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1 **Catalyst synthesis under CO₂ electroreduction favours faceting**
2 **and promotes renewable fuels electrosynthesis**

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21 **Abstract**

22 **The electrosynthesis of C₂₊ hydrocarbons from carbon dioxide has attracted recent**
23 **attention in light of the relatively high market price per unit energy input. Today's low**
24 **selectivities and stabilities towards C₂₊ products at high current densities curtail system**
25 **energy efficiency, which limits their prospects for economic competitiveness. Here we present**
26 **a materials processing strategy based on the *in-situ* electrodeposition of copper under CO₂**
27 **reduction conditions that preferentially exposes and maintains Cu(100) facets which favour**
28 **the formation of C₂₊ products. We observe capping of facets during catalyst synthesis and**
29 **achieve control over faceting, obtaining a 70% increase in the ratio of Cu(100) facets to total**
30 **facet area. We report a 90% Faradaic efficiency for C₂₊ products at a partial current density**
31 **of 520 mA cm⁻² and a full-cell C₂₊ power conversion efficiency of 37%. We achieve nearly**
32 **constant C₂H₄ selectivity over 65-hour operation at 350 mA cm⁻² in a membrane-electrode-**
33 **assembly electrolyser.**

34 **Introduction**

35 The utilization of CO₂ contributes to closing the anthropogenic carbon cycle.
36 Electrochemical reduction is a promising strategy to fulfill this goal by converting CO₂ to fuels
37 and value-added feedstocks using renewable electricity¹. Among products, C₂₊ hydrocarbons and
38 oxygenates – such as ethylene (C₂H₄), ethanol (EtOH) and *n*-propanol (*n*-PrOH) – are attractive in
39 view of their major roles in the chemical industry². However, it remains challenging to catalyze,
40 with high selectivity, the formation of these multi-carbon compounds via the CO₂ reduction
41 reaction (CO₂RR). The multistep reaction, and multiple competing pathways, make the design of
42 catalysts for desired C₂ products a challenging problem³⁻⁵.

43 To date, Cu-based materials have been the most efficient in electrocatalysing the
44 conversion of CO₂ to C₂₊ hydrocarbons and oxygenates⁶⁻⁹. Tailoring the Cu surface using materials
45 chemistry with the goal of directing the intermediate binding in each reaction step offers routes to
46 improve selectivity further towards desired multi-carbon products^{9,10}.

47 Electrochemical reduction of high-oxidation-state copper species offers one avenue to
48 realise selective and active C₂₊ product formation^{7, 11-14}. However, the Faradaic efficiency (FE) for
49 C₂₊ products has, until now, remained near or below 80%^{7, 8, 10}. We sought further means to tune
50 the exposed active sites in a polycrystalline Cu catalyst to enhance the selectivity towards C₂₊
51 products.

52 Cu(100) and step facets, such as Cu(211), are active for CO dimerisation, a key elementary
53 step in producing C₂₊ products¹⁵⁻¹⁸. Colloidally-synthesised Cu nanocubes, rich in Cu(100) facets,
54 have been shown to achieve a ~76% FE toward C₂₊ products (Supplementary Figure 1).

55 In prior approaches to Cu(100)-rich catalyst syntheses, capping agents are used that adsorb

56 on Cu(100) facets, lowering their surface energy^{19, 20}. We reasoned an approach to Cu(100)-rich
57 Cu synthesis – one in which CO₂RR intermediates would have strong interactions with Cu(100)
58 facets – could increase the exposure of surface Cu(100). We pursued the *in-situ* favouring of Cu
59 facets during Cu catalyst synthesis by ensuring the presence of CO₂RR intermediates during the
60 electrodeposition of Cu, and developed an approach that we find herein significantly improves
61 selectivity at high current densities. We increased the proportion of Cu(100) facets by 70%. We
62 achieved consequently a 90% Faradaic efficiency for C₂₊ products at a partial current density of
63 520 mA cm⁻², a full-cell C₂₊ power conversion efficiency of 37%, and nearly constant C₂H₄
64 selectivity for over 65 hours of operation.

65 **Results**

66 **Density functional theory calculations**

67 We first investigated the energetics of Cu facets having low Miller indices by calculating
68 the surface energies using the density functional theory (DFT). On Cu(100), the activation energy
69 and enthalpy change of CO dimerisation are 0.66 eV and 0.30 eV, respectively, which are lower
70 than in the case of either Cu(111) (0.72 and 0.65 eV) or Cu(211) (0.87 and 0.39 eV) (Figure 1a,
71 Supplementary Figure 2-4, and Table 1). Similar trends are seen across relevant applied potentials
72 (Supplementary Table 2). The most stable facet in polycrystalline Cu is Cu(111) according to the
73 calculated surface energies: 1.25 J cm⁻² for Cu(111), 1.43 J cm⁻² for Cu(100), and 1.55 J cm⁻² for
74 Cu(211) (Figure 1b, Supplementary Figure 5 and 6, Table 3-5). Stabilising the less-favoured
75 Cu(100) during the formation of polycrystalline Cu catalysts thus requires a strategy to modulate
76 the relative energies of different facets during materials synthesis.

77 We hypothesised that, under CO₂RR, the intermediates along reductive pathways can shape

78 the formation of different facets, where the adsorption strength of the intermediates plays a role
79 analogous to that of capping agents, traditionally employed to stabilise specific facets¹⁹ in the
80 growth of Cu single crystals.

81 We calculated the adsorption strength of CO₂*, COOH*, CO*, and H* (Supplementary
82 Table 3) and found that the CO₂RR intermediates favour Cu(100) in their adsorption energy, while
83 the adsorption of H* – the intermediate related with hydrogen evolution – is the strongest on
84 Cu(211) (Figure 1c).

85 We then modelled the equilibrium shapes of a Cu crystal using the Wulff construction²¹.
86 With the adsorption of these four intermediates, Cu crystals exhibit an increase of the Cu(100)
87 proportion relative to Cu without intermediates (Figure 1e, f and Supplementary Figure 7 and 8),
88 while no clear changes of Cu(100) exposure are found when HER intermediates are used (Figure
89 1g, h and Supplementary Figure 6 and 7). The trend was retained even when we varied the
90 intermediate ratio (Supplementary Figure 9). These findings motivated us to explore synthesising
91 catalysts in the presence of CO₂RR intermediates.

92 **Intermediate adsorption engineers the Cu facets**

93 Experimentally, we electrodeposited catalyst on gas diffusion layers (GDLs) in a CO₂-flow
94 electrolyser (Supplementary Figure 10). Tartrate anions were added as complexing agents to
95 stabilise the catalyst precursor, Cu²⁺, in alkaline conditions. As seen in Figure 2a, when we applied
96 a cathodic current (400 mA cm⁻²), the Cu(II) ditartrate ions were reduced to Cu metal on the GDL,
97 accompanied by CO₂ electroreduction on the Cu surface.

98 To gain insight into the growth of Cu catalysts during the electrodeposition, we
99 investigated the time-dependent structural evolution of the Cu over the course of catalyst formation

100 (Figure 2b). The starting evaporated Cu seed layer exhibited a nanoparticle morphology with a
101 size of ~10 nm (the left scanning electron microscopic image). After 10 seconds of
102 electrodeposition under CO₂ gas flow, Cu with a particle size of ~20 nm formed (labelled Cu-CO₂
103 in Figure 2b). Cross-sectional secondary electron and backscattered electron (BSE) images
104 confirmed a ~200 nm thickness of this Cu layer (Supplementary Figure 11a). Extending the
105 deposition time to 60 seconds increased the size to ~50 nm, with dendritic structures forming
106 simultaneously. The thickness of the 60-second Cu catalyst layer (labelled Cu-CO₂-60) is ~600
107 nm (Supplementary Figure 11b).

