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Unlocking direct CO_2 electrolysis to C_3 products *via* electrolyte supersaturation

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Keywords

CO_2 electro-reduction, electrocatalysis, multicarbon product, electrochemical deposition, alloy catalyst, energy efficiency, high pressure electrolyzer, *operando* spectroscopy.

Abstract.

The electroreduction of CO_2 has recently achieved notable progress in the formation of C_2 products such as ethylene and ethanol. However, the direct synthesis of C_3 products is considerably limited by the C_2-C_1 coupling reaction and the Faradaic efficiency has remained low. Here, we present a supersaturation strategy for the electrosynthesis of 2-propanol from CO_2 in highly carbonated electrolytes. By controlling the CO_2 concentration above the saturation limit, we developed a co-electrodeposition method with suppressed galvanic replacement to obtain a Cu-Ag alloy catalyst. In supersaturated conditions, the alloy achieved high performance for the production of 2-propanol with a Faradaic efficiency of 56.7 % and $j_{\text{2-propanol}}$ of 59.3 mA cm^{-2}. Our investigations revealed that the presence of dispersed Ag atoms in Cu weakens the surface binding of intermediates in the middle position of the alkyl chain and strengthens the C-O bonds, which favours the formation of 2-propanol over 1-propanol.

Introduction.

The carbon dioxide reduction reaction (CO_2RR) is investigated as a promising route to convert CO_2 into value-added chemicals through electrochemical processes.[1] While the reduction of CO_2 to C_1 and C_2 products has achieved significant progress toward industrial application over recent years, the formation of multicarbon molecules with $C \geq 3$ (C_{3+}) possessing superior energy density and higher commercial values is more desirable but remains challenging.[2] Favourable multicarbon coupling is a prerequisite to unlock the formation of C_3 products and requires the development of catalysts with low energy barriers associated with the C_1-C_1 (C_2) and C_1-C_2 (C_3) coupling reactions.[3] Alternatively, efforts to increase the selectivity towards the formation of C_3 products have focused on replacing CO_2 with CO but such a strategy involves a two-step reaction and complicates the overall CO_2RR process.[4] From a mechanistic point of view, the initial *CO intermediate (* denotes surface bound intermediates) plays a central role in the formation of C-C bonds. Protonation and desorption of *CO are however competing processes to the dimerization of *CO, which is intrinsically limited by a high energy barrier and sluggish kinetics.[5] To date, only a handful of systems have demonstrated the direct conversion of CO_2 to C_3 hydrocarbons and oxygenates, and the corresponding Faradaic efficiency (FE) remains below 20 %. The reaction mechanism for the formation of C_3 products and the associated selectivity is still debated.[6,7] Statistically, larger concentrations of *CO on the catalyst surface increases the probability of further C-C coupling.[8] Previous reports have pointed out that modulating the local CO_2 concentration ([CO_2]) can enhance the C-C coupling in CO_2RR. For example, cavities on the catalyst surface were found to achieve larger selectivity for the formation of propanol thanks to a confinement-derived accumulation of *CO.[9]

Herein, we report a supersaturation strategy for the direct electro-reduction of CO_2 to C_3 products on a CuAg alloy catalyst by using a strongly carbonated electrolyte with [CO_2] above the saturation limit. We developed a co-deposition method under CO_2 supersaturated conditions where CO_2 acts as a surfactant to prevent undesirable galvanic replacement reaction, while favouring the preferential growth of the CO_2RR active CuAg facets. The influence of the [CO_2] on the C-C coupling rate was investigated. We find that performing CO_2RR in strongly carbonated electrolyte translates to a dramatic change in the reaction pathway towards the selective formation of 2-propanol with a record-high $FE_{2\text{-propanol}}$ of 56.7 % at a specific current density of 59.3 mA cm^{-2}. Our hard X-ray absorption (hXAS) spectroscopies revealed the formation of the CuAg alloy with highly dispersed Ag atoms, forming a solid solution, while *operando* Raman spectroscopy indicated the formation of multicarbon products involves the adsorption of *CO on an optimized ratio of atop and bridge sites in the supersaturated electrolyte.[10] We also identified the role of the $*OCH_2CH_3$ intermediate using isotopic labelling and *operando* infrared spectroscopy. Finally, we used DFT calculations to elucidate the critical role of silver atoms in orienting the reaction toward the formation of 2-propanol over 1-propanol. Overall, our investigations revealed that supersaturated conditions promote the formation of *CO species on the surface of catalyst, whereas the CuAg alloy favours the formation of multicarbon products and is responsible for the selective formation of 2-propanol.

Results.

Design and characterizations of bimetallic CuAg catalyst.

The direct conversion of CO_2 to C_3 molecules requires the development of catalysts with low energy barriers for both the C_1-C_1 and C_1-C_2 coupling steps.[11] Cu-based alloys have been identified to enhance the selectivity towards the formation of C_3 products through the modulation of the *CO adsorption.[12] Herein, we designed a favourable catalyst with high C-C coupling activity using CO_2 supersaturated electrolyte based on a synergy effect from Cu and Ag.[13] By analogy with the use of capping agents for the control of the exposed facets of nanocrystals, we hypothesized that the high concentration of CO_2 used for electrodeposition under supersaturated conditions promotes the adsorption of CO_2 on the most favourable facets for the CO_2RR.[14] Under cathodic conditions, the facets with the lowest adsorption energy will be involved in CO_2 conversion, while the less favourable facets will be more likely to be involved in the deposition process. We first explored the adsorption energies of *CO_2 on different Ag and Cu facets by using density functional theory (DFT) calculations (**Fig. 1a**).[15] According to the adsorption energy diagram, CO_2 will preferentially bind on Cu (100) facets rather than Cu (111), Cu (211) facets or Ag (111) and Ag (100) facets. We anticipate that the high surface coverage with CO_2 under supersaturated conditions also prevents galvanic replacement reaction and the formation of segregated domains of Ag and Cu (**Fig. 1b**).[16] Experimentally, Cu and Ag were co-electrodeposited on a gas diffusion layer (GDL) using alternatively CO_2-supersaturated (CO_2-CuAg) or argon-saturated (Ar-CuAg) conditions (**Supplementary Fig. 1, 2, 3a and 3b, Supplementary Note 1 and 2).** The precursor ratio of Cu^{2+} to Ag^+ ions and the deposition current density ($j_{\mathrm{deposition}}$) were adjusted and the CuAg bimetallic electrodes were characterized by inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) (**Supplementary Table 1 and 2, Supplementary Note 3, Supplementary Fig. 3c**). At higher $j_{\mathrm{deposition}}$, the morphology of CuAg bimetallic structure evolved from bulk microcrystals to dendritic structures with high electrochemically active surface area (ECSA) determined by the lead underpotential deposition (Pb-UPD) method (**Supplementary Fig. 3d, Supplementary Table 3 and 4**). Systematic X-ray investigations using XRD and 1D grazing-incidence wide-angle X-ray scattering (GIWAXS) spectroscopy revealed the presence of a single peak at 2θ around 50.9° that is attributed to CuAg (100) facet and is characteristic of a copper-silver based alloy. Conversely, under Ar saturated conditions, the observation of the Ag peak at 38.2° indicates an uncontrollable galvanic replacement reaction (**Supplementary Fig. 4, Supplementary Note 4**). Temperature-programmed desorption (TPD) of CO_2 was also carried out on the CO_2-CuAg and Ar-CuAg, respectively (**Supplementary Fig. 5, Supplementary Note 5**). For CO_2-CuAg, one broad peak was observed from 350 to 720 °C instead of the individual contribution from Ag and Cu, suggesting an alloying characteristic. The XPS spectra show that the position of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ shifted by +0.6 eV for CO_2-CuAg compared with bulk Cu (**Fig. 1c**). Similarly, the binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks shifted by -0.5 eV for CO_2-CuAg compared with bulk Ag (**Fig. 1d**). Such a shift in binding energies is attributed to electron transfer from Cu to Ag atoms, during which Cu atoms act as electron donors and become electron-deficient.[17,18] The existence of electron transfer from Ag to Cu atoms highlights the strong electronic interaction between Cu and Ag and further supports the alloy feature of CO_2-CuAg.[19] We prepared a CuAg alloy: CO_2-10-$Cu_{94}Ag_6$ with a molar ratio of 94 : 6 and a deposition current density of 10 mA cm^{-2}, which exhibited the largest ECSA and a dendritic microstructure (**Fig. 1e to 1g**). The crystal structure of the catalyst was elucidated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and OH^- adsorption profile (**Fig. 1h, Supplementary Fig. 6 and 7, Supplementary Note 6 and 7**). These results indicate that CO_2-10-$Cu_{94}Ag_6$ preferentially exhibits CuAg (100) facets on the surface. Energy-dispersive X-ray (EDX) mapping finally reveals the uniform dispersion of elements in CO_2-CuAg alloy even at high magnification **(Fig. 1i to 1l)**. On the other hand, detailed (S)TEM analyses of the Ar-CuAg sample highlighted the segregation of Ag from the surface of Cu **(Supplementary Fig. 8, Supplementary Note 8)**.[20]

