

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Operando Investigation of Ag-decorated Cu₂O Nanocube Catalysts with enhanced CO₂ Electroreduction toward Liquid Products

Authors: Antonia Herzog, Arno Bergmann, Hyo Sang Jeon, Janis Timoshenko, Stefanie Kühn, Clara Rettenmaier, Mauricio Lopez Luna, Felix T. Haase, and Beatriz Roldán Cuenya

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202017070

Link to VoR: <https://doi.org/10.1002/anie.202017070>

***Operando* Investigation of Ag-decorated Cu₂O Nanocube Catalysts with enhanced CO₂ Electroreduction toward Liquid Products**

Antonia Herzog,^[b] Arno Bergmann,^[b] Hyo Sang Jeon,^[b] Janis Timoshenko,^[b] Stefanie Kühl,^[b] Clara Rettenmaier,^[b] Mauricio Lopez Luna,^[b] Felix T. Haase,^[b] Beatriz Roldan Cuenya*^[a]

[a] Prof. Dr. B. Roldan Cuenya
Department of Interface Science
Fritz-Haber Institute of the Max-Planck Society
Faradayweg 4-6, 14195 Berlin, Germany
E-mail: roldan@fhi-berlin.mpg.de

[b] A. Herzog, Dr. A. Bergmann, Dr. H. S. Jeon, Dr. J. Timoshenko, Dr. S. Kühl, C. Rettenmaier, M. Lopez Luna, F. T. Haase
Department of Interface Science
Fritz-Haber Institute of the Max-Planck Society
Faradayweg 4-6, 14195 Berlin, Germany

Supporting information for this article is given via a link at the end of the document.

Abstract: Direct conversion of carbon dioxide into multicarbon liquid fuels by the CO₂ electrochemical reduction reaction (CO₂RR) can contribute to the decarbonization of the global economy. Here, well-defined Cu₂O nanocubes (NCs, 35 nm) uniformly covered with Ag nanoparticles (5 nm) were synthesized. When compared to bare Cu₂O NCs, the catalyst with 5 at% Ag on Cu₂O NCs displayed a two-fold increase in the Faradaic efficiency for C₂₊ liquid products (30% at -1.0 V_{RHE}), including ethanol, 1-propanol, and acetaldehyde, while formate and hydrogen were suppressed. *Operando* X-ray absorption spectroscopy revealed the partial reduction of Cu₂O during CO₂RR, accompanied by a reaction-driven redispersion of Ag on the CuO_x NCs. *Operando* surface-enhanced Raman spectroscopy data further uncovered significant variations in the CO binding to Cu, which were assigned to Ag-Cu sites formed during CO₂RR that appear crucial for the C-C coupling and the enhanced yield of liquid products.

Accepted Manuscript

Introduction

In the quest for developing a sustainable energy economy, the electrochemical reduction of carbon dioxide (CO₂RR) into value-added chemicals and fuels offers the potential to close the anthropogenic carbon cycle and store renewable energy (wind, solar, hydro) into chemical bonds.^[1] It has been therefore of particular interest to develop efficient and selective electrocatalysts, which reduce the reaction overpotential and steer the reaction toward hydrocarbons and multicarbon oxygenates (C₂₊). The selective generation of liquid products such as ethanol, 1-propanol, and acetaldehyde is highly desirable due to their high energy densities and advantages for storage/transport as compared to gaseous products.^[2]

A variety of metal electrodes can be used to catalyze CO₂RR as demonstrated in the pioneering work by Hori.^[3] While some metals primarily reduce CO₂ to CO (Ag, Au, Zn) or formate (Sn, In, Bi), copper is the only metal yielding products such as methane, ethylene, and ethanol in considerable amounts.^[4] However, the selective conversion to C₂₊ products in the form of liquids (alcohols and carbonyls) still requires high overpotentials, suffers from low current densities that can be achieved, and the generation of parasitic hydrogen through the competing hydrogen evolution reaction (HER). Various strategies have been developed to enhance the performance of Cu-based catalysts, including nanostructuring Cu (control of exposed facets, defects and low-coordinated sites),^[5] engineering the Cu-electrolyte interface (change of local pH),^[6] and adjusting the Cu oxidation state (compositional change).^[7] For example, Cu₂O nanocubes (NCs) with well-ordered (100) facets have been shown to lead to an increase in the selectivity toward ethylene while suppressing methane production.^[5e, 8]

A promising way to further improve the catalyst's performance and selectivity is the introduction of a secondary metal.^[9] Recent studies of Cu-Ag bimetallic systems showed enhanced selectivity for C₂₊ products. In particular, a phase-blended Ag-Cu₂O catalyst had a three times higher Faradaic efficiency (FE) toward ethanol than Ag-free Cu₂O, but suffered from low activity ($|j_{ethanol}| < 1$ mA).^[10] Additionally, Ag-covered Cu₂O nanowires prepared via a galvanic replacement reaction enabled a 1.4 times higher current density toward ethylene production as compared to pure Cu₂O nanowires.^[11] Furthermore, CuAg surface alloys have been found to be more selective for the formation of multicarbon products than pure copper.^[12] The facilitated yield of C₂₊ products in the bimetallic system is usually linked to the suppression of HER due to the enhanced coverage of *CO adsorbates as compared to *H,^[12b] and the diffusion of CO from Ag sites to Cu sites that enables C-C coupling (CO spillover).^[10-11] Note here that a short diffusion path of CO and therefore a homogeneous distribution of Cu and Ag at the surface of the catalyst is essential for an effective CO spillover.^[10, 12b] Nonetheless, although the spatial arrangement of Cu and Ag in these studies seems to play a key role for the different CO₂RR

selectivity trends obtained, the key parameters for achieving an optimal synergy in Cu-Ag bimetallic systems are still unknown. In particular, open questions still remain on the composition and structure of the most active and C₂₊ selective systems under *operando* CO₂RR conditions, including the stability of Cu₂O, which might be modified by introducing Ag.^[13]

In this work, we prepared well-defined Cu₂O NCs (35 nm) uniformly covered with Ag nanoparticles (NPs, 5 nm) by a facile wet-chemical ligand-free synthesis. Employing *ex situ*, *in situ* and *operando* characterization techniques, we gained insights into the morphology, chemical state, composition and adsorbates of the Cu-Ag catalyst under CO₂RR conditions. In particular, we discuss reaction-induced Ag redispersion, Cu-Ag surface alloy formation, the influence of Ag on the reduction of Cu₂O, the adsorption of CO on Cu and Ag and the effect of the former parameters in the CO₂RR activity and selectivity.

Results and Discussion

Figure 1 shows STEM-HAADF and STEM-EDX maps of pure and Ag NP-decorated Cu₂O NCs. The as-prepared Cu₂O NCs have an edge length of 35 ± 7 nm (Figure 1a). The STEM-EDX data (Figure 1b, S1, Table S1) reveal an average Cu:O at% ratio of 66:34, which corresponds to the composition of Cu₂O. In the following, the Cu₂O NCs decorated with 3 and 5 at% of Ag will be denoted 3-Ag/Cu₂O and 5-Ag/Cu₂O. The Ag NPs with a diameter of 4.6 ± 1.1 nm (3-Ag/Cu₂O, Figure 1e, S2) and of 6.0 ± 2.1 nm (5-Ag/Cu₂O, Figure 1i, S3) appear to be uniformly distributed on the surface of the Cu₂O nanocubes. The STEM-EDX maps of the as-prepared 3- and 5-Ag/Cu₂O catalysts (Figure 1f, j) indicate a clear phase separation between the Ag NPs and the Cu₂O NCs.

After 2 h of CO₂RR at -1.0 V_{RHE} in 0.1 M KHCO₃, the cubic morphology appeared less pronounced and hollow structures formed in all cases (Figure 1c, g, k). Simultaneously, the edge length of the NCs decreased in average by 3 nm (Table S2) and the size distribution broadened, as reported in the literature for pure Cu₂O NCs after CO₂RR.^[8] STEM-EDX maps after reaction (Figure 1d, h, l) reveal that Cu₂O is partially reduced to metallic Cu (Table S3) and that the clear phase separation between Ag and Cu is lost. Instead, small Ag clusters are dispersed on the Cu surface. In addition, some Ag-rich areas with sizes of 6.3 ± 1.6 nm (3-Ag/Cu₂O) and 9.5 ± 2.5 nm (5-Ag/Cu₂O) were also found (Table S2).