108 As a control experiment to check whether CO₂ played a role during catalyst synthesis, we
109 grew catalysts whose synthesis was accompanied by H₂ evolution only (labelled Cu-HER) by
110 replacing CO₂ with N₂ gas at the same flow rate. The Cu catalyst layer formed in 10 seconds under
111 N₂ gas exhibited a grain size of ~20 nm with a ~300 nm thickness (Supplementary Figure 12a).
112 After 20 seconds, we observed an aggregate size of ~200 nm, with larger dendrites formed
113 (Supplementary Figure 8a), and the catalyst layer exhibited a thickness of ~500 nm, similar to the
114 thickness of Cu-CO₂ formed in 60 seconds (Supplementary Figure 13b). After 60 seconds, the Cu-
115 HER crystals were predominantly in the form of dendritic structures (Fig. 2b) with a length ranging
116 from 0.5 to 2 μm (Supplementary Figure 12b).

117 Cu(111) and Cu(100) co-exist on both Cu-CO₂ and Cu-HER catalysts, as evidenced in
118 high-resolution transmission electron microscopy (Supplementary Figure 14-16) and grazing-
119 incidence wide-angle X-ray scattering (GIWAXS, Figure 2 c, and Supplementary Figure 17 and
120 18). However, the Cu-CO₂ catalysts exhibited a lower XRD peak intensity than did the Cu-HER
121 counterparts made using the same deposition time (Supplementary Figure 18). The results indicate
122 qualitatively that less Cu was deposited in the presence of CO₂ gas. We further checked the crystal

123 structure of the catalysts using dark-field HRTEM (Supplementary Figure 14-16). The results
124 show that the Cu-CO₂-60 catalysts exhibit less Cu(111) facet exposure compared to Cu-HER-20.

125 We then sought to quantify the difference in the catalyst formation and facet exposure. For
126 real-time monitoring of catalyst formation, we performed a series of *operando* studies. We
127 observed, by *operando* Raman spectroscopy, chemisorbed intermediates when CO₂ was present
128 (Supplementary Figure 19). We used *operando* hard X-ray absorption spectroscopy (hXAS) to
129 track the electrochemical formation of Cu as a function of time (Figure 3a and b). We analysed the
130 X-ray absorption near-edge structure (XANES) of the Cu crystals by linear combination fitting
131 (Supplementary Figure 20, 21 and Table 6 and 7). The starting spectrum exhibits a Cu²⁺ complex
132 feature ascribed to the Cu(II) ditartrate ions in the electrolyte. The ratio of metallic Cu to Cu(II)
133 ditartrate for Cu-CO₂ reaches roughly 50:50 after 60 seconds (Figure 3c, upper panel). However,
134 for Cu-HER, a similar ratio of ~53:47 is obtained at 27 seconds, and it further increases to ~88:12
135 following 60 seconds (Figure 3c, lower panel).

136 Since different Cu facets feature distinctive (and previously-documented²²) OH⁻
137 electrochemical adsorption behaviour, we sought to quantify Cu(100) exposure using the OH⁻
138 electroadsorption technique (Supplementary Figure 22)²³. Linear sweep voltammetry profiles
139 reveal electrochemical OH⁻ adsorption peaks (the oxidation of surface Cu) on Cu(100), (110) and
140 (111) at potentials ~0.37, 0.43, 0.48 V vs. RHE, respectively²³. Using these peaks, we calculated
141 the surface area of each facet (see Methods) for Cu catalysts deposited for different time (Figure
142 3e, f). The growth of Cu(111) is significantly suppressed in the Cu-CO₂-60 sample, with a (111)
143 surface area of less than 0.9 cm² per 1 geometric cm² electrode (Figure 3e). The Cu(100)-to-
144 Cu(111) surface area ratio of Cu-CO₂ is >1.7 times that of Cu-HER (Figure 3f).

145 We also used Pb underpotential deposition (UPD), another surface-sensitive

146 electrochemical technique, and witnessed similar Cu(100):Cu(111) ratios for Cu-CO₂ and Cu-
147 HER catalysts (Supplementary Figure 23). We extended the deposition time to 90 seconds for Cu-
148 CO₂ catalysts, and continued to observe a high Cu(100):Cu(111) ratio of $\sim 0.9 \pm 0.2$
149 (Supplementary Figure 24). From reaction-diffusion modelling, we estimate that the local pH for
150 Cu-CO₂ and Cu-HER are ~ 14.9 and 14.7 (Figure 3g), respectively, which argues against a
151 significant differential impact of local OH⁻ on the catalyst surface structure.

152 We conclude that synthesis under CO₂RR reduced the amount of Cu deposited and changed
153 the surface structure. We propose a role for facet-selective capping by CO₂RR intermediates: the
154 adsorption of CO₂RR intermediates lowers the surface energy of high-energy Cu facets, *e.g.*
155 Cu(100) and Cu(211). This capping effect is similar to that in colloidal crystal synthesis^{24,25}, which
156 modulates Cu growth and increases the fraction of Cu(100) facets.

157 **CO₂ electroreduction performance**

158 We evaluated the catalytic performance of Cu-CO₂ catalysts in 7 M KOH electrolyte
159 (Figure 4), a catholyte in which the energy barrier for CO–CO dimerisation is significantly
160 reduced²⁶. Using samples having similar mass loadings, particle sizes, electrochemically active
161 surface areas (ECSA) (Supplementary Figure 25-27 and Table 8) and Brunauer–Emmett–Teller
162 (BET) surface areas (Supplementary Table 9), we tested Cu-CO₂-60 and Cu-HER-20 catalysts in
163 a 1 cm² active area CO₂RR flow cell.

164 To characterise the intrinsic activity of the catalysts, we normalised current densities using
165 their ECSA (Supplementary Figure 27 and Table 6). The ECSA-normalised C₂H₄ and C₂₊ partial
166 current densities of Cu-CO₂-60 are 1.3 times higher than those of Cu-HER-20 (Figure 4b).

167 On Cu-CO₂-60, the FE for C₂₊ products reaches its peak value of $90 \pm 1\%$ (Figure 4c) at -

168 0.67 V vs. RHE (a full-cell voltage of 2.85 V without iR correction, Supplementary Figure 28),
169 with a C_{2+} partial current density of $\sim 280 \text{ mA cm}^{-2}$. The C_{2+} liquid products include EtOH, PrOH
170 and acetate (AcO^- , Supplementary Figure 29). This result translates to a $\sim 37\%$ C_{2+} full-cell power
171 conversion efficiency (PCE) (Figure 4d and Supplementary Table 10). At -0.71 V, Cu-CO₂-60
172 exhibits a partial current density of $\sim 520 \text{ mA cm}^{-2}$ with a similarly high FE and a 29% PCE for
173 C_{2+} products (Figure 4c).