2D-GIWAXS was then performed to elucidate the surface structure of the exposed crystal facets for both the CO_2-CuAg and Ar-CuAg (**Fig. 2a and 2b**).[21] Using CO_2 supersaturated deposition solution, a series of intense single peaks are detected at q_z = 29.42, 33.98, 48.03 and 56.85 nm^{-1} in agreement with the presence of the CuAg alloy (111), (200), (220) and (310) facets, respectively. Conversely, when the co-deposition is carried out under argon, all peaks split into two components. We monitored the evolution of the coordination environment during the co-deposition process using time-resolved 2D Fourier-transformed *operando* extended X-ray absorption fine structure (EXAFS) (**Fig. 2c and 2d**).[22] By fitting the Cu K-edge EXAFS spectra, we identified the contribution of the Cu-Ag bond as evidenced by the shoulder peak at 2.63 Å in agreement with the decrease of the Cu-Cu coordination number for the CO_2-CuAg alloy (**Supplementary Fig. 9 to 14**, **Supplementary Table 5 and 6, Supplementary Note 9 to 11**). The combined analysis of the GIWAXS and EXAFS results allowed us to discriminate the contributions from the alloy, galvanic replacement and pure Cu formation during the co-deposition process.[23] We estimated that 88.4 % alloying occurs when preparing CO_2-CuAg. Without CO_2 as the capping agent, alloying decreases to only 5.5 % whereas Cu-Cu formation and uncontrollable galvanic replacement processes account for 52.2 % and 42.3 %, respectively in the case of Ar-CuAg (**Supplementary Fig. 15 and 16, Supplementary Note 12 and 13**). We then carried out *ex-situ* Ag K-edge EXAFS spectra and the corresponding wavelet transformation (WT) EXAFS contour spectra to further highlight the Ag-Cu bonding (**Supplementary Fig. 17, Supplementary Table 7, Supplementary Note 14 and 15**). As shown in **Fig. 2e**, the peak at 2.45 Å for the CO_2-CuAg unambiguously confirms the existence of the Ag-Cu bond with a coordination number of 2.43, while no contribution of the Ag-Ag bond was detected.[24] As demonstrated by **Fig. 2f** and **2g**, the Ag K-edge WT-EXAFS spectra demonstrate one intensity maximum associated with the Ag-Cu contribution, which is consistent with the formation of a CuAg alloy. Taken together, these results suggest that the co-deposition of Ag and Cu under CO_2 supersaturated conditions leads to the formation of a CuAg alloy with CO_2RR active (100) facets being preferentially exposed.

CO_2RR under atmospheric pressured CO_2 supersaturation.

The CO_2RR electrocatalytic activity was evaluated using an H-type cell in a standard three-electrode configuration with a catalyst loading amount of 5 mg cm^{-2}.[25] To avoid any cross effect from the pressure, all the measurements were performed at atmospheric pressure. We evaluated the relationship between the equilibrium concentrations of CO_2-HCO_3-CO_3^{2-} together with the electrolyte pH for increasing partial pressure of the CO_2 (**Supplementary Fig. 18, Supplementary Note 16**).[26] Electrochemical activation was carried out before the reaction to remove the surface oxides (**Supplementary Fig. 19, Supplementary Note 17**). The experimental quantification of the [CO_2] in the electrolyte was determined using a CO_2-specific reference electrode (**Inset Fig. 3a**). **Fig. 3a** presents the linear sweep voltammetry (LSV) curves for CO_2-10-$Cu_{94}Ag_6$ recorded in 1.0 mol L^{-1} $CsHCO_3$ with [CO_2] of 0, 0.05 and 0.3 mol L^{-1} that correspond to Ar-saturated, CO_2-saturated and CO_2-supersaturated electrolytes, respectively. The onset potential measured in the CO_2 supersaturated electrolyte extracted from the LSV curves appeared positively shifted by 46 mV compared with that measured in the CO_2 saturated electrolyte. To further quantify the CO_2RR performance, the Faradaic efficiency (FE) was estimated using pre-calibrated gas chromatography (GC) and nuclear magnetic resonance (NMR) analyses (**Supplementary Fig. 20 to 22, Supplementary Note 18 and 19**).[27] In CO_2 saturated electrolyte, the FE_{C2H4} reached 23.2%, while no C_3 product was detected (**Fig. 3b**). Conversely, using a CO_2 supersaturated solution, C_3 products were systematically detected for potentials larger than -0.4 V *versus* the reversible hydrogen electrode (*vs.* RHE) with the 2-propanol being the main product (**Supplementary Fig. 23**).[28] The $FE_{2\text{-propanol}}$ exhibits a volcano-shaped dependence with the applied potentials and reached a maximum of 39.6 % at -0.73V *vs.* RHE (**Fig. 3c**). Importantly, deuterium isotopic labelling experiments under the same CO_2RR condition confirmed the formation of 2-propanol-D8 and ruled out any possible contamination (**Supplementary Fig. 24 and 25, Supplementary Note 20 and 21**). **Fig. 3d** compares the ECSA-normalized specific current density (*j*) of CO_2-10-$Cu_{94}Ag_6$ for the different CO_2RR products. The $j_{ECSA\text{-2-propanol}}$ reaches 12.03 mA cm_{ECSA}^{-1} with a corresponding partial energy efficiency (EE) of 22.7 %. These results outperform the previous reports from the literature for the direct conversion of CO_2-to-C_3 products (**Supplementary Table 8**).[29-31]

To better gauge the CO_2RR properties of CO_2-10-$Cu_{94}Ag_6$ in CO_2 supersaturated 1.0 mol L^{-1} $CsHCO_3$, we then analyzed the FEs of the different products as a function of the [CO_2] for different applied potentials

