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# Unlocking direct CO<sub>2</sub> electrolysis to C<sub>3</sub> products via electrolyte supersaturation

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## Keywords

CO<sub>2</sub> electro-reduction, electrocatalysis, multicarbon product, electrochemical deposition, alloy catalyst, energy efficiency, high pressure electrolyzer, *operando* spectroscopy.

**Abstract.**

The electroreduction of CO<sub>2</sub> has recently achieved notable progress in the formation of C<sub>2</sub> products such as ethylene and ethanol. However, the direct synthesis of C<sub>3</sub> products is considerably limited by the C<sub>2</sub>-C<sub>1</sub> coupling reaction and the Faradaic efficiency has remained low. Here, we present a supersaturation strategy for the electrosynthesis of 2-propanol from CO<sub>2</sub> in highly carbonated electrolytes. By controlling the CO<sub>2</sub> 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  $j_{2\text{-propanol}}$  of 59.3 mA cm<sup>-2</sup>. 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<sub>2</sub>RR) is investigated as a promising route to convert CO<sub>2</sub> into value-added chemicals through electrochemical processes.<sup>1</sup> While the reduction of CO<sub>2</sub> to C<sub>1</sub> and C<sub>2</sub> products has achieved significant progress toward industrial application over recent years, the formation of multicarbon molecules with C ≥ 3 (C<sub>3+</sub>) possessing superior energy density and higher commercial values is more desirable but remains challenging.<sup>2</sup> Favourable multicarbon coupling is a prerequisite to unlock the formation of C<sub>3</sub> products and requires the development of catalysts with low energy barriers associated with the C<sub>1</sub>-C<sub>1</sub> (C<sub>2</sub>) and C<sub>1</sub>-C<sub>2</sub> (C<sub>3</sub>) coupling reactions.<sup>3</sup> Alternatively, efforts to increase the selectivity towards the formation of C<sub>3</sub> products have focused on replacing CO<sub>2</sub> with CO but such a strategy involves a two-step reaction and complicates the overall CO<sub>2</sub>RR process.<sup>4</sup> 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.<sup>5</sup> To date, only a handful of systems have demonstrated the direct conversion of CO<sub>2</sub> to C<sub>3</sub> hydrocarbons and oxygenates, and the corresponding Faradaic efficiency (FE) remains below 20 %. The reaction mechanism for the formation of C<sub>3</sub> products and the associated selectivity is still debated.<sup>6,7</sup> Statistically, larger concentrations of \*CO on the catalyst surface increases the probability of further C-C coupling.<sup>8</sup> Previous reports have pointed out that modulating the local CO<sub>2</sub> concentration ([CO<sub>2</sub>]) can enhance the C-C coupling in CO<sub>2</sub>RR. 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.<sup>9</sup>