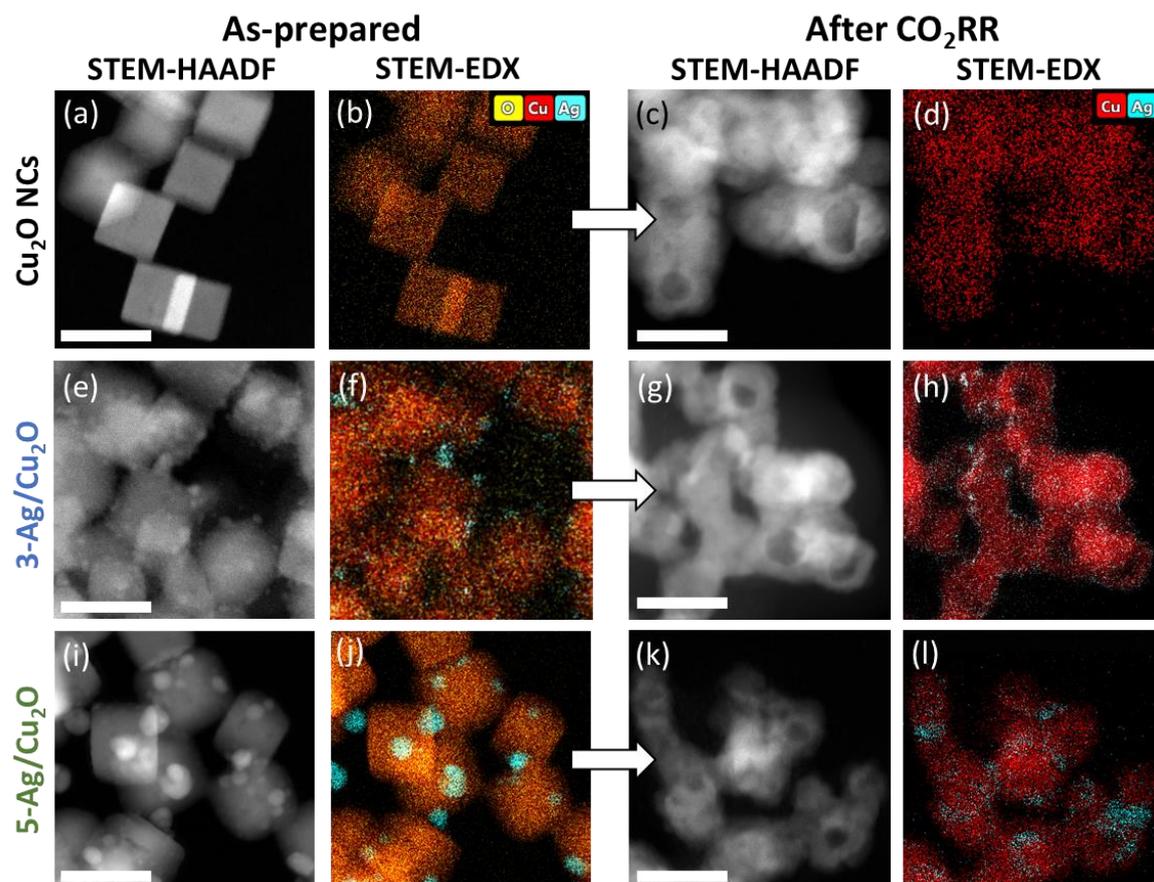


Figure 1. STEM-HAADF images with corresponding EDX maps of Cu_2O NCs, 3-Ag/ Cu_2O and 5-Ag/ Cu_2O in the upper, middle and lower panels, respectively. As-prepared samples are shown on the left (a, e, i) with EDX maps in (b, f, j) and samples after 2 h of CO_2RR at $-1.0 V_{\text{RHE}}$ on the right (c, g, k) with EDX maps in (d, h, l). The scale bars given correspond to 50 nm.

X-ray diffraction (XRD) was applied to confirm the phase purity of the catalysts and to track the evolution of the crystal structure after CO_2RR . Figure S4 shows the XRD pattern of the as-prepared Cu_2O NCs and Ag/ Cu_2O with the main Cu_2O reflections assigned to (111) at 36.4° and (200) at 42.3° . The presence of metallic Ag can be seen by the Ag(111) at 38.2° and Ag(200) at 44.5° for the Ag/ Cu_2O . The low intensity of the *fcc* Ag reflections can be attributed to the low Ag loading and XRD peak broadening due to small particle sizes.

Table 1 shows the as-prepared composition and coherence length derived from Rietveld refinement of the XRD pattern. The coherence length of the Cu_2O agrees well with the size distribution obtained by STEM analysis, although it is slightly smaller than the mean NC edge length. The atomic fractions of metallic Ag in the as-prepared Ag/ Cu_2O agree well with the Cu:Ag composition obtained by ICP-MS (Table S5). This confirms that the majority of the added Ag from the AgNO_3 solution was incorporated in the Ag NPs, and that the initial ratios of the metal salts utilized were maintained.

Table 1. Atomic fraction and structural coherence length of Cu₂O and metallic Cu and Ag phases derived from Rietveld refinement of *ex situ* XRD patterns of as-prepared Cu₂O NCs, 3-Ag/Cu₂O and 5-Ag/Cu₂O, and of 5-Ag/Cu₂O deposited on carbon paper after 2 h of CO₂RR at -1.0 V_{RHE}.

Sample	Atomic fraction [at%]			Structural coherence length [nm]		
	Cu ₂ O	<i>fcc</i> Cu	<i>fcc</i> Ag	Cu ₂ O	<i>fcc</i> Cu	<i>fcc</i> Ag
<i>As-prepared</i>						
Cu₂O NC	100	-	-	32.6(3)	-	-
3-Ag/Cu₂O	97.55(9)	-	2.45(6)	32.3(7)	-	5.9(7)
5-Ag/Cu₂O	95.1(7)	-	4.9(5)	23.1(3)	-	6(2)
<i>After CO₂RR</i>						
5-Ag/Cu₂O	56(16)	24(9)	20(7)	6.8(3)	9(2)	4.4(5)

The structural evolution of the 5-Ag/Cu₂O catalyst was investigated before and after 2 h of CO₂RR using *ex situ* grazing incidence (GI) XRD (Figure 2, Table 1) and shows the reduction of Cu₂O to metallic Cu as prominently seen in the Cu(111) reflection at 43.2°. The background arises from the carbon paper support (Figure S5). Rietveld refinement of 5-Ag/Cu₂O after CO₂RR suggests a mixture of Cu₂O and metallic Cu and a significant increased Ag fraction, while ICP-MS did not show changes in the catalyst composition (Table S6). Thus, we are missing a considerable fraction of Cu/Cu_x after reaction by XRD. This suggests that Cu might be present in non-crystalline domains, resulting in an increased Ag:Cu ratio. Additionally, there is a slight contraction of the Ag lattice (4.092 ± 0.003 to 4.088 ± 0.003 Å) which could be explained by the incorporation of Cu into the Ag lattice (Table S4). Notably, the coherence length of Cu₂O decreased strongly from 23.1 nm (as-prepared) to 6.8 nm (after CO₂RR), reaching a similar value to the coherence length of the metallic Cu phase (9 nm). We conclude that the hollow structures after CO₂RR (Figure 1) might consist of a mixture of Cu₂O and Cu crystallites as seen in XRD. The coherence length of the metallic Ag phase in average slightly decreased after CO₂RR, which agrees with the partial re-dispersion of Ag on the Cu surface and the Ag-rich domains likely being formed from multiple Ag NPs.

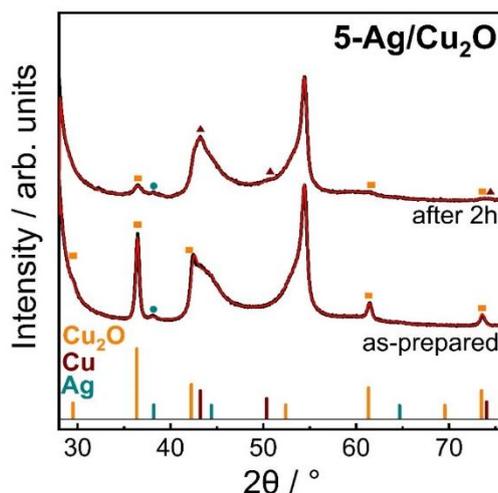


Figure 2. *Ex situ* XRD pattern of 5-Ag/Cu₂O deposited on carbon in the as-prepared state and after 2 h of CO₂RR at -1.0 V_{RHE}. Red lines correspond to Rietveld fits.