(**Fig. 4a-e**).[32] The FE_{H2} for the hydrogen evolution reaction (HER) is found to be larger than 90 % over the measured potential range when the $[CO_2] \leq 0.05$ mol L^{-1} (**Fig. 4a**). The FE for C_1 and C_2 products (FE_{C1} and FE_{C2}) are clearly increased in CO_2-supersaturated electrolytes (**Fig. 4b and 4c**). When $[CO_2] \geq 0.2$ mol L^{-1} – equivalent to 8.8×10^3 parts *per* million (ppm) – C_3 products are detected at potentials as low as -0.4 V *vs.* RHE. (**Fig. 4d**). These findings highlight the role of the $[CO_2]$ on the reaction pathway (**Fig. 4e, Supplementary Note 22**).[26] Importantly, we identified that $[CO_2] \geq 0.2$ mol L^{-1} unlocks the C_1-C_2 coupling reaction to form C_3 products, which emphasizes the benefit of performing the CO_2RR in the supersaturated electrolyte.[33]

To discriminate the role of CO_2, we systematically examined the CO_2RR performance of CO_2-10-$Cu_{94}Ag_6$ with and without supersaturation as well as the influence of the current density for the co-deposition of the alloy (**Supplementary Fig. 26 and 27, Supplementary Note 23**). The results revealed that the C_3 products are only detected when both the co-deposition and the CO_2RR measurements are performed in a CO_2-supersaturated condition. We investigated the role of the cations on the reaction selectivity under supersaturated conditions (**Supplementary Fig. 28 to 31, Supplementary Note 24 to 26**). Although the $[CO_2]$ is found to be largely independent of the nature of the cations, C_3 products could only be detected in the presence of Cs^+, while the FE_{C3} moderately increased with the electrolyte concentration. This finding is attributed to the larger radius of the Cs^+ cations that can interact with two *CO.[34] To clarify the importance of controlling proton and CO_2 concentrations, we also assessed the CO_2RR performance of CO_2-10-$Cu_{94}Ag_6$ using flow-cells and membrane electrode assembly (MEA) electrolyzers with the triple-phase interface.[35] No C_3 products could be detected, which suggests that the elevated $[CO_2]$ and optimal proton concentration are necessary conditions for the formation of C_3 species (**Supplementary Fig. 32 to 34, Supplementary Note 27 and 28**).[36]

The stability of CO_2-10-$Cu_{94}Ag_6$ was evaluated over 24 hours at a potential of -0.73 V *vs.* RHE in CO_2-supersaturated 1.0 M $CsHCO_3$ under atmospheric pressure (**Fig. 4f, Supplementary Fig. 35 to 39 and Supplementary Table 9 to 10, Supplementary Note 29 to 32**). The current was continuously measured while the liquid products were collected and quantified by NMR. The performance was found to be stable with nearly constant cathodic current density and minimal drop of the $FE_{2\text{-propanol}}$. After 24 hours, the retention of the current density and the $FE_{2\text{-propanol}}$ reach 98.4 % and 89.6 %, respectively. 2D Fourier-transformed *operando* EXAFS of the CO_2-10-$Cu_{94}Ag_6$ catalyst during the CO_2RR in CO_2-supersaturated electrolyte highlights the absence of signals from the Cu-O bonds (expected at 2.0 Å) and confirms that the coordination environment for Cu K-edge is preserved during the CO_2RR process (**Fig. 4g**).

Investigations of CO_2 reduction reaction mechanism.

It is generally accepted that the formation of multicarbon products during the electro-reduction of CO_2 proceeds *via* C-C coupling of the *CO intermediates, which has been proved to be a crucial step for achieving higher selectivity towards the formation of the multicarbon products.[37,38] To investigate the reaction mechanism in the supersaturated electrolyte, the surface of the catalysts was probed by *operando* Raman spectroscopy (**Supplementary Fig. 40**). We first recorded the [CO_2] and potential-dependent Raman responses of CO_2-10-$Cu_{94}Ag_6$ (**Supplementary Fig. 41 and 42, Supplementary Note 33 and 34**). A qualitative comparison of *CO intermediate around 2000 cm^{-1} during the CO_2RR revealed that the *CO signatures are enhanced when the [CO_2] $\geq$ 0.2 mol L^{-1} (**Fig. 5a**). It is worth noting that the region with the most intense *CO contribution overlaps with that of the largest $FE_{2\text{-propanol}}$ (**Fig. 5a**, **Supplementary Fig. 43, Supplementary Note 35**). This observation suggests that increasing [CO_2] translates to a higher concentration of *CO absorbed on the surface of the alloy catalyst. We then examined the interactions between the catalyst surface and adsorbed *CO by recording the potential-resolved 2D Raman heatmap in supersaturated 1.0 mol L^{-1} $CsHCO_3$ with a constant [CO_2] of 0.3 mol L^{-1} (**Fig. 5b**).[6] The *CO stretching modes on CO_2-10-$Cu_{94}Ag_6$ alloy with CO_2RR under supersaturated conditions were found to extend over a much larger frequency range from 1900 to 2100 cm^{-1} compared with those measured in CO_2- and Ar-saturated conditions, suggesting a multisite binding mechanism favourable to the multicarbon product formation (**Supplementary Fig. 44 to 46**).[39]

To gain further insight into the nature of the *CO binding on the catalyst surface, we deconvoluted the *CO stretching modes into two regions corresponding to *CO bound on defect-like sites ($^*CO_{bridge}$) and *CO bound on top of terrace-like sites ($^*CO_{atop}$) at a frequency below 2080 cm^{-1} and above 2080 cm^{-1}, respectively.[40,41] The ratio of $^*CO_{bridge}$ to $^*CO_{atop}$ linearly increases with the [CO_2] once the electrolyte enters the supersaturated regime; pointing out a possible correlation between 2-propanol selectivity with the local concentration and stretching mode of *CO (**Supplementary Fig. 47 to 49, Supplementary Note 36**). We further evaluated how the evolution of *CO stretching modes influence the $FE_{2\text{-propanol}}$ under different potentials (**Fig. 5c**).[42] A volcano-shaped relationship centred around the optimal potential of -0.73V *vs.* RHE was found between the $^*CO_{bridge}$-to-$^*CO_{atop}$ ratio, the $FE_{2\text{-propanol}}$ and the applied potential. The results reveal a possible optimization of the proportion of $^*CO_{bridge}$ to $^*CO_{atop}$ for activating the C-C coupling at high *CO density on the catalyst surface.[43]

We then aimed to elucidate the reaction mechanism for the formation of 2-propanol by combining the isotopic labelling experiments and *operando* Fourier-transform infrared (FTIR) spectroscopy. We hypothesized that $^*OCH_2CH_3$ is involved in the formation of C_3 species during the CO_2RR. We added hexadeuteroethanol (ethanol-D6) to the electrolyte as a simulant of $^*OCH_2CH_3$ before the reaction and performed ^{13}C NMR spectroscopy after 24 hours at -0.70 V *vs.* RHE under the 1.0 M $CsDCO_3$, D_2O electrolyte (**Fig. 5d, Supplementary Fig. 50, Supplementary Note 37**). Remarkably the formation rate of

2-propanol-D8 increases in presence of ethanol-D6 in the electrolyte as evidenced by the increase of the corresponding NMR signals, while the integrated peak area from ethanol-D6 decreased after the reaction, suggesting a direct involvement of ethanol-D6 in the reaction process. To confirm the role of $*OCH_2CH_3$, we performed the same reaction using ethanol-D6 in a 1.0 M $CsHCO_3$, H_2O electrolyte. We found that the ^{13}C NMR peak for methyl-carbon splits into two peaks with a difference of chemical shift of 121 ppb, which is attributed to the hydrogen / deuterium-isotope effects.[44] These investigations thus confirm the detection of partially deuterated 2-propanol-D3, which is formed *via* the first dehydrogenative adsorption of ethanol-D6 ($*OCD_2CD_3$ as intermediate) followed by the C_1-C_2 coupling with *CO adsorbed on the catalyst surface.

