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Structural properties of Au/Cu₂O catalysts for electrochemical CO₂ reduction to C₂ products

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Improving the selectivity towards multi-carbon products for the electrochemical reduction reaction of CO₂ (CO₂RR) with Cu-based catalysts remains a significant topic of scientific interest. It is known that using a secondary metal can provide some control over selectivity, with the structure of the bimetallic catalysts playing an important role in product distribution. In this study, we synthesized Au/Cu₂O catalysts *via* a precipitation method followed by galvanic replacement using varying Au concentrations. This approach enabled a systematic investigation of the restructuring of Cu₂O phases decorated with highly dispersed Au, Au-Cu alloys, and Au clusters and their impact on the catalytic activity. Among the tested catalysts, the Cu₂O catalyst with highly dispersed Au exhibited the highest Faradaic efficiency towards ethylene and ethanol. *In situ* X-ray absorption spectroscopy (XAS) and quasi-*in situ* X-ray photoelectron spectroscopy (XPS) measurements revealed that the presence of Au influenced the reduction of Cu₂O, where the catalyst with highly dispersed Au displayed the highest fraction of cationic Cu species. Furthermore, *in situ* X-ray diffraction (XRD) was employed to study the structural evolution of crystalline phases of the catalysts during CO₂RR, which suggests that significant restructuring and redispersion of Au takes place. This work highlights the relevance of *in situ* studies to understand the dynamic interplay between the structure and the catalytic behavior during the reaction.

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Introduction

The electrochemical CO₂ reduction reaction (CO₂RR) offers a promising method to close carbon cycles.¹ This process involves the conversion of waste CO₂ into valuable chemical building blocks and fuels powered by renewable electricity. Copper stands out as an electrocatalyst for this reaction due to its unique ability to form multi-carbon hydrocarbons and oxygenates (*e.g.*, ethylene and ethanol). However, the exclusive formation of one of such products has not been realized yet.²

Bimetallic catalysts have been extensively studied to tune the catalytic performance and improve the C₂ selectivity.^{3,4} The morphology and composition of these catalysts can be readily modified to control the product distribution of the CO₂RR.^{5–7} In particular, adding Ag,^{8,9} Au,^{10,11} and Zn^{12,13} as a second metal can facilitate the conversion of CO₂ to carbon monoxide (CO).^{14–18} The enhanced C₂ selectivity observed with bimetallic catalysts is generally attributed to the role of

CO as a crucial intermediate, facilitating C–C bond formation *via* CO dimerization during the CO₂RR.^{19,20} This constitutes a tandem reaction in which CO₂ is reduced to CO on the secondary metal, with CO spilling over to the Cu sites where the C₂ products can be formed. Besides CO spillover, it has been postulated that adding a second metal alters the electronic properties of Cu, impacting the adsorption energies of key intermediates.^{21,22} For instance, Cu–Au alloys were reported to form more CO than monometallic Au catalysts.^{23,24} Cu–Au alloys can also be formed from Au/Cu₂O catalysts during CO₂RR, enhancing C₂ product formation, especially when small amounts of Au are close to Cu sites.²⁵

Aspects such as the importance of structural properties and CO spillover mechanism for enhanced C₂ product formation have also been mentioned for Cu–Ag alloys.^{26,27} For such alloys, it has been discussed that the stabilization of a Cu₂O overlayer on Ag improves C–C coupling kinetics.²⁷ The promoting effect of residual cationic Cu species, presumably due to incomplete reduction of oxidic Cu precursor during CO₂RR, has also been reported for other Ag/Cu catalysts.¹⁴ Numerous studies have investigated the role of cationic Cu species, especially Cu⁺, on the selectivity to products containing C–C bonds. It has been mentioned that active sites containing Cu⁺ exhibit different adsorption

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$$FE = z \times n \times F/Q$$

where z represents the number of electrons involved in the formation of the product (e.g. $z = 2$ for CO and $z = 12$ for C_2H_4), n is the number of moles for a specific product, F is the Faraday constant (96485 C mol^{-1}) and Q is the total charge (C) for the measurement.

Results and discussion

The Cu_2O nanocrystals with cubic shape were prepared by a ligand-free precipitation method.¹⁴ The Au/ Cu_2O composites were synthesized by a galvanic replacement reaction between $H AuCl_4$ and the Cu_2O nanocrystals ($6 H^+(aq) + 2 AuCl_4^-(aq) + 3 Cu_2O(s) = 6 Cu^{2+}(aq) + 8 Cl^-(aq) + 2 Au(s) + 3 H_2O(l)$).³⁵ In parallel, the disproportionation reaction of Cu_2O into Cu and CuO takes place ($Cu_2O(s) = Cu(s) + CuO(s)$) in the acidic environment. The galvanic replacement was performed in an ethanol–water mixture, because ethanol is known to slow the reactions, thereby stabilizing the Cu_2O surface.^{36–38} As a result, the Au and Cu atoms can form Au–Cu alloys at ambient conditions. As the Au content increases, the Au atoms cluster not only with Cu atoms, but also with each other, forming Au particles. For this study, we synthesized Au/ Cu_2O composites with Au contents of 1, 5 and 10 mol% based on the metal content. This resulted in the formation of well-defined Cu_2O catalysts decorated with highly dispersed Au in 1Au/ Cu_2O , Au–Cu alloys in 5Au/ Cu_2O and Au clusters in 10Au/ Cu_2O , allowing for a systematic study of monitoring the restructuring of these phases during CO_2RR and its impact on the catalytic performance. The characterization of the as-prepared catalysts will be discussed below.