174 In contrast, on the Cu-HER-20 catalyst, the highest C_{2+} FE and partial current density are
175 $77 \pm 2\%$ and 337 mA cm^{-2} (Figure 4c and Supplementary Figure 30). The corresponding C_{2+} full-
176 cell PCE is 31% (Figure 4c).

177 Considering the similarity of CO₂ and CO reduction reaction, we also electrodeposited Cu
178 under CO gas, and obtained $68 \pm 4\%$ and $83 \pm 2\%$ FE for C₂H₄ and C_{2+} products (Supplementary
179 Figure 31a and b). The CO₂RR performance on the 50 nm Cu seeds were also investigated
180 (Supplementary Figure 32). Detailed CO₂RR performance for each catalyst is shown in
181 Supplementary Table 13-17.

182 Since the chemisorbed CO is further converted to C_{2+} products^{11, 27}, we plotted the
183 potential-dependent CO and C_{2+} selectivity trend (Figure 4e). Compared to Cu-HER-20, Cu-CO₂-
184 60 exhibits a higher CO selectivity, peaking at $35 \pm 1\%$ at lower overpotentials, which is ~ 1.7
185 times as high as that on Cu-HER-20 (Supplementary Table 11 and 14). The higher CO production
186 on the Cu-CO₂-60 catalyst at lower overpotentials agrees with a picture of higher CO* intermediate
187 availability when we move to higher overpotentials. Since the Cu-CO₂-60 catalysts differs from
188 the Cu-HER-20 principally in terms of the surface exposure of Cu(100) and Cu(111) facets, this
189 selectivity difference at lower potentials agrees with the view that the higher performance on Cu-
190 CO₂ arises from optimised facet exposure.

191 Alkaline conditions provide high selectivity for C₂₊ products (Supplementary Figure 33)
192 and lowered overpotentials for CO₂RR and oxygen evolution at the anode, which lowers the full-
193 cell voltage (Supplementary Figure 28). However, CO₂ reacts with KOH and forms carbonates
194 under alkaline conditions, and this requires additional energy costs for its regeneration
195 (Supplementary Figure 34). Neutral CO₂RR reduces the carbonate formation problem. We
196 developed Cu-CO₂-60 catalysts having a 5 cm² active area integrated with a membrane electrode
197 assembly (MEA) and used these in an electrolyser with 0.15 M KHCO₃ anolyte. We achieved 65
198 hours of stable operation with constant C₂H₄ FE of 60 ± 2% at an applied full-cell voltage of -3.7
199 V and current density of 350-300 mA cm⁻² (Figure 5f and Supplementary Figure 35). This
200 translates to a 25-fold increase in stability at current densities higher than 300 mA cm⁻² compared
201 to the best prior reports of high-current-density CO₂-to-C₂₊ product electroreduction^{6, 7, 9, 10, 12}
202 (Supplementary Table 10).

203 We also found that, following 1000-second CO₂RR operation, the Cu(100):Cu(111) ratio
204 was well retained (Supplementary Figure 36), while destructive morphological changes to the Cu
205 nanocubes were seen after CO₂RR (Supplementary Figure 37). Higher overpotentials and current
206 densities cause more frequent electron exchanges between the catalyst and intermediates, different
207 surface energies for the different facets, and increased diffusion of Cu atoms and surface bubble
208 formation. Cu nanocubes could also be susceptible to morphological reconstruction as high
209 alkaline conditions may culminate in regions that are less accessible to CO₂ at the catalytic
210 interface²⁶.

211 When a catalyst is operated under CO₂RR, the intermediate coverages on Cu(111), Cu(100)
212 and Cu(211) facets are 0.01, 0.33, and 0.29 ML (Supplementary Figure 6 and 9a) – these coverages
213 are based on a previous study of Nørskov and co-workers²⁸. With a 0.01 ML CO₂RR intermediate

214 coverage, the Cu(111) facet has a surface energy of 1.25 J cm^{-2} , and is 0.16 J cm^{-2} more stable than
215 Cu(100) with the same coverage (Figure 1a and Supplementary Figure 6). The direct conversion
216 of Cu(111) to Cu(100) is therefore not favoured under CO₂RR conditions.

217 In contrast, when we electrodeposit under CO₂-rich conditions, we are no longer required
218 to convert non-(100) facets to Cu(100); instead, we redirect Cu²⁺-to-Cu electroreduction toward
219 Cu(100). The surface energy associated with Cu(100) decreases to 1.0 J cm^{-2} , which is 0.26 J cm^{-2}
220 more stable than that of Cu(111), due to a 0.33 ML CO₂RR intermediate coverage
221 (Supplementary Figure 9a).

222 The Wulff constructions present the thermodynamic equilibrium shapes of Cu crystals with
223 different intermediate coverages (Figure 1d-h, and Supplementary Figure 7-9). The experiments
224 agree with this picture, with a Cu(100):Cu(111) ratio up to 1.4:1 in the Cu-CO₂ catalyst (Figure
225 3f).

226 Over the course of CO₂ electroreduction, the Cu₂O feature resulting from post-oxidation
227 (Supplementary Figure 38) diminishes quickly once the potential is applied (Supplementary Figure
228 39-42). This, when combined with the *operando* Raman results (Supplementary Figure 19),
229 indicates that the CO₂RR activity on both catalysts originates from metallic Cu. As a similar
230 coordination number (CN) was observed for the two catalysts (Supplementary Table 18 and 19),
231 neither the size effect²⁹ nor the subsurface oxygen of Cu appears to determine the differences in
232 selectivity and activity⁷. Catalysts with different deposition times under the same gas also exhibit
233 similar FE for C₂H₄ product (Supplementary Figure 31b, c and 43). This result further argues
234 against a major effect of size on the CO₂RR selectivity reported herein.

235 To explore the wider application of this CO₂RR-tailored catalyst synthesis strategy, we

236 further prepared oxide-derived Ag under CO₂RR conditions and HER conditions (Ag-CO₂ and
237 Ag-HER, Supplementary Figure 44). We observed a 1.5x increase in the area of Ag(110) facet (~3
238 cm²) – the most active facet for CO₂-to-CO on Ag^{ref. 5} – on Ag-CO₂ (Supplementary Figure 44g,
239 h). The maximum FE for CO was ~92% on Ag-CO₂, 1.4 time higher than on Ag-HER (~66%)
240 (Supplementary Figure 44i).

241 **Conclusion**

242 This work presents a catalyst materials synthesis strategy that seeks to expose and maintain
243 C₂₊-selective Cu(100) facets preferentially, and selectively produce thereby C₂₊ products at high
244 current via CO₂RR. We capitalised on CO₂RR intermediate adsorption to tune which Cu facets are
245 exposed. We demonstrate that CO₂RR intermediates (*e.g.* CO) can be used to regulate the
246 crystallisation of materials beyond noble metals³⁰⁻³². We offer a physical picture in which the
247 intermediates function in analogy with capping agents, regulating the growth of catalysts to
248 produce a highly active catalyst with a high proportion of Cu(100). Only as a result do we achieve
249 high-selectivity-at-high-current-density CO₂ electroreduction to C₂₊ products and C₂H₄ on Cu
250 catalysts. Specifically, we obtain a FE for total C₂₊ products of ~90% at current densities exceeding
251 580 mA cm⁻² and full-cell PCE for C₂₊ products of ~37%. We achieved a constant C₂H₄ FE for 65
252 hours of operation. We demonstrated the wider applicability of this CO₂RR-processed catalyst
253 faceting strategy, increasing (110) facet exposure on Ag catalysts and achieving as a result 92%
254 CO FE. *In-situ* materials processing provides an avenue to expose preferentially and maintain the
255 active sites needed in reactions, contributing additional principles for designing selective and
256 active catalysts. The topic warrants further study to deepen and extend physical models of capping
257 using intermediates during catalyst synthesis vs. catalyst operation, including through the use of
258 advanced *operando* methods that simultaneously monitor both the presence of intermediates, and

259 of catalyst facets and shape, *in situ*.