To get a further understanding of the C_1-C_2 coupling process, we examined the dynamic evolution of the *CO and $*OCH_2CH_3$ intermediates during the CO_2RR by performing *operando* FTIR spectroscopy under CO_2-supersaturated conditions (**Supplementary Fig. 51, Supplementary Note 38**). Clear signals attributed to the *CO stretching band and the $*OCH_2CH_3$ bending band were detected at 1950-2150 cm^{-1} and ~1340 cm^{-1}, respectively.[45,46] When the potential decreases from -0.2 to -0.73 V *vs.* RHE, both the *CO and $*OCH_2CH_3$ bands become progressively more intense, which points to higher formation rates of the intermediates (**Fig. 5e**). Remarkably, the increase of the *CO and $*OCH_2CH_3$ signals is accompanied by a decrease of the FE_{CO} and $FE_{ethanol}$ together with an increase of the $FE_{2\text{-propanol}}$ (**Fig. 5f**). These findings suggest that under CO_2-supersaturation conditions, the high density of *CO and $*OCH_2CH_3$ intermediates triggers the formation of 2-propanol instead of CO or ethanol. At larger overpotentials, fewer *CO and $*OCH_2CH_3$ intermediates are generated according to the decrease in FTIR signals, which decreases the probability of C_1-C_2 coupling and leads to a rapid decrease in 2-propanol formation.

In the light of the above experiments and the identification of the role of $*OCH_2CH_3$ in the formation of 2-propanol, we proposed in **Fig. 6a** the mechanism toward 2-propanol. DFT calculations were performed with an implicit solvent to evaluate the formation energy of each intermediate with the computational hydrogen electrode, under a potential of -0.7 V *vs.* RHE. We performed calculations on Cu and $Cu_{92}Ag_8$ slabs to model pure Cu and CuAg catalysts (**Supplementary Table 11**). We note that the $Cu_{92}Ag_8$ slab was formed by swapping two of the closest Cu atoms to the oxygen atom of intermediate I2 ($*OCH_2CH_3$) by Ag. We found that the adsorption of the intermediate *via* the O atom pointing to a hollow site of Cu is more stable by 0.79 eV compared to the adsorption *via* only one C atom. On both Cu and CuAg catalysts, the thermodynamic pathway occurs *via* the formation of intermediates I2, I2', I2'', I3, I6 and I8, leading to the formation of 2-propanol (red arrows, the corresponding energies are summarized in **Supplementary Table 12 and 13**).

Although the formation energies provide a potential route to the formation of 2-propanol on $Cu_{92}Ag_8$, they do not demonstrate the selective effect of the catalyst, as 1-propanol is not thermodynamically predicted on pure Cu. Indeed, kinetic effects, governed by transition barriers along the pathway, also control the reaction selectivity. According to our proposed mechanism and the literature, the formation of 1-propanol occurs *via* the cleavage of the O-C bond of the carbon in the middle carbon position on the C_3 chain, leading to an oxygenated carbon at the end of the alkyl chain.[37,47,48] By contrast, the formation of 2-propanol must proceed by the hydrogenation of the middle oxygen (in position 2 of the C_3). We evaluated the strength of the O-C bond with respect to the strength of the Cu*-O bond as a key descriptor of the propanol formation kinetics. To illustrate this general effect, we considered the intermediate I2.[49] The energy of I2 was first calculated as a function of Cu*-O or O-C bonds distance on the Cu catalyst (**Fig. 6b**). The dissociation energy is defined as the lowest energy value when shifting the dissociated state to 0.0 eV. We further defined the difference between dissociation energies of *Cu-O and O-C bonds as $\Delta E_{diss.}$ We found that on a pure Cu catalyst, the dissociation energy of Cu*-O is greater than that of O-C on pure Cu. This implies that a weaker O-C bond will preferentially break, striping the oxygen atom in the position 2 of the C_3 chain, thus leading to the formation of 1-propanol *via* the I7 intermediate, which is consistent with the previous experimental reports.[48]

We then generated a library of CuAg slabs by replacing 1, 2 and 3 Cu atoms of the 2 first surface layers with Ag atoms, which is combinatorial with symmetry, leading to the $Cu_{96}Ag_4$, $Cu_{92}Ag_8$ and $Cu_{88}Ag_{12}$ structure, respectively. For the 127 slabs generated, we computed the dissociation energy of Cu*-O and O-C bonds for I2, and the energy differences ΔE_{diss} as a function of the distance to Ag are plotted in **Fig. 6c** (**Supplementary Table 14**). The distance to Ag is defined as the averaged distance between the oxygen atom of I2 and the Ag atoms in the catalyst. We realized that as the I2 intermediates get closer to the Ag atoms, the dissociation energy corresponding to the CuAg*-O bond decreases and that of the O-C bond increases (i.e. ΔE_{diss} decreases). Interestingly, for configurations where I2 is very close to Ag sites, ΔE_{diss} becomes negative, suggesting that the O-C bond becomes stronger than the CuAg*-O bond (inset in Fig 6c, **Supplementary Fig. 52**). By contrast, for configurations where I2 is far from Ag sites, ΔE_{diss} tends to 0.4 eV, which is similar to the energy we computed on pure Cu catalyst (dashed line in Fig. 6c). Therefore, when I2 is in the vicinity of the Ag sites, the weaker CuAg*-O bond will dissociate preferentially, and the stronger O-C bond will stabilize intermediates such as I5 and I8, leading to the selective formation of 2-propanol. It is important to note that C_2 and C_3 intermediates will be located close to Ag sites of the CuAg alloy as it has been previously demonstrated that Ag provides low energy barriers for C_1-C_1 and C_1-C_2 coupling.[2]

To further demonstrate and validate the effect of Ag proximity to CuAg*-O and O-C bonds in a realistic environment, we performed *operando* DFT calculations with explicit water (**Supplementary Fig. 53 to 59,**

Supplementary Table 15 to 17). Our simulations include the explicit effect of water, electrochemical potential, ions, and CO_2 (Please see the markup of SI for more information). Overall, the results provide strong validations of the implicit solvent model and suggest minor effects of dissolved cation and CO_2 to the stabilization of the intermediate I2. To summarize, our experimental and computational approaches demonstrate that both CO_2-supersaturated conditions and the alloy characteristics of CO_2-CuAg are responsible for the enhanced formation rates of *CO and $*OCH_2CH_3$ intermediates (I2) close to Ag sites of the alloy, which further combine and lead to the formation of I3. The proximity of Ag sites strengthens the C-O bond of the carbon in position 2 of the C_3 chain while destabilizing the CuAg*-O bond, leading to the preferential formation of 2-propanol. According to our experimental and DFT calculation results, the origin of the unique selectivity of CO_2-to-2-propanol conversion can be attributed to the combined effect on the modulation of the *CO adsorption and formation of the key $*OCH_2CH_3$ intermediate induced by both the alloy nature of the catalyst and the CO_2 supersaturation of the electrolyte.

