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Bio-inspired hydrophobicity promotes CO₂ reduction on a Cu surface

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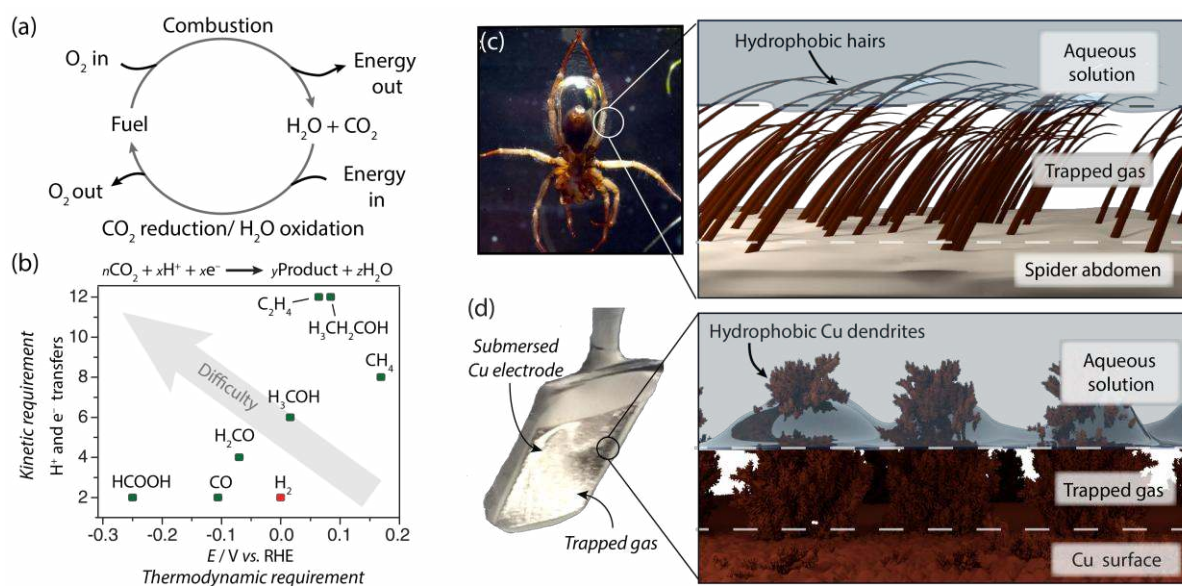
Abstract

Aqueous electrocatalytic reduction of CO₂ into alcohol and hydrocarbon fuels presents a sustainable route towards energy-rich chemical feedstocks. Cu is the only material able to catalyse the substantial formation of multi-carbon products (C₂/C₃), however competing proton reduction to hydrogen is an ever-present drain on selectivity. Herein, a superhydrophobic surface was generated by 1-octadecanethiol treatment of hierarchically structured Cu dendrites, inspired by the structure of gas-trapping cuticles on subaquatic spiders. The hydrophobic electrode attained 56% Faradaic efficiency for ethylene and 17% for ethanol production at neutral pH, compared to 9% and 4% on a hydrophilic, wettable equivalent. These observations are assigned to trapped gases at the hydrophobic Cu surface, which increase the concentration of CO₂ at the electrode|solution interface and consequently increase CO₂ reduction selectivity. Hydrophobicity is thus proposed as a governing factor in CO₂ reduction selectivity and can help explain trends seen on previously reported electrocatalysts.

23 Introduction

24 Figure 1a shows a theorized sustainable energy cycle propagated through the storage of renewable
25 energies as CO₂-derived fuel. Such a process would provide relief to numerous environmental
26 concerns, both current and impending,¹ and curtail dependency on fossil fuel. The cycle is driven
27 through aqueous CO₂ electrolysis, wherein electrons and protons from water oxidation are used in
28 the reduction of CO₂ to hydrocarbons and alcohols. Contemporary research now seeks an efficient
29 and inexpensive catalyst for this reduction.

30 Cu remains the paradigmatic surface for CO₂ reduction, with the ability to produce C₂ and C₃ species,
31 such as ethylene, ethanol and *n*-propanol.² Formation of such products has various thermodynamic
32 and kinetic demands and requires multiple proton and electron transfers (Figure 1b). These are
33 readily facilitated in water, however proton reduction to H₂ is more facile than CO₂ reduction (red
34 dot, Figure 1b).³ Water is also in substantial excess, due to the low solubility of CO₂ (33 mM at room
35 temperature),⁴ and as a result Cu electrodes will typically lose >30% Faradaic efficiency (FE) to H₂
36 production.⁵



37

38 **Figure 1 | CO₂ reduction as a source of sustainable fuel and an introduction to the 'plastron effect'.**

39 (a) The generation of renewable fuel through CO₂ reduction and H₂O oxidation. (b) The
 40 thermodynamic vs. kinetic requirement of various CO₂-reduction reactions.³ The plotted values are
 41 based on the reaction equation given above the graph, made stoichiometric according to the
 42 product composition. (c, d) The 'plastron effect'; use of a hydrophobic surface to trap a layer of gas
 43 between the solution|solid interface. This is illustrated on a naturally occurring diving bell spider for
 44 subaquatic breathing in (c), and a hydrophobic dendritic Cu surface for aqueous CO₂ reduction in (d).
 45 Photo of the diving bell spider was adapted from reference 6 with permission by The Company of
 46 Biologists.