260 **Methods**

261 **Density functional theory calculations.** In this work, all the DFT calculations were carried out
262 with a periodic slab model using the Vienna *ab initio* simulation program (VASP)³³⁻³⁶. The
263 generalised gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE)
264 exchange-correlation functional³⁷. The projector-augmented wave (PAW) method^{38, 39} was used
265 to describe the electron-ion interactions, and the cut-off energy for the plane-wave basis set was
266 450 eV. In order to illustrate the long-range dispersion interactions between the adsorbates and
267 catalysts, we employed the D3 correction method by Grimme et al⁴⁰ with Becke-Jonson damping⁴¹.
268 Brillouin zone integration was accomplished using a 3×3×1 Monkhorst-Pack k-point mesh.

269 Adsorption geometries were optimised using a force-based conjugate gradient algorithm, while
270 transition states (TSs) were located with a constrained minimisation technique⁴²⁻⁴⁴. For the
271 modelling of copper, the crystal structure was optimised and the equilibrium lattice constants were
272 found to be $a_{\text{Cu}} = 3.631 \text{ \AA}$. Three low Miller index planes were cleaved, including Cu(100),
273 Cu(111), and Cu(211). For Cu(100), a periodic six-layer model with the 3 lower layers fixed and
274 3 upper layers relaxed was used, and a p(3×3) super cell was chosen. For Cu(111), we used a 4-
275 layer model with p(3×3) super cell with the 2 upper layers relaxed and 2 lower layers fixed. The
276 convergence test of different layers is detailed in Supplementary Table 5. Cu(211) was modelled
277 with a periodic 12-layer p(1×3) model with the 6 lower layers fixed and 6 upper layers relaxed. At
278 all intermediate and transition states, one charged layer of water molecules was added to the
279 surface to take the combined field and solvation effects into account⁴⁵. The charged layer of water
280 molecules was optimised at all intermediate and transition states. In the CO dimerisation, there is
281 no proton or electron transfer, thus the computational hydrogen electrode was not used in this
282 work.

283 For the full solvent calculations, the total number of water considered is 25 water for Cu(100), 21
284 water for Cu(111), and 21 water for Cu(211), as seen in Supplementary Figure 4. We used the
285 reactive force field to run a 1 ns molecular dynamic on all facets. The force field developed by van
286 Duin and co-workers⁴⁶ was chosen as this force field was used by Goddard and co-workers to
287 describe water-surface interface conditions⁴⁷.

288 To describe the effect of applied potentials on adsorption and reaction energies, the charge-
289 asymmetric nonlocally determined local-electric (CANDLE) solvation model⁴⁸. We used the same
290 settings as the CO₂RR mechanism study work by Goddard and co-workers⁴⁹. For the effect of
291 potential, we used the grand canonical electronic DFT⁵⁰ implemented in JDFTX⁵¹ to evaluate the
292 adsorption energies at different applied potentials.

293 To evaluate the stability of one surface, the surface energy was used as defined below:

$$E_{surface} = \frac{E_{total} - nE_{ref} - E_{ads}}{2A} \quad (1)$$

294 where E_{total} is the total energy of this surface from DFT calculations, and E_{ref} is the reference
295 energy of unit composition from bulk calculation. E_{ads} is the sum of the adsorption energies of
296 the intermediates at given coverages. A and n are the surface area and the number of unit
297 composition in this surface, respectively. Given this definition, the more positive the surface
298 energy is for a surface, the less stable this surface is.

299 Wulff constructions were performed using the Python Materials Genomics (pymatgen) materials
300 analysis library⁵². In this work, CO₂RR intermediates refer to CO₂*, CO*, COOH*, and H*, while
301 HER intermediates are H*. Surface energies with adsorption of four intermediates states were

302 calculated by assuming the coverages of all the four intermediates are the same. For example, the
303 coverage of all the intermediates were assumed to be 0.05 ML for all the four intermediates at 0.2
304 ML total coverage. The total coverage value of CO₂RR intermediates, 0.2 ML, is chosen because
305 it is the total coverage of each intermediate adsorbing on one side of a 3×3 surfaces. 211 surface
306 is assumed to be have 9 sites to keep consistent 111 and 100. In realistic system, the coverage of
307 the species should be larger, and the values for different intermediates should be diverse. Nørskov
308 and co-workers reported the coverage of CO is ~0.3 ML on Cu surfaces based on a micro-kinetic
309 modelling²⁸. The value of 0.2 ML is considered only to show the trend that Cu(100) concentration
310 increases even at low coverage of intermediates. The surface energies with intermediates are
311 calculated in respect of Cu(111).

312 **Catalyst preparation.** Cu-CO₂ catalysts were prepared through an electrodeposition approach
313 under CO₂ gas flow (50 standard cubic centimetres per minute, s.c.c.m.). Catalysts were
314 electrodeposited at a constant current of -0.4 A cm⁻² for 60 s on a gas diffusion layer (Freudenberg
315 H14C9, for characterisations) or a polytetrafluoroethylene (PTFE) membrane (pore size 450 nm)
316 with 50 nm sputtered Cu seeds (for electrochemical tests). The solution consisted of 0.1 M copper
317 bromide (98%, Sigma-Aldrich), 0.2 M sodium tartrate dibasic dihydrate (purum p.a., ≥98.0% NT,
318 Sigma-Aldrich) and 1 M KOH. For Cu-CO and Cu-HER, the catalyst was synthesised under
319 identical conditions as Cu-CO₂, but with CO and N₂ or Ar at the same flow rate instead of CO₂.

320 For Cu nanocubes, 46 mg hexadecyltrimethylammonium chloride (CTAC, ≥98.0% NT, Sigma-
321 Aldrich) was dissolved in 9.8 mL deionised water. 50 μL 0.1 M copper acetate (97%, Sigma-
322 Aldrich) and 0.2 mL 0.5 M (+)-sodium L-ascorbate (≥98.0% NT, Sigma-Aldrich) aqueous solution
323 were then added. The solution was transferred into a gas-light vial and kept in a 100 °C oven for 1

324 h. The reddish Cu nanocubes were then centrifugated, washed using deionised water, and dried in
325 vacuum. 6 mg Cu nanocubes were obtained in 200 mL precursor solution. The Cu nanocubes were
326 then mixed with 10 μ L Nafion resin solution in 1 mL methanol, sonicated for 30 min, and then
327 sprayed onto a 5×5 cm² PTFE membrane with the 50 nm sputtered Cu layer.

328 For Ag catalysts, the precursor Ag₂O was prepared by mixing 25 mL 0.05 M AgNO₃ (98%, Sigma-
329 Aldrich) with 1.4 g KOH. Then, the as-made Ag₂O particles were spray-coated on 1 cm² GDL
330 with a mass loading of 0.3 mg cm⁻². Ag-CO₂ and Ag-HER catalysts were prepared by
331 electroreducing Ag₂O nanoparticle at the constant current of -0.2 A cm⁻² for 30 s under CO₂ and
332 N₂, respectively.