Quasi-*in situ* X-ray photoelectron spectroscopy (XPS) measurements were performed to gain deeper insight into the surface composition and chemical state of the Ag NP-decorated and pure Cu₂O NCs before and after 2 h of CO₂RR. Figure 3 presents the Ag 3d and Cu Auger LMM spectra, while Figure S6 shows the Cu 2p spectra. The Ag 3d core level regions of 3- and 5-Ag/Cu₂O (Figure 3a, b) reveal that Ag is in the metallic state before and after CO₂RR, which is also consistent with the XRD results. The Ag:Cu surface composition ratios were determined by integrating the peak areas of Ag 3d_{5/2} and Cu 2p_{3/2}. As expected for Ag NPs decorating the surface of Cu₂O NCs, the Ag:Cu ratio extracted from the surface-sensitive XPS technique was higher than the bulk composition obtained from the XRD and ICP-MS analysis. After CO₂RR, the Ag:Cu XPS ratios further increased from 4:96 to 7:93 at% in 3-Ag/Cu₂O and from 9:91 to 11:89 in 5-Ag/Cu₂O. Thus, we conclude that a more homogenous distribution of Ag (redispersion) on the Cu₂O surface takes place during CO₂RR. Furthermore, we can exclude significant preferential dissolution of Cu during CO₂RR due to the constant bulk Ag:Cu ratio before and after CO₂RR as demonstrated by ICP-MS (Table S6). The higher Ag signal observed after CO₂RR agrees with the formation of smaller Ag NPs and clusters and an enhanced Ag dispersion, as also revealed by the STEM and XRD data.

Additionally, deconvolution of the Cu LMM spectra (Figure 3c,d, Tables S7) was carried out to distinguish Cu(0), Cu(I), and Cu(II) near-surface species. In the as-prepared state, the samples consisted mainly of Cu₂O with a contribution of CuO. After 2 h of CO₂RR, the near-surface of the Cu₂O NCs and Ag/Cu₂O samples were fully reduced to metallic Cu within the error margin. In contrast to prior studies, our samples were not exposed to air after CO₂RR, since our electrochemical cell is directly connected

to the XPS chamber. Thus, even though no potential is applied during the XPS measurement, re-oxidation in air can be excluded.

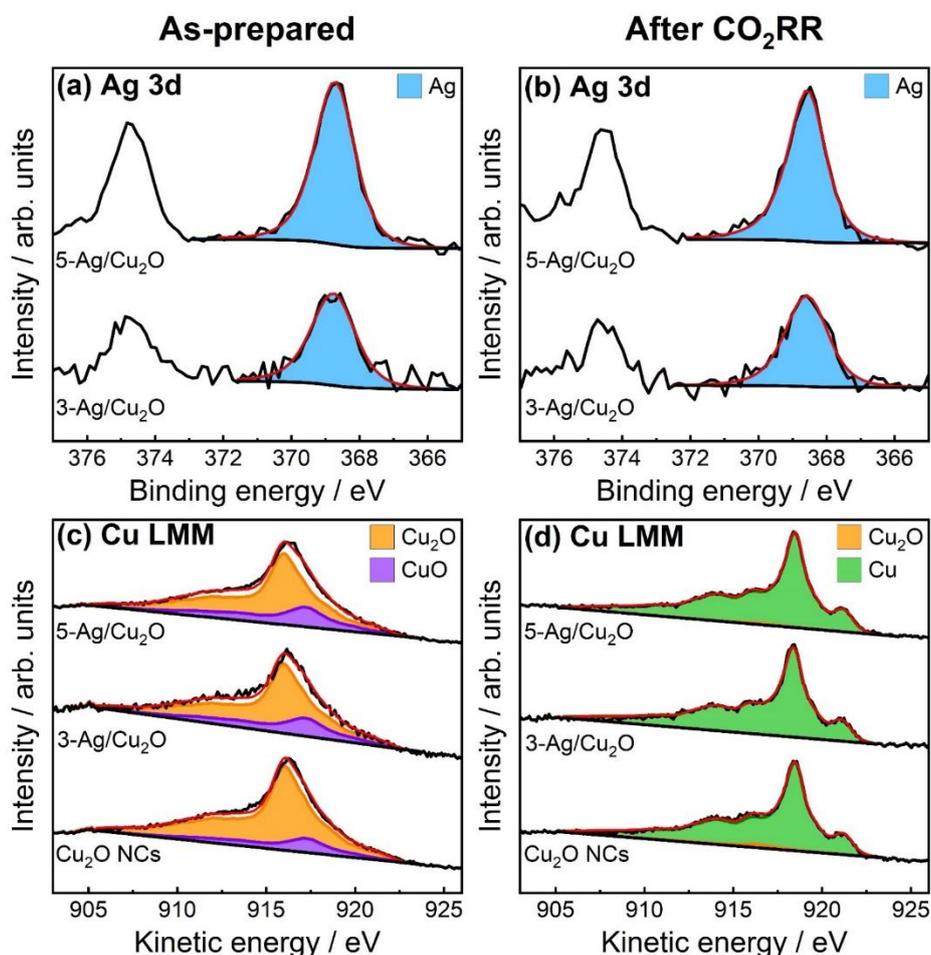


Figure 3. Quasi-*in situ* Ag 3d and Cu LMM XPS spectra of Cu₂O NCs, 3-Ag/Cu₂O and 5-Ag/Cu₂O (a, c) in as-prepared state and (b, d) after 2 h of CO₂RR at -1.0 V_{RHE} (without air exposure) with corresponding fits (red line) and reference spectra.

The electrocatalytic performance of Ag NP-decorated and pure Cu₂O NCs deposited on carbon paper was evaluated by chronoamperometry measurements for 2 h at potentials between -0.7 and -1.1 V_{RHE} in a CO₂-saturated 0.1 M KHCO₃ electrolyte (Figures 4, S7-S11, Table S8). Figure 4 displays the Faradaic efficiencies (FEs) of the main C₂ and C₃ products, namely, ethanol, 1-propanol and ethylene, as well as the combined FEs of all C₂₊ products, of the C₂₊ liquid products, and of the C₂₊ carbonyl products. See also Figure S8 (C₁ products), S9 (minor C₂₊ products), S10 (sum of all liquid products), S11 (geometric and mass current densities).

The production of ethanol at -1.0 V_{RHE} increases significantly with the amount of Ag. Cu₂O NCs, 3- and 5-Ag/Cu₂O reach 10%, 13% and 17% FE for ethanol at -1.0 V_{RHE}, respectively (Figures 4a, S7a). Thus, FE_{ethanol} increased 1.5 times by the addition of 5 at% of Ag to Cu₂O NCs. Additionally, the production of

1-propanol is doubled in the Ag/Cu₂O samples with FE of 5-6% at -0.9 V_{RHE} compared to 3% for the Cu₂O NCs (Figure 4b). This increase in alcohol yield has been previously linked to CO spillover from Ag to Cu, since the weaker binding between Ag and the *CO intermediate is considered to facilitate CO production as compared to the moderate binding energy between Cu and the *CO intermediate leading to the formation of hydrocarbons.^[4, 10] Also in our case, the Ag/Cu₂O samples show higher FEs for CO at low overpotentials, with almost 40% FE at -0.7 V_{RHE} in comparison to 20% FE for the pure Cu₂O NCs (Figure S8b). At higher overpotentials, the FE_{CO} decreases for all catalysts, and starting from -1.0 V_{RHE} the selectivity for CO of the Ag/Cu₂O is even similar to that of the bare Cu₂O NCs (FE_{CO}=3-5%). We note that 3-Ag/Cu₂O shows a better ability to transform CO₂ into C₂₊ products at lower overpotentials than 5-Ag/Cu₂O, which is also related to a lower FE of CO starting from -0.83 V_{RHE} (Figure S8b). These differences might originate from the different sizes of the Ag NPs in the two samples as extracted by STEM analysis (Table S2), which can affect the CO₂ to CO electrocatalytic reduction as well as the CO spillover to the Ag/Cu interface.

