts at the system where more efficient CO2RR (less HER) can occur with higher CO2RR FE and partial current density such as flow cell. In current status, I think that it is difficult to agree with this phenomenon as a general behavior of CO2RR catalysts because of relatively high HER portion and poor CO2RR stability. Therefore, investigating the restructuring of catalysts at the more efficient CO2RR condition would be helpful to verify the

hypothesis of this work.

5. Authors explained that Cu ions tend to migrate onto Ag domains, generating more abundant of Ag-Cu interface at higher *CO concentration. How does high *CO concentration can promote the Cu migration onto Ag domains? Authors needs to provide direct experimental evidence about this explanation.

6. It seems that the CO2RR results in Figure 2a and 2b are not same with the results in contour map in Figure 2e. For example, Ag0.5-Cu0.5 exhibited the optimal alcohol FE at -1.05 V (vs RHE) in Figure 2a and 2b. However, in the contour map, the optimal FE for alcohol is located at the potential range between -0.9 and -1.0 V (vs RHE). Authors need to explain this mismatch.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript has undergone significant improvements and is now ready for publication.

Reviewer #2

(Remarks to the Author)
The Authors have clarified the raised point and made needed changes to amend the issue. The Authors also provided enough explanations on the novelty of their work. I have no further remarks/comments to make. The paper can be accepted for publication in the present form.

Reviewer #3

(Remarks to the Author)
The authors have made substantial revisions to the manuscript and addressed all concerns. I therefore recommend its publication in Nature Communications without the need for further revisions.

Reviewer #4

(Remarks to the Author)
Revised manuscript now addresses the concerns from this reviewer. I recommend the acceptance of this manuscript in Nature Communications.

Author's response

Intermediate-regulated dynamic restructuring at Ag-Cu biphasic interface enables selective CO_2 electroreduction to C_{2+} fuels

We appreciate the editor and reviewers for your time considering and providing the constructive comments. Here we provide a point-to-point response to the comments/suggestions. In this document, the *italics* are the comments from the reviewers, and the underlined are changes made in the manuscript.

Response to Reviewer #1's comments:

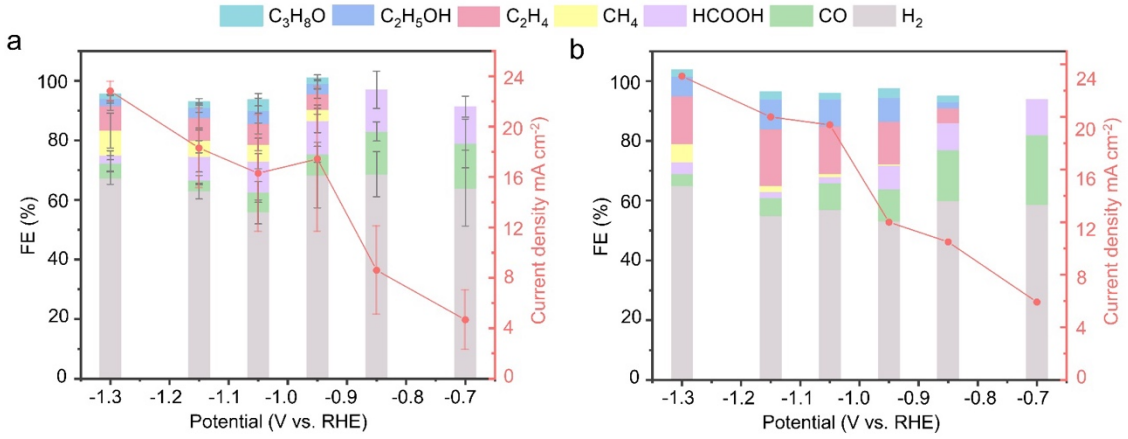
*This manuscript performed electrochemical CO_2RR on a neat biphasic Ag/Cu interface, with a main focus on imaging the dynamic reconstruction of catalyst and deciphering the accurate structure-function correlation. This topic, is of high importance to the scientific community and general readers, given that electrocatalysts usually undergo surface reconstruction, which strongly impedes understanding the structure-performance correlation. In this paper, structural characterization is very impressive. Using highly-resolved HAADF-STEM imaging, the authors gained elegant insight into the atomic structural transformations of catalysts that were shown to influence the selectivity of C_{2+} fuels. Also, the *CO intermediate-regulated interfacial restructuring mechanism was thoroughly explained and supported by solid evidences. This work will contribute to the fundamental understanding of tandem CO_2-to-C_{2+} conversion by highlighting the dynamic restructuring of bimetallic interface. Overall, I would support the acceptance of this manuscript in Nat. Commun. Prior to publication, I have a few questions that require further clarification.*

We appreciate your positive evaluation, and the point-to-point response is appended below.

1. Could the authors provide more explanations on the self-assembly process, e.g., why the bipy can successfully assemble Ag and Cu together? Will the bipy-function layer affect the performance evaluation of CO_2RR?

We appreciate your thoughtful comment. The 4,4-bipyridine (bipy) molecules can successfully assemble Cu and Ag together because of forming strong coordination bonds between the nitrogen atoms of bipy ligands and metal surface. This assembly strategy has been successfully demonstrated in fabricating multiple nanostructures (*J. Am. Chem. Soc.* 1997, **119**, 2524-2533; *Cryst. Growth Des.* 2010, **10**, 4642-4649; *Dalton Trans.* 2015, **44**, 19041-19055; *Angew. Chem. Int. Ed.* 2019, **58**, 14100-14103). To clarify this point, we have added these references and the following descriptions to the revised text (*Paragraph 2, Page 4*): … Here, Ag nanoparticles (Ag NPs) were assembled onto Cu nanowires (Cu NWs) with 4,4'-bipyridine (bipy) serving as a linker (see Experimental Procedures). The bipy molecules could successfully bring Cu and Ag together by forming strong coordination bonds between the nitrogen atoms of bipy ligands and the metal surface[32-35]. …

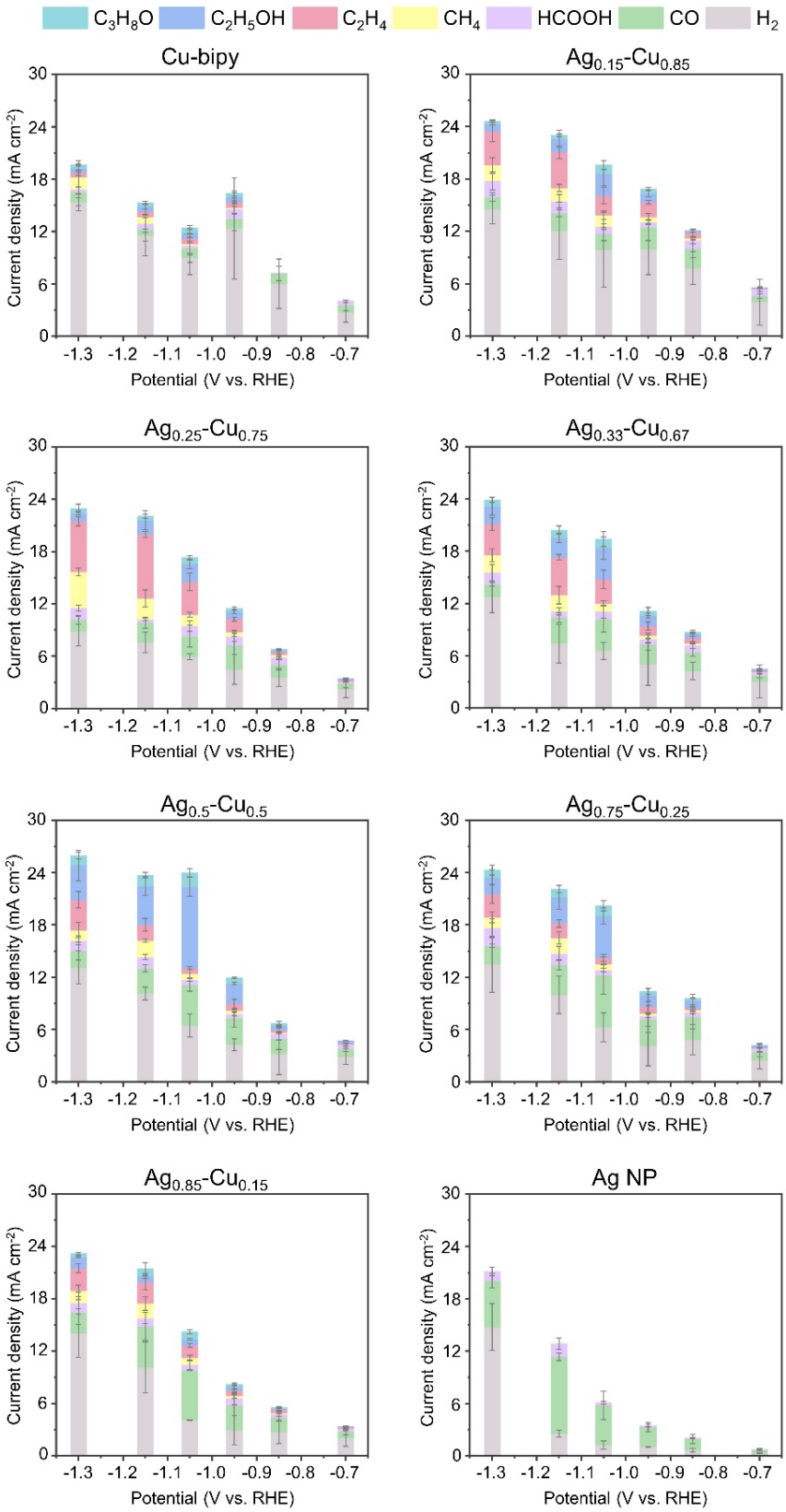
We performed electrochemical CO_2R on both bipy-functionalized Cu (denoted as Cu-bipy) and pristine Cu nanowires, and observed that bipy-functionalization slightly promoted the generation of C_1 products, *e.g.*, CH_4, CO and HCOOH, whereas suppressed the production of C_{2+} fuels including C_2H_5OH and C_2H_4, particularly under a higher negative potential < -0.9 V *vs*. RHE. The following figure has been added to the revised manuscript as Supplementary Figure 10, and the main text was modified accordingly (*Paragraph 3, Page 5*): … As shown in Figure 2a, Cu-bipy exhibited a wider product distribution, although bipy-functionalization slightly reduced the production of C_{2+} fuels, as compared to pure Cu[36] (Supplementary Figure 10). …