333 **Materials characterisation.** Scanning electron microscopy (Hitachi S-5200) and transmission
334 electron microscopy (Hitachi HF3300) were employed to observe the morphology of the samples.
335 X-ray photoelectron spectroscopy (XPS) measurements were carried out on a K-Alpha XPS
336 spectrometer (PHI 5700 ESCA System), using Al K α X-ray radiation (1486.6 eV) for excitation.
337 *Operando* hard X-ray absorption measurements were performed at the 9BM beamline, and
338 Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements were conducted at the
339 12D-D beamline of the Advanced Photon Source (APS) located in the Argonne National
340 Laboratory (Lemont, IL). Raman measurements were conducted using a Renishaw inVia Raman
341 Microscope and a water immersion objective (63x) with a 785 nm laser.

342 **Electrochemical OH⁻ adsorption, Pb UPD and ECSA evaluation.** Electrochemical OH⁻
343 adsorption was performed in N₂-saturated 1 M KOH electrolyte by a linear sweep voltammetry
344 method at a sweep rate of 100 mV s⁻¹ for Cu and 20 mV s⁻¹ for Ag catalysts. The potential ranged
345 from -0.2 to 0.6 V vs. RHE for Cu. All Cu catalysts were reduced at -0.6 V vs. RHE for 2 min

346 before performing the OH⁻ adsorption measurement. Single-crystal Cu(100) and Cu(111)
347 substrates were measured using the same method. The facet area was calculated by normalising
348 the OH⁻ adsorption charge of each facet on Cu catalysts to that on single crystals. For Ag, catalysts
349 were first reduced at -0.6 V vs. RHE for 30 s, and the potential range was 0.83 to 0.93 V vs. RHE.
350 N₂ was kept being purged during the measurement.

351 For Pb UPD, a N₂-saturated 0.1 M HClO₄ aqueous solution with 10 mM Pb(ClO₄)₂ was used as
352 the electrolyte. The potential was first set at -0.15 V vs. RHE for 150 seconds. Linear sweep
353 voltammetry with a sweep rate of 10 mV s⁻¹ was used for measurements. The potential ranged
354 from 0.17 to 0.2 V vs. RHE. N₂ was purged during these measurements. The facet area was
355 calculated by normalising the Pb UPD charge of each facet on Cu catalysts to that on Cu single
356 crystals.

357 For ECSA, the electrochemical double layer capacitance method was employed. All catalysts were
358 reduced at -0.6 V vs. RHE for 2 min, and scanned in the potential range of -0.07 to 0.13 V and
359 0.83 to 0.93 V vs. RHE for Cu and Ag catalysts in N₂-saturated 1 M KOH for 10 cycles at the
360 sweep rate of 20, 40, 60, 80, and 100 mV s⁻¹. N₂ was purged during the measurement. The anodic
361 and cathodic current densities at 0.03 V vs. RHE for Cu and 0.88 V vs. RHE for Ag in the last scan
362 cycle were recorded. The differences in these two current densities (Δj) at different sweep rates
363 were then calculated and plotted against the sweep rates for each catalyst. By linear fitting, we
364 calculated the slopes of the Δj vs. sweep rate curves, which are the double layer capacitances for
365 different catalysts. The double layer capacitance of electropolished Cu foil was obtained from
366 previous reports⁵³.

367 **Local pH simulation.** The local pH was simulated based on previous reports⁵⁴ and accounted for

368 $\text{CO}_{2\text{aq}}$, CO_3^{2-} , HCO_3^- , and OH^- evolution as $\text{CO}_{2\text{aq}}$ is reduced via electrocatalysis in 1 M KOH. We
 369 modelled the four ionic species using the Transport of Dilute Species physics in a two-dimensional
 370 rectangular domain. A time-dependent study was performed to simulate species evolution away
 371 from the interface. At the left boundary, the gas-catalyst-electrolyte interface, the $\text{CO}_{2\text{aq}}$
 372 concentration was specified according to Henry's Law and the Sechenov effect⁵⁵⁻⁵⁷, with zero flux
 373 imposed for CO_3^{2-} , HCO_3^- , and OH^- . The top and right boundaries allow for species outflow, and
 374 the bottom boundary concentrations are those of the bulk solution.

375 To model CO_2RR , a thin vertical catalyst layer was imposed over which the $\text{CO}_{2\text{aq}}$ is reduced and
 376 OH^- is produced according to the reactions:

$$R_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{aq}}}{[\text{CO}_2]_{\text{aq},0}} \frac{j}{F} \frac{\epsilon}{L_{\text{cat}}} \frac{1}{2e^-} \text{CO}_2 \quad (2)$$

$$R_{\text{OH}} = \frac{j}{F} \frac{\epsilon}{L_{\text{cat}}} \frac{2\text{OH}^-}{2e^-} \quad (3)$$

377
 378 where $[\text{CO}_2]_{\text{aq}}$ is the equilibrium $\text{CO}_{2\text{aq}}$ concentration in the bulk electrolyte, j is the current density
 379 applied, F is Faraday constant, ϵ is the catalyst porosity (0.6), and L_{cat} is the size of the catalyst
 380 layer (varied from 10 nm to 300 nm). The left $\text{CO}_{2\text{aq}}$ boundary condition in conjunction with OH^-
 381 production in the catalyst layer supports carbonate formation, producing a diffusion layer that
 382 grows away from the left boundary. We assume a $2e^-$ process for the reduction of CO_2 (Eq. 2) to
 383 CO with 100% Faradaic efficiency. The production of OH^- (Eq. 3) depends only on the current
 384 density since both CO_2RR and HER produce OH^- . The species' diffusion coefficient, as well as
 385 the chemical dissociation reaction equations of $\text{CO}_{2\text{aq}}$ were found in previous literature⁵⁸.

386 **XAS fitting.** An IFEFFIT package was used to analyse the hXAS spectra^{59, 60}. Standard data-
387 processing including energy calibration and spectral normalisation of the raw spectra was
388 performed using Athena software. To track the Cu valence distribution, a linear combination fitting
389 analysis, included in Athena, was carried out using the hXAS spectra of various Cu-based
390 standards. To extract the Cu bonding information, a Fourier transform was applied to convert the
391 hXAS spectra from an energy space to a radial distance space. Then, a standard fitting analysis of
392 the first shell between 1.6 and 3.0 Å was carried out using Artemis software. The phase and
393 amplitude functions of Cu-Cu was calculated with FEFF, S_0/σ^2 values of 0.89/0.00825 for Cu was
394 determined from Cu foil, which then was applied to the Cu hXAS fitting.

395 **GIWAXS measurements.** Grazing incidence wide-angle X-ray scattering (GIWAXS)
396 measurements were performed at beamline 12-ID-D of the Advanced Photon Source (APS) at the
397 Argonne National Laboratory. The catalyst samples were mounted on a Huber six-circle
398 diffractometer that can precisely control the X-ray angle of incidence to achieve the grazing
399 incidence condition for GIWAXS. The scattering patterns were obtained at an incident angle of
400 0.3°. The XRD measurements were conducted at the X-ray energy of 20 keV with the beam profile
401 of 500 µm (horizontal) × 70 µm (vertical). The sample stage was rotated by 180° along the out-of-
402 plane axis during the measurement and scattering patterned were recorded at every 2°. 90 patterns
403 were acquired and integrated to obtain a single scattering pattern for each sample.