The HAADF-STEM images of the freshly prepared catalysts are shown in Fig. 1. Representative bright-field TEM images are shown in Fig. S1. The Cu_2O nanocrystals display a cubic morphology and are enclosed with six (100) crystal planes.³⁹ The cubes have an edge length of approximately 30 nm. Huang *et al.* showed that, although the cubic shape was preserved in the presence of Au, the Cu_2O surface became rougher.³⁷ For 1Au/ Cu_2O , we observed that the Cu_2O surface looks similar to that of the Au-free sample, likely due to the low Au loading. This suggests a high dispersion of Au atoms on the Cu_2O nanocubes. At higher Au loading (5 mol% Au), small Au nanoparticles with a size of 5 nm appeared on the

Cu_2O surface. Many such nanometer-sized particles were observed on the sample containing 10 mol% Au. This latter sample also contained some larger agglomerates of Au particles.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were performed to identify the presence of a Cu_2O phase with highly dispersed Au species, Au–Cu alloys and larger Au clusters in the as-prepared samples (Fig. 2). The crystalline phases in the as-prepared Cu_2O nanocubes and Au/ Cu_2O composites were determined by synchrotron powder XRD. The diffractograms shown in Fig. 2a and S2 clearly demonstrate the crystalline nature of the materials. The main Cu_2O reflections attributed to the (111) and (200) diffraction planes are found at q values of 2.55 \AA^{-1} and 2.94 \AA^{-1} , respectively. As the patterns only contain reflections of Cu_2O , it can be concluded that crystalline Au- and Au–Cu-containing phases are absent in the 1Au/ Cu_2O sample, in line with the high Au dispersion suggested by the EM images. In contrast, the XRD patterns of 5Au/ Cu_2O and 10Au/ Cu_2O contain characteristic (111) reflections of AuCu alloy at $q = 2.78 \text{ \AA}^{-1}$ and CuO at $q = 2.68 \text{ \AA}^{-1}$. The 10Au/ Cu_2O sample also contains a diffraction peak at $q = 2.60 \text{ \AA}^{-1}$, which can be assigned to the Au(111) reflection. The low intensity of the peaks related to CuO, AuCu, and Au shows that they are minority phases. The broad peaks indicate the small size of the crystalline domains and suggest the high dispersion of these phases. The sizes of the Cu_2O and Au/ Cu_2O crystallites derived from XRD data were in the range of 25–30 nm and are in good agreement with electron microscopy data (Table S1). XPS analysis was performed on the fresh samples to study the surface of the catalysts (Fig. 2b–d). From the peak at 932.2 eV in the Cu $2p_{3/2}$ XPS spectra (Fig. 2b), it can be judged that metallic Cu^0 and/or Cu^+ species are present on the surface. Furthermore, Cu^{2+} species were detected as can be seen from the shoulder at 934.0 eV and the characteristic satellite feature in the 939–945 eV range.³³ The existence of Cu^{2+} species is most likely due to the air exposure of the sample. To distinguish between Cu^0 and Cu^+ , we analyzed the Cu LMM spectrum (Fig. 2c). This spectrum demonstrated the absence of Cu^0 species and revealed the presence of a mixture of Cu^+ and Cu^{2+} . With increasing Au content, the fraction of Cu^{2+} species on the surface increased. This is revealed by the corresponding Cu $2p_{3/2}$ spectra, which display a higher relative intensity of the

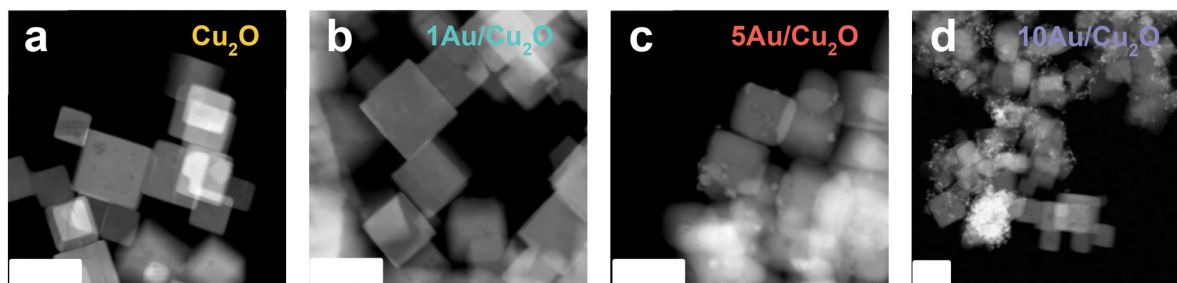


Fig. 1 HAADF-STEM images of (a) Cu_2O , (b) 1Au/ Cu_2O , (c) 5Au/ Cu_2O and (d) 10Au/ Cu_2O . The scale bar corresponds to 50 nm.





Fig. 2 (a) Synchrotron X-ray diffractograms of the as-prepared samples ($\lambda = 0.0165312$ nm). (b) Cu $2p_{3/2}$, (c) Cu LMM and (d) Au 4f XPS spectra of the as-prepared samples.

Cu^{2+} to the $\text{Cu}^{0/+}$ peaks and the strong satellite feature. Besides air exposure, Cu^{2+} can be formed by the reactions taking place during Au introduction, *i.e.*, galvanic replacement reaction and Cu_2O disproportionation, as described earlier.³⁵ Au 4f XPS spectra provide evidence for Au species on the surface of the Cu_2O nanocubes (Fig. 2d). The Au content at the surface determined from these XPS spectra was close to the targeted theoretical values (Table S2). However, at higher Au loadings, the amount of Au ending up in the sample is significantly lower than the targeted value. We surmise that this is caused by the simultaneous

formation of CuO due to disproportionation. CuO does not participate in the galvanic replacement reaction, *i.e.*, CuO will not react with HAuCl_4^- . The shift of the Au $4f_{7/2}$ peak from 84.7 to 84.2 eV with increasing Au loading revealed the formation Au–Cu alloys and/or Au clusters.^{40–42} Thus, we speculate that the Au or Au–Cu alloy particles are highly dispersed in the 1Au/ Cu_2O sample. These observations are in line with the results from HAADF-STEM and XRD.