Supplementary Figure 10 The product distribution and current density of CO_2R at different potentials on Cu NWs with (a) and without (b) bipy-functionalization.

2. In addition to the product selectivity, the current density on various Ag_x-Cu_y electrodes at different potentials should be provided.

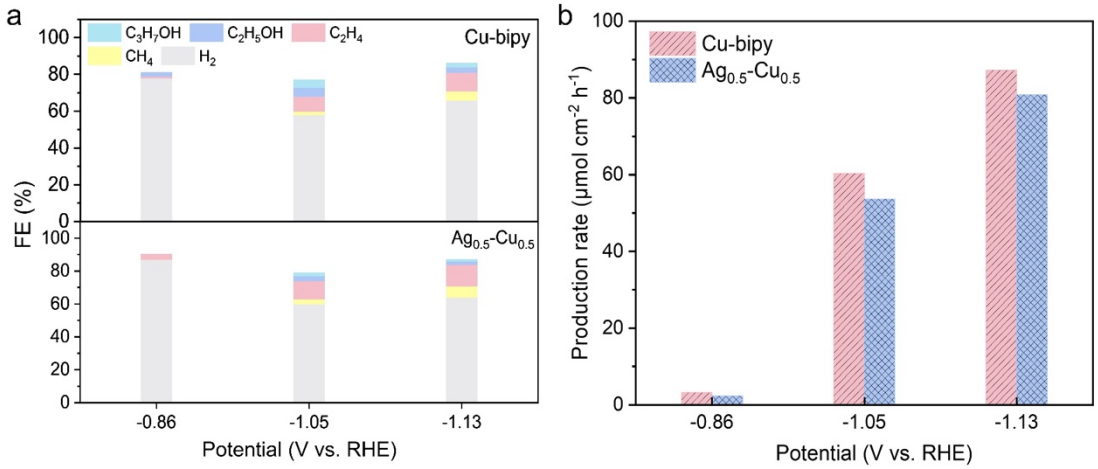
We appreciate your suggestion. In the revised manuscript, we have added the potential-dependent current density for Ag_x-Cu_y, Cu-bipy and Ag electrodes as Supplementary Figure 9 (shown below). Accordingly, we modified the main text (*Paragraph 2, Page 5*): … Supplementary Figures 8-9 summarized the product distributions and current densities of different catalysts at each applied potential.



Supplementary Figure 9 Potential-dependent partial current densities of multiple products on Cu-bipy, Ag and variable Ag_x-Cu_y electrodes. The error bars along Y axis correspond to one standard deviation of triplicate measurements.

3. As an important control experiment, the authors may need to consider comparing the activity difference of CORR on Cu and $Ag_{0.5}$-$Cu_{0.5}$ under multiple potentials.

Thank you for this insightful comment. In the revised manuscript, we have performed electrochemical CO reduction on both Cu and $Ag_{0.5}$-$Cu_{0.5}$ under multiple potentials, and the production rates of C_{2+} alcohols were compared as follows (Supplementary Figure 13). It was observed that the Cu-bipy exhibited a comparable C_{2+} alcohols production rate with $Ag_{0.5}$-$Cu_{0.5}$ across a broad potential window. This observation is distinguished with that in electrochemical CO_2R, where $Ag_{0.5}$-$Cu_{0.5}$ was more favorable to generate alcohol products. Therefore, our results experimentally demonstrated the importance of locally enriched *CO at the interface, which could not be simply replaced by the CO-supplying reagent. Accordingly, we modified the manuscript (*Paragraph 2, Page 6*): … We found that such locally produced *CO could not be simply replaced by the CO-supplying reagent, because no significant differences occurred in the C_{2+} selectivity and production rate between Cu-bipy and $Ag_{0.5}$-$Cu_{0.5}$ under multiple potentials in direct CO reduction (Supplementary Figure 13). These observations experimentally confirmed the promoted C_{2+} alcohols production on Ag-Cu biphasic heterostructure follows a tandem CO_2R pathway. …



Supplementary Figure 13 The FE (a) and production rate (b) of C_{2+} fuels on $Ag_{0.5}$-$Cu_{0.5}$ and Cu-bipy in electrochemical CO reduction under different potentials.

4. The charge transfer between Ag and Cu is an interesting observation. It is better to provide detailed deconvolutions of the XPS signal in Figures 3d-f.

Thank you for this comment. In the revised manuscript, we have provided detailed deconvolutions of XPS signals in Figures 3d-f. The updated Figure 3 was shown below, and the main text was modified accordingly (*Paragraph 2, Page 7*): ... We compared the X-ray photoelectron spectra (XPS) of $Ag_{0.25}$-$Cu_{0.75}$, $Ag_{0.33}$-$Cu_{0.67}$, and $Ag_{0.5}$-$Cu_{0.5}$ before and after electrolysis (Figures 3d-f). All three samples exhibited a Cu^{2+} signal at 935 eV and a Cu^{+}/Cu signal at 932.5 eV. The peaks at 368.2 and 374.2 eV were ascribed to Ag $3d_{5/2}$ and $3d_{3/2}$, respectively. …