The production of ethylene on the Cu₂O NCs peaks at -0.95 V_{RHE} with 40% FE (Figures 4c, S7c), while for the 3-Ag/Cu₂O the FE is slightly larger (45%). In contrast, 5-Ag/Cu₂O shows a lower FE_{ethylene} (34%), paralleled by an enhancement in the ethanol production. Consequently, the FE_{ethanol}:FE_{ethylene} ratio at -1.0 V_{RHE} increases with Ag loading from 0.28 for Cu₂O NCs, 0.33 for 3-Ag/Cu₂O, to 0.49 for 5-Ag/Cu₂O. The C₂₊ selectivity is the highest for the two Ag/Cu₂O samples with a FE of 65% at -0.98 V_{RHE}, which is an increase of 10% compared to pure Cu₂O NCs (Figure 4d, S7d).

Furthermore, the parasitic HER (Figure S8a) and the production of formate (the only C₁ liquid, Figure S8d) were (slightly) suppressed. The latter has been also recently observed for AgCu foam catalysts as compared to pure Cu foams.^[14] In contrast, the formation of acetaldehyde (Figure S9a) and propionaldehyde (Figure S9b) significantly increases for the 5-Ag/Cu₂O, which results in an enhancement of the carbonyl C₂₊ products by a factor of three (Figure 4f, S7f). Overall, introducing Ag increases the FE of the desired C₂₊ liquid products (Figure 4e, S7e) for 5-Ag/Cu₂O by 15% in comparison to Cu₂O NCs at -1.0 V_{RHE}. This is assigned to the enhanced production of ethanol, 1-propanol, allyl alcohol and carbonyl C₂₊ products (Figure 4a, 4b, 4f, S9c). We additionally performed long-term CO₂RR measurements for 12 h at -1.0 V_{RHE} to track the stability of the catalytic performance (Figure S12) and found a good stability for all catalysts. For the Ag/Cu₂O samples, the amount of C₂₊ liquid products over time remains stable with a decrease of the aldehydes and increase of 1-propanol as well as acetate for the 5-Ag/Cu₂O catalyst.

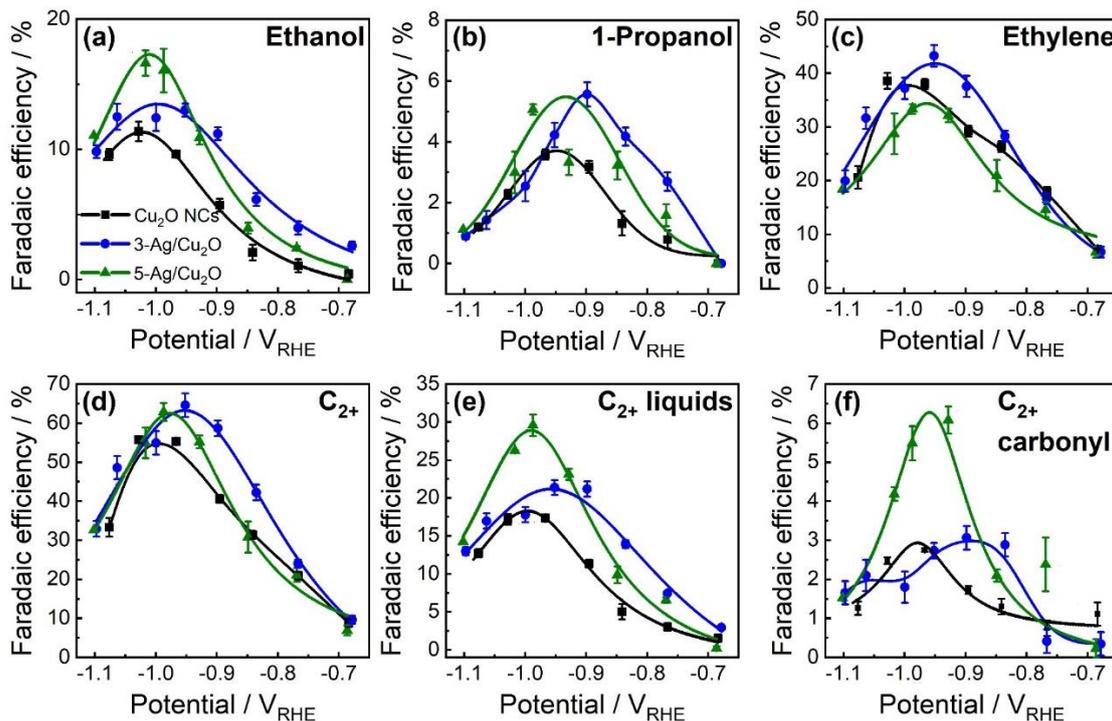


Figure 4. Potential-dependent Faradaic efficiencies of (a) ethanol, (b) 1-propanol, (c) ethylene, (d) C₂ + C₃ products (C₂₊), (e) C₂₊ liquid products and (f) C₂₊ carbonyl products of Cu₂O NCs (black), 3-Ag/Cu₂O (blue) and 5-Ag/Cu₂O (green) after 2 h of electrolysis in CO₂-saturated 0.1 M KHCO₃. Solid lines are a guide for the eye.

In order to further examine the Cu-Ag interaction and its role in the CO₂RR selectivity, we also investigated the catalytic performance of the pure Cu₂O NCs deposited on a polished Ag foil (Cu₂O/Ag). In this configuration (Figure S13), the production of C₂₊ liquids is also enhanced on the Cu₂O/Ag sample at -1.0 V_{RHE}, indicating again the importance of the CO generated at the Ag sites on the further hydrogenation of the C-C products generated on the Cu sites. However, the Cu₂O/Ag sample shows a drastic increase of HER as compared to the 5-Ag/Cu₂O, namely from 20 to 40% FE, and a suppression of the ethylene FE from 30% to 20%. This might be correlated to the decrease of the total area of the Ag/Cu interfaces, which decreases the atomic interaction and synergy between Ag and Cu. Consequently, the well-distributed Ag NPs but redispersed on the surface of our Cu₂O NCs appear to play a significant role in the synergistic effect observed and C-C coupling mechanism.

Further insight into the Ag-Cu interaction can be extracted from *operando* X-ray absorption spectroscopy (XAS) data. Figure 5 depicts the normalized Cu K-edge and Ag K-edge X-ray absorption near edge structure (XANES) spectra of the Ag NP-decorated and pure Cu₂O NCs in their as-prepared state (Figure 5a, c) and during CO₂RR in a steady-state after 5 h of the reaction (Figure 5b, d). The position of the absorption edge in the Cu K-edge XANES spectra of the as-prepared Cu₂O NCs compared

to the reference spectra show that the NCs exhibit mainly a Cu(I) oxidation state, with the characteristic pre-edge feature at 8981 eV. Linear combination analysis (LCA) of Cu K-edge XANES revealed the presence of Cu(I) and Cu(II) species (Figure S14), as already seen in the more surface sensitive XPS analysis. The decoration with the Ag NPs does not change the Cu XANES spectra (Figure 5c). Ag K-edge XANES spectra, in turn, confirm the metallic state of Ag, with all XANES features resembling those of the Ag foil. These findings are consistent with the previous STEM, XRD and XPS results, emphasizing the lack of significant interaction between the Cu₂O and Ag species in the as-prepared state.

The reduction of the Cu₂O NCs was investigated during CO₂RR at -1.0 V_{RHE} for 5 h (Figure S14). In the final state, the Cu K-edge XANES spectrum resembles that of the metallic Cu foil reference (Figure 5b). We tracked the evolution of the Cu(0):Cu(I):Cu(II) ratios by LCA (Figure S14b, c) and our analysis revealed that a significant fraction of Cu(I) was preserved under CO₂RR reaction conditions, with 15-25% of Cu(I) present in all samples. Figure 5d shows the Ag K-edge XANES spectra under CO₂RR conditions at -1.0 V_{RHE} after reaching stationary conditions. Ag remained metallic, but an attenuation of the post-edge oscillations is visible during CO₂RR, explainable by a decrease in the size of the Ag NPs due to their redispersion on the Cu₂O NC surface.^[15]

To achieve a deeper understanding of the local atomic structure, Fourier transformed- (FT-) EXAFS spectra of the Ag NP-decorated and pure Cu₂O NCs are shown in Figure 6 with the corresponding Fourier-filtered EXAFS spectra in Figure S15. The peaks at 1.5 Å and 2.8 Å (phase uncorrected) in Cu K-edge FT-EXAFS and at 2.8 Å in Ag K-edge FT-EXAFS for the as-prepared samples indicate the presence of Cu-O bonds (typical for Cu₂O) and Ag-M bonds (here M is Ag or Cu), respectively, in agreement with the XANES analysis.