47 Improving selectivity towards CO₂ reduction, particularly towards products containing multiple
 48 carbons, remains a major priority in this field. Hitherto implemented strategies have included
 49 surface modifications,^{7,8} adjusting surface pH⁹ and the use of non-aqueous solvents,¹⁰ however the
 50 most effective approaches can be summarised into three categories: (1) *Morphology*: nanowires,¹¹
 51 nanowhiskers,¹² nanoparticles,¹³ nanoprisms¹⁴ and nanodendrites^{15,16} present high catalytic surface
 52 areas that have shown appreciable selectivity. (2) *Carbon supports*: carbon frameworks and gas
 53 diffusion layers loaded with Cu have shown generation of C₂ products up to 80%.¹⁷⁻²⁰ (3) *Oxide*

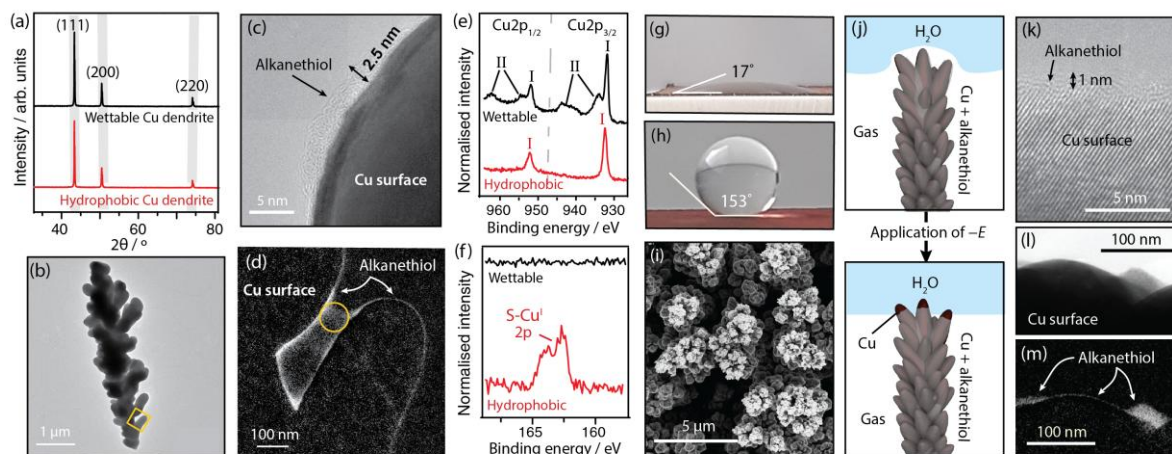
54 *layers*: Surface oxides serve as precursors to active Cu catalysts, leading to efficiencies as high as 60%
55 for ethylene formation.^{21–23}

56 These strategies may also increase the hydrophobicity of an electrode, however this is rarely
57 discussed as a determinant on selectivity.² Submerged hydrophobic surfaces trap appreciable
58 amounts of gas at the nanoscale,^{24,25} and even at the microscale if the Cassie-Baxter regime is
59 reached,²⁶ allowing trapped CO₂ to accumulate at the Cu|solution interface. Recent reports have
60 exploited gas|electrode|solution triple-phase boundaries to increase the CO₂ reduction activity of
61 Cu on gas diffusion electrodes with hydrophobic polytetrafluoroethylene layers,^{19,20} however it is
62 difficult to assign this enhancement solely to hydrophobicity over other factors, such as their
63 porosity and increased mass transport.²⁷ Herein, we thus study hydrophobicity as an isolated
64 parameter on a Cu surface to establish its role in promoting gas-trapping and consequently selective
65 CO₂ reduction.

66 Taking nature as inspiration, we introduce hydrophobicity based on the ‘plastron effect’ used by
67 aquatic arachnids, such as the diving bell spider in Figure 1c.²⁸ These plastrons are composed of
68 hydrophobic hairs that trap air, thereby allowing the spider to respire underwater. The gas-trapping
69 phenomenon occurs when hydrophobic surface chemistry is presented on the microscale and
70 nanoscale simultaneously.²⁹ We achieve an analogous multi-scale hydrophobic surface through
71 modification of hierarchically structured dendritic Cu with a monolayer of waxy alkanethiol. The
72 resultant electrode visibly traps CO₂ gas at the electrolyte|electrode interface, forming a triple-
73 phase boundary (Figure 1d). As a result, H₂ evolution was substantially lowered in CO₂-saturated
74 electrolyte compared to an unmodified hydrophilic equivalent, from 71% FE to 10%, while CO₂
75 reduction increased from 24% to 86%, of which C₂ products comprised 74%. The drastically
76 increased CO₂ concentration at the hydrophobic Cu surface was identified as key to the increased
77 catalytic selectivity, which we propose is present in other reported systems.

78 **Preparation and characterization of the hydrophobic Cu dendrite**

79 Cu dendrite scaffolds were grown using previously reported aqueous electrodeposition procedures,
80 forming hierarchical architectures with both micro and nanoscale features (Supplementary Figure
81 1).^{30,31} Powder X-ray diffraction (PXRD) measurements confirmed the structure to be metallic Cu
82 (Figure 2a), although a small amount of Cu₂O was visible (Supplementary Figure 2). The hydrophobic
83 treatment was undertaken by submersing the dendritic Cu into liquid 1-octadecanethiol at 60°C for
84 15 minutes to form an alkanethiol layer. Transmission electron microscopy (TEM) of the dendritic Cu
85 after treatment confirmed the nanostructure remained intact (Figure 2b) and was coated with a
86 monolayer between 2-3 nm in thickness (Figure 2c), consistent with a surface of 1-octadecanethiol
87 molecules bound upright (chain length is 2.3 nm between surface-bound S and terminal C). The
88 carbonaceous nature of the coating was confirmed by energy-filtered transmission electron
89 microscopy (EF-TEM) at the C-K edge (Figure 2d). X-ray energy-dispersive spectroscopy (XEDS) of the
90 area indicated in Figure 2d displayed S and C environments within the layer (Supplementary Figure
91 3) and no carbonaceous layer was present on untreated Cu dendrite (Supplementary Figure 4).