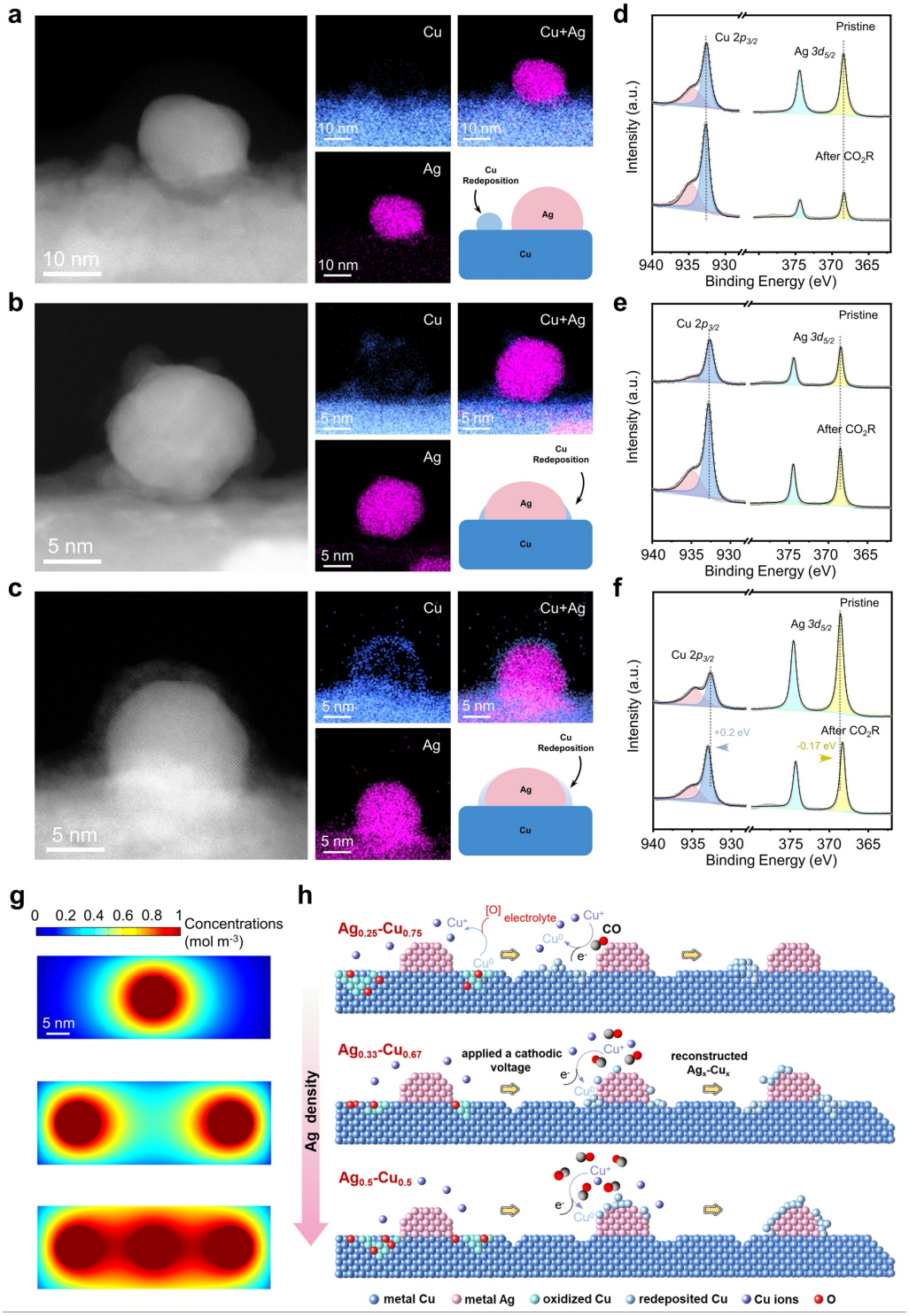


Figure 3 Dynamic restructuring of Ag-Cu biphasic interface. a-c, HAADF-STEM images and corresponding EDS elemental maps of $Ag_{0.25}$-$Cu_{0.75}$ (a), $Ag_{0.33}$-$Cu_{0.67}$ (b), $Ag_{0.5}$-$Cu_{0.5}$ (c) after restructuring at -1.05 V *vs*. RHE. Insets show schematics of the reconstructed Ag-Cu interface. **d-f,** XPS spectra of $Ag_{0.25}$-$Cu_{0.75}$ (d), $Ag_{0.33}$-$Cu_{0.67}$ (e), and $Ag_{0.5}$-$Cu_{0.5}$ (f) before and after electrolysis. **g,** A top-view of the concentration and flux distribution of *CO on Ag-Cu heterostructures with different Ag densities via the FEM simulation. **h,** Proposed restructuring mechanisms of Ag-Cu heterostructures with different Ag densities.

5. Ag seems to play an important role in the dynamic restructuring. How does the structure of Ag NPs change during CO_2RR?

We thank you for this comment. The concern on the structural evolution of Ag was addressed in the original text, which is clarified below. The topographical structure of Ag barely changed after CO_2R, as confirmed from the HAADF-STEM characterizations shown in Figures 3a-c. In terms of electronic structure, we performed XPS to compare the valence states of Ag before and after CO_2R (Figures 3d-f). For all pristine Ag-Cu electrode, the Ag 3d spectra can be fitted into two symmetric peaks with binding energies of 368.2 ($3d_{5/2}$) and 374.2 ($3d_{3/2}$) eV, respectively, indicative of the existence of Ag(0). After CO_2R, the spectra of Ag exhibited scarcely evolution on both $Ag_{0.25}$-$Cu_{0.75}$ and $Ag_{0.33}$-$Cu_{0.67}$, suggesting the stable valence state of Ag(0). In contrast, a binding energy shift of -0.17 eV was observed on $Ag_{0.5}$-$Cu_{0.5}$, which was attributed to the partial electron transfer from Cu to Ag.

6. For the mechanism discussion, this paper illuminated different active sites for C_{2+} production: The Cu-rich interface favors ethylene production, while the in-situ formed CuAg interface favors alcohol production. Is it possible that the re-deposited Cu provides another independent pathway to directly convert CO_2 to C_{2+} fuels, instead of the tandem process?

We thank you for this comment. Compared with Ag-Cu tandem system, the monometallic Cu surface generally favors the production of ethylene over ethanol/n-propanol (*Energy Environ. Sci.* 2012, **5**, 7050-7059; *Nat. Commun.* 2014, **5**, 4948). In our control experiment on monometallic Cu, we observed higher hydrocarbon production than oxygenates (Supplementary Figure 10), consistent with the conclusions in previous reports. In contrast, the production of C_{2+} alcohols outperformed that of hydrocarbons on $Ag_{0.5}$-$Cu_{0.5}$ at low overpotentials (Figures 2a and 2e), suggesting the active sites to produce C_{2+} alcohols were not the redeposited Cu. Instead, we proposed that the production of C_{2+} alcohols was from a tandem pathway including *CO buildup and *CO-to-C_{2+} alcohols conversion, wherein the local *CO enrichment is a key step to keep the durable production of C_{2+} alcohols.

Response to Reviewer #2's comments:

The manuscript presents a detailed study on CO_2 electroreduction on bimetallic Ag-Cu substrate, providing insights onto the reconstruction of the Ag-Cu substrate, at different Ag:Cu ratios, after operation. Despite the level of English used must be improved, the work is sound and all characterizations are well addressed. Unfortunately, after a careful and thorough reading of the manuscript I found unsettling similarities with the following paper: Wei, Daixing, et al. "Decrypting the controlled product selectivity over Ag−Cu bimetallic surface alloys for electrochemical CO_2 reduction." Angewandte Chemie 135.19 (2023): e202217369. In particular, Figure 2c-d of the presented manuscript are by far too similar, almost identical, to the Figure 2 of the aforementioned

paper, in terms of style, colors and way to present experimental data. Stated that, I do not believe the presented material meets the required level of novelty needed to be accepted for publication on Nature Communications.

We sincerely appreciate you for the effort in reviewing our manuscript, and apologize for referring the data analysis protocols, *e.g.*, 3D diagrams and contour maps, from the previously published work. First, to address your concern on the novelty of our paper, we would like to emphasize that the innovation points of our work are very different from the *Angew. Chem. Int. Ed.* paper. Our work aims **to track the empirical atomic-scale structural evolution at the Ag-Cu biphasic interface during CO_2 electrolysis, and demonstrate the interfacial structure-steered reduction pathway**. In particular, we unraveled the crucial role of *CO intermediate in modulating the Cu restructuring behavior at the interface, which has been rarely emphasized in previous reports. This *Angew. Chem. Int. Ed.* paper performed elegant experiments to decipher the surface composition-dependent product distributions on AgCu intermetallic alloys, without emphasizing the influence of structural evolution on electrochemical CO_2R performance. After comparing with this *Angew. Chem. Int. Ed.* paper side-by-side, we would like to highlight the advancement of our work as follows:

(1) We showed the structural evaluation of Ag-Cu biphasic interface under CO_2 electrolysis, deciphering the real active sites, and thus rationalized the C_{2+} product (*i.e.* C_2H_4 and alcohols) disparities on different reconstructed Ag-Cu heterostructures. Previous works on Ag-Cu bimetallic interface, including the *Angew. Chem. Int. Ed.* paper, have demonstrated substantially discrepant product distributions. Our work employed the aberration-corrected HAADF-STEM to reveal the biphasic interface of Ag-Cu heterostructure, and performed in-depth analysis on the empirical atomic-scale structural evolution during electrolysis. Experimentally, we excluded the atomic interdiffusion between Ag and Cu atoms, and ambiguously manifested the porous core-shell Ag@Cu nanostructure as well as the discernable charge transfer between two elements after electrocatalysis, which is crucial for understanding the interfacial structure-steered CO_2R pathway.

(2) More importantly, we emphasized the crucial role of *CO intermediate as an impetus for the structural evolution at such a biphasic interface. As far as we know, this is the first time to experimentally highlight the critical role of *CO-coverage in the dynamic restructuring of bimetallic interface during CO_2 electrolysis. We experimentally unraveled that the *CO intermediate can strongly regulate the electrochemical restructuring behavior, *e.g.*, Cu tends to migrate onto the neighboring Ag under a locally high *CO concentration, forming abundant of Ag-Cu interface. Collectively, we proved that the evolving structure and enriched *CO intermediate strongly altered the oxyphilic characteristic at the interface, which profoundly determined the hydrogenation energetics of CO_2, leading to disparate C_{2+} product distributions.

(3) Distinguished with the *Angew. Chem. Int. Ed.* paper choosing to study AgCu alloy, we implemented an Ag-Cu biphasic interface without intermetallic alloy as a model system, which was fabricated through a novel surface assembly strategy at the room temperature. This Ag-Cu heterostructure possesses a well-defined surface, benefiting to track the dynamic restructuring

during electrocatalysis. From the mechanistic side, The CO_2R on this biphasic interface followed a tandem pathway, wherein the accumulation of *CO was crucial to influence the following reduction step. This tandem catalysis was also different from the one-step reduction on the bimetallic alloy surface, where the binding strength of intermediates determined by the position of d-band center dominated the ultimate product distributions.

To further address your concern on the data presentation protocol, in the revised text, we reanalyzed our electrochemical results to differentiate our work. The updated Figures 2c-f was shown below. Once again, we sincerely apology for the similarity of data presentation protocol with the published work, and greatly appreciate your thoughtful comments on our paper.