Herein, we report a supersaturation strategy for the direct electro-reduction of CO<sub>2</sub> to C<sub>3</sub> products on a CuAg alloy catalyst by using a strongly carbonated electrolyte with [CO<sub>2</sub>] above the saturation limit. We developed a co-deposition method under CO<sub>2</sub> supersaturated conditions where CO<sub>2</sub> acts as a surfactant to prevent undesirable galvanic replacement reaction, while favouring the preferential growth of the CO<sub>2</sub>RR active CuAg facets. The influence of the [CO<sub>2</sub>] on the C-C coupling rate was investigated. We find that performing CO<sub>2</sub>RR 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<sub>2-propanol</sub> of 56.7 % at a specific current density of 59.3 mA cm<sup>-2</sup>. 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.<sup>10</sup> We also identified the role of the \*OCH<sub>2</sub>CH<sub>3</sub> 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<sub>2</sub> to C<sub>3</sub> molecules requires the development of catalysts with low energy barriers for both the C<sub>1</sub>-C<sub>1</sub> and C<sub>1</sub>-C<sub>2</sub> coupling steps.<sup>11</sup> Cu-based alloys have been identified to enhance the selectivity towards the formation of C<sub>3</sub> products through the modulation of the \*CO adsorption.<sup>12</sup> Herein, we designed a favourable catalyst with high C-C coupling activity using CO<sub>2</sub> supersaturated electrolyte based on a synergy effect from Cu and Ag.<sup>13</sup> 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<sub>2</sub> used for electrodeposition under supersaturated conditions promotes the adsorption of CO<sub>2</sub> on the most favourable facets for the CO<sub>2</sub>RR.<sup>14</sup> Under cathodic conditions, the facets with the lowest adsorption energy will be involved in CO<sub>2</sub> 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<sub>2</sub> on different Ag and Cu facets by using density functional theory (DFT) calculations (**Fig. 1a**).<sup>15</sup> According to the adsorption energy diagram, CO<sub>2</sub> 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<sub>2</sub> under supersaturated conditions also prevents galvanic replacement reaction and the formation of segregated domains of Ag and Cu (**Fig. 1b**).<sup>16</sup> Experimentally, Cu and Ag were co-electrodeposited on a gas diffusion layer (GDL) using alternatively CO<sub>2</sub>-supersaturated (CO<sub>2</sub>-CuAg) or argon-saturated (Ar-CuAg) conditions (**Supplementary Fig. 1, 2, 3a and 3b, Supplementary Note 1 and 2**). The precursor ratio of Cu<sup>2+</sup> to Ag<sup>+</sup> ions and the deposition current density ( $j_{\text{deposition}}$ ) 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  $j_{\text{deposition}}$ , 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  $2\theta$  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<sub>2</sub> was also carried out on the CO<sub>2</sub>-CuAg and Ar-CuAg, respectively (**Supplementary Fig. 5, Supplementary Note 5**). For CO<sub>2</sub>-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<sub>3/2</sub> and Cu 2p<sub>1/2</sub> shifted by +0.6 eV for CO<sub>2</sub>-CuAg compared with bulk Cu (**Fig. 1c**). Similarly, the binding energies of Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> peaks shifted by -0.5 eV for CO<sub>2</sub>-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.<sup>17,18</sup> 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<sub>2</sub>-CuAg.<sup>19</sup> We prepared a CuAg alloy: CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> with a molar ratio of 94 : 6 and a deposition current density of 10 mA cm<sup>-2</sup>, 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<sup>-</sup> adsorption profile (**Fig. 1h, Supplementary Fig. 6 and 7, Supplementary Note 6 and 7**). These results indicate that CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> preferentially exhibits CuAg (100) facets on the surface. Energy-dispersive X-ray (EDX) mapping finally reveals the uniform dispersion of elements in CO<sub>2</sub>-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**).<sup>20</sup>

2D-GIWAXS was then performed to elucidate the surface structure of the exposed crystal facets for both the CO<sub>2</sub>-CuAg and Ar-CuAg (**Fig. 2a and 2b**).<sup>21</sup> Using CO<sub>2</sub> supersaturated deposition solution, a series of intense single peaks are detected at  $q_z = 29.42, 33.98, 48.03$  and  $56.85 \text{ nm}^{-1}$  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**).<sup>22</sup> By fitting the Cu K-edge EXAFS spectra, we identified the contribution of the Cu-Ag bond as evidenced by the shoulder peak at  $2.63 \text{ \AA}$  in agreement with the decrease of the Cu-Cu coordination number for the CO<sub>2</sub>-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.<sup>23</sup> We estimated that 88.4 % alloying occurs when preparing CO<sub>2</sub>-CuAg. Without CO<sub>2</sub> 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  $2.45 \text{ \AA}$  for the CO<sub>2</sub>-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.<sup>24</sup> 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<sub>2</sub> supersaturated conditions leads to the formation of a CuAg alloy with CO<sub>2</sub>RR active (100) facets being preferentially exposed.