CO_2RR under elevated pressured CO_2 supersaturation.

CO_2RR investigations have previously been performed under elevated pressure to avoid the diffusion limit of the CO_2 during the electrochemical reactions, but there is limited in-depth discussion in the literature regarding the origin of the activity enhancement under high CO_2 partial pressure.[50-53] In the light of the above performance and the mechanism investigations, we further evaluated the CO_2RR properties of the catalyst at higher [CO_2]. According to Henry's law, under constant temperature, the amount of a given gas that dissolves in a given volume of liquid is directly proportional to the partial pressure of gas in equilibrium with the liquid.[54] Therefore, the catalytic measurements were carried out using a two-compartment high-pressure reactor with CO_2 pressures up to 20-bar and Nafion-117 membrane as cation exchange membrane (**Supplementary Fig. 60 and 61, Supplementary Note 39**). To better assess the performance of CO_2-10-$Cu_{94}Ag_6$ in CO_2 supersaturated 1.0 mol L^{-1} $CsHCO_3$ under high pressure, we first evaluated the $FE_{2\text{-propanol}}$ as a function of the [CO_2] and for different applied potentials (**Supplementary Fig. 62 to 64**). As shown in **Fig. 7a**, the $FE_{2\text{-propanol}}$ exhibits a volcano shape relationship with the potential and the CO_2 pressures and reaches a record-high value of 56.7 % at a potential of -0.70 V *vs.* RHE and ~3.0 mol L^{-1} of CO_2 corresponding to a pressure of 10 bar. To highlight the role of the [CO_2] on the catalyst behaviour, the j_{total}, j_{H2} and $j_{2\text{-propanol}}$ were calculated (**Fig. 7b)**. The j_{total} for all products continuously increased with the elevation of the [CO_2]. For a [CO_2] of 3.0 mol L^{-1}, the CO_2-10-$Cu_{94}Ag_6$ electrodes demonstrated a value of $j_{2\text{-propanol}}$ as high as 59.3 mA cm^{-2}. By comparing the performance metrics of CO_2-10-$Cu_{94}Ag_6$ under CO_2 supersaturated electrolyte with previous literature benchmarks, we observed that the supersaturation strategy outperforms previous reports from the literature even including CO-to-C_3 systems and set a record-high direct CO_2-to-C_3 conversion rate of 0.71 μmol h^{-1} cm^{-2} (**Fig. 7c**).[55,56] The robustness of the CO_2-10-$Cu_{94}Ag_6$ catalyst was investigated under continuous operation with a CO_2

pressure of 10 bar, a feed rate of 100 standard cubic centimetres *per* minute (sccm) and an applied cell voltage of -0.70 V *vs.* RHE (**Fig. 8a**). We further used EDX-mapping, XPS, *ex-situ* XRD and *operando* hXAS analyses to confirm the stability of the surface oxidation state as well as the coordination environment of the catalyst during operation (**Supplementary Fig. 65 to 68, Supplementary Table 18, Supplementary Note 40 and 41**). NMR analyses were carried out along reaction time and the corresponding amount of 2-propanol produced from the conversion of CO_2 was estimated (**Fig. 8b and 8c**). Under high-pressure operation, the system was found to be stable over 200 hours with retentions of the $FE_{2\text{-propanol}}$ and $j_{2\text{-propanol}}$ of 98.3 % and 97.5 %, respectively, which translates to a steady CO_2-to-C_3 conversion rate of 0.71 μmol h^{-1} cm^{-2}.

Conclusions.

Overall, we introduced a CO_2 supersaturation strategy for the direct conversion of CO_2-to-C_3 products. Supersaturation conditions with CO_2 allow for the controllable co-deposition of a CuAg alloy by suppressing the galvanic replacement reaction responsible for the segregation of Cu and Ag. Performing the electro-reduction of CO_2 under supersaturation conditions also orients the reaction pathway towards the formation of 2-propanol. The mechanism responsible for the high selectivity towards the formation of C_3 products was explored in detail using *operando* Raman, FTIR and hXAS spectroscopy together with *ex-situ* isotopic labelling experiments and DFT calculations. These results led to the identification of the role of *CO for C_1-C_1 coupling and $^*OCH_2CH_3$ as a key intermediate for the selective formation of 2-propanol. Our experimental and calculation results highlight the importance of the CuAg alloy catalyst on the formation of 2-propanol and emphasize the advantage of the supersaturation strategy to increase the local [CO_2] during the CO_2RR, which improves the formation rate of *CO intermediates. We achieved a record-high selectivity with the Faradaic efficiency for 2-propanol of 56.7 % and a specific current density of 59.3 mA cm^{-2} together with operating stability for 200 hours. Our investigations provide the opportunity for fine-tuning the reaction pathway by controlling the local CO_2 concentration and the formation rate of the catalytic favourable intermediates. We believe that the supersaturation strategy holds promise for applications in large-scale carbon fixation, the production of high-market value, energy-dense multicarbon molecules and the storage of energy in the form of chemical fuels.

Methods.

Structural characterization and compositional analysis.

Scanning electron microscopy (SEM) images were obtained using a Hitachi SU-8010 ultra-high resolution (1.0 nm) scanning electron microscope. Transmission electron microscopy (TEM) measurements were conducted with a JEOL 1400 microscope equipped with an emission gun operating at 120 kV. High-resolution transmission electron microscope (HRTEM) was performed on the FEI Tecnai G^2 F20 TEM operating at 200 kV. The samples were prepared by dropping ethanol dispersions onto 300 mesh lacey carbon-coated gold grids. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were acquired using a JEOL-ARM200F TEM operated at 200 kV. The attainable spatial resolution of the microscope was 78 pm with a probe spherical-aberration corrector. The images were acquired with an illumination semi-angle of 25 mrad and a probe current of 100 pA. The dwell time for image acquisition was set at 10 μs per pixel to ensure a desirable signal-to-noise ratio. The collection angles for the HAADF images were fixed at 90-250 mrad. To obtain high-quality scanning transmission electron microscopy (STEM) images with atomic resolution, the material was pre-treated at 60 °C in a vacuum oven for 4 hours to remove any organic contaminants on its surface. A field emission scanning electron microscope (TESCAN Mira3) was employed to observe the morphology of samples. Aberration-corrected high-resolution (scanning) transmission electron microscopy imaging (HR-(S)TEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using an FEI Titan Cubed Themis microscope which was operated at 200 kV. The Themis is equipped with a double Cs aberration corrector, a monochromator, an X-FEG gun, a super EDS detector, and an Ultra-High Resolution Energy Filter (Gatan Quantum ERS) which allows for working in Dual-EELS mode. HR-STEM imaging was performed by using HAADF and annular dark-field (ADF) detectors. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB-250 instrument (Thermo Fisher Scientific, USA) with a monochromatic Al-Kα (1486.6 eV) radiation source and a hemisphere detector with an energy resolution of 0.1 eV. Peak positions were all corrected to the position of the C 1s peak at 284.8 eV. X-ray diffraction (XRD) analyses were performed on an Xpert Pro apparatus (Philips Pana Analytical, Cu Kα; $\lambda = 1.5418$ Å) operating at 40 kV and 20 mA with a scan rate of 8° *per* minute. Inductively coupled plasma mass spectrometry (ICP-MS) data were determined using an ELAN 9000/DRC ICP-MS system (PerkinElmer, USA).