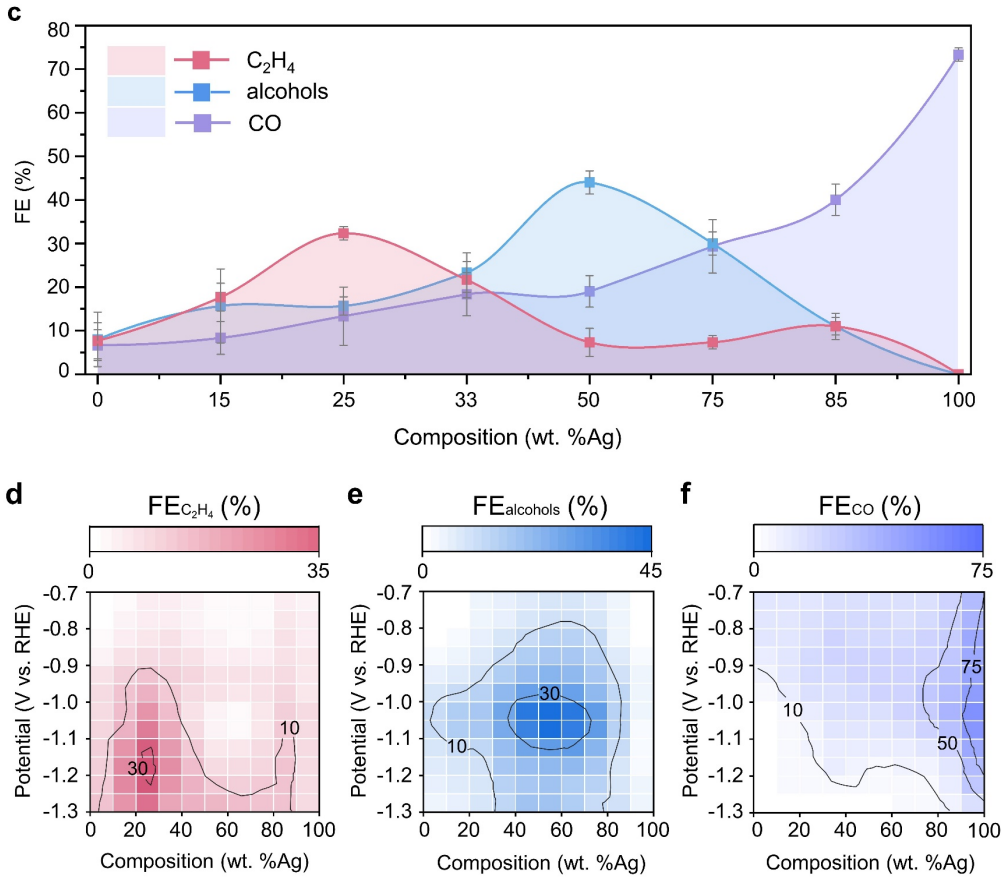


Figure 2 Electrochemical CO_2R product quantification. c, The FEs of C_2H_4, alcohols and CO as a function of Ag fraction. **d-f,** The corresponding contour maps for FEs of different products: C_2H_4 (d), alcohols (e) and CO (f) *versus* Ag fraction and applied potential.

Response to Reviewer #3's comments:

The submitted manuscript entitled "Intermediate-regulated dynamic restructuring at Ag-Cu biphasic interface enables selective CO_2 electroreduction to C_{2+} fuels" discusses the use of a bimetallic heterostructure, specifically an Ag-Cu biphasic interface, for the electroreduction of CO_2 to produce multi-carbon (C_{2+}) fuels. The authors investigate the interfacial structure and its role in determining the selectivity of the CO_2 electroreduction pathway. The manuscript is interesting.

However, there are numerous questions/issues to be discussed prior to acceptance.

Thank you for your positive evaluation of our work, and the point-by-point response is appended below.

1. The authors should provide more discussion about other Ag-Cu interfaces, clarifying what has been done and what is missing. It will also help to clarify the novelty of this work.

We appreciate you for this excellent comment. We would like to highlight that the novelty of our work is to track the empirical atomic-scale structural evolution at the Ag-Cu bimetallic interface during CO_2 electrolysis, and demonstrate the interfacial structure-steered reduction pathway. In particular, we unraveled the crucial role of *CO intermediate in modulating the Cu restructuring behavior at the interface, which has been rarely explored in previous reports. To further clarify the innovation points, we have modified the introduction as follows (*Paragraph 2, Page 3*): … A tandem catalysis strategy has been proposed to improve C_{2+} fuels production on an Ag-Cu heterostructure, wherein CO_2 can be reduced into *CO on Ag and then transferred to Cu for further reduction into C_{2+} products[16-17]. Although previous studies on AgCu alloy and Ag-Cu/CuO_x heterostructures have established the important role of bimetallic interface in promoting C_{2+} fuels[23-26]/C_1 hydrocarbon production[26,27] and suppressing hydrogen evolution[28], precisely tracking the atomic-scale structural evolution during electrolysis remains lacking at the bimetallic interface, which is crucial for understanding the interfacial structure-steered CO_2R pathway. Particularly, the impetus of structural evolution at such a biphasic interface has rarely been explored. …

2. It also remains a question of why Cu nanowires exhibit CO_2R activity alike Bulk Cu.

Thank you for this comment. Previous works have shown that the product distribution of CO_2R on Cu was strongly influenced by the size and surface structures (*J. Am. Chem. Soc.* 2014, **136,** 6978-6986; *Angew. Chem. Int. Ed.* 2016, **55,** 5789-5792; *Acc. Chem. Res.* 2022, **55,** 629-637). The size-dependent selectivity on Cu highlighted the crucial role of low-coordinated Cu sites in determining the product distribution. However, in our work, we implemented Cu nanowires with a diameter of ~50 nm and a length >0.5 μm. The lack of low-coordinated active sites rendered Cu NWs demonstrating the performance alike bulk Cu.

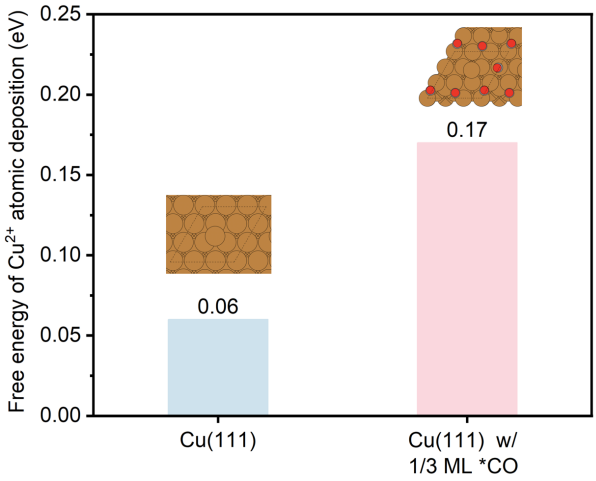
3. Overall, the authors claim that the enhanced selectivity is due to the existence interface of Ag/Cu. Also, in Line 215, the authors claim that "The enrichment of Cu on Ag surface could already be observed after 0.5 h electrolysis. While the electrolysis time extended to 3 hours, more Cu species migrated onto Ag, resulting in a thicker Cu layer (~4 nm). The growing Cu layer is responsible for the decreased alcohol selectivity with prolonged time". The migration of Cu on Ag is not justified. The authors should provide a valid explanation of why Cu is migrating on Ag surface. Additionally, the SI figure discussing time-dependent CO_2R product distribution shows no alcohol products after

0.5 hours.

We are grateful for your insightful comments. The concern on the impetus of Cu restructuring has been addressed in the original text (*Paragraph 1, Page 8*), which is clarified below. Cu atoms demonstrate a high mobility in CO_2 electrolysis, experiencing dissolution and subsequent redeposition either on the catalyst surface or at diverse locations under negative potentials (*Nat. Commun*. 2018, **9,** 3117; *J. Am. Chem. Soc.* 2023, **145,** 10116-10125; *Nat. Catal*. 2023, **6,** 837-846). In our study, a continuous oxidation-reduction process at the Ag-Cu interface was accountable for the dynamic restructuring of the surface. Under a cathodic bias, the electrochemical reduction resulted in a redeposition of Cu ions from the electrolyte, yet such redeposition was prone to occur at different places depending on the local *CO concentration. With a higher local *CO concentration, Cu ions tend to migrate onto the Ag domains, generating more abundant of Ag-Cu interface. We have experimentally confirmed this phenomenon by performing HAADF-STEM and EDS analysis after electrocatalysis on the Ag-Cu heterostructures with varying Ag surface compositions (Figure 3a-c). Results have shown that the formation of Cu layer strongly correlated with the *CO concentration, which was determined by the surface composition of Ag. We also performed electrocatalysis with a gas feeding having different CO_2 fractions on $Ag_{0.5}$-$Cu_{0.5}$, and observed scarcely any Cu overlayer was formed when the fraction of CO_2 is low (see Supplementary Figure 21).