### CO<sub>2</sub>RR under atmospheric pressured CO<sub>2</sub> supersaturation.

The CO<sub>2</sub>RR electrocatalytic activity was evaluated using an H-type cell in a standard three-electrode configuration with a catalyst loading amount of 5 mg cm<sup>-2</sup>.<sup>25</sup> 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<sub>2</sub>-HCO<sub>3</sub><sup>-</sup>-CO<sub>3</sub><sup>2-</sup> together with the electrolyte pH for increasing partial pressure of the CO<sub>2</sub> (**Supplementary Fig. 18, Supplementary Note 16**).<sup>26</sup> 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<sub>2</sub>] in the electrolyte was determined using a CO<sub>2</sub>-specific reference electrode (**Inset Fig. 3a**). **Fig. 3a** presents the linear sweep voltammetry (LSV) curves for CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> recorded in 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> with [CO<sub>2</sub>] of 0, 0.05 and 0.3 mol L<sup>-1</sup> that correspond to Ar-saturated, CO<sub>2</sub>-saturated and CO<sub>2</sub>-supersaturated electrolytes, respectively. The onset potential measured in the CO<sub>2</sub> supersaturated electrolyte extracted from the LSV curves appeared positively shifted by 46 mV compared with that measured in the CO<sub>2</sub> saturated electrolyte. To further quantify the CO<sub>2</sub>RR 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**).<sup>27</sup> In CO<sub>2</sub> saturated electrolyte, the FE<sub>C<sub>2</sub>H<sub>4</sub></sub> reached 23.2%, while no C<sub>3</sub> product was detected (**Fig. 3b**). Conversely, using a CO<sub>2</sub> supersaturated solution, C<sub>3</sub> 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**).<sup>28</sup> The FE<sub>2-propanol</sub> 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<sub>2</sub>RR condition confirmed the formation of 2-propanol-D<sub>8</sub> 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<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> for the different CO<sub>2</sub>RR products. The *j*<sub>ECSA-2-propanol</sub> reaches 12.03 mA cm<sup>-1</sup><sub>ECSA</sub> 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<sub>2</sub>-to-C<sub>3</sub> products (**Supplementary Table 8**).<sup>29-31</sup>

To better gauge the CO<sub>2</sub>RR properties of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> in CO<sub>2</sub> supersaturated 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub>, we then analyzed the FEs of the different products as a function of the [CO<sub>2</sub>] for different applied potentials

(**Fig. 4a-e**).<sup>32</sup> The  $FE_{H_2}$  for the hydrogen evolution reaction (HER) is found to be larger than 90 % over the measured potential range when the  $[CO_2] \leq 0.05 \text{ mol L}^{-1}$  (**Fig. 4a**). The FE for  $C_1$  and  $C_2$  products ( $FE_{C_1}$  and  $FE_{C_2}$ ) are clearly increased in  $CO_2$ -supersaturated electrolytes (**Fig. 4b and 4c**). When  $[CO_2] \geq 0.2 \text{ mol L}^{-1}$  – equivalent to  $8.8 \times 10^3$  parts *per* million (ppm) –  $C_3$  products are detected at potentials as low as  $-0.4 \text{ V vs. RHE}$ . (**Fig. 4d**). These findings highlight the role of the  $[CO_2]$  on the reaction pathway (**Fig. 4e**, **Supplementary Note 22**).<sup>26</sup> Importantly, we identified that  $[CO_2] \geq 0.2 \text{ mol L}^{-1}$  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.<sup>33</sup>

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  $FE_{C_3}$  moderately increased with the electrolyte concentration. This finding is attributed to the larger radius of the  $Cs^+$  cations that can interact with two  $*CO$ .<sup>34</sup> 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.<sup>35</sup> 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**).<sup>36</sup>