92

93 **Figure 2 | Characterization of the electrode surface.** (a) PXRD of Cu dendrite with and without
 94 hydrophobic surface treatment. (b,c) TEM and high-resolution TEM images of a 1-octadecanethiol-
 95 treated Cu dendrite showing the layer of alkanethiol attached to the Cu surface, the yellow square in
 96 (b) indicates the area observed in (d). (d) EF-TEM using the C-K edge of an alkanethiol-treated Cu
 97 dendrite surface, the yellow circle indicates the area used for TEM-XEDS analysis in Supplementary
 98 Figure 3. (e) XPS spectra in the Cu regions showing peaks assigned to I and II oxidation states. (f) XPS
 99 spectra showing the presence of S on the alkanethiol-treated Cu surface. (g) and (h) show contact
 100 angle measurements of the *wettable* and *hydrophobic dendrite* respectively. (i) SEM image of the
 101 *hydrophobic dendrite* after 2.5 hours of applied cathodic potential in 0.1 M CsHCO₃ (CO₂ saturated,
 102 pH 6.8, room temperature) with a CO₂ flow of 10 ml min⁻¹. (j) Illustration of the *hydrophobic dendrite*
 103 gaining a solid|liquid interface upon application of negative potential. (k), (l) and (m) show the
 104 equivalent images from (c) and (d) after electrolysis in 0.1 M CsHCO₃ (CO₂ saturated, pH 6.8, room
 105 temperature) with a CO₂ flow of 10 ml min⁻¹ for 30 minutes at -1.4 V vs. RHE.

106 The alkanethiolation removes Cu oxide from the surface, leaving Cu-S bonds, as illustrated by X-ray
 107 photoelectron spectroscopy (XPS, Figure 2e).³² Before treatment, the Cu dendrite shows
 108 environments consistent with Cu₂O at 932.5/952.4 eV and Cu^{II}O at 934.6/955.0 eV and 942.8/962.7
 109 eV. Analysis of the Cu LMM Auger showed no evidence of metallic Cu⁰ at the surface (Supplementary
 110 Figure 5).³³ After reaction with 1-octadecanethiol all Cu^{II} environments are removed, forming a

111 surface of Cu^I (Figure 2e and Supplementary Table 1), and a new S 2p peak is visible at 163.0 eV,
112 consistent with Cu–S bonds (Figure 2f).³³ The presence of the alkanethiol layer was further
113 confirmed through attenuated total reflectance infrared (ATR-IR) spectroscopy (Supplementary
114 Figure 6).

115 Contact angle measurements illustrated that without 1-octadecanethiol modification the Cu
116 dendrite surface is hydrophilic; a deposited water droplet sat with a contact angle of 17° (Figure 2g).
117 The alkanethiol-treated electrode is not susceptible to the same wetting, with a drastically increased
118 contact angle of 153° (Figure 2h), falling into the regime of superhydrophobicity where trapped
119 gases are expected on both the micro and nanoscale.³⁴ For clarity, these electrodes will be referred
120 to as the *wettable dendrite* and *hydrophobic dendrite* for the hydrophilic and hydrophobic dendritic
121 Cu surfaces, respectively.

122 Initial characterization of the dendrites' electrochemical properties revealed a significant decrease in
123 electrochemically-active surface area (ECSA) upon introduction of hydrophobicity. Capacitance
124 measurements of the *hydrophobic dendrite* indicated the surface had very limited electrical contact
125 with the solution, displaying an ECSA of $3 \times 10^{-3} \text{ cm}^2 \text{ cm}^{-2}$, much lower than the $21 \text{ cm}^2 \text{ cm}^{-2}$ obtained
126 on the *wettable dendrite* (where $\text{cm}^2 \text{ cm}^{-2}$ indicates the ECSA of the dendritic electrode vs. that of a
127 flat electrode, Supplementary Figure 7). BET analysis through Kr adsorption measurements revealed
128 that the ECSA disparity is not from a loss in geometric surface area upon alkanethiol treatment, as
129 these remained similar: $90 \text{ cm}^2 \text{ cm}^{-2}$ and $92 \text{ cm}^2 \text{ cm}^{-2}$ for the *wettable dendrite* and *hydrophobic*
130 *dendrite*, respectively (where $\text{cm}^2 \text{ cm}^{-2}$ indicates the BET-derived surface area of the dendritic
131 electrode vs. the area of a flat electrode). The decrease in ECSA is therefore induced by gas trapping
132 at the interface between the *hydrophobic dendrite* and solution, as illustrated in Figure 2j (top
133 panel).

134 Upon application of reducing potential over 60 minutes in aqueous electrolyte (0.1 M CsHCO₃, CO₂
135 saturated) the ECSA of the *hydrophobic dendrite* electrode increased to $0.2 \text{ cm}^2 \text{ cm}^{-2}$ (Supplementary

136 Figure 7b), which can also be seen through linear sweep voltammetry (LSV, Supplementary Figure 8).
137 This increase is assigned to loss of 1% of alkanethiol when reaching labile Cu^0 oxidation states, as the
138 ECSA is 1% of the *wettable dendrite* ($21 \text{ cm}^2 \text{ cm}^{-2}$). This loss occurs at the point of the electrode
139 closest to the electrolyte, as suggested through SEM images that show brighter Cu regions at the tips
140 of the dendrite (Figure 2i and Supplementary Figure 9). Similar activation has been documented on
141 other hydrophobic electrodes.²⁶ The *hydrophobic dendrite* therefore requires an initial application of
142 potential to generate a stable liquid|electrode|gas triple-phase boundary at the top of the dendrite
143 where electrochemical reactions take place, as illustrated in Figure 2j. This activation was monitored
144 through one day of repeated LSV scans, wherein the current at -1.4 V vs. RHE stabilised 3-5 times
145 lower than that of the *wettable* equivalent (Supplementary Figure 10).