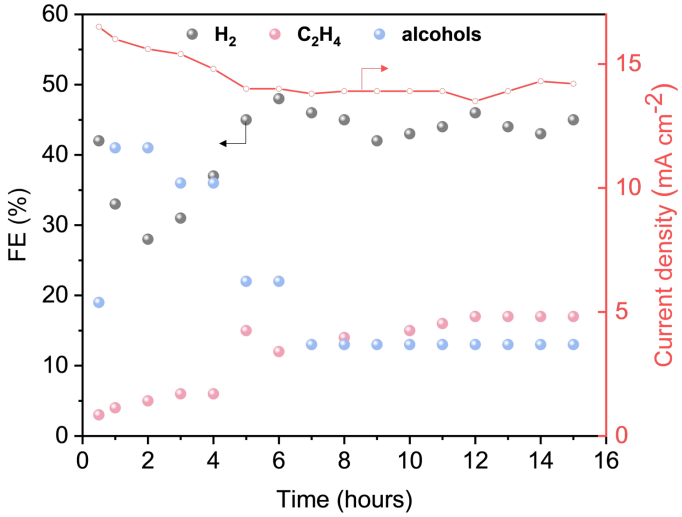
We rationalized that the selective-deposition behavior of Cu ions stems from the distinct binding energies of *CO on Cu and Ag surfaces, *e.g.*, comparing with Cu, Ag possesses a much lower binding energy toward *CO (*Phys. Chem. Chem. Phys.* 2014, **16,** 4720-4727; *Chem*, 2018, **4,** 1809-1831). Consequently, under CO_2R operating condition, *CO is expected to desorb from Ag, and preferentially adsorbs on Cu, which would hinder the deposition of Cu ions on Cu NWs. As shown in the following figure, we compared the free energy evolution upon the deposition of dissolved Cu ions onto pure Cu and Cu-*CO. It was observed that the deposition on Cu was endothermic, and the degree of endothermicity increased when *CO adsorbed on Cu. Therefore, the higher *CO coverage would hinder the deposition of Cu ions on Cu, thus promoting the formation of Ag-Cu interface. To clarify this point, we added the following description to the revised text (*Paragraph 2, Page 8*): … We rationalized that the selective-deposition behavior of Cu ions stems from the distinct binding energies of *CO on Cu and Ag surfaces, *e.g.*, comparing with Cu, Ag possesses a much lower binding energy toward *CO[22,45]. Consequently, under CO_2R operating condition, *CO is expected to desorb from Ag, and preferentially adsorbs on Cu, which would hinder the deposition of Cu ions on Cu NWs. We calculated and compared the free energy evolution upon the deposition of dissolved Cu ions on pure Cu and Cu-*CO. It was observed that the deposition on Cu was endothermic, and the degree of endothermicity increased when *CO adsorbed on Cu (Supplementary Figure 22). Therefore, higher *CO coverage would suppress the deposition of Cu ions on Cu NWs, instead, it promotes the migration of Cu to the neighboring clean Ag surface, leading to the formation of Ag-Cu interface. These results can well explain our experimental observations: With a higher local *CO

concentration, Cu ions tend to migrate onto Ag NPs, generating more abundant of Ag-Cu interface. …



Supplementary Figure 22 The free energy evolution of Cu ion deposition on Cu(111) and Cu(111) with 1/3 ML *CO.

We feel sorry for the misleading figure in Supplementary Figure 14, wherein the liquid products were not collected after 0.5 h electrolysis in the original text. To provide a more detailed temporal profile, we have now included the distribution of CO_2R products after 0.5 h. Alcohol products were detectable at this early time point, consistent with TEM characterizations (Supplementary Figure 18), indicating that the structural reconstruction had already occurred after 0.5 h electrolysis.



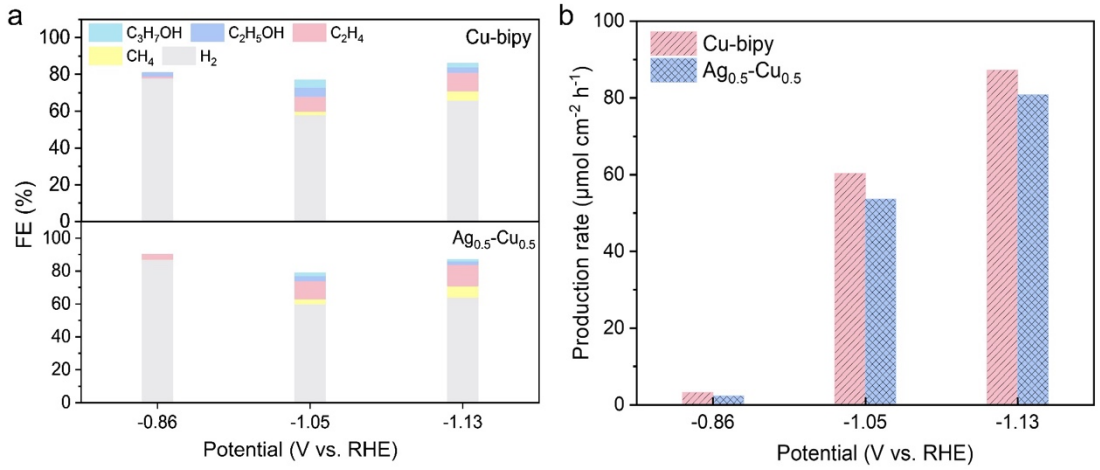
Supplementary Figure 14 The current density and product distribution evaluation during 15 h CO_2 electrolysis catalyzed by $Ag_{0.5}$-$Cu_{0.5}$ at -1.05 V *vs.* RHE.

4. Moreover, stability remains an issue as deposition of Cu over Ag nanoparticle counited even after 4 hours. Why do Cu atoms keep migrating and depositing on Ag nanoparticles?

We greatly appreciate your thoughtful comment. First, we would like to emphasize that the innovation point of this work is not to develop a high-performance and stable CO_2 electrocatalyst, but to track the empirical atomic-scale structural evolution at the bimetallic interface, and demonstrate the interfacial structure-steered reduction pathway. In particular, we unraveled the crucial role of *CO intermediate in modulating the Cu restructuring behavior at the interface, which has been rarely explored in previous reports. To further address your concern on Cu deposition, we believe a continuous oxidation-reduction process at the Ag-Cu interface was accountable for the dynamic restructuring of the surface. As stated in the response to your Comment 3, under a higher *CO concentration, Cu tends to deposit on Ag surface, forming a Cu shell. Even after 4 h electrolysis, the continuous oxidation-reduction of Cu remains occurring. Although the deposited Cu shell itself underwent a dynamic restructuring involving dissolution and redeposition, the rate of redeposition was greater, resulting in an increasing Cu shell thickness. This phenomenon is an important observation of our study, which can well explain the CO_2R performance evolution with time, *e.g.*, the continuous deposition of Cu on Ag resulted in a dropped Ag-Cu active interface, thereby decreasing the selectivity of alcohols in CO_2R.

5.Line314: the author mentioned "Ag-Cu biphasic heterostructure for tandem electrochemical CO_2R". There is no evidence of tandem CO_2R behavior.

We appreciate you for this comment, and apologize for the unclear description, which is clarified below. We have performed electrochemical CO reduction on both Cu and $Ag_{0.5}$-$Cu_{0.5}$ under multiple potentials, and the production rates of C_{2+} alcohols were compared as follows (Supplementary Figure 13). It was observed that the Cu-bipy exhibited a comparable C_{2+} alcohols production rate with $Ag_{0.5}$-$Cu_{0.5}$ across a broad potential window. This observation is distinguished with that in electrochemical CO_2R, where $Ag_{0.5}$-$Cu_{0.5}$ was more favorable to generate alcohol products. Therefore, our results experimentally demonstrated the promoted alcohols production on Ag-Cu biphasic heterostructure follows a tandem CO_2R pathway wherein the locally enriched *CO at the Ag-Cu interface, which cannot be simply replaced by the CO-supplying reagent, is a key step to keep the durable production of C_{2+} alcohols. Our observations on tandem catalytic mechanism were also consistent with previous observations on Cu-based bimetallic interfaces (*Nat. Catal.* 2018, **1**, 764-771; *Chem* 2022, **8**, 3288-3301). To clarify, we modified the main text (*Paragraph 2, Page 6*): … We found that such locally produced *CO could not be simply replaced by the CO-supplying reagent, because no significant differences occurred in the C_{2+} selectivity and production rate between Cu-bipy and $Ag_{0.5}$-$Cu_{0.5}$ under multiple potentials in direct CO reduction (Supplementary Figure 13). These observations experimentally confirmed the promoted C_{2+} alcohols production on Ag-Cu biphasic heterostructure follows a tandem CO_2R pathway. …



Supplementary Figure 13 The FE (a) and production rate (b) of C_{2+} fuels on $Ag_{0.5}$-$Cu_{0.5}$ and Cu-bipy in electrochemical CO reduction under different potentials.

Response to Reviewer #4's comments:

*X. Gao, et al. reported the investigation about the restructuring of Cu-Ag bimetallic alloy during CO_2 reduction reaction (CO_2RR). Reconstruction (restructuring) in heterogeneous CO_2RR catalysts is key issue because this impedes to understand the real catalytic active sites which steers the CO_2RR reaction pathway. Therefore, understanding the reconstruction especially for Cu alloy is essential for the selective C_{2+} chemicals production. Cu-Ag has received great attention because of spillover effect to tune the selectivity between ethylene and ethanol by increasing *CO intermediates. In this point of view, the topic of unveiling the reconstruction behavior of Cu-Ag can be of interest to catalysis society. This work provides an insight to understand the CO_2RR selectivity trend (C_2H_4, C_2H_5OH, CO) with increasing Ag contents as the degree of Cu dissolution and redeposition on the Ag active sites. The topic of this work seems quite interesting, but this reviewer has several concerns about the novelty and explanation in this work. I can't recommend the accept of this manuscript in its current form. This can be reconsidered after major revision. Details are as follows.*

We appreciate you for the positive assessment and valuable comments, and the point-to-point response is appended below.