The stability of  $CO_2$ -10- $Cu_{94}Ag_6$  was evaluated over 24 hours at a potential of  $-0.73 \text{ V vs. RHE}$  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  $2.0 \text{ \AA}$ ) 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<sub>2</sub> 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.<sup>37,38</sup> 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<sub>2</sub>] and potential-dependent Raman responses of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> (**Supplementary Fig. 41 and 42, Supplementary Note 33 and 34**). A qualitative comparison of \*CO intermediate around 2000 cm<sup>-1</sup> during the CO<sub>2</sub>RR revealed that the \*CO signatures are enhanced when the [CO<sub>2</sub>] ≥ 0.2 mol L<sup>-1</sup> (**Fig. 5a**). It is worth noting that the region with the most intense \*CO contribution overlaps with that of the largest FE<sub>2-propanol</sub> (**Fig. 5a, Supplementary Fig. 43, Supplementary Note 35**). This observation suggests that increasing [CO<sub>2</sub>] 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<sup>-1</sup> CsHCO<sub>3</sub> with a constant [CO<sub>2</sub>] of 0.3 mol L<sup>-1</sup> (**Fig. 5b**).<sup>6</sup> The \*CO stretching modes on CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> alloy with CO<sub>2</sub>RR under supersaturated conditions were found to extend over a much larger frequency range from 1900 to 2100 cm<sup>-1</sup> compared with those measured in CO<sub>2</sub>- and Ar-saturated conditions, suggesting a multisite binding mechanism favourable to the multicarbon product formation (**Supplementary Fig. 44 to 46**).<sup>39</sup>

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<sub>bridge</sub>) and \*CO bound on top of terrace-like sites (\*CO<sub>atop</sub>) at a frequency below 2080 cm<sup>-1</sup> and above 2080 cm<sup>-1</sup>, respectively.<sup>40,41</sup> The ratio of \*CO<sub>bridge</sub> to \*CO<sub>atop</sub> linearly increases with the [CO<sub>2</sub>] 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<sub>2-propanol</sub> under different potentials (**Fig. 5c**).<sup>42</sup> A volcano-shaped relationship centred around the optimal potential of -0.73V *vs.* RHE was found between the \*CO<sub>bridge</sub>-to-\*CO<sub>atop</sub> ratio, the FE<sub>2-propanol</sub> and the applied potential. The results reveal a possible optimization of the proportion of \*CO<sub>bridge</sub> to \*CO<sub>atop</sub> for activating the C-C coupling at high \*CO density on the catalyst surface.<sup>43</sup>

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<sub>2</sub>CH<sub>3</sub> is involved in the formation of C<sub>3</sub> species during the CO<sub>2</sub>RR. We added hexadeuteroethanol (ethanol-D<sub>6</sub>) to the electrolyte as a simulant of \*OCH<sub>2</sub>CH<sub>3</sub> before the reaction and performed <sup>13</sup>C NMR spectroscopy after 24 hours at -0.70 V *vs.* RHE under the 1.0 M CsDCO<sub>3</sub>, D<sub>2</sub>O 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  $^*\text{OCH}_2\text{CH}_3$ , we performed the same reaction using ethanol-D6 in a 1.0 M  $\text{CsHCO}_3$ ,  $\text{H}_2\text{O}$  electrolyte. We found that the  $^{13}\text{C}$  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.<sup>44</sup> These investigations thus confirm the detection of partially deuterated 2-propanol-D3, which is formed *via* the first dehydrogenative adsorption of ethanol-D6 ( $^*\text{OCD}_2\text{CD}_3$  as intermediate) followed by the  $\text{C}_1$ - $\text{C}_2$  coupling with  $^*\text{CO}$  adsorbed on the catalyst surface.