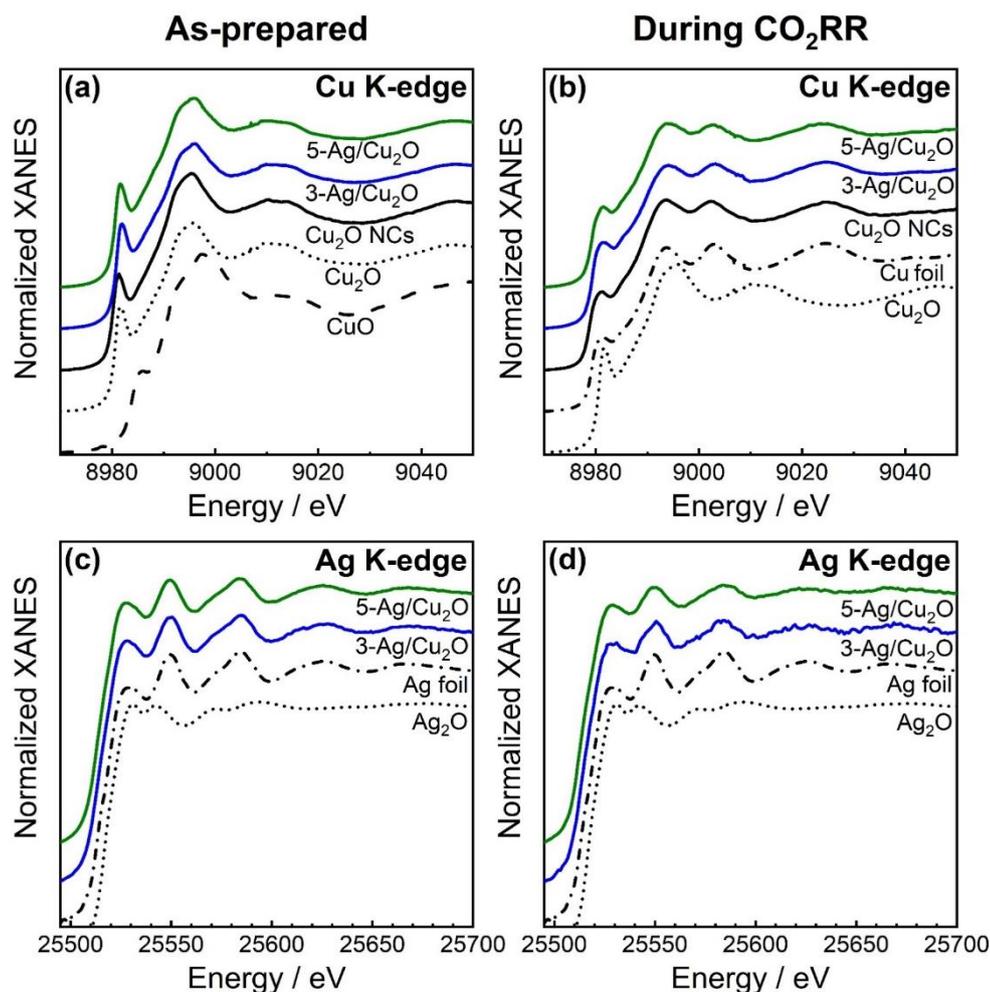


Figure 5. Normalized Cu and Ag K-edge XANES spectra of Cu₂O NCs (black), 3-Ag/Cu₂O (blue) and 5-Ag/Cu₂O (green) in as-prepared state (a, c) and in the final state under CO₂RR at -1.0 V_{RHE} (b, d). Reference spectra of Cu₂O, CuO, Cu foil, Ag₂O and Ag foil are shown for comparison.

Under CO₂RR conditions at -1.0 V_{RHE}, a strong peak at 2.2 Å (phase uncorrected) appeared in the Cu K-edge FT-EXAFS, which can be attributed to the Cu–Cu contribution in metallic Cu. The Ag–M peak position at 2.8 Å in Ag K-edge FT-EXAFS did not change significantly, and no additional peaks appeared. Nonetheless, the comparison of the FT-EXAFS before and during CO₂RR shows a decrease in the Ag–M peak intensities. Moreover, the intensity of both, the Cu–Cu and Ag–M peaks decreases with an increase in Ag loading (Figure 6). These differences suggest structural changes in the Ag and Cu atomic environment under CO₂RR conditions, which we further investigated using quantitative fitting of the EXAFS spectra to obtain the structural parameters presented in Tables S10–S11. For the as-prepared state, we obtained a Cu–O coordination number (N_{Cu-O}) of ~2 and a Cu–O distance (R_{Cu-O}) of ~1.87 Å, which agree with the values of these parameters in bulk Cu₂O. Furthermore, in the as-prepared samples, the N_{Ag-Ag} decreased from 12 in the Ag foil over 11.4 ± 0.4 in 3-Ag/Cu₂O to 10.5 ± 0.3 in 5-

Ag/Cu₂O, indicating an enhanced disorder within the Ag NPs. However, the R_{Ag-Ag} distances in all samples are comparable to that of the Ag foil, $2.833 \pm 0.003 \text{ \AA}$, which means that there is no significant lattice contraction due to alloying in the as-prepared state.

Under stationary CO₂RR conditions, the Cu-Cu coordination number of ~ 9 is lower than that of the Cu foil reference (12). We also observe Cu-O bonds with $N_{Cu-O} \sim 0.3$. The Cu-Cu distance (R_{Cu-Cu}) during CO₂RR is with $2.524 \pm 0.003 \text{ \AA}$ comparable to that in the bulk Cu foil reference ($2.527 \pm 0.002 \text{ \AA}$). The Cu(0) to Cu(I) ratio under CO₂RR, as obtained from the EXAFS analysis, agrees well with the XANES data (Table S9), showing the partial reduction of the Cu₂O to metallic Cu under CO₂RR conditions. Our primary finding from the Cu K-edge is the increasing disorder of the Cu-Cu bond with higher Ag loading and thus, reveals the decoration of the Cu₂O NCs with Ag NPs during CO₂RR, but one cannot exclude that this could also be a result of incomplete CuO_x reduction.

One of the main goals of this study is to explore the interaction between Cu and Ag at the atomic scale under CO₂RR conditions. Due to the low concentration of Ag as compared to Cu, information on the interplay between Ag and Cu atoms can be best extracted from the analysis of Ag EXAFS data (Figure 6c,d, S16). During CO₂RR, we identified an additional contribution of Ag-Cu bonds with R_{Ag-Cu} of $2.623 \pm 0.005 \text{ \AA}$ (3-Ag/Cu₂O) and $2.596 \pm 0.008 \text{ \AA}$ (5-Ag/Cu₂O), while the bond-lengths in the more prominent Ag-Ag component did not contract significantly for the 3-Ag/Cu₂O ($2.840 \pm 0.005 \text{ \AA}$), but did so for the 5-Ag/Cu₂O ($2.787 \pm 0.007 \text{ \AA}$). The Ag-Ag coordination number decreased from 12 (bulk) to 9, and an Ag-Cu coordination number (N_{Ag-Cu}) of up to 1 was obtained under CO₂RR conditions, being larger for the 3-Ag/Cu₂O sample than for 5-Ag/Cu₂O. The obtained Ag-Cu bond-length is in between the values for Cu-Cu distance in bulk Cu ($2.527 \pm 0.002 \text{ \AA}$) and the Ag-Ag distance in bulk Ag ($2.833 \pm 0.003 \text{ \AA}$). The Ag-Cu bond lengths as well as the coordination numbers suggest the partial incorporation of Ag into Cu-rich domains either as an AgCu phase or as dispersed particles or clusters on the Cu surface under CO₂RR conditions. Furthermore, the reduced total Ag-M coordination numbers with respect to those in the as-prepared samples suggests an increase in the disorder in the Ag-Ag component during CO₂RR, which agrees well with a smaller particle size and/or Ag redispersion during CO₂RR, as shown by the STEM results. Thus, we observe the partial miscibility of Cu and Ag under CO₂RR conditions by using *operando* Ag K-edge XAS, which was not provided in comparable studies so far.