1. It seems that restructuring of Cu-Ag has been studied by investigating the HAADF-STEM images after CO_2RR. However, in the manuscript, it is difficult to find the CO_2RR condition (such as potential, current density, etc) for this post CO_2RR characterization. In the CO_2RR, -1.05 V (vs. RHE) seems the potential where the dramatic CO_2RR selectivity change occurs. Therefore, it is important to see the material study needs to be proceeded after CO_2RR at -1.05 V (vs. RHE).

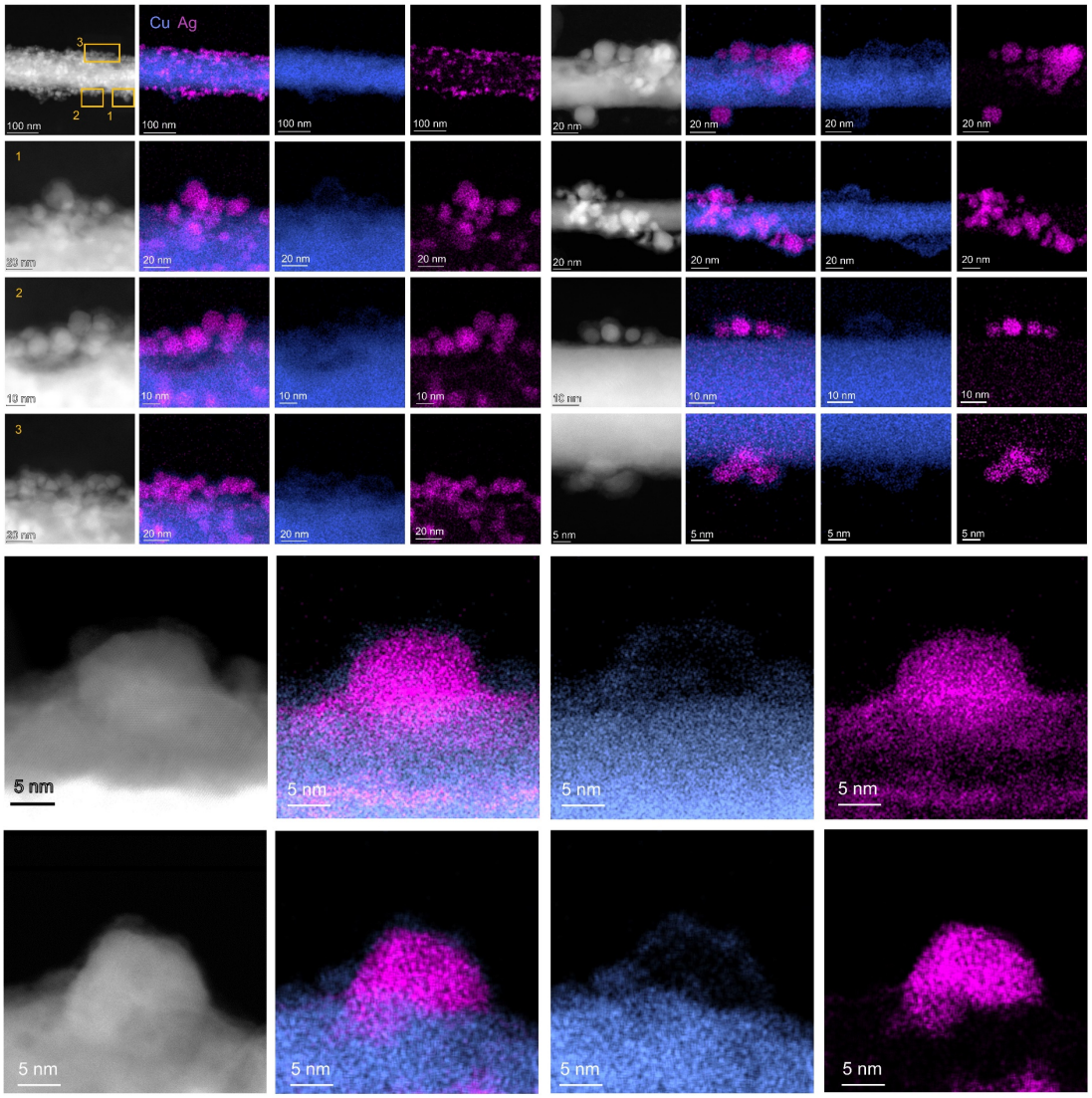
We appreciate you for the great comment, and apologize for missing to report the applied potential for the post CO_2R characterizations. We selected -1.05 V *vs.* RHE as the potential to check the morphology of Ag-Cu heterostructure after electrolysis, considering it is the potential that the discrepant product distributions occurred. To clarify, we have added the details of sample treatment

for post-TEM characterizations in the revised text (*Paragraph 3, Page 6*): … Aberration-corrected STEM was employed to reveal the biphasic interfaces of $Ag_{0.25}$-$Cu_{0.75}$, $Ag_{0.33}$-$Cu_{0.67}$, and $Ag_{0.5}$-$Cu_{0.5}$, respectively, after electrocatalysis at the potential of -1.05 V *vs*. RHE for one hour. …

2. Authors should provide more quantitative information about the Cu redeposition. Analysis of the Ag surface by HAADF-STEM does not represent the overall trend of restructuring because this only shows the narrow spot in whole catalysts. I think that there can be deviation in the Cu redeposition according to the Ag nanoparticle site. To generalize the behavior of Cu redeposition in the Ag nanoparticles-decorated Cu NWs, statistical results are essential.

Thank you for this thoughtful comment. We fully agree that HAADF-STEM is a local characterization technique, and there may be deviations at different positions. However, at the current stage, the characterization regarding encapsulation at the interface (*e.g.*, the Cu re-deposition in this work or strong metal support interaction) largely depends on the electron microscopy tools, since the interfacial feature cannot be well reflected in spectroscopy methods, which generally average data across the entire region, including the interface and bulk materials.

To provide a more comprehensive and rigorous assessment, we conducted additional experiments and incorporated more extensive HAADF-STEM characterization data at various locations in the revised text. An in-depth analysis, as clearly illustrated in the following figure, revealed that the reconstruction behavior involving the dissolution and redeposition of Cu on the $Ag_{0.5}$-$Cu_{0.5}$ heterostructure is not an occasional but a universal phenomenon across the whole surface. This behavior is consistently observed at various sites on a single nanowire and in randomly selected regions across multiple nanowires. These statistical HAADF-STEM and EDS analysis have been incorporated in the revised text as Supplementary Figure 16. Accordingly, the main text has been modified (*Paragraph 1, Page 7*): … Such a structural evolution occurred over the entire surface, and more results collected from other regions were summarized in Supplementary Figure 16. …



Supplementary Figure 16. HAADF-STEM images and corresponding EDS elemental maps at different locations showing the reconstructed core-shell nanostructure on $Ag_{0.5}$-$Cu_{0.5}$.

3. It seems that CuNWs are coated with bipyridine functional group. In this condition, how does Cu dissolves to the electrolyte? Can authors investigate the coverage of bipyridine functional group?

Thank you for this comment. We believe the decorated bipyridine functional groups are unable to cover the entire surface of Cu NWs, therefore Cu dissolution cannot be fully suppressed. To estimate the surface coverage of bipyridine functional group, we explored the thermogravimetric and specific surface analysis. As shown in the following thermogravimetric figure, bipyridine can be fully decomposed before 225 °C, corresponding to 1.28% weight fraction in Cu-bipy, *e.g.*, 0.11 mg of bipy was decorated on the surface of 8.14 mg of Cu NWs. To estimate the surface area of Cu NWs, we conducted the specific surface area test, and found that the Langmuir surface area of as-obtained Cu NWs was 2.12 m^2/g. According to the above results, the surface area of 8.14 mg of Cu NWs was estimated to be 0.017 m^2.

The bipy molecules could successfully functionalize Cu by forming strong coordination bonds

between the nitrogen atoms of bipy ligands and the metal surface. If we suppose that all bipy molecules vertically attached onto Cu NWs, the surface coverage of bipy molecules can be estimated through

$$coverage\ (bipy) = \frac{S_{bipy}}{S_{Cu}} = \frac{N_{bipy} \times S_{bipy(SGL)}}{S_{Cu}} = \frac{m_{bipy} \times N_A \times 3.14 \times (R_N)^2}{M_{bipy} \times S_{Cu}}$$

S_{bipy}: total cross-sectional area of as-obtained bipy, m^2

S_{Cu}: the Langmuir surface area of as-obtained Cu NWs, m^2

N_{bipy}: atomic number of as-obtained bipy

$S_{bipy(SGL)}$: cross-sectional area of a single N atom, m^2

m_{bipy}: the mass of bipy obtained from the TG curve, g

N_A: Avogadro constant = 6.02×10^{23} mol^{-1}

R_N: radius of an N atom, m

M_{bipy}: the molar mass of bipy, 156.18 g/mol

Therefore, for 0.11 mg of bipy on 8.14 mg of Cu NWs, we can estimate the coverage of bipyridine functional group to be 0.44 ML.