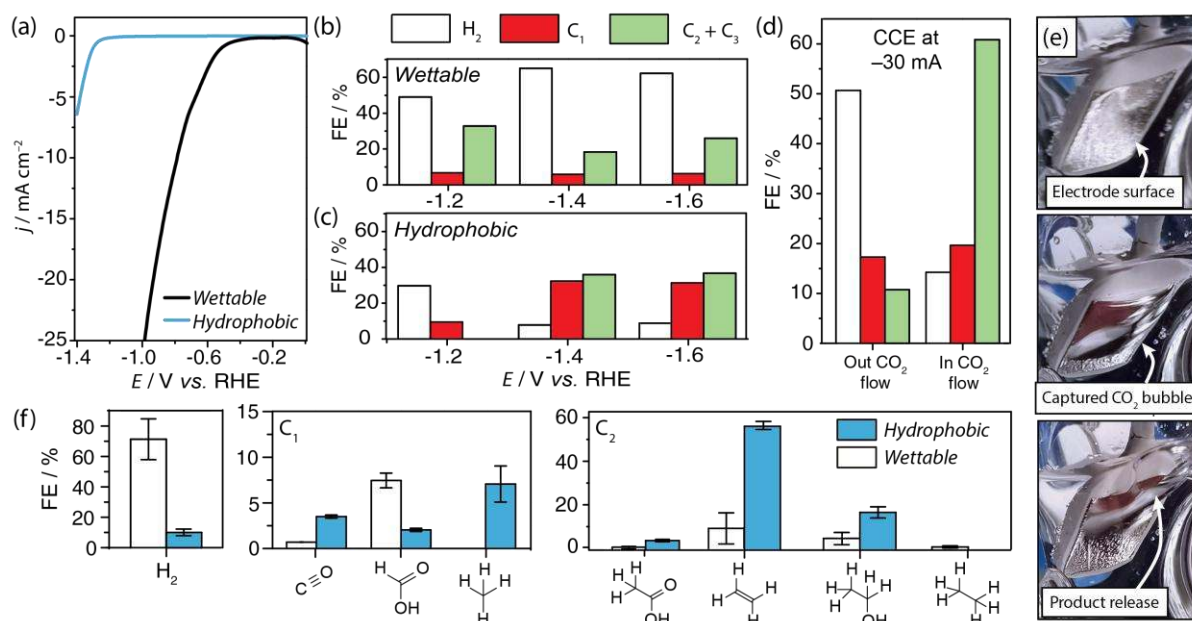
146 To ensure the *hydrophobic dendrite* maintained its hydrophobicity upon application of potential,
147 contact angle measurements were carried out after 12 hours of electrolysis at -15 mA cm^{-2}
148 (Supplementary Figure 11). The resultant angle of 143° indicated that the hydrophobic surface
149 treatment was not removed. Furthermore, $^1\text{H-NMR}$ spectroscopy showed no 1-octadecanethiol
150 within the electrolyte after electrolysis (Supplementary Figure 12), although some dissolved
151 alkanethiol may be present below the detection limit of the experiment. XPS analysis before and
152 after electrolysis showed similar ratios of Cu:S on the sample (Supplementary Table 2), however a
153 portion of the 1-octadecanethiol is converted into alkanesulfonates (Supplementary Figure 5c, 168.6
154 eV), which is known to occur upon exposure of alkanethiol monolayers to air.³⁵ Nevertheless, HR-
155 TEM and EF-TEM at the C-K edge (Figure 2k, l and m) do show the monolayer loses density and that
156 large carbonaceous deposits are present on the nanostructure after electrolysis. We thus propose
157 that the majority of the C_{18} -alkane chain does not dissolve from the electrode surface, but a portion
158 may move across the surface to form aliphatic agglomerates, explaining how the surface maintains
159 hydrophobicity whilst allowing current to pass.

160

161 **Comparing the catalytic activity of *hydrophobic* and *wettable* Cu dendrites**

162 Figure 3a shows the LSV of the *hydrophobic dendrite* and equivalent *wettable dendrite* in CO₂-
163 saturated CsHCO₃ electrolyte (0.1 M, pH 6.8). Cs⁺ cations were used due to their superior ability to
164 buffer pH changes at the electrode|solution interface during electrolysis compared to other
165 cations,³⁶ thereby eliminating changes in surface pH as a determinant on selectivity. To reach a
166 current of -5 mA cm^{-2} , the *wettable dendrite* required a potential of -0.68 V vs. RHE , while the
167 *hydrophobic dendrite* required a more negative potential of -1.38 V vs. RHE . The lowered current at
168 a given potential can be partly explained by the significantly lower ECSA of the *hydrophobic dendrite*
169 but should also be assigned to the lack of proton reduction activity exhibited by this electrode.
170 Controlled potential electrolysis (CPE) confirmed this, as even at highly cathodic potentials the
171 *hydrophobic dendrite* has vastly lowered H₂ evolution activity: At -1.6 V vs. RHE , the *hydrophobic*
172 *dendrite* displays H₂ evolution activity below 10%, while the *wettable* displays values above 60%
173 (Figure 3b and 3c). In place of H₂ evolution, the *hydrophobic dendrite* presents superior CO₂
174 reduction efficiency for both C₁ and C₂ products (Figures 3b and c), except at -1.2 V vs. RHE , at which
175 point current was too low for detection of C₂ products (Supplementary Figure 13). To confirm that
176 the optimal CO₂ reduction selectivity on the *wettable dendrite* was not attained at lower potentials,
177 CPE at less cathodic biases was carried out (Supplementary Figure 14).

