

1 Oxidation State and Surface Reconstruction of Cu under CO₂ 2 Reduction Conditions from *In Situ* X-ray Characterization

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Cite This: <https://dx.doi.org/10.1021/jacs.0c10017>



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6 **ABSTRACT:** The electrochemical CO₂ reduction reaction (CO₂RR) using Cu-based catalysts holds great potential for producing
7 valuable multi-carbon products from renewable energy. However, the chemical and structural state of Cu catalyst surfaces during the
8 CO₂RR remains a matter of debate. Here, we show the structural evolution of the near-surface region of polycrystalline Cu
9 electrodes under *in situ* conditions through a combination of grazing incidence X-ray absorption spectroscopy (GIXAS) and X-ray
10 diffraction (GIXRD). The *in situ* GIXAS reveals that the surface oxide layer is fully reduced to metallic Cu before the onset potential
11 for CO₂RR, and the catalyst maintains the metallic state across the potentials relevant to the CO₂RR. We also find a preferential
12 surface reconstruction of the polycrystalline Cu surface toward (100) facets in the presence of CO₂. Quantitative analysis of the
13 reconstruction profiles reveals that the degree of reconstruction increases with increasingly negative applied potentials, and it persists
14 when the applied potential returns to more positive values. These findings show that the surface of Cu electrocatalysts is dynamic
15 during the CO₂RR, and emphasize the importance of *in situ* characterization to understand the surface structure and its role in
16 electrocatalysis.

17 **C**opper is known as the only monometallic heterogeneous
18 electrocatalyst that can convert CO₂ into more valuable
19 multi-carbon products.¹ To produce C₂₊ products at
20 economically feasible reaction rates requires a significant
21 overpotential for CO₂RR.² During the CO₂RR, the structure
22 and chemical state of the Cu surface has shown dynamic
23 changes in response to the local environment and applied
24 potential.³ The Cu valence state at the surface is of particular
25 interest since recent computational studies have shown that the
26 presence of subsurface oxygen or an oxide phase can improve
27 CO₂RR activity and steer the selectivity into C₂₊ products.^{4–7}
28 Based on such a hypothesis, several studies have tried to probe
29 the oxidation state of Cu-based catalysts by utilizing *ex situ* and
30 *in situ/operando* spectroscopy or microscopy.^{8–12} However,
31 these studies have not reached a consensus on whether the
32 oxide phase is present and stable at the catalyst surface under
33 realistic operating conditions where the CO₂RR performance is
34 measured. The rapid reoxidation of the Cu surface upon
35 exposure to O₂ makes it difficult to reach a robust conclusion
36 on this topic, and most of the *in situ/operando* techniques
37 employed struggle to distinguish whether the oxygen is located
38 at the surface or buried in the bulk. Therefore, measurements
39 that can specifically probe the active catalytic surface to
40 determine the oxidation states of Cu present under CO₂RR
41 rates similar to those used for performance evaluation are
42 needed.

43 In addition to the Cu valence state, the surface can
44 dynamically reconstruct through its interaction with the local
45 environment.^{13,14} Since Cu has low cohesive energy and high
46 surface mobility, the Cu atoms at the surface can easily

migrate. CO, which is a key intermediate in the CO₂RR, has
47 been shown to exacerbate this reconstruction in near-ambient
48 pressure conditions.¹⁵ Surface reconstructions can affect
49 product selectivity because the Cu(111) surface preferentially
50 yields CH₄, whereas the Cu(100) surface produces C₂H₄ with
51 a lower onset potential.¹⁶ To probe the surface structure under
52 CO₂RR conditions, electrochemical scanning tunneling mi-
53 croscopy (ECSTM) has been utilized to image Cu surfaces
54 with atomic resolution and has successfully demonstrated that
55 polycrystalline Cu (hereafter referred to as Cu(pc))
56 reconstructs into Cu(100) surfaces in N₂-purged electrolytes.¹⁷
57 However, one of the limitations of ECSTM is its limited field
58 of view, and it is unclear whether these changes occur globally.
59 Therefore, to understand the structural dynamics of Cu
60 surfaces more fully, it is imperative to elucidate both the local
61 atomic structure and long-range order under realistic CO₂RR
62 conditions. Here, we characterize the near-surface structure of
63 a Cu(pc) thin film (50 nm thickness) under CO₂RR
64 conditions by utilizing *in situ* grazing incidence X-ray
65 absorption spectroscopy (GIXAS) and X-ray diffraction
66 (GIXRD). The Cu(pc) thin film is utilized as an electrocatalyst
67 because it has been demonstrated that the roughness of the Cu
68 thin film is low enough to allow sensitivity to a few nm of the
69