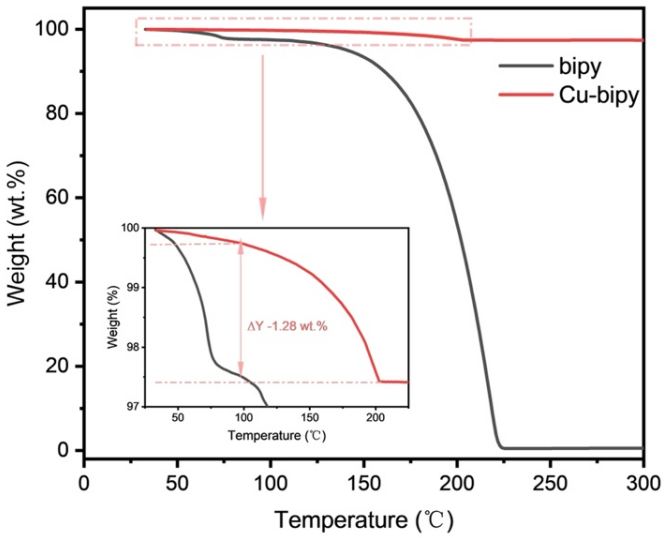
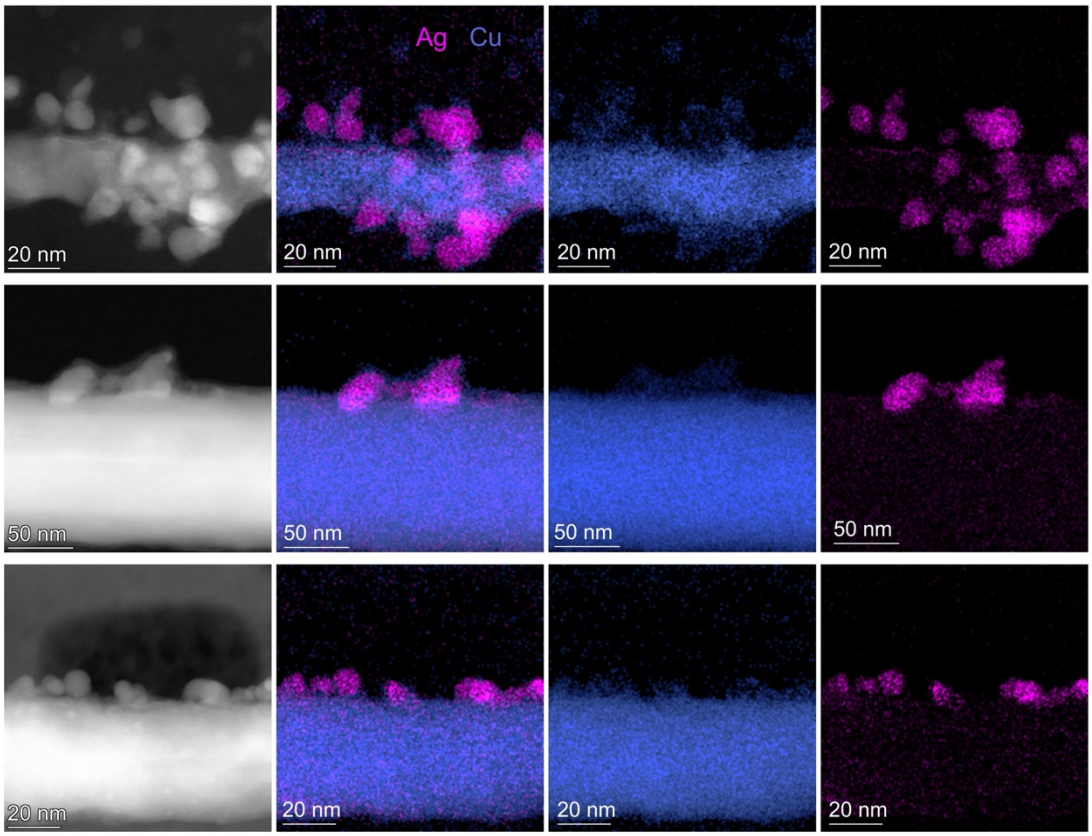


Figure Thermogravimetric analysis of Cu-bipy and pure bipy.

4. As authors mentioned, it seems that CO_2RR intermediates can affect the restructuring of Cu active sites. In the CO_2RR of Cu-Ag catalysts, most representative products are H_2 in general (Figure S8). I recommend authors to investigate the restructuring behavior of Cu-Ag catalysts at the system where more efficient CO_2RR (less HER) can occur with higher CO_2RR FE and partial current density such as flow cell. In current status, I think that it is difficult to agree with this phenomenon as a general behavior of CO_2RR catalysts because of relatively high HER portion and poor CO_2RR stability. Therefore, investigating the restructuring of catalysts at the more efficient CO_2RR condition would be helpful to verify the hypothesis of this work.

We appreciate your insightful comments. We fully agree with you on the importance of investigating

the restructuring of Ag-Cu heterostructure in a flow cell, where more efficient CO_2R occurs. In the revised text, we performed CO_2R on $Ag_{0.5}$-$Cu_{0.5}$ in a flow cell at -1.05 V *vs.* RHE, followed by HAADF-STEM imaging and EDS analysis. Our results revealed that the catalyst underwent more significant restructuring under a high current density. Specifically, we still observed Cu deposition on Ag surface, which aligns well with our findings in a H-cell. The following figure showing the restructuring of $Ag_{0.5}$-$Cu_{0.5}$ under electrolysis in a flow cell has been incorporated to the revised manuscript as Supplementary Figure 17. The revised text has been modified accordingly (*Paragraph 1, Page 7*): …The migration of Cu onto Ag surface has also been observed in a flow cell geometry, where a large current density and higher *CO concentration was produced (Supplementary Figure 17). …



Supplementary Figure 17 HAADF-STEM images and corresponding EDS elemental maps of $Ag_{0.5}$-$Cu_{0.5}$ in a flow cell at -1.05 V *vs.* RHE.

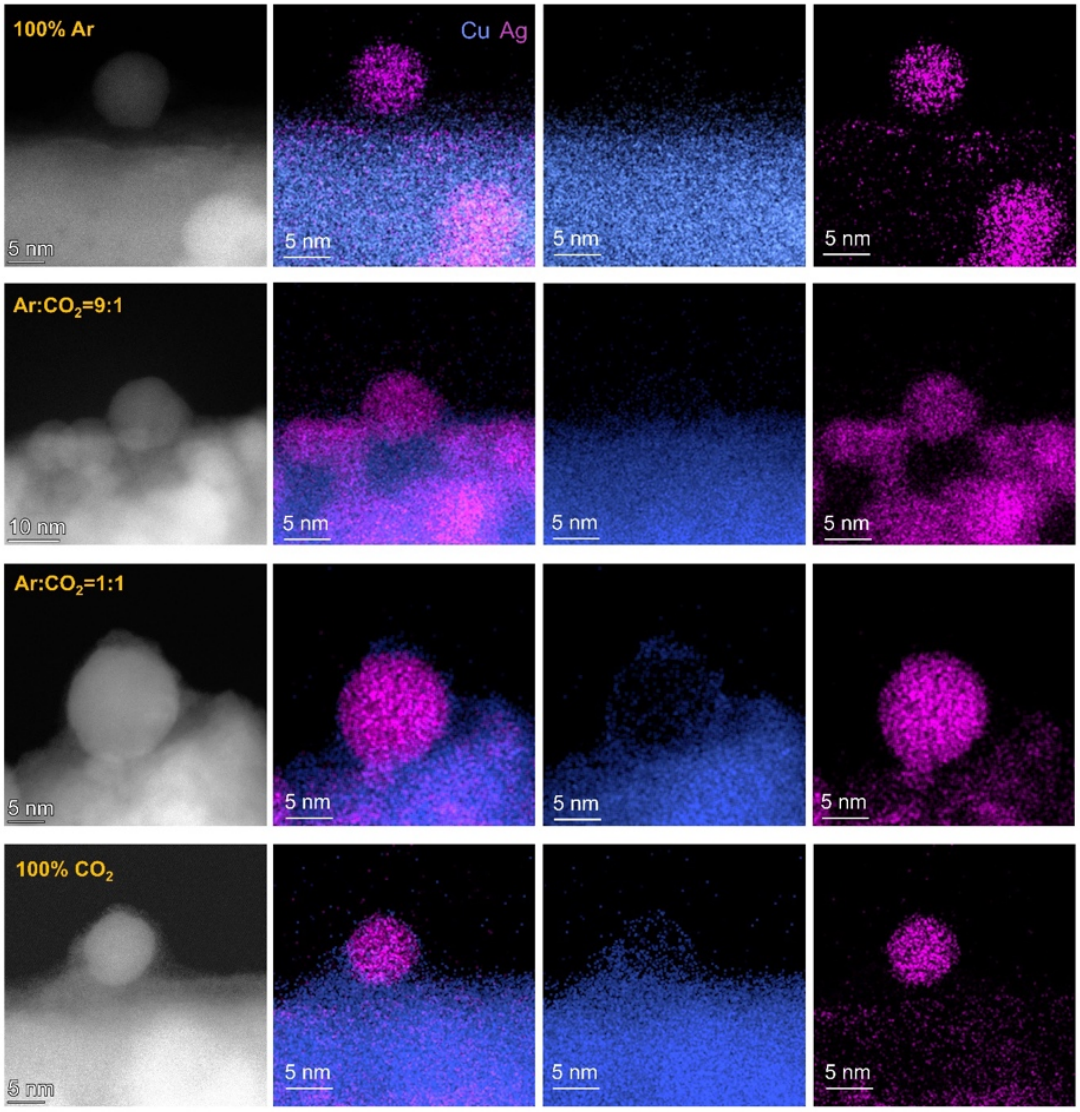
In addition, we apologize for the lack of clarity in the original figure annotations. We need to clarify that, even in a H-cell, CO_2R dominated the reaction on the surface of $Ag_{0.5}$-$Cu_{0.5}$, where H_2 was only a byproduct with a Faradaic efficiency of less than 30% at -1.05 V *vs.* RHE (Supplementary Figure 8). Therefore, we believe that the results we demonstrated in the H-cell can represent the restructuring behavior of Ag-Cu heterostructure under CO_2R. Furthermore, in the original text, we also designed an experiment without CO_2 supply to the system, wherein only HER occurs. It was observed that in the absence of *CO, the surface of Cu NW after electrolysis was smooth, and the

porous Ag@Cu core-shell structure was undetectable (Supplementary Figure 21). These results can further prove the critical role of *CO-coverage in the dynamic restructuring of bimetallic interface during CO_2 electrolysis. Thank you again for your valuable feedback, which will undoubtedly help us to improve and refine our work.