404 **Electrocatalytic measurement of CO₂ reduction.** The electrocatalytic measurements were
405 carried out in a 1 cm² electrochemical flow cell using a three-electrode configuration with 90% *iR*
406 correction. The flow cell was connected to an electrochemical workstation (Autolab PGSTAT204)
407 equipped with 10 A current booster. The flow cell consisted of three compartments: gas chamber,
408 catholyte chamber, and anolyte chamber. The gas and cathodic compartments were separated by

409 the Cu (or Ag) electrode. Catholyte and anolyte chambers were separated by an anion-exchange
410 membrane (Fumapem FAA-3-PK-130). The CO₂RR catalyst, Ag/AgCl electrode (3.5 M KCl used
411 as the filling solution) and NiFe hydroxides on Ni mesh were employed as working, reference, and
412 counter electrodes, respectively. The full-cell voltages were tested in a two-electrode configuration.
413 The thickness of the catholyte chamber was ~5 mm. Carbon/Nafion and graphite/Nafion mixtures
414 were sequentially sprayed on the catalyst layer on PTFE support. The applied potentials were
415 converted to the reversible hydrogen electrode (RHE) scale through the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl (3.5 M KCl)}} + 0.059 \times \text{pH} + 0.205 \quad (4)$$

416
417 Aqueous KOH (7 M or 1 M), K₂CO₃ (0.5 M) or KHCO₃ (1 M) electrolyte was used as the both
418 catholyte and anolyte. The flow rate of the CO₂ gas was fixed at 50 s.c.c.m. The gaseous products
419 were separated by gas chromatography (PerkinElmer Clarus 600), and detected by a thermal
420 conductivity detector (TCD) and a flame ionisation detector (FID). High-purity Argon (99.99%)
421 was used as the carrier. Liquid products were quantified by H-nuclear magnetic resonance (H-
422 NMR) technic (Agilent DD2 600) using Dimethyl sulfoxide (DMSO) as the internal standard.
423 Faradaic efficiency of gas product was calculated based on the following equation:

$$\text{Faradaic efficiency} = \frac{i_x}{i_{\text{tot}}} = \frac{n_x v_{\text{gas}} c_x F}{i_{\text{tot}} V_m} \quad (5)$$

424
425 where i_x is the partial current of product x ; i_{tot} is the total current; n_x represents the number of
426 electron transfer toward the formation of 1 mol of product x ; v_{gas} is the CO₂ flow rate (s.c.c.m); c_x

427 represents the concentration of product x detected by the gas chromatography (p.p.m); F is the
428 Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$); V_m is the unit molar volume, which is $24.5 \text{ L}\cdot\text{mol}^{-1}$ at room
429 temperature (298.15 K).

430 The power conversion efficiency (PCE) was defined as the ratio of fuel energy to applied electrical
431 power, which was calculated with the following equation:

$$\text{PCE}_x = \frac{P_{chem}}{P_{applied}} = \frac{(1.23 - E_x^0)FE_x}{\text{Applied voltage}} \quad (6)$$

432

433 where P_{chem} stands for the power used for CO_2RR ; $P_{applied}$ stands for the input electrical energy;
434 E_x^0 represents the equilibrium potential of CO_2 electroreduction to each C_{2+} product, which is 0.08
435 V for ethylene, 0.09 V for ethanol, and -0.26 V for acetate. FE_x is the Faradaic efficiency for each
436 C_{2+} product.

437 For tests in MEA electrolyzers, the experimental setup used was a commercial MEA electrolyzer
438 (Dioxide Materials[®], 5 cm^2 active area). The MEA consisted of a cathode electrode, anion
439 exchange membrane (AEM, Sustainion[®] X37-50 grade 60), and anode electrode (IrO_2 -Ti mesh).
440 The anode electrode was prepared by following a methodology similar to that described in the
441 previous report⁶¹. The resulting cathode and anode electrodes were then mounted on their
442 respective flow fields, separated from each other via the AEM, and assembled in the MEA
443 electrolyzer. CO_2 was then supplied with a flow rate of 80 s.c.c.m. through the flow channels in
444 the cathode flow field, while the 0.15 M KHCO_3 was fed into the anode flow channels with a flow
445 rate of 20 ml min^{-1} . The applied potential was increased gradually from -3.0 V to -4.2 V, with
446 constant negative potential increments of -0.1 V. Stability test were performed at a constant full

447 cell potential of -3.7 V.

448 **Data availability**

449 The datasets generated and/or analysed during the current study are available from the
450 corresponding author on reasonable request.

451 **References**

- 452 1 Bushuyev, O. S. *et al.* What should we make with CO₂ and how can we make it? *Joule*
453 **2**, 1-8 (2018).
- 454 2 Mistry, H., Varela, A. S., Kühl, S., Strasser, P., & Cuenya, B. R. Nanostructured
455 electrocatalysts with tunable activity and selectivity. *Nat. Rev. Mater.* **1**, 16009 (2016).
- 456 3 Schouten, K., Kwon, Y., Van der Ham, C., Qin, Z., Koper, M. A new mechanism for
457 the selectivity to C₁ and C₂ species in the electrochemical reduction of carbon dioxide
458 on copper electrodes. *Chem. Sci.* **2**, 1902-1909 (2011).
- 459 4 Hori, Y. in *Modern aspects of electrochemistry*, Berlin, Germany 89-189 (Springer,
460 2008).
- 461 5 Wang, Y., Liu, J., Wang, Y., Al-Enizi, A. M., Zheng, G. Tuning of CO₂ reduction
462 selectivity on metal electrocatalysts. *Small* **13**, 1701809 (2017).
- 463 6 Hoang, T. T. H., Ma, S., Gold, J. I., Kenis, P. J. A., Gewirth, A. A. Nanoporous copper
464 films by additive-controlled electrodeposition: CO₂ reduction catalysis. *ACS Catal.* **7**,
465 3313-3321 (2017)
- 466 7 De Luna, P. *et al.* Catalyst electro-redeposition controls morphology and oxidation
467 state for selective carbon dioxide reduction. *Nat. Catal.* **1**, 103-110 (2018).
- 468 8 Mistry, H. *et al.* Highly selective plasma-activated copper catalysts for carbon dioxide
469 reduction to ethylene. *Nat. Commun.* **7**, 12123 (2016).
- 470 9 Hoang, T. T. H *et al.* Nano porous copper-silver alloys by additive-controlled electro-
471 deposition for the selective electroreduction of CO₂ to ethylene and ethanol. *J. Am.*
472 *Chem. Soc.* **140**, 5791-5797 (2018).
- 473 10 Zhuang, T.-T. *et al.* Steering post-C-C coupling selectivity enables high efficiency