178 During electrolysis, CO₂ was introduced as a stream of gas from the bottom of the cell (illustration
179 provided in Supplementary Figure 15). When using the *hydrophobic dendrite*, the capture and
180 retention of the gaseous CO₂ stream was observed, causing a bubble to engulf the entire electrode
181 surface (Figure 3e, Supplementary Video 1). If the gas flow was not incident to the *hydrophobic*
182 *dendrite* to constantly refill this bubble, formation of C₁ and C₂ products was severely reduced
183 (Figure 3d), indicating that the captured CO₂ at the electrode surface is the predominant substrate of
184 the *hydrophobic dendrite*. At lower partial pressures of CO₂ in the gas stream, the CO₂ reduction rate
185 dropped accordingly (Supplementary Figure 16).



186

187 **Figure 3 | The effect of hydrophobicity on electrocatalytic CO₂ reduction.** (a) Linear sweep
 188 voltammogram of the *wettable* and *hydrophobic dendrite* ($v = 20 \text{ mV s}^{-1}$). (b,c) Controlled potential
 189 electrolysis product FEs from the *wettable* and *hydrophobic dendrite* at various potentials. (d)
 190 Product formation FE at the *hydrophobic dendrite* after controlled current electrolysis at -30 mA cm^{-2}
 191 ² inside of and outside of the CO₂ flow at 2.5 ml min^{-1} . (e) Photos of the capture and release of a CO₂
 192 bubble on the *hydrophobic dendrite* surface. (f) Product formation FEs at the *hydrophobic vs.*
 193 *wettable dendrite* when passing an overall current density of -30 mA cm^{-2} . In all cases the
 194 electrolyte was CO₂-saturated CsHCO₃ (0.1 M, pH 6.8, room temperature). Unless stated otherwise, a
 195 CO₂ flow rate of 5 ml min^{-1} was used throughout electrolysis. Gaseous products were analysed after
 196 10 and 30 minutes and liquid products after 35 minutes of electrolysis. Error bars are based on the
 197 standard deviation of 3 individual measurements.

198 Control experiments without hierarchical Cu surface morphology were undertaken using a flat Cu
 199 electrode treated with 1-octadecanethiol. Neither gas trapping nor large contact angles were
 200 observed (contact angle: 90° , Supplementary Figure 17) and the electrode did not show a drastic
 201 increase in selectivity for CO₂ reduction compared to a pristine Cu electrode (see Supplementary

202 Table 3). The combination of hydrophobic treatment and hierarchical morphology therefore
203 facilitate gas trapping.

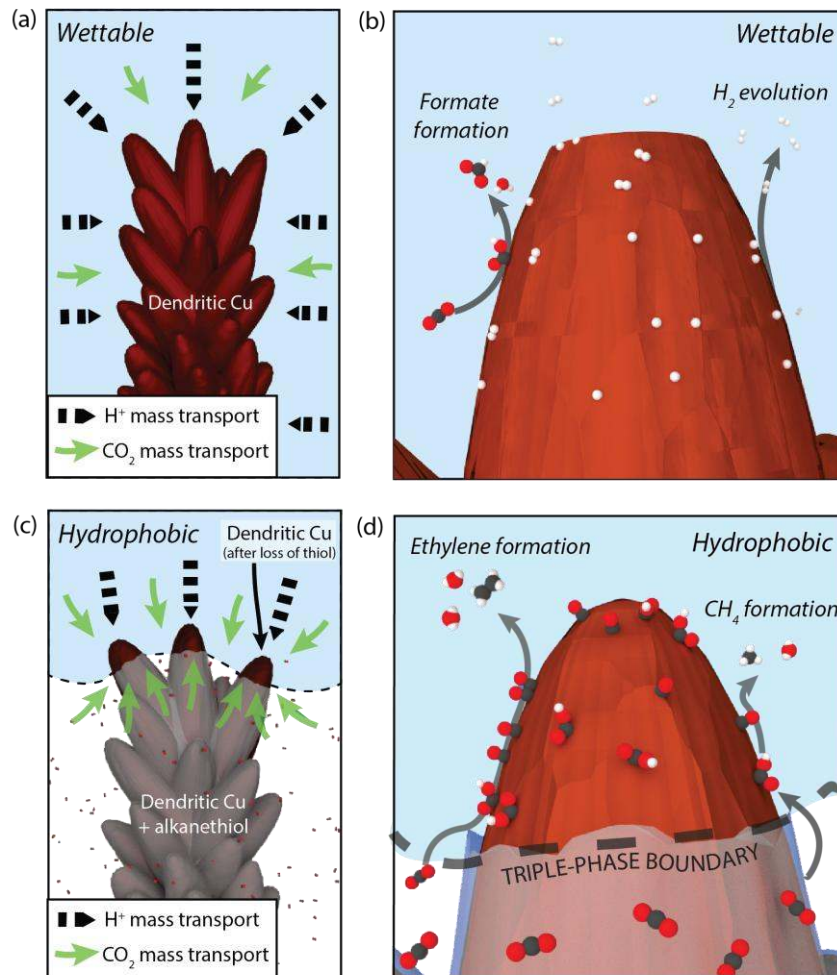
204 Controlled current electrolysis (CCE) at -30 mA cm^{-2} for the two Cu dendrites was undertaken to
205 understand their selectivity while exerting the same mass transport pressure on the solution (Figure
206 3f). The *hydrophobic dendrite* required a higher cathodic applied potential to reach -30 mA cm^{-2} ($E =$
207 $-1.1 \text{ V} - 1.5 \text{ V}$ vs. RHE, IR corrected), but had much higher selectivity for CO_2 reduction: CO (3%
208 *hydrophobic*; 1% *wettable*), methane (7% *hydrophobic*; 0% *wettable*), ethylene (56% *hydrophobic*;
209 9% *wettable*) ethanol (17% *hydrophobic*; 4% *wettable*) and acetic acid (1% *hydrophobic*; 0.4%
210 *wettable*). In contrast, the *wettable dendrite* required a less cathodic potential to reach -30 mA cm^{-2}
211 ($E = -0.8 \text{ V} - 1.0 \text{ V}$ vs. RHE, IR corrected) as it carried out mostly H_2 evolution (10% *hydrophobic*; 71%
212 *wettable*), however it also showed the highest selectivity for formate (2% *hydrophobic*; 7%
213 *wettable*), ethane (0 % *hydrophobic*; 0.5% *wettable*) and *n*-propanol formation (0 % *hydrophobic*; 2%
214 *wettable, not pictured*). The *hydrophobic dendrite's* selectivity for C_2 products (74% total) rivals that
215 of state-of-the-art gas-diffusion electrode systems in alkaline conditions (66% ethylene, 11%
216 ethanol, 6% acetate),²⁰ however the achieved currents and overpotentials are poorer in the neutral
217 pH electrolyte.