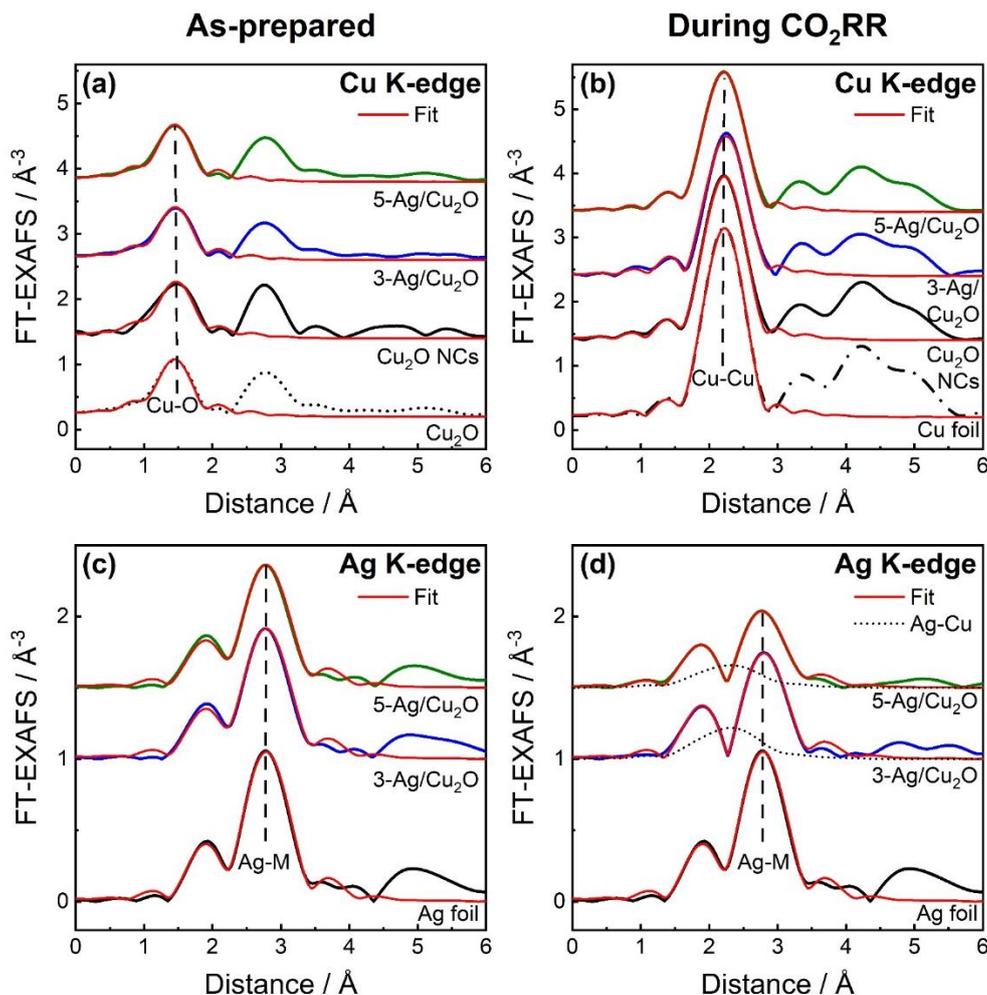


Figure 6. Moduli of Fourier transformed- (FT-) Cu and Ag K-edge EXAFS spectra of Cu_2O NCs (black), 3-Ag/ Cu_2O (blue) and 5-Ag/ Cu_2O (green) in as-prepared state (a, c) and in the final state under *operando* CO_2 reduction conditions at $-1.0 V_{\text{RHE}}$ (b, d) with corresponding fits (red). Partial contribution of Ag-Cu bonds, as obtained from EXAFS data fitting, is also shown in (d) with dotted lines. Reference spectra of Cu_2O , Cu and Ag foils are shown for comparison.

We furthermore followed the reduction of the Cu_2O species and the CO or CO-like intermediates chemisorbed on Cu and Ag at different potentials and during CO_2RR via *operando* surface enhanced Raman spectroscopy (SERS). Figure 7 presents potential-dependent SERS spectra of the Ag NP-decorated and pure Cu_2O NCs acquired at open circuit potential (ocp) and between -0.4 and $-1.1 V_{\text{RHE}}$ from $150\text{-}700\text{ cm}^{-1}$ and $1850\text{-}2350\text{ cm}^{-1}$ (see also Figure S17).

In the as-prepared state, the characteristic peaks of Cu_2O are observed at 415 cm^{-1} , 527 cm^{-1} , and 624 cm^{-1} .^[16] The Cu_2O peaks vanished for all samples after applying a reductive potential of $-0.4 V_{\text{RHE}}$, which indicates a prompt reduction of the surface Cu_2O species independently from the Ag loading. The latter is in agreement with the quasi-*in situ* XPS analysis.

At more negative potentials, the *operando* SERS data of the Ag NP-decorated Cu₂O NCs exhibit significant differences compared to the bare Cu₂O NCs during CO₂RR: (1) At higher Raman shifts during CO₂RR, a broad band of the C-O vibrations appeared at 2088 cm⁻¹ for Cu₂O NCs, while for the Ag/Cu₂O a shoulder at 2031 cm⁻¹ is more pronounced. This might be assigned to the multisite binding mechanism on the AgCu surface, where each binding configuration has a different electron back-donating ability.^[17] (2) For the Ag NP-decorated Cu₂O NC samples, two additional peaks at 490 and 530 cm⁻¹ appeared, which might be assigned to Ag-CO vibrations.^[11, 18] (3) Two peaks evolve differently at 280 cm⁻¹ and 366 cm⁻¹, caused by the Cu-CO frustrated rotation and stretching vibration, respectively.^[16b, 18] Thus, we can track the CO adsorbed on Cu and Ag separately by using *operando* SERS and identified significant differences in the CO adsorption characteristics on Cu in the presence of dispersed Ag atoms during CO₂RR as interestingly, the peak intensity ratio of the two Cu-CO Raman peaks shifts towards the Cu-CO stretching vibration with decreasing electrode potential. A similar trend can also be seen with increasing Ag content at -1.0 V_{RHE}. These drastic changes might originate from the way that CO predominantly binds to the Cu. While on pure Cu₂O NCs the CO binding configuration is similarly prone to the Cu-CO rotation and stretching, the presence of Ag sites gives rise to a CO binding configuration that facilitates the Cu-CO stretching with thus, stronger lateral confinement. We anticipate that the latter plays a critical catalytic role to enhance the C-C coupling of neighboring CO adsorbates and thus, increases the C₂₊ liquid product formation.

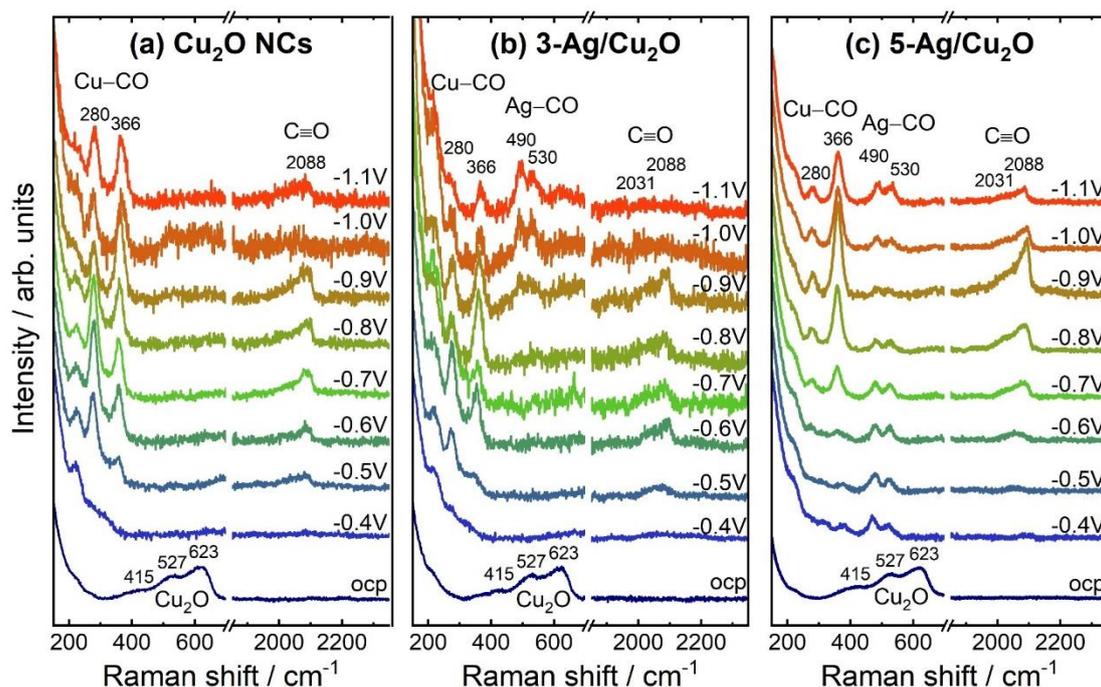


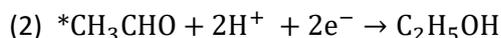
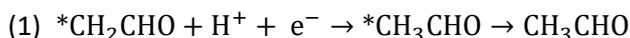
Figure 7. *Operando* surface-enhanced Raman spectra of (a) Cu_2O NCs, (b) 3-Ag/ Cu_2O and (c) 5-Ag/ Cu_2O at open circuit potential (ocp) and under different applied potentials in CO_2 -saturated 0.1 M KHCO_3 . All potentials are given with reference to RHE.