The performance of the electrocatalysts was assessed using chronoamperometry at fixed potentials in an H-type cell with CO_2 -saturated 0.1 M KHCO_3 (pH 6.8) as the supporting electrolyte. The catalytic tests were carried out at potentials between -0.9 to -1.2 V vs. RHE with intervals of 0.1 V. The FE for CO, ethylene and ethanol obtained after 1 h of CO_2RR are shown in Fig. 3. The FE for other products formed during electrolysis can be found in Fig. S3. In all cases, C_2 products were formed during CO_2RR , as commonly observed for Cu-based catalysts.^{43–45} The introduction of Au and the increase of the Au loading resulted in a higher FE towards CO, especially at less negative potentials. The FE towards ethylene was slightly enhanced for 1Au/ Cu_2O as compared to Cu_2O . 5Au/ Cu_2O showed only an increase in ethylene formation at more negative potentials. However, the addition of Au to Cu_2O had a more pronounced effect on the FE towards ethanol. The incorporation of 1 mol% of Au resulted in a significant 1.6-fold increase in ethanol formation at -1.0 and -1.1 V vs. RHE, achieving FEs of 15% and 17%, respectively. Notably, a higher Au loading (10 mol% Au) resulted in the lowest FEs for ethylene and ethanol across the entire potential range. To understand the influence of the electrochemical surface area (ECSA) on the product distribution, we carried out double-layer capacitance measurements after CO_2RR (Fig. S4 and S5 and Table S3). All catalysts exhibit similar ECSAs, suggesting that differences in ECSA cannot account for the observed variations in catalytic performance. Based on the FE data, we hypothesize that the

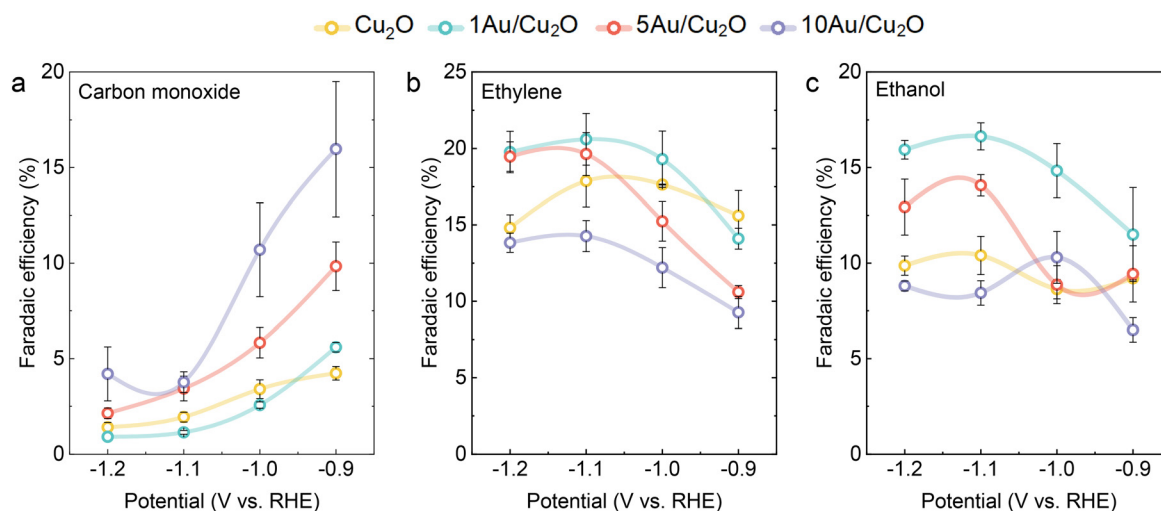


Fig. 3 Faradaic efficiencies as a function of the applied potential for (a) carbon monoxide (b) ethylene and (c) ethanol. The potentials were kept constant for 1 hour in CO_2 -saturated 0.1 M KHCO_3 electrolyte. Solid lines are a guide for the eye.



high dispersion of Au or Au–Cu alloys in the as-prepared samples enhances catalytic performance towards C_2 products. Placing CO-producing sites close to Cu sites facilitates CO spillover, resulting in improved C_2 FE. Au–Cu alloys were reported to outperform Au in terms of CO formation, resulting in a high local CO concentration in the double layer, which facilitates C–C coupling.²⁴ Furthermore, it is known that the morphology and size of Au particles can affect the CO_2RR performance, resulting in different CO/ H_2 ratios in the product mixture.^{46,47} We postulate that the larger Au particles in the 10Au/ Cu_2O sample favor CO and H_2 production, the abundance of such particles on the reduced

Cu phase potentially blocking the active Cu sites for C–C coupling. To further examine the interactions between Cu and Au, which could be responsible for the observed differences in the catalytic performance, we employed a variety of *in situ* and quasi-*in situ* characterization methods.

The evolution of the crystalline phases under CO_2RR conditions was followed by *in situ* synchrotron XRD. The *in situ* XRD cell has been described in the literature.⁴⁸ For this study, we continuously bubbled CO_2 in an external reservoir with 0.1 M $KHCO_3$ electrolyte (pH 6.8). The diffractograms of the initial state of the catalysts (Fig. S6) are in good agreement with the *ex situ* XRD data shown in Fig. 2a. Due to