218 Extended CO_2 reduction on the *hydrophobic dendrite* over 5 hours at a controlled current density of
219 -30 mA cm^{-2} showed a high ethylene and ethanol efficiency of 30%-55% and 12-22%, respectively
220 (Supplementary Figure 18). During the experiment, C_2 product formation was again sensitive to
221 interaction with inbound CO_2 : drops in C_2 production were observed when CO_2 flow fell out of line
222 with the electrode surface (Supplementary Figure 18, as indicated), however the stream could be
223 adjusted to restore activity. Despite this, a gradual decrease in C_2 production activity was apparent,
224 coinciding with destruction of regions of the dendrite surface (Supplementary Figure 19). This
225 destruction is assigned to the mechanical stress imposed by continual collision of bubbles with the
226 electrode surface. Engineering-efforts using vapor-fed electrodes to relieve this stress are ongoing.

227 The gas-trapping of the *hydrophobic dendrite* could also be exploited for CO reduction, where low
228 substrate concentration is particularly problematic ($[\text{CO}] = 1 \text{ mM}$ at 1 atm at room temperature).⁴
229 CCE at -30 mA cm^{-2} in a CO flow on the *hydrophobic dendrite* showed 23.5% FE for CO reduction,
230 compared to 0.88% on the *wettable dendrite* in 1 M KOH (Supplementary Figure 20, Supplementary
231 Table 4). Further experiments showed that C_2 selectivity during CO reduction on the *hydrophobic*
232 *dendrite* is greatly promoted in pH 14 solution (1 M KOH $\text{C}_1:\text{C}_2$ ratio = 1:24), in comparison to pH 7
233 (0.1 M KPi $\text{C}_1:\text{C}_2$ ratio = 1:1.7, Supplementary Figure 20). Additional CO_2 reduction experiments in
234 more acidic conditions (pH 4.6, CO_2 -saturated 0.1 M KPi) similarly showed a decrease in C_2 selectivity
235 ($\text{C}_1:\text{C}_2$ ratio = 1:0.8, Supplementary Figure 21, Supplementary Table 5). Formic acid reduction
236 experiments produced only H_2 , excluding it as a source of C_2 products (Supplementary Table 6).

237 Explanation of the reported data is given in Figure 4a-d, which show a single strand of the dendritic
238 Cu in its *wettable* (Figure 4a and b) and *hydrophobic* form (Figure 4c and d). Since highly cathodic
239 potentials are applied, it is assumed that both the dendrites react rapidly with either H^+ or CO_2 to
240 form Cu-H^* or Cu-COOH^* intermediates respectively,³⁷ and therefore selectivity is controlled by
241 mass transport of the two substrates. The *wettable dendrite* has a large liquid|electrode interface
242 therefore only dissolved H^+/CO_2 are substrates (Figure 4a). A higher proportion of Cu-H^* groups is
243 then expected, which promotes H_2 formation (Figure 4b). On the other hand, the electrolyte is
244 pushed away from the *hydrophobic dendrite* Cu surface, forming an electrolyte|solid|gas triple-
245 phase boundary at the electrode (Figure 4c). CO_2 mass transport is then omnidirectional, while H^+
246 comes unilaterally from bulk solution, which drastically increases the local CO_2 concentration. The
247 surface concentration of Cu-COOH^* and the subsequently formed Cu-CO^* is then greatly increased
248 over Cu-H^* . This promotes C-C coupling and therefore the efficiency for C_2 products is increased
249 (Figure 4d). Reduction of CO without coupling is also possible, explaining the enhanced CH_4
250 production. Based on the presented CO reduction experiments, the selectivity for C_2 over CH_4 can be
251 increased with high solution pH, corroborating recent reports that C_2 formation at high overpotential

252 is dependent on high concentrations of Cu-CO^* , while CH_4 formation requires a rate-limiting
253 electron-proton transfer to a Cu-CHOH^* intermediate.³⁸



254

255 **Figure 4 | The proposed role of hydrophobicity in promoting CO_2 reduction over proton reduction.**

256 (a,b) The *wettable dendrite* under operation, showing reactant mass transport and product
257 formation on the electrode surface. (c, d) The operation of the *hydrophobic dendrite*, illustrating the
258 enhanced CO_2 mass transport from the triple-phase boundary between electrolyte, electrode and
259 gaseous CO_2 and the resultant formation of key products on the surface.