To get a further understanding of the  $\text{C}_1$ - $\text{C}_2$  coupling process, we examined the dynamic evolution of the  $^*\text{CO}$  and  $^*\text{OCH}_2\text{CH}_3$  intermediates during the  $\text{CO}_2$ RR by performing *operando* FTIR spectroscopy under  $\text{CO}_2$ -supersaturated conditions (**Supplementary Fig. 51, Supplementary Note 38**). Clear signals attributed to the  $^*\text{CO}$  stretching band and the  $^*\text{OCH}_2\text{CH}_3$  bending band were detected at  $1950\text{-}2150\text{ cm}^{-1}$  and  $\sim 1340\text{ cm}^{-1}$ , respectively.<sup>45,46</sup> When the potential decreases from  $-0.2$  to  $-0.73\text{ V vs. RHE}$ , both the  $^*\text{CO}$  and  $^*\text{OCH}_2\text{CH}_3$  bands become progressively more intense, which points to higher formation rates of the intermediates (**Fig. 5e**). Remarkably, the increase of the  $^*\text{CO}$  and  $^*\text{OCH}_2\text{CH}_3$  signals is accompanied by a decrease of the  $\text{FE}_{\text{CO}}$  and  $\text{FE}_{\text{ethanol}}$  together with an increase of the  $\text{FE}_{2\text{-propanol}}$  (**Fig. 5f**). These findings suggest that under  $\text{CO}_2$ -supersaturation conditions, the high density of  $^*\text{CO}$  and  $^*\text{OCH}_2\text{CH}_3$  intermediates triggers the formation of 2-propanol instead of CO or ethanol. At larger overpotentials, fewer  $^*\text{CO}$  and  $^*\text{OCH}_2\text{CH}_3$  intermediates are generated according to the decrease in FTIR signals, which decreases the probability of  $\text{C}_1$ - $\text{C}_2$  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  $^*\text{OCH}_2\text{CH}_3$  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  $-0.7\text{ V vs. RHE}$ . We performed calculations on Cu and  $\text{Cu}_{92}\text{Ag}_8$  slabs to model pure Cu and CuAg catalysts (**Supplementary Table 11**). We note that the  $\text{Cu}_{92}\text{Ag}_8$  slab was formed by swapping two of the closest Cu atoms to the oxygen atom of intermediate I2 ( $^*\text{OCH}_2\text{CH}_3$ ) 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  $0.79\text{ eV}$  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<sub>92</sub>Ag<sub>8</sub>, 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<sub>3</sub> chain, leading to an oxygenated carbon at the end of the alkyl chain.<sup>37,47,48</sup> By contrast, the formation of 2-propanol must proceed by the hydrogenation of the middle oxygen (in position 2 of the C<sub>3</sub>). 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.<sup>49</sup> 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  $\Delta E_{\text{diss}}$ . 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, stripping the oxygen atom in the position 2 of the C<sub>3</sub> chain, thus leading to the formation of 1-propanol *via* the I7 intermediate, which is consistent with the previous experimental reports.<sup>48</sup>

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<sub>96</sub>Ag<sub>4</sub>, Cu<sub>92</sub>Ag<sub>8</sub> and Cu<sub>88</sub>Ag<sub>12</sub> 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  $\Delta E_{\text{diss}}$  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.  $\Delta E_{\text{diss}}$  decreases). Interestingly, for configurations where I2 is very close to Ag sites,  $\Delta E_{\text{diss}}$  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,  $\Delta E_{\text{diss}}$  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<sub>2</sub> and C<sub>3</sub> 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<sub>1</sub>-C<sub>1</sub> and C<sub>1</sub>-C<sub>2</sub> coupling.<sup>2</sup>

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<sub>2</sub> (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<sub>2</sub> to the stabilization of the intermediate I2. To summarize, our experimental and computational approaches demonstrate that both CO<sub>2</sub>-supersaturated conditions and the alloy characteristics of CO<sub>2</sub>-CuAg are responsible for the enhanced formation rates of \*CO and \*OCH<sub>2</sub>CH<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub>-to-2-propanol conversion can be attributed to the combined effect on the modulation of the \*CO adsorption and formation of the key \*OCH<sub>2</sub>CH<sub>3</sub> intermediate induced by both the alloy nature of the catalyst and the CO<sub>2</sub> supersaturation of the electrolyte.