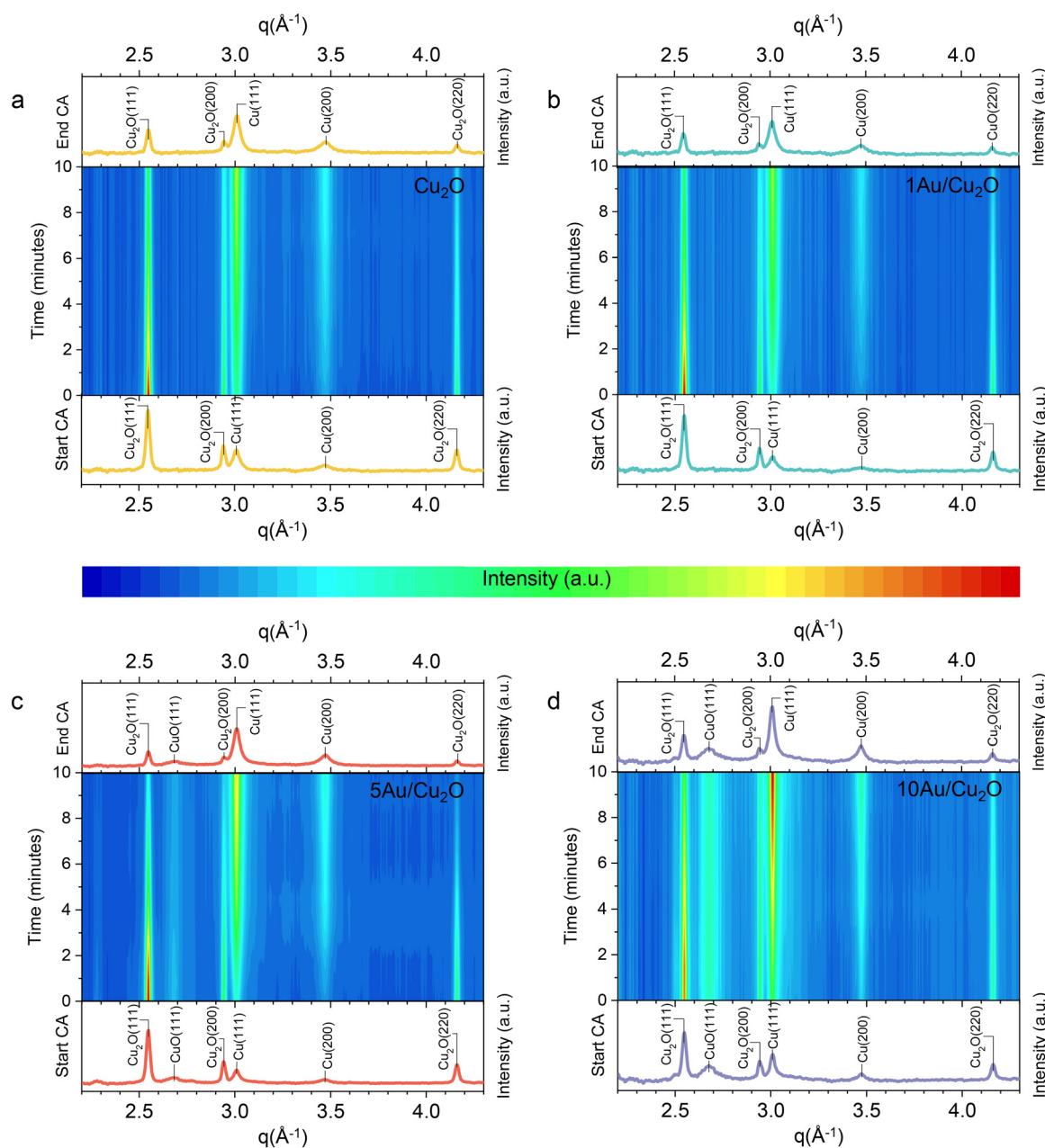


Fig. 4 Evolution of the X-ray diffractograms during the chronoamperometry measurement at -0.9 V vs. RHE for (a) Cu_2O , (b) 1Au/ Cu_2O , (c) 5Au/ Cu_2O and (d) 10Au/ Cu_2O .