260 Perhaps more interesting are the products from CO_2 reduction produced solely on the *wettable*
261 *dendrite*: ethane and *n*-propanol, albeit in small quantities (below 5%). The lack of these products on
262 the *hydrophobic dendrite*, as well as other highly efficient C_2 -forming electrodes,²⁰ suggests that

263 hydrogen transfer is a rate limiting step in their formation and therefore they require a high
264 concentration of Cu-H*. This is supported by recent reports that show high efficiencies for CO₂
265 reduction to *n*-propanol with relatively high H₂-evolution activity³⁹ and also reports of ethane
266 formation on surfaces that generate large quantities of H₂.⁴⁰

267 The presented experiments led us to consider other reported catalysts for C₂ product formation,
268 which have been traditionally Cu oxides.²³ Many explanations for their activity are available, but we
269 hypothesize that the combination of nanostructured surfaces with hydrophobic Cu₂O⁴¹ creates
270 similar gaseous voids that trap CO₂ to create an electrolyte|electrode|gas triple-phase boundary.
271 Regions not in contact with electrolyte solution on these surfaces would explain why oxides are still
272 spectroscopically visible *in operando*,¹² despite their expected removal at cathodic potential.⁴² It may
273 also explain the low long-term stability of such surfaces, as removal of the oxides increases surface
274 wettability. Further support for this concept is illustrated by stable C₂ production on gas-diffusion
275 electrodes,²⁰ whose hydrophobicity is not as susceptible to reduction and as such maintain their
276 electrolyte|electrode|gas interfaces.

277

278 **Conclusion**

279 In summary, a hydrophobic coating of long-chain alkanethiols on dendritic Cu, with no further
280 modification, leads to a drastic increase in CO₂ reduction selectivity. The difference is a result of a
281 plastron effect; a gaseous layer trapped at the surface of the electrode that increases the local CO₂
282 concentration, allowing the Cu dendrite to match the high selectivity for C₂ products reported on Cu-
283 loaded gas-diffusion electrodes.²⁰ In the present form, the electrode suffers from some drawbacks
284 for implementation in technological devices and future work will focus on promoting stable
285 hydrophobicity on high-surface-area microporous electrodes to further increase activity.

286 We conclude that hydrophobicity, and the resultant gaseous voids that it introduces, is thus a
287 governing factor of CO₂ reduction selectivity on Cu and should be considered in the future design
288 and understanding of electrocatalytic surfaces for both CO₂ and CO reduction.

289 **Methods**

290 **General:** SEM images were performed on a SU-70 Hitachi FEGSEM fitted with an X-Max 50 mm²
291 Oxford EDX spectrometer. PXRD was performed in Bragg-Brentano geometry using a BRUKER D8
292 Advance diffractometer with Cu K α radiation ($\lambda K\alpha_1=1.54056$ Å, $\lambda K\alpha_2=1.54439$ Å) and a Lynxeye XE
293 detector. Contact angle measurements were made on a slow-motion video camera with 15 μ l of
294 H₂O. XPS spectra were performed using a Thermo ESCALAB 250 X-ray photoelectron spectrometer
295 with a monochromatic Al-K α X-ray source ($h\nu=1486.6$ eV).

296 **Preparation of Cu dendrites:** Square Cu surfaces of 1 cm² surface area were prepared from a Cu
297 plate (GoodFellow, 99.999%, 1 mm thickness) that had its sides, back and backside electrical contact
298 encased in epoxy resin (Loctite, Henkel). The surface was polished mechanically using alumina
299 micropolish on a polishing cloth (3 μ m, Struers) followed by copious rinsing in water. Dendrite
300 deposition was subsequently undertaken by applying -0.5 A cm⁻² to the electrode for 120 s in a
301 solution containing 0.1 M CuSO₄·5H₂O (99.9%, Sigma Aldrich) in 1.5 M H₂SO₄ (Sigma Aldrich)
302 followed by rinsing under a gentle stream of water, then acetone. The electrode was then dried
303 under a stream of air.

304 **Alkanethiol deposition:** Application of 1-octadecanethiol (Sigma, 98%) was undertaken by first
305 melting the waxy solid under vacuum at 60 °C. The electrode to be treated was then submerged into
306 the liquid under Ar and left for 15 minutes at 60 °C. After this point the electrode was moved to a
307 solution of ethyl acetate at 60 °C to remove excess 1-octadecanethiol and allowed to dry in ambient
308 conditions.

309 **Electrocatalytic analysis:** Electrochemical analysis was carried out in an air-tight two compartment
310 electrochemical cell separated by a Nafion membrane (Alfa Aesar, N115) or bipolar membrane (Fuel
311 cell store, Fumasep FBM). The counter electrode was a Pt wire (GoodFellow) and the reference a
312 Ag/AgCl wire in KCl (3 M KCl, palmsens). The electrolyte was deaerated/saturated with CO₂/CO/Ar
313 before each experiment by bubbling CO₂ (≥ 99.998%, Linde), CO (Linde) or Ar (Linde) for at least 10
314 minutes.

315 During electrolysis the electrodes were placed at a 45° incidence to the CO₂ inlet, as this ensured all
316 bubbles of CO₂ from the bottom of the vessel would collide with the electrode surface. CO₂ was
317 flowed through the cathode compartment of the cell using a mass flow controller (Brooks
318 Instruments) and the solution was stirred. The headspace was connected to a gas chromatograph
319 (GC, discussed below) and was typically sampled at 10 and 30 minutes. The liquid phase was
320 analysed for products by ¹H-NMR after 35 minutes (see below). Faradaic efficiency was calculated
321 based on the time before injection that was required to fill the GC injector sample loops (1 mL). This
322 is summarised in Equation 1.

323

$$324 \quad \text{Faradaic efficiency (\%)} = \frac{n_{\text{product}} \times n_{\text{electrons}} \times F}{(Q_{t=0} - Q_{t=x})} \times 100 \quad \text{Equation 1}$$

325

326 Where n_{product} is the product measured (mol), $n_{\text{electrons}}$ is the number of electrons to make said
327 product from CO₂/H₂O or CO/H₂O, F is the Faraday constant (C mol⁻¹), $Q_{t=0}$ is the charge passed at the
328 point of injection (C) and $Q_{t=x}$ is the charge passed at x seconds before injection, (x being the time
329 required to fill the GC sample loop based on sample loop size and gas flow rate, C).