*5. Authors explained that Cu ions tend to migrate onto Ag domains, generating more abundant of Ag-Cu interface at higher *CO concentration. How does high *CO concentration can promote the Cu migration onto Ag domains? Authors needs to provide direct experimental evidence about this explanation.*

We appreciate your thoughtful comments and suggestions. The concern on the impetus of Cu restructuring has been addressed in the original text, which is clarified below. Cu atoms demonstrate a high mobility in CO_2 electrolysis, experiencing dissolution and subsequent redeposition either on the catalyst surface or at diverse locations under negative potentials (*Nat. Commun*. 2018, **9,** 3117; *J. Am. Chem. Soc*. 2023, **145,** 10116-10125; *Nat. Catal*. 2023, **6,** 837-846). In our study, a continuous oxidation-reduction process at the Ag-Cu interface was accountable for the dynamic restructuring of the surface. Under a cathodic bias, the electrochemical reduction resulted in a redeposition of Cu ions from the electrolyte, yet such redeposition was prone to occur at different places depending on the local *CO concentration. With a higher local *CO concentration, Cu ions tend to migrate onto the Ag domains, generating more abundant of Ag-Cu interface (Figure 3).

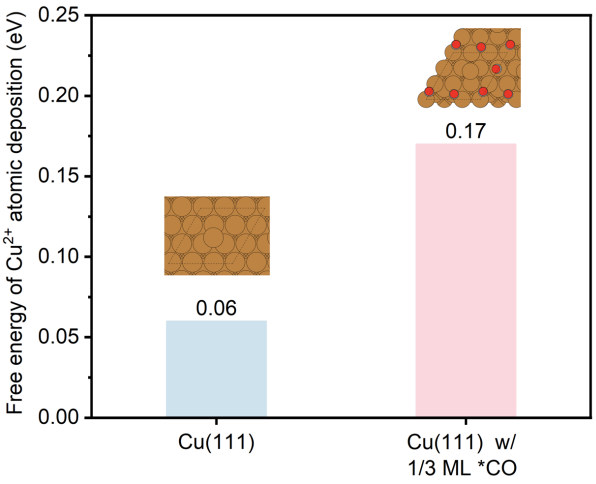
To experimentally support our conclusion, we designed and conducted more experiments in the revised text. We fed a gas mixture with varying CO_2/Ar ratios to the electrochemical cell, and characterized the interface by using HAADF-STEM and EDS analysis after CO_2 electrolysis under the same potential. As shown in Supplementary Figure 21, the surface of Cu NW after electrolysis in the absence CO_2 supply (100% Ar) was smooth, and the porous Ag@Cu core-shell structure was undetectable. Under the condition of Ar:CO_2=9:1, Cu reconstruction remained barely distinguishable. The migration of Cu onto Ag became obvious with an elevating CO_2 fraction, for instance, at Ar:CO_2=1:1, we started to observe Cu restructuring by forming porous Ag@Cu core-shell structure, while feeding pure CO_2, a thicker Cu shell could be evidenced. To this end, we conclude the crucial role of *CO intermediate in modulating the Cu restructuring behavior, wherein a higher *CO concentration leads to the generation of more Ag-Cu interfaces. Accordingly, we have added the following descriptions to the main text (*Paragraph 2, Page 8*): … To confirm our hypothesis, the electrochemical reconstruction of $Ag_{0.5}$-$Cu_{0.5}$ was investigated in gas mixtures with varying Ar and CO_2 ratios (see Experimental Procedure and Supplementary Figure 21). In the absence of *CO, the surface Cu NWs after electrocatalysis even demonstrated a smoother surface than the reconstructed $Ag_{0.25}$-$Cu_{0.75}$ under CO_2R wherein a low concentration of *CO was produced. The migration of Cu to Ag became more pronounced with an increasing CO_2 composition (from Ar : CO_2 = 9:1 to 1:1). …



Supplementary Figure 21 HAADF-STEM images and corresponding EDS elemental maps of $Ag_{0.5}$-$Cu_{0.5}$ after one hour electrolysis in gas mixtures with different ratios of Ar and CO_2.

We rationalized that the selective-deposition behavior of Cu ions stems from the distinct binding energies of *CO on Cu and Ag surfaces, *e.g.*, comparing with Cu, Ag possesses a much lower binding energy toward *CO (*Phys. Chem. Chem. Phys.* 2014, **16,** 4720-4727; *Chem*, 2018, **4,** 1809-1831). Consequently, under CO_2R operating condition, *CO is expected to desorb from Ag, and preferentially adsorbs on Cu, which would hinder the deposition of Cu ions on Cu NWs. As shown in the following figure, we compared the free energy evolution upon the deposition of dissolved Cu ions onto pure Cu and Cu-*CO. It was observed that the deposition on Cu was endothermic, and the degree of endothermicity increased when *CO adsorbed on Cu. Therefore, the higher *CO coverage would hinder the deposition of Cu ions on Cu, thus promoting the formation of Ag-Cu interface. To clarify this point, we added the following description to the revised text (*Paragraph 2, Page 8*): … We rationalized that the selective-deposition behavior of Cu ions stems from the distinct binding

energies of *CO on Cu and Ag surfaces, *e.g.*, comparing with Cu, Ag possesses a much lower binding energy toward *CO[22,45]. Consequently, under CO_2R operating condition, *CO is expected to desorb from Ag, and preferentially adsorbs on Cu, which would hinder the deposition of Cu ions on Cu NWs. We calculated and compared the free energy evolution upon the deposition of dissolved Cu ions on pure Cu and Cu-*CO. It was observed that the deposition on Cu was endothermic, and the degree of endothermicity increased when *CO adsorbed on Cu (Supplementary Figure 22). Therefore, higher *CO coverage would suppress the deposition of Cu ions on Cu NWs, instead, it promotes the migration of Cu to the neighboring clean Ag surface, leading to the formation of Ag-Cu interface. These results can well explain our experimental observations: With a higher local *CO concentration, Cu ions tend to migrate onto Ag NPs, generating more abundant of Ag-Cu interface. …



Supplementary Figure 22 The free energy evolution of Cu ion deposition on Cu(111) and Cu(111) with 1/3 ML *CO.

6. It seems that the CO_2RR results in Figure 2a and 2b are not same with the results in contour map in Figure 2e. For example, $Ag_{0.5}$-$Cu_{0.5}$ exhibited the optimal alcohol FE at -1.05 V (vs. RHE) in Figure 2a and 2b. However, in the contour map, the optimal FE for alcohol is located at the potential range between -0.9 and -1.0 V (vs. RHE). Authors need to explain this mismatch.

We sincerely appreciate your careful checking, and apologize for this mistake. The data order on Y axis in the original contour map was reversed, which has been corrected in the revised text. We have further carefully checked all data graphs included in the manuscript to ensure the accuracy. Once again, we are grateful for your diligent review of our article.

Author's response

Intermediate-regulated dynamic restructuring at Ag-Cu biphasic interface enables selective CO_2 electroreduction to C_{2+} fuels

We appreciate the editor and reviewers for your time reviewing this manuscript. Here we provide a point-to-point response. In this document, the *italics* are the comments from the reviewers.

Response to Reviewer #1's comments:

The manuscript has undergone significant improvements and is now ready for publication.

We appreciate your positive evaluation and your support to accept our work for publication.

Response to Reviewer #2's comments:

The Authors have clarified the raised point and made needed changes to amend the issue. The Authors also provided enough explanations on the novelty of their work. I have no further remarks/comments to make. The paper can be accepted for publication in the present form.

We sincerely appreciate your support to accept our manuscript for publication.

Response to Reviewer #3's comments:

The authors have made substantial revisions to the manuscript and addressed all concerns. I therefore recommend its publication in Nature Communications without the need for further revisions.

Thank you for your support. We appreciate your efforts in reviewing our work.

Response to Reviewer #4's comments:

Revised manuscript now addresses the concerns from this reviewer. I recommend the acceptance of this manuscript in Nature Communications.

We appreciate you for the positive assessment and your support to accept our work.