### **CO<sub>2</sub>RR under elevated pressured CO<sub>2</sub> supersaturation.**

CO<sub>2</sub>RR investigations have previously been performed under elevated pressure to avoid the diffusion limit of the CO<sub>2</sub> during the electrochemical reactions, but there is limited in-depth discussion in the literature regarding the origin of the activity enhancement under high CO<sub>2</sub> partial pressure.<sup>50-53</sup> In the light of the above performance and the mechanism investigations, we further evaluated the CO<sub>2</sub>RR properties of the catalyst at higher [CO<sub>2</sub>]. 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.<sup>54</sup> Therefore, the catalytic measurements were carried out using a two-compartment high-pressure reactor with CO<sub>2</sub> 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<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> in CO<sub>2</sub> supersaturated 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> under high pressure, we first evaluated the FE<sub>2-propanol</sub> as a function of the [CO<sub>2</sub>] and for different applied potentials (**Supplementary Fig. 62 to 64**). As shown in **Fig. 7a**, the FE<sub>2-propanol</sub> exhibits a volcano shape relationship with the potential and the CO<sub>2</sub> pressures and reaches a record-high value of 56.7 % at a potential of -0.70 V vs. RHE and ~3.0 mol L<sup>-1</sup> of CO<sub>2</sub> corresponding to a pressure of 10 bar. To highlight the role of the [CO<sub>2</sub>] on the catalyst behaviour, the  $j_{total}$ ,  $j_{H2}$  and  $j_{2-propanol}$  were calculated (**Fig. 7b**). The  $j_{total}$  for all products continuously increased with the elevation of the [CO<sub>2</sub>]. For a [CO<sub>2</sub>] of 3.0 mol L<sup>-1</sup>, the CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> electrodes demonstrated a value of  $j_{2-propanol}$  as high as 59.3 mA cm<sup>-2</sup>. By comparing the performance metrics of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> under CO<sub>2</sub> supersaturated electrolyte with previous literature benchmarks, we observed that the supersaturation strategy outperforms previous reports from the literature even including CO-to-C<sub>3</sub> systems and set a record-high direct CO<sub>2</sub>-to-C<sub>3</sub> conversion rate of 0.71 μmol h<sup>-1</sup> cm<sup>-2</sup> (**Fig. 7c**).<sup>55,56</sup> The robustness of the CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> catalyst was investigated under continuous operation with a CO<sub>2</sub>

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<sub>2</sub> 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<sub>2-propanol</sub> and  $j_{2-propanol}$  of 98.3 % and 97.5 %, respectively, which translates to a steady CO<sub>2</sub>-to-C<sub>3</sub> conversion rate of 0.71 μmol h<sup>-1</sup> cm<sup>-2</sup>.

## Conclusions.

Overall, we introduced a CO<sub>2</sub> supersaturation strategy for the direct conversion of CO<sub>2</sub>-to-C<sub>3</sub> products. Supersaturation conditions with CO<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub> 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<sub>1</sub>-C<sub>1</sub> coupling and \*OCH<sub>2</sub>CH<sub>3</sub> 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<sub>2</sub>] during the CO<sub>2</sub>RR, 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<sup>-2</sup> together with operating stability for 200 hours. Our investigations provide the opportunity for fine-tuning the reaction pathway by controlling the local CO<sub>2</sub> 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<sup>2</sup> 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  $\mu$ s 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-K $\alpha$  (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 K $\alpha$ ;  $\lambda = 1.5418 \text{ \AA}$ ) 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  $Q = 4\pi (\sin \theta) / \lambda$ ,  $\theta$  is half of the total scattering angle and  $\lambda$  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  $1.0 \times 0.5$  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  $I_2$  chamber) were used for measurements in transmission mode in the case of the reference samples. The energy resolution ( $\Delta E / E$ ) for the incident X-ray photons was estimated to be  $2.0 \times 10^{-4}$ . 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<sub>94</sub>Ag<sub>6</sub> 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<sub>3</sub> was used as the electrolyte for the  $CO_2$ RR 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  $\sim 900 \times 300 \mu m^2$ . 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  $2 \times 10^{-4}$ . 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<sub>94</sub>Ag<sub>6</sub> 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<sub>3</sub> was used as the electrolyte for the  $CO_2$ RR 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  $1 \text{ \AA}^{-1}$  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.<sup>57</sup> All EXAFS spectra (*in-situ* and *ex-situ*) were fit for distances ( $\Delta R$ ), coordination number (CN), and mean-square displacement of interatomic distance ( $\sigma^2$ ) 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 ( $\Delta E_0$ ) and Debye-Waller factor ( $\sigma^2$ ) 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  $R\text{-factor} = \Sigma(\chi_{\text{data}} - \chi_{\text{fit}})^2 / \Sigma(\chi_{\text{data}})^2$  and good fits occur for  $R\text{-factor} < 0.05$ . For the wavelet transform analysis, the  $\chi(k)$  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  $\text{\AA}$ , k range = 0 to 13  $\text{\AA}^{-1}$ ; k weight = 2 and Morlet function with  $k = 10$ ,  $\sigma = 1$  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,  $\times 50$ ) 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  $\text{CO}_2$ -