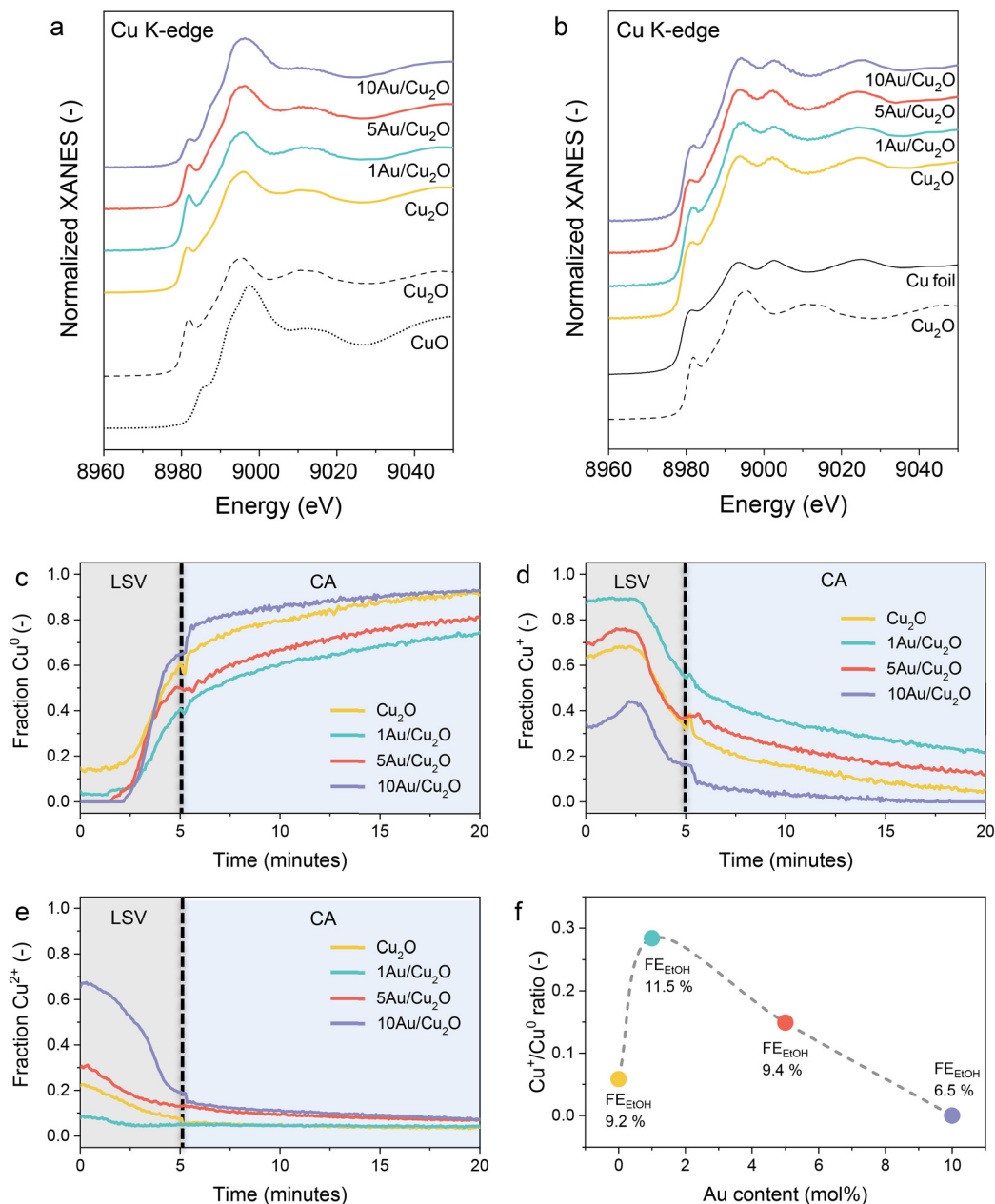


Fig. 5 Normalized Cu K-edge XANES spectra of the (a) fresh samples and (b) in the final state during CO₂RR at -0.9 V vs. RHE. References (black) are shown for comparison. Time-dependent fractions of (c) Cu⁰, (d) Cu⁺ and (e) Cu²⁺ during linear sweep voltammetry (LSV) (+0.6 V to -0.9 V vs. RHE, scan rate: 5 mV s⁻¹) followed by chronoamperometry (CA) at -0.9 V vs. RHE. The dotted lines represent the end of the LSV and the beginning of the CA (f) Cu⁺/Cu⁰ ratio versus the theoretical Au loading and the FE for EtOH at -0.9 V vs. RHE. Dashed grey line is a guide for the eye.

CO₂RR, the fresh catalysts are similar to the measured Cu₂O reference, which agrees with the MCR-ALS XANES analysis. The main contributions at 1.5 Å and 2.8 Å correspond to Cu–O and Cu–Cu bonds, respectively, in Cu₂O. The EXAFS fitting parameters are presented in Table S5. The Cu–O coordination number ($N_{\text{Cu-O}}$) of the fresh samples is approximately 2, closely matching that of bulk Cu₂O. The Cu–O distance ($R_{\text{Cu-O}}$) was determined to be 1.86 Å, which aligns with the Cu–O distance in bulk Cu₂O.⁴⁹ During the CA at -0.9 V vs. RHE, a new intense contribution emerged at 2.2 Å in the Cu K-edge FT-EXAFS for all samples. This peak can

be ascribed to the first Cu–Cu shell in metallic Cu.⁵⁰ The highest Cu–Cu coordination number ($N_{\text{Cu-Cu}}$) for this metallic Cu shell was observed for 10Au/Cu₂O (8.7 ± 0.5). Lower $N_{\text{Cu-Cu}}$ values were reported for Cu₂O (8.5 ± 0.6), 1Au/Cu₂O (7.4 ± 0.6) and 5Au/Cu₂O (8.5 ± 0.6). The lowest $N_{\text{Cu-Cu}}$ for 1Au/Cu₂O can be explained by partial preservation of the Cu₂O phase. The Au L₃-edge XAS spectra of the Au/Cu₂O catalysts, recorded before and during CO₂RR, are shown in Fig. S13. Although the Au signal is relatively weak due to the low Au content, the XANES spectra of the fresh samples exhibit a notable increase in the white-line intensity between





Fig. 6 Fourier-transformed Cu K-edge EXAFS of the (a) fresh samples and (b) in the final state during CO₂RR at -0.9 V vs. RHE with the corresponding fits (black). The reference spectra of Cu₂O and Cu foil are shown for comparison.

11920 and 11940 eV compared to the Au foil reference (Fig. S14a). This increase is indicative of electron transfer from Au to Cu, which is commonly associated with Au-Cu alloy formation.^{35,51} During CO₂RR, a clear decrease in white-line intensity is observed for 10Au/Cu₂O (Fig. S14c), suggesting a shift toward more metallic Au under reaction conditions. For 5Au/Cu₂O (Fig. S14b), this trend is more difficult to resolve, likely due to the lower Au content and associated signal-to-noise limitations. However, the FT-EXAFS data also reveal significant differences in the local structure of Au in the as-prepared samples relative to Au foil, with both spectra only beginning to resemble Au foil under CO₂RR conditions (Fig. S13d, Table S6). These observations suggest dynamic restructuring and possible dealloying during CO₂RR, which is in line with the *in situ* XRD results. For the 1Au/Cu₂O sample, reliable data acquisition during CO₂RR was challenging due to the low Au content, resulting in poor signal-to-noise ratios. Therefore, this data was excluded from our analysis.