Wide-angle X-ray scattering measurements.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out at beam-line 07A of the National Synchrotron Radiation Research Centre (NSRRC), Taiwan. In the GIWAXS measurements, the incident angle to each thin film was aligned precisely to 0.3° for investigating the whole layer and minimizing the background from the Si substrate. The scattering intensities were reduced through standard calibration and background subtraction and are expressed as a function of the scattering vector, Q, where $Q = 4\pi (\sin \theta) / \lambda$, θ is half of the total scattering angle and λ is the X-ray wavelength. The photon energy of the beam used is 15 keV. To ascertain the reproducibility of the experimental data, at least three scan sets were collected and compared for each sample.

Ex-situ and *Operando* X-ray absorption spectroscopy measurements.

Ex-situ and *Operando* X-ray absorption spectroscopy (XAS) for Cu K-edge data were collected at room temperature at SAMBA beamline (Synchrotron SOLEIL) equipped with a double-crystal Si (111) monochromator at the Cu K-edge for energy selection. The beam size was 1.0 × 0.5 mm. The signals were collected in fluorescence mode using a 13-channel Ge detector. The intensity of the incident radiation was measured with an ionization chamber (I_0) filled with an N_2 (500 mbar) / He (500 mbar) mixture. Two additional ionization chambers filled with 1700 mbar N_2 (in I_1 chamber) and an Ar (150 mbar) / N_2 (850 mbar) mixture (in I_1 chamber) were used for measurements in transmission mode in the case of the reference samples. The energy resolution (ΔE / E) for the incident X-ray photons was estimated to be 2.0×10^{-4}. A custom-designed electrochemical cell (Zahner, PECC-2) was used for the *operando* Cu-K edge XAS measurements. The applied potential was controlled by a VSP potentiostat (Bio-Logic Science Instruments). A platinum wire and Ag/AgCl electrode (3 M KCl) were used as counter and reference electrodes, respectively. For the XAS studies, the CO_2-10-$Cu_{94}Ag_6$ was *in-situ* electrodeposited on the gas diffusion layer (GDL, Sigracet 22 BB, Fuel Cell Store). The GDL was then mounted on a graphite foil by polyamide tape as both a working electrode and window for the pass-through of the X-ray. The CO_2 supersaturated 1.0 M $CsHCO_3$ was used as the electrolyte for the CO_2RR with continuously purging by CO_2 during the measurements and the electrolyte was refreshed every two hours to maintain the CO_2 supersaturation. Time-resolved spectra were recorded every 10 mins, to ascertain the reproducibility of the experimental data, at least three scan sets were collected and compared for each sample.

Ex-situ and *Operando* XAS for Ag K-edge were collected at Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14W1. The storage ring is operated at an electron energy of 2.5 GeV with a beam current of 250 mA. A Si (111) double-crystal monochromatic was applied. The beam size used at the sample position was ~900 × 300 μm^2. All the data were collected at ambient temperature and applied in fluorescence mode. The energy resolution ($\Delta E/E$) for the incident X-ray photons was estimated to be 2×10^{-4}. To ascertain the reproducibility of the experimental data, at least three scan sets were collected and compared for each sample. A custom-designed electrochemical cell (Zahner, PECC-2) was used for the *operando* Ag-K edge XAS measurements under atmospheric pressure. The applied potential was controlled by a VSP potentiostat (Bio-Logic Science Instruments). A platinum wire and Ag/AgCl electrode (3 M KCl) were used as counter and reference electrodes, respectively. For the XAS studies, the CO_2-10-$Cu_{94}Ag_6$ was *in-situ* electrodeposited on the GDL. The GDL was then mounted on a graphite foil using polyamide tape. Graphite foils were used as both a working electrode and window for the pass-through of the X-ray. The CO_2 supersaturated 1.0 M $CsHCO_3$ was used as the electrolyte for the CO_2RR and the solution was purged with CO_2 during the measurements. The electrolyte was refreshed every two hours to maintain the CO_2 supersaturation. Time-resolved spectra were recorded every 10 mins, to ascertain the reproducibility of the experimental data, at least three scan sets were collected and compared for each sample.

Extended X-ray absorption fine structure curve fitting and data analysis.

Extended X-ray absorption fine structures (EXAFS) curve fitting and data analysis were performed with the Artemis and IFEFFIT software. Standard data-processing, including energy calibration and spectral normalization of the raw spectra was performed using the Athena program. Each sample of XAS data was aligned and processed using the Athena program. Spectra were baseline corrected using a linear pre-edge function between -200 and -50 eV and normalized using a linear or quadratic function between 150 and 700 eV, including a flattening function in the post-edge region. To track the copper and silver valence state distribution, a linear combination fitting analysis, included in Athena, was carried out using the hXAS spectra of various copper-based and silver-based standards. The XAFS signal was isolated from the adsorption edge background using a fit to a cubic spline with nodes defined by the AUTOBKG function in IFEFFIT, with a k-weight of 3 and with the Rbkg parameter set to 1. Fourier transformations of k^3-weighted spectra were using a Kaiser-Bessel window with a 1 Å^{-1} sill width. The magnitude parts of the Fourier transformed spectra are shown throughout this manuscript with a radial distance scale that is not corrected for phase shift. For EXAFS fitting, theoretical scattering paths were calculated with FEFF6 using Artemis.[57] All EXAFS spectra (*in-situ* and *ex-situ*) were fit for distances (ΔR), coordination number (CN), and mean-square displacement of interatomic distance (σ^2) using the Artemis interface with a fixed amplitude reduction factor (S_0^2) of 0.707 to 1.000. The parameters such as interatomic distance (R), CN, the difference in threshold energy (ΔE_0) and Debye-Waller factor (σ^2) were first established with reasonable guesses and then were fitted in R-space. The error in the overall fits was determined using the R-factor, the goodness-of-fit parameter, in which R-factor = $\Sigma(\chi_{data} - \chi_{fit})^2 / \Sigma(\chi_{data})^2$ and good fits occur for R-factor < 0.05. For the wavelet transform analysis, the χ(k) exported from Athena was imported into the Hama Fortran code available on the European Synchrotron Radiation Facility (ESRF) website (http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM20/Software/Wavelets/HAMA). The parameters were listed as follow: R range = 1 to 4 Å, k range = 0 to 13 Å^{-1}; k weight = 2 and Morlet function with k = 10, σ = 1 was used as the mother wavelet to provide the overall distribution.

Operando Raman spectroscopy measurements.