- 474 electroreduction of carbon dioxide to multi-carbon alcohols. *Nat. Catal.* **1**, 421-428
475 (2018)
- 476 11 Li, C. W., Ciston, J., Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel
477 on oxide-derived nanocrystalline copper. *Nature* **508**, 504-507 (2014).
- 478 12 Jiang, K. *et al.* Metal ion cycling of Cu foil for selective C–C coupling in
479 electrochemical CO₂ reduction. *Nat. Catal.* **1**, 111-119 (2018).
- 480 13 Li, C. W., Kanan, M. W. CO₂ reduction at low overpotential on Cu electrodes resulting
481 from the reduction of thick Cu₂O films. *J. Am. Chem. Soc.* **134**, 7231-7234 (2012).
- 482 14 Reller, C. *et al.* Selective electroreduction of CO₂ toward ethylene on nano dendritic
483 copper catalysts at high current density. *Adv. Energy Mater.* **7**, 1602114 (2017).
- 484 15 Pérez Gallent, E., Marcandalli, G., Figueiredo, M. C., Calle-Vallejo, F., Koper, M.
485 Structure- and Potential-Dependent Cation Effects on CO Reduction at Copper Single-
486 Crystal Electrodes. *J. Am. Chem. Soc.* **139**, 16412-16419 (2017).
- 487 16 Pérez Gallent, E., Figueiredo, M. C., Calle-Vallejo, F., Koper, M. Spectroscopic
488 observation of a hydrogenated CO dimer intermediate during CO reduction on Cu(100)
489 electrodes. *Angew. Chem. Int. Ed.* **56**, 3621-3624 (2017).
- 490 17 Hori, Y., Takahashi, I., Koga, O., & Hoshi, N. Electrochemical reduction of carbon
491 dioxide at various series of copper single crystal electrodes. *J. Mol. Catal. A: Chem.*
492 **199**, 39-47 (2003).
- 493 18 Roberts, F. S., Kuhl, K. P., Nilsson, A. High selectivity for ethylene from carbon
494 dioxide reduction over copper nanocube electrocatalysts. *Angew. Chem. Int. Ed.* **54**,
495 5179-5182 (2015).
- 496 19 Jin, M. *et al.* Shape-controlled synthesis of copper nanocrystals in an aqueous solution

497 with glucose as a reducing agent and hexadecylamine as a capping agent. *Angew. Chem.*
498 *Int. Ed.* **50**, 10560-10564 (2011).

499 20 Huang, J. *et al.* Potential-induced nanoculstering of metallic catalysts during
500 electrochemical CO₂ reduction. *Nat. Commun.* **9**, 3117 (2018).

501 21 Tran, R. *et al.* Surface energies of elemental crystals. *Sci. Data* **3**, 160080 (2016).

502 22 Droog, J. M. M., & Schlenter, B. Oxygen electrosorption on copper single crystal
503 electrodes in sodium hydroxide solution. *J. Electroanal. Chem.* **112**, 387-390 (1980).

504 23 Raciti, D. *et al.* Low-overpotential electroreduction of carbon monoxide using copper
505 nanowires. *ACS Catal.* **7**, 4467-4472 (2017).

506 24 Yin, Y., Alivisatos, A. P. Colloidal nanocrystal synthesis and the organic-inorganic
507 interface. *Nature* **437**, 664-670 (2005).

508 25 Zhuang, T.-T. *et al.* 1D colloidal hetero-nanomaterials with programmed
509 semiconductor morphology and metal location for enhancing solar energy conversion.
510 *Small*, **13**, 1602629 (2017).

511 26 Dinh, C.-T. *et al.* CO₂ electroreduction to ethylene via hydroxide-mediated copper
512 catalysis at an abrupt interface. *Science* **360**, 783-787 (2018).

513 27 Cheng, T., Xiao, H. & Goddard III, W. A. Nature of the active sites for CO reduction
514 on copper nanoparticles; suggestions for optimizing performance. *J. Am. Chem. Soc.*
515 **139**, 11642-11645 (2017).

516 28 Liu, X. *et al.* Understanding trends in electrochemical carbon dioxide reduction rates.
517 *Nat. Commun.* **8**, 15438 (2017).

518 29 Reske, R., Mistry, H., Behafarid, F., Roldan Cuenya, B., Strasser, P. Size effects in the
519 catalytic electroreduction of CO₂ on Cu nanoparticles. *J. Am. Chem. Soc.* **136**, 6978-

520 6986 (2014).

521 30 Huang, X. *et al.* Freestanding palladium nanosheets with plasmonic and catalytic
522 properties. *Nat. Nanotechnol.* **6**, 28-32 (2011).

523 31 Kang, Y., Ye, X., Murray, C. B. Size- and Shape-selective synthesis of metal
524 nanocrystals and nanowires using CO as a reducing agent. *Angew. Chem. Int. Ed.* **49**,
525 6156-6159 (2010).

526 32 Cui, C. *et al.* Carbon monoxide-assisted size confinement of bimetallic alloy
527 nanoparticles. *J. Am. Chem. Soc.* **136**, 4813-4816 (2014).

528 33 Kresse, G., Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy
529 calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169-11186 (1996).

530 34 Kresse, G., Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals
531 and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **6**, 15-50 (1996).

532 35 Kresse, G., Hafner, J. *Ab-Initio* Molecular-Dynamics Simulation of the Liquid-Metal
533 Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **49**, 14251-14269
534 (1994).

535 36 Kresse, G., Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **47**,
536 558-561 (1993).

537 37 Perdew, J. P., Burke, K., Ernzerhof, M. Generalized Gradient Approximation Made
538 Simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996).

539 38 Kresse, G., Joubert, D. From ultrasoft pseudopotentials to the projector augmented-
540 wave method. *Phys. Rev. B* **59**, 1758-1775 (1999).

541 39 Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953-17979 (1994).

542 40 Grimme, S., Antony, J., Ehrlich, S., Krieg, H. A consistent and accurate *ab initio*

543 parametrization of density functional dispersion correction (DFT-D) for the 94
544 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).

545 41 Grimme, S., Ehrlich, S., Goerigk, L. Effect of the damping function in dispersion
546 corrected density functional theory. *J. Comp. Chem.* **32**, 1456-1465 (2011).

547 42 Michaelides, A. *et al.* Identification of general linear relationships between activation
548 energies and enthalpy changes for dissociation reactions at surfaces. *J. Am. Chem. Soc.*
549 **125**, 3704-3705 (2003).

550 43 Liu, Z. P., Hu, P. General rules for predicting where a catalytic reaction should occur
551 on metal surfaces: A density functional theory study of C-H and C-O bond
552 breaking/making on flat, stepped, and kinked metal surfaces. *J. Am. Chem. Soc.* **125**,
553 1958-1967 (2003).

554 44 Alavi, A., Hu, P. J., Deutsch, T., Silvestrelli, P. L., Hutter, J. CO oxidation on Pt(111):
555 An *ab initio* density functional theory study. *Phys. Rev. Lett.* **80**, 3650-3653 (1998).

556 45 Montoya, J. H., Shi, C., Chan, K., Nørskov, J. K. Theoretical Insights into a CO
557 Dimerization Mechanism in CO₂ Electroreduction. *J. Phys. Chem. Lett.* **6**, 2032-2037
558 (2015).

559 46 van Duin, A. C. T. *et al.* Development and validation of a reaxFF reactive force field
560 for Cu cation/water interactions and copper metal/metal oxide/metal hydroxide
561 condensed phases. *J. Phys. Chem. A* **114**, 9507-9514 (2010).

562 47 Cheng, T., Xiao, H., Goddard, W. A. Full atomistic reaction mechanism with kinetics
563 for CO reduction on Cu(100) from *ab initio* molecular dynamics free energy calculation
564 at 298 K. *Proc. Natl. Acad. Sci.* **114**, 1795-1800 (2017).