The surface composition and the chemical state of the electrocatalysts after 1 h of CO₂RR at -0.9 V vs. RHE were investigated with quasi-*in situ* XPS. A CO₂-saturated 0.1 M KHCO₃ solution was used as a supporting electrolyte. The quasi-*in situ* approach allows for the analysis of the surface of the samples without exposure to air. The XPS spectra were recorded directly after the electrochemical measurements and sample transfer to the analysis chamber, performed under an inert atmosphere of Ar to prevent oxidation of the samples. The Cu 2p_{3/2} and Cu LMM spectra in Fig. 7a and b show that all Cu²⁺ species at the surface were reduced, as follows from the absence of the characteristic peaks and satellite feature corresponding to Cu²⁺.³³ The single Cu 2p_{3/2} feature at 932.3 eV for all catalysts indicates that the surface of the samples only contained Cu⁺ and/or Cu⁰ species. The Cu LMM spectra show that the surface is predominantly made up of metallic Cu (Fig. 7b). The relative intensities of the features at kinetic energies of 917.0 eV and 918.9 eV



Fig. 7 Quasi-*in situ* XPS spectra of the (a) Cu 2p_{3/2}, (b) Cu LMM and (c) Au 4f regions (spectra recorded after 1 h CO₂RR at -0.9 V vs. RHE, transfer through vacuum system without air exposure).



suggest the presence of residual surface Cu^+ species. The 1Au/Cu₂O sample contained the largest amount of Cu^+ species, which is consistent with the observations from the XAS analysis. The Au 4f spectra shown in Fig. 7c reveal that Au is in the metallic state. The surface composition ratios after CO₂RR were comparable to those in the fresh samples (Table S2). This indicates that, despite the disappearance of bulk Au according to *in situ* XRD, Au dissolves and redeposits on the surface. All catalysts displayed a Au 4f_{7/2} maximum peak intensity at a binding energy of 83.9 eV. The shift towards lower binding energies for 1Au/Cu₂O, compared to the fresh sample, can indicate sintering of the dispersed Au particles during CO₂RR.

General discussion

This work shows that Au can have a promoting role in Cu-based electrocatalysts for CO₂RR, where a 1.6-fold increase in the FE towards ethanol was observed for the 1Au/Cu₂O sample as compared to Cu₂O alone. Au is introduced on Cu₂O nanocubes by galvanic replacement, which results in Au and Au–Cu particles dispersed on Cu₂O. Under CO₂RR conditions, the combined results from (quasi)-*in situ* spectroscopy reveal that a significant fraction of Cu₂O is reduced to metallic Cu, while residual Cu^+ surface species remain and redeposition of Au occurs. Although the experimental protocols and conditions of each technique differ slightly, they offer a complementary and coherent view of the dynamic evolution of the catalysts. This integrated approach provides valuable insights into the much-debated origin of Au's promoting effect on Cu. For instance, it has been suggested that changes in the binding energies of adsorbates and key reaction intermediates at the Cu–Au interface facilitate C–C coupling.^{41,52} This may be linked to the presence of a Au–Cu alloy, which was also observed by XRD. Others pointed out that C–C coupling is facilitated by a high dispersion of the CO-producing metal on Cu, enhancing CO spillover.^{16,25} Au is a selective electrocatalyst for the reduction of CO₂ to CO, typically exhibiting CO FEs higher than 80% in the potential range of –0.5 V to –0.9 V *vs.* RHE.^{11,53,54} A high local concentration of CO at the surface of the reduced Au/Cu₂O catalysts promotes C–C coupling at less negative potentials than in the absence of Au.⁵⁵ This effect was demonstrated by a study of Jaramillo's group, who showed that a bimetallic Au/Cu catalyst prepared by chemical vapor deposition of Au on a polycrystalline Cu foil displayed higher FEs towards C₂₊ alcohols at lower overpotentials than the Cu foil without Au.¹⁸ Our 1Au/Cu₂O sample exhibited a higher FE towards ethanol at –0.9 V *vs.* RHE compared to the Cu₂O sample, with the promoting effect of Au becoming more substantial at more negative potentials. Besides CO spillover, it has been frequently put forward that residual cationic Cu^+ species in the reduced Cu catalysts are associated with higher rates of C–C coupling during CO₂RR. Our observations from *in situ* XAS and quasi-*in situ* XPS measurements indicate that Au stabilizes residual Cu^+

species at the Cu surface under reducing conditions. Stabilization of cationic Cu species by Ag under CO₂RR conditions has previously been reported, also resulting in enhanced C₂ product formation.^{14,26,27} Density function theory (DFT) calculations have indicated that Cu^+ can stabilize CO on the Cu surface, thereby promoting its subsequent hydrogenation to *CHO and coupling with *CO, and suppressing the competitive HER reaction.^{56–58} Although it is not possible to distinguish the roles of CO spillover and Cu^+ species to enhanced C₂ product formation, our findings show that a too high Au content leads to a smaller promoting effect and a shift of the product distribution from C₂ products to CO. This is most likely due to the increasing abundance of CO-producing Au particles, which likely cover the Cu sites responsible for further CO reduction reaction, including C–C coupling reactions.

Conclusion

In this study, we demonstrated the effectiveness of bimetallic Au/Cu₂O catalysts for the electrochemical reduction of CO₂. By employing various *ex situ* and (quasi)-*in situ* measurements, we show that galvanic replacement of Au results in the formation of highly dispersed Au, Au–Cu alloys, and Au clusters. Under CO₂RR conditions, pronounced restructuring of the catalysts is observed, including dealloying of AuCu phases and redispersion of Au. The Cu₂O sample with highly dispersed Au (1Au/Cu₂O) showed the highest FE towards the desired C₂ products, while higher Au loadings (10Au/Cu₂O) decreased the C₂ FE, along with an increased FE towards CO and H₂. Here, highly dispersed Au was proposed to enhance the CO₂RR performance by providing active sites for the reduction of CO₂ to CO, which can spill over to the nearby Cu sites. In addition, the highly dispersed Au helps stabilize Cu^+ species, which were linked to improved C₂ FE. Further increasing the surface coverage of Au improved CO formation rates at the expense of the number of Cu^+ species, resulting in poorer C₂ FE. This work sheds light on the dynamics of the catalytic structure during electrolysis by utilizing a variety of advanced *in situ* characterization techniques. These insights highlight the effectiveness of bimetallic Cu-based catalysts, which will aid in the design of more active and selective catalysts for the CO₂RR.