Operando Raman measurements were carried out on a Renishaw inVia Raman microscope equipped with an objective (Leica, ×50) under a 633 nm laser. The catalyst was electrochemically deposited on the GDL whereas the backside and edges of the GDL were covered with epoxy to prevent the parasitic hydrogen evolution reaction. The modified GDL with the catalyst was then used as a working electrode and installed in a custom-designed *operando* Raman cell (Gaossunion, *operando* spectrum cell). The electrochemical measurements were performed using a Solartron SI-1286 potentiostat. Ag/AgCl (KCl saturated) and Pt foil were applied as reference and counter electrodes, respectively. The cell was then filled with a CO_2-

supersaturated 1.0 mol L^{-1} $CsHCO_3$ solution and the electrolyte was refreshed for each applied potential to keep the CO_2 supersaturation state. The laser power was kept below 1.5 mW to protect the sample from laser damage and the probe size was estimated to be 1.9 μm^2. To ensure a low noise-to-signal ratio, spectra were obtained from an average of 10 scans with an accumulation time of 10 seconds. Raman data was analyzed using the Renishaw WiRE (version 5.2) software and the assignment of Raman signals is based on cross-referenced literature.[58]

Operando electrochemical FTIR measurements

Before catalyst loading, an Au film was deposited directly on the reflecting plane of the Si prism using a chemical deposition method. First, the Si prism was polished with a slurry of 0.5 μm Al_2O_3 and sonicated in acetone and deionized water, respectively. After polishing, the Si prism was soaked in a piranha solution (3:1 volumetric ratio of 98% H_2SO_4 and H_2O_2) for 60 min to remove the organic contaminants. Following cleaning, the reflecting plane of the Si prism was dried with a nitrogen gas flow and immersed in 40% NH_4F solution for 150 s to create a hydrogen-terminated surface to improve the adhesion of the Au film. Then the reflecting surface was immersed in a mixture of the Au plating solution (5.75 mM $NaAuCl_4\cdot 2H_2O$ + 0.025 M NH_4Cl + 0.075 M Na_2SO_3 + 0.025 M $Na_2S_2O_3$ + 0.026 M NaOH) and a 2 wt. % HF solution at 55 °C for 10 min. After the deposition, the Au film was rinsed with deionized water and dried by nitrogen gas flow.

The *operando* electrochemical Fourier-transform infrared (FTIR) spectroscopy measurements were performed using a thermoelectric IR spectrometer (Thermo Fisher IS50) equipped with a liquid nitrogen-cooled Mercury-Cadmium-Telluride (MCT-A) detector. A customized spectra-electrochemical cell was assembled on top of the Si prism to carry out the *operando* measurement process. A silicon prism crystal loaded with catalysts, a platinum plate, and Ag/AgCl (saturated KCl solution filling) was used as the working electrode, counter electrode, and reference electrode, respectively. The CO_2-supersaturated 1.0 M $CsHCO_3$ was used as the electrolyte and purged with a constant flow (10 sccm) throughout the test to enable the balance of the reaction environment. The catalysts (200 mg) scraped from the GDL were dispersed in a hybrid solution including 750 µL of deionized water, and 100 µL of Nafion (5 wt. %) to create the catalyst ink. Then 100 µL of catalyst ink was cast onto the Au film modified Si prism reflecting surface. FTIR spectra were obtained from an average of 32 scans with a resolution of 8 cm^{-1}, and the range of wavenumbers of collected spectra was set from 1100 to 2400 cm^{-1}. The background spectrum was recorded under the potential of open circuit voltage (OCV) conditions. The spectra under *operando* conditions were obtained by applying single potential steps and collected after running 90 s.

Temperature-programmed desorption measurements.

Temperature-programmed desorption (TPD) measurements of CO / CO_2 on the CuAg bimetallic material surface were conducted with an adsorption/desorption system. In a typical experiment, 120 mg of sample was placed in a U-shaped quartz microreactor followed by pre-heating at 300 °C for 30 min under a He stream (flow rate: 40 mL min^{-1}) to clean the surface of the sample and then cooled to 50 °C. The outlet of the U-shaped quartz microreactor was connected to the gas chromatography (GC-2014, Shimadzu) equipped with a thermal conductivity detector (TCD) through an automatic six-port valve. Afterwards, the CO / CO_2 stream was injected into the U-shaped quartz microreactor and purged for 60 min, followed by flushing of the sample by the He stream until a stable baseline of GC was obtained. TPD measurements were then conducted from 50 to 800 °C with a ramp rate of 10 °C min^{-1}.

CO_2RR performance measured under the high-pressure electrolyzer configuration.

High-pressure CO_2RR experiments were carried out in a custom-designed one-compartment two-cell high-pressure electrolyzer (350 mL in total volume, Parr Instrument Company). Ag wire and Pt wire were applied as reference and counter electrodes, respectively. The anode and cathode were separated by a Nafion-117 proton exchange membrane to avoid any potential cross-contamination or the oxidation of the reaction products at the anode. The experiment was carried out in 150 mL of electrolyte, which was supersaturated with CO_2 under the targeted pressure before each of the electrolysis experiments with a CO_2 flow rate of 100 standard cubic centimetres *per* minute (sccm). The pressurized vessel was left for 30 minutes to saturate the solution before the measurements. We estimated the reading error for the pressure to be 10 % based on the accuracy of the manometer. The Faradaic efficiency was determined by performing chronoamperometric analyses for at least 60 minutes. A small-volume antechamber was connected to the gas outlet of the vessel and was used to depressurize the gas outlet to atmosphere pressure before injecting it into the GC. The resultant gas composition was then used to calculate the amount of gases generated in the pressurized cell during the CO_2RR.

Data availability

All data can be found in the public figshare repository (https://doi.org/10.6084/m9.figshare.22002014.v1) or from the corresponding authors upon reasonable request.

Code availability

All code used within the article can be found in the public figshare repository (https://doi.org/10.6084/m9.figshare.22083551.v1) or from the corresponding authors upon reasonable request.

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Author Contributions Statement

D.V. and K. Q. designed and directed the research. K. Q., Y. Z., H. L. W. and Y. P. Z. synthesized the materials and performed the materials property characterization. N. O., W. S. W. and J. L. carried out and analyzed the DFT calculation. E. P. and C. S. carried out the liquid NMR spectroscopy measurements. L. L., X. Q. C. and Y. W. performed the TEM characterization and analyzed the data. K. Q. and D. V. wrote the manuscript. K. Q., J. F. L., G. R. J., J. D. W., J. Y. M. and J. C. F. performed the hXAS measurements and fitting. D. V. supervised the project and established the final version of the paper. All authors contributed to the manuscript and have approved the final version of the manuscript.

Competing Interests Statement

The authors declare that they have no competing interests.

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Fig. 1. ***Operando*** **deposition and structure characterization of CuAg bimetallic catalysts. a**, Adsorption energies of the *CO_2 on different low-index facets of Cu and Ag. **b**, Schematic illustration of *CO_2 adsorption assisted alloy formation. High-resolution XPS spectra of **c**, Cu 2P and **d**, Ag 3d for the CO_2-CuAg catalyst compared with the standard monometallic sample (Cu foil and Ag powder). **e**, Cross-section and **f**, top-viewed SEM images of CO_2-10-$Cu_{94}Ag_6$ *in-situ* grown on the surface of gas diffusion layer in CO_2-supersaturated deposition solution. **g**, TEM image of CO_2-10-$Cu_{94}Ag_6$ catalyst. **h**, Aberration-corrected HAADF-STEM image of CO_2-10-$Cu_{94}Ag_6$, inset fast Fourier transform of the HRTEM image showing superlattice reflections of (200) and (020) facets. **i-l**, HAADF-STEM and EDX-mapping images of CO_2-10-$Cu_{94}Ag_6$.