565 48 Sundararaman, R., Goddard III, W. A. The charge-asymmetric nonlocally determined

566 local-electric (CANDLE) solvation model. *J. Chem. Phys.* **142**, 064107 (2015).

567 49 Xiao, H., Cheng, T., Goddard III, W. A. Atomistic mechanisms underlying selectivities
568 in C₁ and C₂ products from electrochemical reduction of CO on Cu(111). *J. Am. Chem.*
569 *Soc.* **139**, 130-136 (2017).

570 50 Sundararaman, R., Goddard II, W. A., Arias, T. A. Grand canonical electronic density-
571 functional theory: algorithms and applications to electrochemistry. *J. Chem. Phys.* **146**,
572 114104 (2017).

573 51 Sundararaman, R. *et al.* JDFTx: software for joint density-functional theory. *SoftwareX*
574 **6**, 278-284 (2017).

575 52 Ong, S. P. *et al.* Python Materials Genomics (pymatgen): A robust, open-source python
576 library for materials analysis. *Comp. Mater. Sci.* **68**, 314-319 (2013).

577 53 Verdaguer-Casadevall, A. *et al.* Probing the active surface sites for CO reduction on
578 oxide-derived electrocatalysts. *J. Am. Chem. Soc.* **137**, 9808-9811 (2015).

579 54 Millero, F. J., & Rabindra, N. R. A chemical equilibrium model for the carbonate
580 system in natural waters. *Croat. Chem. Acta* **70**, 1-38 (1997).

581 55 Millero, F. j., Graham, T. B., Huang, F., Bustos-Serrano, H., & Pierrot, D. Dissociation
582 constants of carbonic acid in seawater as a function of salinity and temperature. *Mar.*
583 *Chem.* **100**, 80-94 (2006).

584 56 Weisenberger, S., Schumpe, A. Estimation of gas solubilities in salt solutions at
585 temperatures from 273 K to 363 K. *AIChE J.* **42**, 298-300 (1996).

586 57 Mehrbach, C., Culberson, C. H., Hawley, J. E., Pytkowicz, R. M. Measurement of the
587 apparent dissociation constants of carbonic acid in seawater at atmospheric pressure.
588 *Limnol. Oceanogr.* **18**, 897-907 (1973).

- 589 58 Burdyny, T. *et al.* Nanomorphology-enhanced gas-evolution intensifies CO₂ reduction
590 electrochemistry. *ACS Sustainable Chem. Eng.* **5**, 4031-4040 (2017).
- 591 59 Ravel, B., Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
592 ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **12**, 537-541 (2005).
- 593 60 Li, J. *et al.* Revealing the Synergy of Mono/Bimetallic PdPt/TiO₂ Heterostructure for
594 Enhanced Photoresponse Performance *J. Phys. Chem.* **121**, 24861-24870 (2017).
- 595 61 Luc, W., Rosen, J., Jiao, F. An Ir-based anode for a practical CO₂ electrolyzer. *Catal.*
596 *Today* **288**, 79-94 (2017).

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624

625 **Author contributions**

626 E.H.S supervised the project. Y.W., and C.-T.D. designed the experiments. Y.W. carried out the
627 catalyst synthesis, electrochemical tests, electrocatalysis tests, and SEM measurements. Z.W.
628 performed DFT calculations. J.L. performed all the XAS measurements and analysed the results.
629 A.O. performed the tests in MEA electrolysers. M.G.K. prepared evaporated Cu seeds. Y.L. and
630 F.L. prepared sputtered Cu seeds. C.-S.T. performed TEM measurements and data analysis. A.S.
631 and C.M.G carried out the *operando* Raman measurements. M.C.L synthesised Cu nanocubes.
632 C.M. performed the local pH simulations. Y.W, H.Z, M.X.L., A.P. and A.J. performed GIWAXS
633 measurements and data analysis. A.P., and P.T. carried out the XPS measurements. All authors
634 discussed, commented on and revised the manuscript.

635

636 **Author information**

637 Reprints and permissions information is available at www.nature.com/reprints. The authors
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642

643 **Figures legends**

644 **Figure 1. Density functional theory calculations.** **a** Energy profiles of CO dimerisation on
645 Cu(111), Cu(100), and Cu(111). **b** Surface energy changes with the surface coverage of CO₂RR
646 (assuming same coverages for all the 4 intermediates) and HER intermediates. **c** Adsorption
647 energies of four intermediates on three facets of Cu. Wulff construction clusters of Cu **d** without
648 adsorption and with adsorption of **e-f** CO₂RR and **g-h** HER intermediates.

649 **Figure 2. Intermediate adsorption influences Cu clustering.** **a** Schematic illustration of
650 intermediate adsorption controlling which Cu facets are exposed. The chemisorbed intermediates
651 (*e.g.* CO*) act as a capping agent, leading to a high portion of Cu(100) in the forming catalyst. **b**
652 The time-dependent morphological change of Cu-CO₂ (upper arrows) and Cu-HER (lower arrows)
653 during electrodepositions at 400 mA cm⁻² in 1 M KOH containing the Cu precursor. The scale bars
654 are 100 nm for the evaporated Cu seeds and 10 sec samples, 200 nm for the 60 sec Cu samples. **c**
655 2D GIWAXS patterns of the Cu-CO₂ catalysts with respect to deposition time.

656 **Figure 3. Analysis of the catalyst formation and the surface structures.** **a, b** Fourier
657 transformed *operando* hXAS spectra of the formation of intermediate Cu-CO₂ and Cu-HER with

658 respect to time at 400 mA cm^{-2} in 1 M KOH containing the Cu precursor. **c** The ratio of metallic
659 Cu to Cu precursor over the course of catalyst formation. **d** Charge distribution during the
660 electrochemical catalyst synthesis. **e, f** The surface area and ratio of Cu(100) and Cu(111) facets
661 quantified by OH^- electroadsorption. **g** Local pH modelling during catalyst growth. Error bars in **e**
662 and **f** correspond to the standard deviation of 3 independent measurements.

663 **Figure 4. CO₂ electroreduction performance.** **a** j - V plots of C_2H_4 and C_{2+} product partial current
664 density vs. potential (with 90% iR correction) on Cu-CO₂-60 and Cu-HER-20 in 7 M KOH. **b**
665 Electrochemical active surface area (ECSA) normalised C_2H_4 and C_{2+} product partial current
666 density. **c** Faradaic efficiency for each CO₂RR product and H_2 on Cu-CO₂-60 at various potential
667 ranging from -0.38 to -0.74 V vs. RHE in 7 M KOH. **d** Comparison of C_2H_4 and C_{2+} full-cell
668 power conversion efficiency (PCE) on Cu-CO₂-60 and Cu-HER-20 in the current density range of
669 130 to 780 mA cm^{-2} without iR correction in 7 M KOH. **e** Comparison of C_2H_4 , C_{2+} and CO
670 Faradaic efficiency on Cu-CO₂-60 and Cu-HER-20 catalysts in 7 M KOH. **f** Stability obtained at
671 -3.7 V (without iR correction) in a 5 cm^2 MEA electrolyser. The anolyte was 0.15 M KHCO_3 .
672 Error bars in **c-e** correspond to the standard deviation of 3 independent measurements.