330 During LSVs the electrode was placed outside of the CO₂ inlet, no stirring was applied and CO₂ flow
331 was decreased to 0.2 ml min⁻¹.

332

333 Potentials were converted to the Reversible Hydrogen Electrode (RHE) using the relationship: E
334 (RHE) = E (Ag/AgCl) + 0.197 + (pH × 0.059). IR-drop correction of the potentials applied during
335 controlled current electrolysis was undertaken manually using the resistance measured immediately
336 after electrolysis was completed. The reported potentials are those measured at the time point of
337 GC analysis (typically 10 or 30 minutes). IR-drop correction was not applied during controlled
338 potential electrolysis, LSVs or CVs.

339 **Electrochemically active surface area measurements:** Electrochemically active surface area was
340 measured through the capacitance of the electrodes in a 0.1 M solution of CsHCO₃ (Sigma, 99.9%)
341 saturated with CO₂. Capacitance was measured by analysis of the electrode cyclic voltammogram at
342 –0.15 V vs. the standard hydrogen electrode (SHE) using Equation 2:

343
$$\frac{i_a - i_c}{2} = Cv$$
 Equation 2

344 Where C is the capacitance (F), i_a is the anodic current at –0.15 V vs. SHE (A), i_c is the equivalent
345 cathodic current (A) and v is the scan rate (V s⁻¹). The capacitance was found by plotting the left side
346 of Equation 2 against scan rate. Electrochemically-active surface area was then determined from the
347 difference between the capacitance of the nanostructured surfaces relative to a flat 1 cm² Cu
348 surface.

349 **Gas chromatography:** Gas chromatography was carried out on an SRI instruments MG#5 GC with Ar
350 carrier gas. H₂ was quantified using a thermal conductivity detector and separated from other gases
351 with a HaySepD precolumn attached to a 3 m molecular sieve column. All carbon-based products
352 were detected using a flame-ionisation detector equipped with a methanizer and were separated
353 either using a 3 m molecular sieve column (CO, CH₄) or a 5 m HaySepD column (C₂H₄, C₂H₆).
354 Calibration was performed using a custom mixture of each gas in CO₂.

355 **¹H-NMR:** ¹H-NMR spectroscopy was undertaken on a Bruker Avance III 300 MHz spectrometer at 300
356 K. A sample of the liquid phase electrolyte was taken and D₂O was added as a locking solvent, along
357 with an aqueous terephthalic acid solution that served as a reference for quantification. A Pre-
358 SAT180 water suppression method was carried out to remove the water peak from each spectrum.⁴³

359 **BET:** Surface areas were obtained from analysis of Kr adsorption isotherms measured on a BelSorp
360 Max set-up at 77 K. Prior to the measurement, samples were treated under vacuum at 130°C for at
361 least 7 h. Surface areas were estimated using the BET model (Kr cross-sectional area 0.210 nm²). The
362 BET sample was prepared by undertaking the described dendrite preparation procedure on a large
363 Cu surface (3x3 cm²) to grow enough dendrite for measurement. Alkanethiol treatment of the large
364 electrode was carried out by covering the dendrite in a powder of 1-octadecanethiol and inserting
365 the resultant surface horizontally in a vacuum oven at 100°C for 15 minutes. The electrode was
366 subsequently removed and left in a bath of warm ethyl acetate at 60 °C for 5 minutes. Once dry, the
367 dendritic Cu was carefully scraped off the underlying Cu support for analysis. The value derived from
368 the BET measurement, reported in m² g⁻¹, was converted to cm² cm⁻² by multiplying it by the mass
369 of deposited dendrite onto the 1 cm² flat Cu support (5 mg for the *wettable dendrite* and 4 mg for
370 the *hydrophobic dendrite*).

371 **TEM/STEM:** Transmission electron microscopy images and chemical maps were acquired with a Jeol
372 2100F microscope operated at 200 kV and equipped with a UHR pole piece. XEDS spectra were
373 acquired in STEM mode with the same microscope, equipped with a Jeol system for X-ray detection
374 and cartography. Energy-Filtered TEM images at zero loss and C-K edge were acquired using a Gatan
375 GIF 2991 spectrometer. Samples for TEM were prepared by shaking a lacey carbon TEM grid in a vial
376 containing a small amount of Cu dendrite powder.

377 **ATR-FTIR:** Attenuated total reflectance-Fourier transform infrared spectroscopy was carried on a
378 0.5 mm thick Si-prism coated with 3-5 nm of Cu in a metal vacuum-evaporation apparatus.

379 Alkanethiolation of the prism was undertaken as described above. ATR-FTIR was undertaken while
380 the front of the prism was exposed to a solution of 0.1 M CsHCO₃ under CO₂.

381

382 **Data Availability Statement**

383 Raw data used in preparation of this manuscript is available to download at (TO BE FILLED AT PROOF
384 STAGE).

385

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488

489 **Supplementary Information**

490 Supplementary Figures 1-21, Supplementary Tables 1-6 and Supplementary Video 1 are provided as
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500 **Author contributions**

501 D.W., M.F. and V.M. conceived the research. D.W. and S.L. performed electrocatalysis and
502 characterization. N.M. carried out TEM measurements. F.O., S.L. and D.W. carried out IR
503 experiments. XPS was carried out by D.M. and P.M. All authors analyzed the data. D.W. wrote the
504 manuscript. S.L., M.F. and V.M. added to the discussion and contributed to the preparation of the
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506 **Competing interests:** Authors declare no competing interests.

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513 END OF MANUSCRIPT