Fig. 2. Surface facet and coordination environment characterization of CuAg bimetallic catalysts. a-b, 2D GIWAXS patterns of the CuAg bimetallic structures prepared in CO_2-supersaturated (**a**) and Ar-saturated (**b**) deposition solution, respectively. **c-d**, 2D Fourier-transformed *operando* EXAFS spectra of the CuAg bimetallic catalysts prepared in CO_2-supersaturated (**c**) and Ar-saturated (**d**) deposition solution, respectively. Inset shows the calculated percentages associated with the different processes during co-deposition. **e**, Fourier transformed Ag K-edge EXAFS spectra of the CuAg bimetallic catalyst and Ag-based reference samples in R space. **f-g**, Ag K-edge WT-EXAFS contour spectra of the CuAg bimetallic catalysts prepared in CO_2-supersaturated (**f**) and Ar-saturated (**g**) deposition solution, respectively. The wavelet transformed analysis of the EXAFS data was performed with HAMA Fortran package from the European Synchrotron Radiation Facility (ERSF) website. Parameters used in these WT analyses were the Morlet function, $\sigma = 1$, and $k = 10$.

Fig. 3. CO_2RR performance in H-cell under atmospheric pressure CO_2 supersaturated electrolyte. a, Linear scan voltammetry curves of CO_2-10-$Cu_{94}Ag_6$ measured in 1.0 mol L^{-1} $CsHCO_3$ for different CO_2 concentrations corresponding to argon- and CO_2-saturated electrolyte compared with CO_2 supersaturated electrolyte. Inset shows the calibration curve and the quantification of the CO_2 concentration in the liquid electrolyte. **b-c**, Potential dependent CO_2RR Faradaic efficiency on CO_2-10-$Cu_{94}Ag_6$ for CO_2 concentrations of 0.05 mol L^{-1} and 0.3 mol L^{-1} corresponding to CO_2-saturated and CO_2-supersaturated electrolyte, respectively. The inset shows the Ag content dependence of the C_{2+} product selectivity in a 0.05 mol L^{-1} CO_2-saturated electrolyte. **d**, ECSA normalized specific current density (*j*) for different products formed on CO_2-10-$Cu_{94}Ag_6$ in a 0.3 mol L^{-1} CO_2-supersaturated electrolyte. Error bars represent the

standard deviation of three independent measurements and the mean values (centre point) are presented together with denoting the standard deviation (bar height).

Fig. 4. CO_2RR activity maps and the stability measurement. a-d, 2D heatmaps of FE_{H2}, FE_{C1}, FE_{C2} and FE_{C3} on CO_2-10-$Cu_{94}Ag_6$ for different CO_2 concentrations and potentials. **e**, Superposition of the different maps showing the preferential zones for the hydrogen evolution, the C_1 formation, the C_1-C_1 coupling (C_2 formation) and the C_1-C_2 coupling (C_3 formation). **f**, Long-term stability measurement for CO_2-10-$Cu_{94}Ag_6$ in 0.3 mol L^{-1} CO_2-supersaturated 1.0 mol L^{-1} $CsHCO_3$ electrolyte at a potential of -0.73 V *vs.* RHE. **g**, Time-dependent *operando* Cu K-edge Fourier-transformed EXAFS spectra the CO_2-10-$Cu_{94}Ag_6$ catalyst during the CO_2RR in CO_2-supersaturated electrolyte.

Fig. 5. Investigations of the CO_2 reduction reaction mechanism using *ex-situ* and *operando* spectroscopy. a, 2D heatmap for the intensity of the *CO stretching modes on CO_2-10-$Cu_{94}Ag_6$ during CO_2RR for different CO_2 concentrations. The dark-grey dashed line indicates the distribution of $FE_{2\text{-propanol}}$. **b**, Potential-resolved Raman mapping of CO_2-10-$Cu_{94}Ag_6$ in CO_2-supersaturated 1.0 mol L^{-1} $CsHCO_3$ during CO_2RR. **c**, Volcano relationship between the ratio of $*CO_{bridge}$ to $*CO_{atop}$ and the $FE_{2\text{-propanol}}$ with the applied potentials for a $[CO_2]$ = 0.3 mol L^{-1}. **d**, ^{13}C-NMR spectra of the electrolyte aliquots after the isotopic labelling experiments for 1.0 M $CsHCO_3$ ($[CO_2]$ = 3.0 mol L^{-1}). The blue and red curves correspond to experiments with ethanol-D6 in D_2O or H_2O, respectively. **e**, Relationship between the integrated area of the *CO and $*OCH_2CH_3$ signals measured using *operando* FTIR at different applied potentials under $[CO_2]$ = 0.3 mol L^{-1}. **F**, Relationship between the FE_{CO} (*via* *CO desorption), the $FE_{ethanol}$ (*via* $*OCH_2CH_3$ hydrogenation) and the $FE_{2\text{-propanol}}$ (*via* C_1-C_2 coupling between $*OCH_2CH_3$ and *CO) and the applied potentials under $[CO_2]$ = 0.3 mol L^{-1}. Error bars represent the standard deviation of three independent measurements and the mean values (centre point) are presented together with denoting the standard deviation (bar height).

Fig. 6. Theoretical calculations of the C-C coupling and the formation of 2-propanol. a, Proposed reaction pathways for the C_1-C_2 coupling and the formation of C_3 products. The formation energy of each intermediate is given in brackets. The intermediates labelled in red correspond to the most favourable thermodynamic pathway. **b**, The energy of the $*OCH_2CH_3$ intermediate adsorbed on Cu (100) facet as a function of Cu*-O and O-C bond distances. **c**, ΔE_{diss} as a function of the averaged distance between intermediate $*OCH_2CH_3$ and Ag atoms for various alloying contents of CuAg.

Fig. 7. CO_2RR performance in high-pressure electrolyzer under elevated CO_2 concentration. **a**, 2D heatmap for the $FE_{2\text{-propanol}}$ on CO_2-10-$Cu_{94}Ag_6$ with different CO_2 concentrations and applied potentials. **b**, Evolution of the j_{total} and $j_{2\text{-propanol}}$ at -0.70 V *vs.* RHE from CO_2-10-$Cu_{94}Ag_6$ with different CO_2 concentrations in 1.0 mol L^{-1} $CsHCO_3$. Error bars represent the standard deviation of three independent measurements and the mean values (centre point) are presented together with denoting the standard deviation (bar height). **c**, Comparison of the performance metrics with the literature benchmarks for the CO_2/CO-to-C_3 conversion. **d**, Long-term stability measurement of CO_2-10-$Cu_{94}Ag_6$ at -0.70 V *vs.* RHE in CO_2-supersaturated ($[CO_2]$ = 3.0 mol L^{-1}, 10 bar) 1.0 M $CsHCO_3$. **e**, NMR spectra of the electrolyte centred around the signals of 2-propanol for different reaction times. The presence of a septet signature at 4.13 ppm is characteristic of 2-propanol. **f**, Total quantity and formation rate of 2-propanol over 200 hours using a 6.0 cm^2 electrode modified with CO_2-10-$Cu_{94}Ag_6$. The volume of the electrolyte was 150 mL.

Fig. 8. CO_2RR stability measurement and quantity the formation rate of 2-propanol. **a**, Long-term stability measurement of CO_2-10-$Cu_{94}Ag_6$ at -0.70 V *vs.* RHE in CO_2-supersaturated ($[CO_2]$ = 3.0 mol L^{-1}, 10 bar) 1.0 M $CsHCO_3$. **b**, NMR spectra of the electrolyte centred around the signals of 2-propanol for different reaction times. The presence of a septet signature at 4.13 ppm is characteristic of 2-propanol. **c**, Total quantity and formation rate of 2-propanol over 200 hours using a 6.0 cm^2 electrode modified with CO_2-10-$Cu_{94}Ag_6$. The volume of the electrolyte was 150 mL.

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