







Reply To: Confined molecular catalysts provide an alternative interpretation to the electrochemically reversible demetallation of copper complexes

Zhe Weng ^{1,4}, Yueshen Wu^{1,5}, Maoyu Wang^{2,6}, Gary W. Brudvig ¹, Victor S. Batista ¹, Yongye Liang ^{3✉}, Zhenxing Feng ^{2✉} & Hailiang Wang ^{1✉}

REPLYING TO E. Boutin et al. *Nature Communications* <https://doi.org/10.1038/s41467-022-31661-1> (2022)

In the Matters Arising (MA) by Robert and Boutin (henceforth abbreviated RB) on our article entitled “Active Sites of Copper-Complex Catalytic Materials for Electrochemical Carbon Dioxide Reduction” published in *Nature Communications* more than four years ago in January 2018 (the article)¹, RB questioned our interpretation of a portion of our results and offered an alternative explanation. Specifically, based on our in situ X-ray absorption spectroscopy (XAS) results, we proposed that at reductive electrode potential (−1.06 V vs RHE, all potentials below are with respect to RHE unless otherwise stated), reduction of copper phthalocyanine (CuPc) leads to the formation of small Cu nanoparticles (NPs) that are electrocatalytically active for CO₂ reduction to CH₄; subsequently, after release of the reductive potential, oxidation of the Cu NPs and re-coordination with the empty Pc ligands occur to regenerate CuPc (Table 1). It is this latter point that RB disagree with. They argue that upon reoxidation, all the Cu NPs leach into the electrolyte as Cu²⁺ ions and the XAS signal for CuPc arises solely from the unreacted part of CuPc that is not reduced at the previous reductive potential (Table 1). However, in their MA, RB do not provide any original data; nor do they show any evidence that can directly support their argument. Therefore, the original results and conclusions of the article are not affected. Nevertheless, we would like to take this opportunity to update readers with additional data we collected in our earlier experiments as well as results from more recently published independent studies from other research groups that have directly confirmed our conclusions in the article.

Figure 1 shows the original unnormalized XAS spectra of our CuPc electrode at the initial open circuit voltage (OCV), at −1.06 V and then back to OCV. The unnormalized edge jumps of the Cu K absorption spectra can be used to quantitatively compare the amount of Cu species on the electrode. At the initial OCV, the unnormalized intensity is 1.5 with 100% of the Cu

element in the CuPc form, corresponding to the initial state. At −1.06 V, the absorption intensity has decreased to 1.2, which is not uncommon for this kind of multi-hour measurement^{2,3}. One likely reason for the loss is gas bubbling stripping active material off the electrode. Analysis shows that the material at −1.06 V contains 80% Cu NPs and 20% CuPc, which directly leads to the conclusion that a large part of the CuPc on the electrode has been reduced to Cu NPs. After measurements at negative potentials, the electrode was left at OCV (labeled as OCV-2 to distinguish from the initial OCV) for several hours before the final XAS spectrum was taken. Note that the 0.64 V label in the original article was inaccurate and the description “upon release of the negative electrode potential” was ambiguous (0.64 V was the value of the initial OCV which should differ from that of OCV-2; we apologize to the readers for this negligence). At OCV-2, the absorption intensity has further decreased to 0.8 with 100% CuPc. Note that at −1.06 V the unreacted CuPc accounts for an intensity of 0.24 (20% of total intensity 1.2). Therefore, at least a significant part of the Cu NPs at −1.06 V has been converted back to CuPc (conclusion of the article). It is impossible that the CuPc signal at OCV-2 is entirely from unreacted CuPc (the RB claim) whose theoretical maximum contribution to absorption intensity is 0.24. These experimental results directly prove that RB’s argument in their MA is incorrect.

Over the past several years since the publication of the article, there have been a considerable number of independent studies from other research groups that directly or indirectly confirm our restructuring conclusions. In their work published in *ChemSusChem* in 2020, Mougél and Fontecave et al. studied a polymer of CuPc coated on carbon nanotubes for electrochemical CO₂ reduction⁴. With in-situ XAS, they also observed reduction to Cu NPs under working conditions and restoration of the original CuN₄ coordination structure upon reoxidation (Fig. 2a, b). In

¹Department of Chemistry and Energy Sciences Institute, Yale University, New Haven, Connecticut 06511, USA. ²School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR 97331, USA. ³Department of Materials Science and Engineering, South University of Science and Technology of China, Shenzhen 518055, China. ⁴Present address: Tianjin University, Tianjin, China. ⁵Present address: Twelve, Berkeley, CA, USA. ⁶Present address: Argonne National Laboratory, Lemont, IL, USA. ✉email: lianggyy@sustc.edu.cn; zhenxing.feng@oregonstate.edu; hailiang.wang@yale.edu

Table 1 Original conclusions of the article and key points raised by RB's MA.**Our original conclusions**

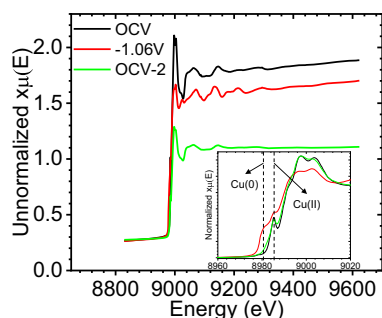
At reductive potential (-1.06 V), CuPc is reduced to Cu NPs which are the active catalyst for CO_2 reduction to CH_4 .