From the *ex situ* and *operando* studies performed under CO_2RR we gained a detailed insight into the structural evolution of the Ag NP-decorated Cu_2O NC catalysts. In their as-prepared state, the Cu_2O NCs as well as the Ag NP-decorated samples mainly consist of Cu_2O , with some contribution of CuO. During CO_2RR , Cu_2O partially reduces to metallic Cu, while the contribution of CuO vanishes. In fact, the *operando* XANES data evidenced the incomplete reduction of Cu_2O in all samples after five hours of CO_2RR (up to 30% of Cu_2O remained in the 3-Ag/ Cu_2O sample). However, we did not find a correlation between the content of Cu_2O (in the bulk, XAS data) and the increased selectivity for C_2+ liquid products, which might be due to the complete reduction (XPS, SERS) of the surface Cu_2O species to metallic Cu during CO_2RR .

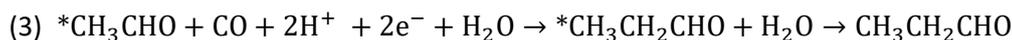
Since the fraction of Ag in the near-surface is low (< 11 at%) intermixing is plausible although a precise determination of the Ag:Cu ratio in the $\text{Ag}_x\text{Cu}_{1-x}$ regions is not possible. Therefore, our system consists of three classes of potentially active sites during CO_2RR : Ag/AgCu/Cu.

To further understand how the structural/chemical rearrangements influence the reaction mechanism, it is useful to correlate such changes with the formation and stability of different intermediates during CO_2RR . The production of CO increased at lower overpotentials with increasing Ag content in the samples.^[19] It has been suggested that $^*\text{CO}$, which is a key intermediate for the C-C coupling mechanism,^[19] might couple with $^*\text{CH}_x$ ^[20] to form the $^*\text{CH}_2\text{CHO}$ intermediate, which plays a

central role in the formation of C₂₊ liquid products.^[21] The *CH₂CHO intermediate can be hydrogenated to *CH₃CHO and form acetaldehyde (1) or be further hydrogenated to yield ethanol (2).



If *CH₃CHO couples with another *CO, propionaldehyde (3) and 1-propanol (4) can be formed.



On Cu surfaces, acetaldehyde and propionaldehyde are usually hydrogenated to ethanol, and 1-propanol and are only detected with FE ~1%, as seen for the Cu₂O NCs. Therefore, we can relate the enhancement of the two aldehyde selectivities to the dispersion of the Ag atoms/small clusters on the Cu surface during CO₂RR, which induces locally strained Cu sites with expanded Cu-Ag interatomic distances compared to Cu-Cu interatomic distances and most importantly, differences in the predominant CO binding motifs. DFT calculations of our previous study showed that an expanded Cu lattice increases the binding energies for the intermediates of CO₂RR (e.g. CO* on Cu).^[22] Additionally, Ag incorporation in Cu weakens the binding energies of the reduced aldehyde intermediates and inhibits their further reduction to ethanol and 1-propanol as demonstrated in a recent DFT study.^[23] However, the structural analysis of the catalysts showed that the surface partially consists of Cu/Ag areas, which also leads to the formation of ethanol and 1-propanol at the Cu sites, since they are expected to have higher binding energies for the oxygenated intermediates as compared to the Ag-Cu mixed regions. Therefore, having Ag/AgCu/Cu interfaces as active surface sites appear to enhance the yield of C₂₊ liquid products.

Conclusion

In summary, Ag NP-decorated Cu₂O nanocubes displayed enhanced selectivity toward C₂₊ liquid products, while the production of formate and hydrogen was suppressed. By means of *ex situ*, *quasi-in situ* and *operando* spectroscopy studies under CO₂RR conditions, we could gain insight in the structural and chemical transformations of these catalysts that were shown to influence the selectivity trends. In particular, we found the redispersion of the Ag NPs on Cu and a certain Cu-Ag miscibility, leading to expanded Cu-Ag interatomic distances compared to metallic Cu-Cu distances. Such structural rearrangements were found to result in an enhanced formation of alcohols and aldehydes.

By comparing the selectivity of pure Cu₂O and Ag NP-decorated Cu₂O NCs we concluded that even though Cu₂O species were partially preserved under reaction conditions, they are not the solely species responsible for the enhancement in the C₂₊ liquid products, which is favored when large Ag/Cu interfaces are formed. Importantly, we correlate the enhancement to variations in the predominant CO adsorption motif on Cu in the presence of dispersed Ag atoms.

Our work contributes to the fundamental understanding of the CO₂RR by highlighting the intricate interplay of different parameters affecting the selectivity. These include the content of residual Cu₂O species, the presence of a secondary metal near Cu where efficient CO spillover can take place, and the alloying of Cu with another metal that is able to increase locally the interatomic distance, leading to a change in the binding energies of adsorbates and intermediates, and favoring thus the formation of C₂₊ liquid products.

Acknowledgements

We would like to thank Dr. See Wee Chee (FHI) and Dr. Osman Karslioglu (FHI) for their support with the acquisition of some of the STEM images as well as Dr. Chao Zhan (FHI) for his helpful suggestions during the acquisition and analysis of the SERS data. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project no. 406944504 – SPP 2080 and Germany's Excellence Strategy – EXC 2008 – 390540038 – UniSysCat. Additional financial support from the European Research Council under grant ERC-OPERANDOCAT (ERC-725915) is also greatly appreciated. Herzog, Rettenmaier and Haase acknowledge support by the IMPRS Functional Interfaces in Physics and Chemistry. We acknowledge SOLEIL for provision of synchrotron radiation facilities and thank the "SAMBA" beamline staff for their great assistance. Experiments were also performed at CLAES beamline at ALBA synchrotron with the excellent collaboration of ALBA staff.

Keywords: *Operando* X-ray absorption spectroscopy • *Operando* surface enhanced Raman spectroscopy • CO₂ electroreduction • CuAg alloy • Cu₂O

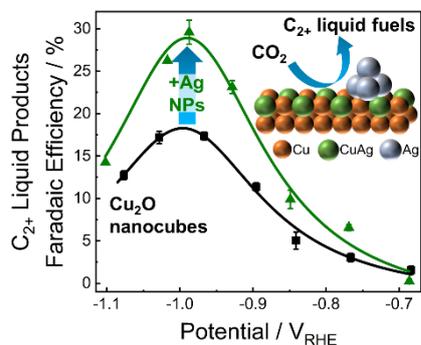
References

- [1] a) S. Chu, Y. Cui, N. Liu, *Nat. Mater.* **2017**, *16*, 16-22; b) P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, *Science* **2019**, *364*, 350-+.
- [2] a) M. Jouny, W. Luc, F. Jiao, *Ind. Eng. Chem. Res.* **2018**, *57*, 2165-2177; b) S. I. Mussatto, G. Dragone, P. M. R. Guimarães, J. P. A. Silva, L. M. Carneiro, I. C. Roberto, A. Vicente, L. Domingues, J. A. Teixeira, *Biotechnol. Adv.* **2010**, *28*, 817-830.
- [3] Y. Hori, K. Kikuchi, A. Murata, S. Suzuki, *Chem. Lett.* **1986**, 897-898.