supersaturated 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> solution and the electrolyte was refreshed for each applied potential to keep the CO<sub>2</sub> 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<sup>2</sup>. 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.<sup>58</sup>

### ***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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>) 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<sub>4</sub>F 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<sub>4</sub>·2H<sub>2</sub>O + 0.025 M NH<sub>4</sub>Cl + 0.075 M Na<sub>2</sub>SO<sub>3</sub> + 0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> + 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<sub>2</sub>-supersaturated 1.0 M CsHCO<sub>3</sub> 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<sup>-1</sup>, and the range of wavenumbers of collected spectra was set from 1100 to 2400 cm<sup>-1</sup>. 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<sub>2</sub> 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<sup>-1</sup>) 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<sub>2</sub> 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<sup>-1</sup>.

### **CO<sub>2</sub>RR performance measured under the high-pressure electrolyzer configuration.**

High-pressure CO<sub>2</sub>RR 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<sub>2</sub> under the targeted pressure before each of the electrolysis experiments with a CO<sub>2</sub> 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<sub>2</sub>RR.

### **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<sub>94</sub>Ag<sub>6</sub> *in-situ* grown on the surface of gas diffusion layer in  $CO_2$ -supersaturated deposition solution. **g**, TEM image of  $CO_2$ -10-Cu<sub>94</sub>Ag<sub>6</sub> catalyst. **h**, Aberration-corrected HAADF-STEM image of  $CO_2$ -10-Cu<sub>94</sub>Ag<sub>6</sub>, 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<sub>94</sub>Ag<sub>6</sub>.

**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.  $CO_2$ RR performance in H-cell under atmospheric pressure  $CO_2$  supersaturated electrolyte.** **a**, Linear scan voltammetry curves of  $CO_2$ -10-Cu<sub>94</sub>Ag<sub>6</sub> measured in 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> 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  $CO_2$ RR Faradaic efficiency on  $CO_2$ -10-Cu<sub>94</sub>Ag<sub>6</sub> for  $CO_2$  concentrations of 0.05 mol L<sup>-1</sup> and 0.3 mol L<sup>-1</sup> 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<sup>-1</sup>  $CO_2$ -saturated electrolyte. **d**, ECSA normalized specific current density ( $j$ ) for different products formed on  $CO_2$ -10-Cu<sub>94</sub>Ag<sub>6</sub> in a 0.3 mol L<sup>-1</sup>  $CO_2$ -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<sub>2</sub>RR activity maps and the stability measurement.** **a-d**, 2D heatmaps of FE<sub>H<sub>2</sub></sub>, FE<sub>C<sub>1</sub></sub>, FE<sub>C<sub>2</sub></sub> and FE<sub>C<sub>3</sub></sub> on CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> for different CO<sub>2</sub> concentrations and potentials. **e**, Superposition of the different maps showing the preferential zones for the hydrogen evolution, the C<sub>1</sub> formation, the C<sub>1</sub>-C<sub>1</sub> coupling (C<sub>2</sub> formation) and the C<sub>1</sub>-C<sub>2</sub> coupling (C<sub>3</sub> formation). **f**, Long-term stability measurement for CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> in 0.3 mol L<sup>-1</sup> CO<sub>2</sub>-supersaturated 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> electrolyte at a potential of -0.73 V vs. RHE. **g**, Time-dependent *operando* Cu K-edge Fourier-transformed EXAFS spectra the CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> catalyst during the CO<sub>2</sub>RR in CO<sub>2</sub>-supersaturated electrolyte.