After release of the reductive potential, (at least a large part of) Cu NPs are converted back to CuPc.

RB's MA

Agrees with us on what happens at the reductive potential.

After release of the reductive potential, All Cu NPs are oxidized to Cu^{2+} and leach into the electrolyte, no regeneration of CuPc.



[Cu K-edge absorption intensity is proportional to the amount of Cu species on electrode](#)

- i) OCV: intensity 1.5; 100% CuPc
- ii) -1.06 V: intensity 1.2; 80% Cu(0), 20% CuPc
Conclusion: (at least a large part of) CuPc has been reduced to Cu(0)
- iii) Back to OCV: intensity 0.8; 100% CuPc
Conclusion: (at least a large part of) Cu(0) has been converted back to CuPc

Fig. 1 Unnormalized in-situ XAS spectra. CuPc under electrochemical CO_2 reduction conditions with the near edge structure shown as inset (same original data that generated Fig. 2 in the article).

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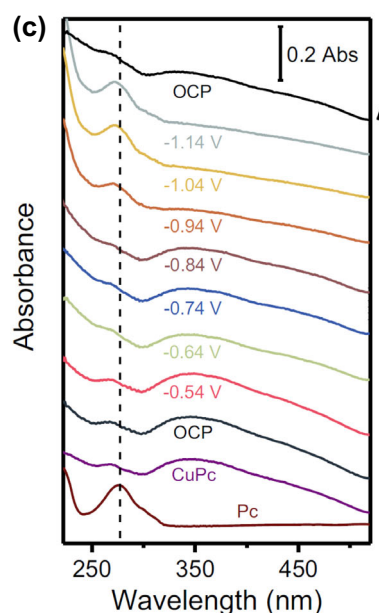
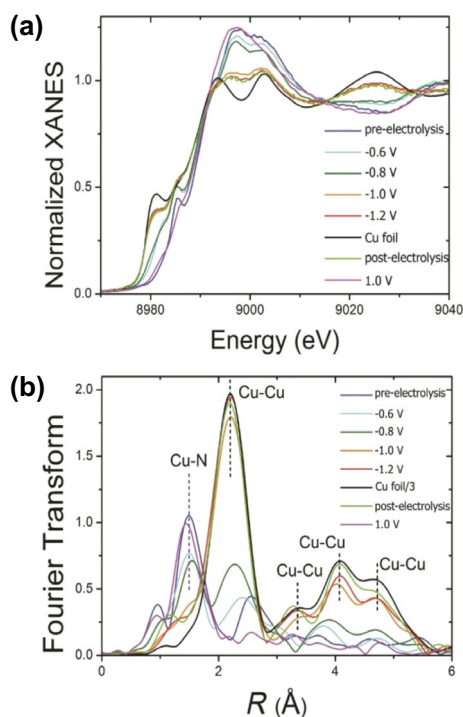


Fig. 2 Two representative recent studies from other research groups that directly support our conclusions. **a**, **b** In-situ XAS results (**a** near edge absorption; **b** Fourier transform of the extended range) of a CuPc polymer catalyst under electrochemical CO_2 reduction conditions. Adapted with permission from Ref. 4. Copyright 2020 Wiley. **c** In-situ UV-vis study of CuPc under electrochemical CO_2 reduction conditions. Adapted with permission from Ref. 5.

another work by Min, Lin, Zhu and co-workers published in *Nature Communications* in 2021, the authors performed in-situ UV-vis spectroscopic measurements of CuPc under electrochemical CO_2 reduction reaction conditions⁵. At reducing electrode potentials < -1.04 V, the CuPc absorption features almost disappear and the B-bands of free-base Pc dominate (Fig. 2c). After release of the reduction potential, the UV-vis profile returns to that of CuPc, which directly confirms our reversible

restructuring finding with a different technique. Similar reversible restructuring between single Cu(II) sites and Cu(0) NPs have also been observed for CO_2 reduction electrocatalysts that can be considered analogs of CuPc, such as single CuN_4 sites embedded in a carbon network⁶ and CuN_2Cl_2 in a covalent triazine framework⁷. More studies as such are summarized in a recent short review article published in *Nature Communications*⁸. All these independent studies clearly support our conclusions in the

article and testify directly against RB's argument. Unfortunately, the results and conclusions of these important studies were overlooked, intentionally or otherwise, by RB.

In conclusion, the reversible restructuring postulation remains as the best interpretation of the results, which is supported by our experimental data and has been confirmed by other independent studies.

Data availability

The data that support the findings of this study are available within the paper or are available from the corresponding authors upon reasonable request.

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Author contributions

Z.W., Y.W., M.W., G.W.B., V.S.B., Y.L., Z.F., and H.W. analyzed the data and wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to Yongye Liang, Zhenxing Feng or Hailiang Wang.

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