Author contributions

Bianca Ligt (conceptualization, investigation, methodology, data analysis, interpretation, and writing the original draft), Floriane A. Rollier (XRD), Tim Wissink (XAS), Wei Chen (quasi-*in situ* XPS), Jason M. J. Heinrichs (HAADF-STEM), Jérôme F. M. Simons (XAS data analysis), Marta Costa Figueiredo (conceptualization, funding acquisition, review & editing), and Emiel J. M. Hensen (conceptualization, funding acquisition, review & editing).



Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cy00476d>.

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References

- M. Y. Lee, K. Park, W. Lee, H. Lim, Y. Kwon and S. Kang, *Crit. Rev. Environ. Sci. Technol.*, 2020, **50**, 769–815.
- K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ. Sci.*, 2012, **5**, 7050–7059.
- D. Karapinar, C. E. Creissen, J. G. Rivera de la Cruz, M. W. Schreiber and M. Fontecave, *ACS Energy Lett.*, 2021, **6**, 694–706.
- H. L. A. Dickinson and M. D. Symes, *Electrochem. Commun.*, 2022, **135**, 107212.
- G. L. De Gregorio, T. Burdyny, A. Loiudice, P. Iyengar, W. A. Smith and R. Buonsanti, *ACS Catal.*, 2020, **10**, 4854–4862.
- W. Tang, A. A. Peterson, A. S. Varela, Z. P. Jovanov, L. Bech, W. J. Durand, S. Dahl, J. K. Nørskov and I. Chorkendorff, *Phys. Chem. Chem. Phys.*, 2012, **14**, 76–81.
- A. H. M. da Silva, S. J. Raaijman, C. S. Santana, J. M. Assaf, J. F. Gomes and M. T. M. Koper, *J. Electroanal. Chem.*, 2021, **880**, 114750.
- S. Liu, H. Tao, L. Zeng, Q. Liu, Z. Xu, Q. Liu and J.-L. Luo, *J. Am. Chem. Soc.*, 2017, **139**, 2160–2163.
- S. Liu, C. Sun, J. Xiao and J. L. Luo, *ACS Catal.*, 2020, **10**, 3158–3163.
- R. Shi, J. Guo, X. Zhang, G. I. N. Waterhouse, Z. Han, Y. Zhao, L. Shang, C. Zhou, L. Jiang and T. Zhang, *Nat. Commun.*, 2020, **11**, 1–10.
- W. Zhu, R. Michalsky, O. Metin, H. Lv, S. Guo, C. J. Wright, X. Sun, A. A. Peterson and S. Sun, *J. Am. Chem. Soc.*, 2013, **135**, 16833–16836.
- D. H. Won, H. Shin, J. Koh, J. Chung, H. S. Lee, H. Kim and S. I. Woo, *Angew. Chem.*, 2016, **128**, 9443–9446.
- W. Luo, J. Zhang, M. Li and A. Züttel, *ACS Catal.*, 2019, **9**, 3783–3791.
- A. Herzog, A. Bergmann, H. S. Jeon, J. Timoshenko, S. Kühl, C. Rettenmaier, M. Lopez Luna, F. T. Haase and B. Roldan Cuenya, *Angew. Chem., Int. Ed.*, 2021, **60**, 7426–7435.
- S. Juntrapirom, J. Santatiwongchai, A. Watwiangkham, S. Suthirakun, T. Butburee, K. Faungnawakij, P. Chakthranont, P. Hirunsit and B. Rungtawevevoranit, *Catal. Sci. Technol.*, 2021, **11**, 8065.
- D. Ren, B. S. H. Ang and B. S. Yeo, *ACS Catal.*, 2016, **6**, 8239–8247.
- E. L. Clark, C. Hahn, T. F. Jaramillo and A. T. Bell, *J. Am. Chem. Soc.*, 2017, **139**, 15848–15857.
- C. G. Morales-Guio, E. R. Cave, S. A. Nitopi, J. T. Feaster, L. Wang, K. P. Kuhl, A. Jackson, N. C. Johnson, D. N. Abram, T. Hatsukade, C. Hahn and T. F. Jaramillo, *Nat. Catal.*, 2018, **1**, 764–771.
- L. Wang, S. A. Nitopi, E. Bertheussen, M. Ozarov, C. G. Morales-Guio, X. Liu, D. C. Higgins, K. Chan, J. K. Nørskov, C. Hahn and T. F. Jaramillo, *ACS Catal.*, 2021, **8**, 7445–7454.
- K. J. P. Schouten, Y. Kwon, C. J. M. Van Der Ham, Z. Qin and M. T. M. Koper, *Chem. Sci.*, 2011, **2**, 1902.
- M. Li, Y. Hu, G. Dong, T. Wu and D. Geng, *Small*, 2023, **19**, 2207242.
- X. G. Zhang, S. Feng, C. Zhan, D.-Y. Wu, Y. Zhao and Z.-Q. Tian, *J. Phys. Chem. Lett.*, 2020, **11**, 6593–6599.
- J. Christophe, T. Doneux and C. Buess-Herman, *Electrocatalysis*, 2012, **3**, 139–146.
- E. Andrews, Y. Fang and J. Flake, *J. Appl. Electrochem.*, 2018, **48**, 435–441.
- C. Rettenmaier, A. Herzog, D. Casari, M. Rüscher, H. S. Jeon, D. Kordus, M. Lopez Luna, S. Kühl, U. Hejral, E. M. Davis, S. W. Chee, J. Timoshenko, D. T. L. Alexander, A. Bergmann and B. Roldan Cuenya, *EES Catal.*, 2024, **2**, 311.
- E. L. Clark, C. Hahn, T. F. Jaramillo and A. T. Bell, *J. Am. Chem. Soc.*, 2017, **139**, 15848–15857.
- T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis and A. A. Gewirth, *J. Am. Chem. Soc.*, 2018, **140**, 5791–5797.
- M.-R. Gao, Z.-Z. Wu and F.-Y. Gao, *Energy Environ. Sci.*, 2021, **14**, 1121.
- R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo and B. Roldan Cuenya, *Nat. Energy*, 2020, **5**, 317–325.
- R. Du, T. Li, Q. Wu, P. Wang, X. Yang, Y. Fan, Y. Qiu, K. Yan, P. Wang, Y. Zhao, W.-W. Zhao and G. Chen, *ACS Appl. Mater. Interfaces*, 2022, **14**, 36527–36535.
- J. J. Velasco-Vélez, J. Poon, D. Gao, C.-H. Chuang, A. Bergmann, T. E. Jones, S.-C. Haw, J.-M. Chen, E. Carbonio, R. V. Mom, D. Ivanov, R. Arrigo, B. Roldan Cuenya, A. Knop-Gericke and R. Schlögl, *Adv. Sustainable Syst.*, 2023, **7**, 2200453.
- M. L. J. Peerlings, K. Han, A. Longo, K. H. Helfferich, M. Ghiasi, P. E. de Jongh and P. Ngene, *ACS Catal.*, 2024, **14**, 10701–10711.
- M. C. Biesinger, *Surf. Interface Anal.*, 2017, **49**, 1325–1334.
- J. Jaumot, A. de Juan and R. Tauler, *Chemom. Intell. Lab. Syst.*, 2015, **140**, 1–12.