- [4] Y. Hori, in *Modern Aspects of Electrochemistry* (Eds.: C. G. Vayenas, R. E. White, M. E. Gamboa-Aldeco), Springer New York, New York, NY, **2008**, pp. 89-189.
- [5] a) H. Mistry, A. S. Varela, S. Kühl, P. Strasser, B. Roldan Cuenya, *Nat. Rev. Mater.* **2016**, *1*, 16009; b) R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, *J. Am. Chem. Soc.* **2014**, *136*, 6978-6986; c) H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B. Roldan Cuenya, *J. Am. Chem. Soc.* **2014**, *136*, 16473-16476; d) H. S. Jeon, I. Sinev, F. Scholten, N. J. Divins, I. Zegkinoglou, L. Pielsticker, B. Roldan Cuenya, *J. Am. Chem. Soc.* **2018**, *140*, 9383-9386; e) A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager, R. Buonsanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 5789-5792; f) Z. Wang, G. Yang, Z. Zhang, M. Jin, Y. Yin, *ACS Nano* **2016**, *10*, 4559-4564.
- [6] a) A. S. Varela, M. Kroschel, T. Reier, P. Strasser, *Catal. Today* **2016**, *260*, 8-13; b) D. Ren, J. Fong, B. S. Yeo, *Nat. Commun.* **2018**, *9*, 925; c) Y. Lum, B. Yue, P. Lobaccaro, A. T. Bell, J. W. Ager, *J. Phys. Chem. C* **2017**, *121*, 14191-14203; d) D. Gao, F. Scholten, B. Roldan Cuenya, *ACS Catal.* **2017**, *7*, 5112-5120; e) J. Resasco, L. D. Chen, E. Clark, C. Tsai, C. Hahn, T. F. Jaramillo, K. Chan, A. T. Bell, *J. Am. Chem. Soc.* **2017**, *139*, 11277-11287.
- [7] a) J.-J. Velasco-Vélez, T. Jones, D. Gao, E. Carbonio, R. Arrigo, C.-J. Hsu, Y.-C. Huang, C.-L. Dong, J.-M. Chen, J.-F. Lee, P. Strasser, B. Roldan Cuenya, R. Schlögl, A. Knop-Gericke, C.-H. Chuang, *ACS Sustain. Chem. Eng.* **2019**, *7*, 1485-1492; b) H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. Roldan Cuenya, *Nat. Commun.* **2016**, *7*, 12123; c) C. Liu, M. P. Lourenço, S. Hedström, F. Cavalca, O. Diaz-Morales, H. A. Duarte, A. Nilsson, L. G. M. Pettersson, *J. Phys. Chem. C* **2017**, *121*, 25010-25017; d) R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo, B. Roldan Cuenya, *Nat. Energy* **2020**, *5*, 317-325.
- [8] a) D. F. Gao, I. Zegkinoglou, N. J. Divins, F. Scholten, I. Sinev, P. Grosse, B. Roldan Cuenya, *ACS Nano* **2017**, *11*, 4825-4831; b) P. Grosse, D. F. Gao, F. Scholten, I. Sinev, H. Mistry, B. Roldan Cuenya, *Angew. Chem. Int. Ed.* **2018**, *57*, 6192-6197.
- [9] a) S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. T. Haasch, J. I. Gold, M. Yamauchi, P. J. A. Kenis, *J. Am. Chem. Soc.* **2017**, *139*, 47-50; b) D. Kim, J. Resasco, Y. Yu, A. M. Asiri, P. Yang, *Nat. Commun.* **2014**, *5*, 4948; c) M. Bernal, A. Bagger, F. Scholten, I. Sinev, A. Bergmann, M. Ahmadi, J. Rossmeisl, B. Roldan Cuenya, *Nano Energy* **2018**, *53*, 27-36; d) H. S. Jeon, J. Timoshenko, F. Scholten, I. Sinev, A. Herzog, F. T. Haase, B. Roldan Cuenya, *J. Am. Chem. Soc.* **2019**, *141*, 19879-19887.
- [10] S. Lee, G. Park, J. Lee, *ACS Catal.* **2017**, *7*, 8594-8604.
- [11] J. Gao, H. Zhang, X. Guo, J. Luo, S. M. Zakeeruddin, D. Ren, M. Grätzel, *J. Am. Chem. Soc.* **2019**, *141*, 18704-18714.
- [12] a) D. Higgins, A. T. Landers, Y. Ji, S. Nitopi, C. G. Morales-Guio, L. Wang, K. Chan, C. Hahn, T. F. Jaramillo, *ACS Energy Lett.* **2018**, *3*, 2947-2955; b) E. L. Clark, C. Hahn, T. F. Jaramillo, A. T. Bell, *J. Am. Chem. Soc.* **2017**, *139*, 15848-15857.
- [13] T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.* **2018**, *140*, 5791-5797.
- [14] a) A. Dutta, I. Z. Montiel, R. Erni, K. Kiran, M. Rahaman, J. Drnec, P. Broekmann, *Nano Energy* **2020**, *68*; b) T. Kottakkat, K. Klingan, S. Jiang, Z. P. Jovanov, V. H. Davies, G. A. M. El-Nagar, H. Dau, C. Roth, *ACS Appl. Mater. Interfaces* **2019**, *11*, 14734-14744.
- [15] J. Timoshenko, S. Roese, H. Hövel, A. I. Frenkel, *Radiat. Phys. Chem.* **2020**, *175*.
- [16] a) Y. Deng, A. D. Handoko, Y. Du, S. Xi, B. S. Yeo, *ACS Catal.* **2016**, *6*, 2473-2481; b) S. Jiang, K. Klingan, C. Pasquini, H. Dau, *Journal of Chemical Physics* **2019**, *150*; c) G. Niaura, *Electrochim. Acta* **2000**, *45*, 3507-3519; d) A. Singhal, M. R. Pai, R. Rao, K. T. Pillai, I. Lieberwirth, A. K. Tyagi, *Eur. J. Inorg. Chem.* **2013**, *2013*, 2640-2651.

- [17] Y. C. Li, Z. Wang, T. Yuan, D.-H. Nam, M. Luo, J. Wicks, B. Chen, J. Li, F. Li, F. P. G. de Arquer, Y. Wang, C.-T. Dinh, O. Voznyy, D. Sinton, E. H. Sargent, *Journal of the American Chemical Society* **2019**, *141*, 8584-8591.
- [18] I. Oda, H. Ogasawara, M. Ito, *Langmuir* **1996**, *12*, 1094-1097.
- [19] a) J. H. Montoya, C. Shi, K. Chan, J. K. Norskov, *J. Phys. Chem. Lett.* **2015**, *6*, 2032-2037; b) D. F. Gao, I. T. McCrum, S. Deo, Y. W. Choi, F. Scholten, W. M. Wan, J. G. G. Chen, M. J. Janik, B. Roldan Cuenya, *ACS Catal.* **2018**, *8*, 10012-+.
- [20] L. R. L. Ting, O. Piqué, S. Y. Lim, M. Tanhaei, F. Calle-Vallejo, B. S. Yeo, *ACS Catal.* **2020**, *10*, 4059-4069.
- [21] a) R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, M. T. M. Koper, *The Journal of Physical Chemistry Letters* **2015**, *6*, 4073-4082; b) R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, M. T. M. Koper, *J. Phys. Chem. Lett.* **2015**, *6*, 4073-4082; c) E. L. Clark, A. T. Bell, *J. Am. Chem. Soc.* **2018**, *140*, 7012-7020.
- [22] M. Bernal, A. Bagger, F. Scholten, I. Sinev, A. Bergmann, M. Ahmadi, J. Rossmeisl, B. R. Cuenya, *Nano Energy* **2018**, *53*, 27-36.
- [23] L. Wang, D. C. Higgins, Y. Ji, C. G. Morales-Guio, K. Chan, C. Hahn, T. F. Jaramillo, *Proc. Natl. Acad. Sci. U.S.A.* **2020**.

Entry for the Table of Contents

Ag/Cu₂O nanocubes for CO₂RR

Cu₂O nanocubes showed a remarkable increase (30%) in the Faradaic efficiency for C₂₊ liquid products after the decoration with Ag nanoparticles. *Operando* spectroscopy revealed a reaction-driven redispersion of Ag on CuO_x as well as a certain Cu-Ag miscibility. These changes were coupled with significant variations in the binding of CO to Cu that favored the enhancement of the liquid product yields.