**Fig. 5. Investigations of the CO<sub>2</sub> reduction reaction mechanism using *ex-situ* and *operando* spectroscopy.** **a**, 2D heatmap for the intensity of the \*CO stretching modes on CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> during CO<sub>2</sub>RR for different CO<sub>2</sub> concentrations. The dark-grey dashed line indicates the distribution of FE<sub>2-propanol</sub>. **b**, Potential-resolved Raman mapping of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> in CO<sub>2</sub>-supersaturated 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub> during CO<sub>2</sub>RR. **c**, Volcano relationship between the ratio of \*CO<sub>bridge</sub> to \*CO<sub>atop</sub> and the FE<sub>2-propanol</sub> with the applied potentials for a [CO<sub>2</sub>] = 0.3 mol L<sup>-1</sup>. **d**, <sup>13</sup>C-NMR spectra of the electrolyte aliquots after the isotopic labelling experiments for 1.0 M CsHCO<sub>3</sub> ([CO<sub>2</sub>] = 3.0 mol L<sup>-1</sup>). The blue and red curves correspond to experiments with ethanol-D<sub>6</sub> in D<sub>2</sub>O or H<sub>2</sub>O, respectively. **e**, Relationship between the integrated area of the \*CO and \*OCH<sub>2</sub>CH<sub>3</sub> signals measured using *operando* FTIR at different applied potentials under [CO<sub>2</sub>] = 0.3 mol L<sup>-1</sup>. **f**, Relationship between the FE<sub>CO</sub> (via \*CO desorption), the FE<sub>ethanol</sub> (via \*OCH<sub>2</sub>CH<sub>3</sub> hydrogenation) and the FE<sub>2-propanol</sub> (via C<sub>1</sub>-C<sub>2</sub> coupling between \*OCH<sub>2</sub>CH<sub>3</sub> and \*CO) and the applied potentials under [CO<sub>2</sub>] = 0.3 mol L<sup>-1</sup>. 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<sub>1</sub>-C<sub>2</sub> coupling and the formation of C<sub>3</sub> 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<sub>2</sub>CH<sub>3</sub> intermediate adsorbed on Cu (100) facet as a function of Cu\*-O and O-C bond distances. **c**, ΔE<sub>diss</sub> as a function of the averaged distance between intermediate \*OCH<sub>2</sub>CH<sub>3</sub> and Ag atoms for various alloying contents of CuAg.

**Fig. 7. CO<sub>2</sub>RR performance in high-pressure electrolyzer under elevated CO<sub>2</sub> concentration.** **a**, 2D heatmap for the FE<sub>2-propanol</sub> on CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> with different CO<sub>2</sub> concentrations and applied potentials. **b**, Evolution of the  $j_{\text{total}}$  and  $j_{2\text{-propanol}}$  at -0.70 V vs. RHE from CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> with different CO<sub>2</sub> concentrations in 1.0 mol L<sup>-1</sup> CsHCO<sub>3</sub>. 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<sub>2</sub>/CO-to-C<sub>3</sub> conversion. **d**, Long-term stability measurement of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> at -0.70 V vs. RHE in CO<sub>2</sub>-supersaturated ([CO<sub>2</sub>] = 3.0 mol L<sup>-1</sup>, 10 bar) 1.0 M CsHCO<sub>3</sub>. **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<sup>2</sup> electrode modified with CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub>. The volume of the electrolyte was 150 mL.

**Fig. 8. CO<sub>2</sub>RR stability measurement and quantity the formation rate of 2-propanol.** **a**, Long-term stability measurement of CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub> at -0.70 V vs. RHE in CO<sub>2</sub>-supersaturated ([CO<sub>2</sub>] = 3.0 mol L<sup>-1</sup>, 10 bar) 1.0 M CsHCO<sub>3</sub>. **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<sup>2</sup> electrode modified with CO<sub>2</sub>-10-Cu<sub>94</sub>Ag<sub>6</sub>. The volume of the electrolyte was 150 mL.

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