- 35 Z. Zhang, T. Cao, L. Luo, R. Song, H. Wang and W. Huang, *ChemNanoMat*, 2016, **2**, 861–865.
- 36 J. J. Teo, Y. Chang and H. C. Zeng, *Langmuir*, 2006, **22**, 7369–7377.
- 37 H. Bao, Z. Zhang, Q. Hua and W. Huang, *Langmuir*, 2014, **30**, 6427–6436.
- 38 Z. Wang, D. Luan, C. M. Li, F. Su, S. Madhavi, F. Y. C. Boey and X. W. Lou, *J. Am. Chem. Soc.*, 2010, **132**, 16271–16277.
- 39 W. Huang, *Acc. Chem. Res.*, 2016, **49**, 520–527.
- 40 Z. Jiang, W. Zhang, L. Jin, X. Yang, F. Xu, J. Zhu and W. Huang, *J. Phys. Chem. C*, 2007, **111**, 12434–12439.
- 41 Q. Sun, Y. Zhao, X. Tan, C. Jia, Z. Su, Q. Meyer, M. I. Ahmed and C. Zhao, *ACS Catal.*, 2023, **13**, 5689–5696.
- 42 A. Yin, C. Wen, W. L. Dai and K. Fan, *J. Mater. Chem.*, 2011, **21**, 8997–8999.
- 43 A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager and R. Buonsanti, *Angew. Chem., Int. Ed.*, 2016, **55**, 5789–5792.
- 44 M. K. Birhanu, M.-C. Tsai, A. W. Kahsay, C.-T. Chen, T. S. Zeleke, K. B. Ibrahim, C.-J. Huang, W.-N. Su and B.-J. Hwang, *Adv. Mater. Interfaces*, 2018, **5**, 1800919.
- 45 Y. Hori, A. Murata and R. Takahashi, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2309–2326.
- 46 H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser and B. Roldan Cuenya, *J. Am. Chem. Soc.*, 2014, **136**, 16473–16476.
- 47 S. Back, M. S. Yeom and Y. Jung, *J. Phys. Chem. C*, 2018, **122**, 4274–4280.
- 48 F. A. Rollier, V. Muravev, N. Kosinov, T. Wissink, D. Anastasiadou, B. Ligt, L. Barthe, M. C. Figueiredo and E. J. M. Hensen, *J. Mater. Chem. A*, 2025, **13**, 2285.
- 49 D. Grandjean, H. L. Castricum, J. C. van den Heuvel and B. M. Weckhuysen, *J. Phys. Chem. B*, 2006, **110**, 16892–16901.
- 50 S.-C. Lin, C.-C. Chang, S.-Y. Chiu, H.-T. Pai, T.-Y. Liao, C.-S. Hsu, W.-H. Chiang, M.-K. Tsai and H. M. Chen, *Nat. Commun.*, 2020, **11**, 1–12.
- 51 L. Meng, C.-W. Kao, Z. Wang, J. Ma, P. Huang, N. Zhao, X. Zheng, M. Peng, Y.-R. Lu and Y. Tan, *Nat. Commun.*, 2024, **15**, 1–10.
- 52 Y. Zhang, F. Chen, X. Hao, Y. Liu, W. Wu, X. Zhang, Z. Zang, H. Dong, W. Wang, F. Lu, Z. Lu, H. Liu, H. Liu, F. Luo and Y. Cheng, *Appl. Catal., B*, 2024, **344**, 123666.
- 53 C. Chen, B. Zhang, J. Zhong and Z. Cheng, *J. Mater. Chem. A*, 2017, **5**, 21955–21964.
- 54 E. R. Cave, J. H. Montoya, K. P. Kuhl, D. N. Abram, T. Hatsukade, C. Shi, C. Hahn, J. K. Nørskov and T. F. Jaramillo, *Phys. Chem. Chem. Phys.*, 2017, **19**, 15856–15863.
- 55 W. Zhu, K. Zhao, S. Liu, M. Liu, F. Peng, P. An, B. Qin, M. Zhou, H. Li and Z. He, *J. Energy Chem.*, 2019, **37**, 176–182.
- 56 Y. Shao, Q. Yuan and J. Zhou, *Small*, 2023, **19**, 2303446.
- 57 H. Feng, C. Chen, S. Wang, M. Zhang, H. Ding, Y. Liang and X. Zhang, *J. Phys. Chem. Lett.*, 2022, **13**, 8002–8009.
- 58 L. Sun, J. Han, Q. Ge, X. Zhu and H. Wang, *RSC Adv.*, 2022, **12**, 19394.