Received: September 18, 2020



70 surface using GIXAS and GIXRD.¹⁸ We employ an electro-
 71 chemical flow cell that has been demonstrated to enable near
 72 surface-sensitive *in situ* characterization at high current
 73 densities by allowing a grazing incidence geometry and
 74 improving mass transport of reactive species to the catalyst.¹⁹
 75 Our results confirmed that no detectable oxide remains at the
 76 near-surface at potentials relevant to the CO₂RR, and,
 77 simultaneously, that potential-dependent surface reconstruc-
 78 tion from Cu(pc) to Cu(100) can be observed across μm – mm
 79 areas of the surface in a CO₂ saturated electrolyte.

80 We first characterized as-prepared Cu(pc) films by using
 81 GIXRD, GIXAS, and X-ray photoelectron spectroscopy
 82 (Figures S1 and S2), and the probe depths were calculated
 83 based on the incidence angles (Figure S3). The CO₂RR
 84 performance of the Cu(pc) thin film is similar to that of Cu foil
 85 reported previously (Figure S4).²⁰ To investigate the changes
 86 of oxidation states and local atomic structure during the
 87 CO₂RR, we performed *in situ* GIXAS measurements on the Cu
 88 thin film in a 0.1 M KHCO₃ electrolyte saturated with CO₂.
 89 The total current densities exceeded 20 mA/cm² at -1.1 V vs
 90 RHE (all the potentials are hereafter noted vs RHE),
 91 conditions under which Cu is known to form CO₂RR products
 92 and which are often employed when reporting CO₂RR
 93 efficiencies (Figure S5). The XANES spectrum at open-circuit
 94 potential (OCP) showed rising edge peaks at both 8982 and
 95 8996 eV, indicating that the surface was composed of a mixture
 96 of metallic Cu and Cu₂O (Figure 1a). These Cu(I) features
 97 disappeared at -0.3 V, which is before the onset potential of
 98 CO₂RR on Cu(pc) (generally ~ -0.63 V).²¹ Over the applied

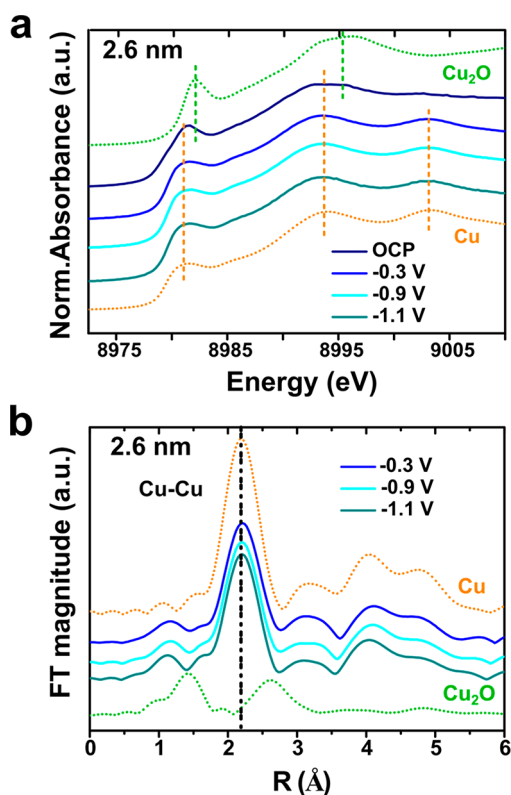


Figure 1. *In situ* GIXAS of Cu(pc) thin-film electrode in CO₂-saturated 0.1 M KHCO₃. XANES (a) and EXAFS (b) spectra of Cu (pc) at a probe depth of 2.6 nm as a function of the applied potentials. The Cu (orange) and Cu₂O (green) reference spectra (dotted line) are plotted for comparison.

potential range relevant to the CO₂RR, we observed only 99
 metallic Cu at the surface. The corresponding extended X-ray 100
 absorption fine structure (EXAFS) spectra displayed a 101
 prominent Cu–Cu scattering peak at 2.2 Å, which matches with 102
 the metallic Cu reference (Figure 1b). Although angle- 103
 dependent overabsorption distorted and dampened XANES 104
 and EXAFS spectra,¹⁹ it did not affect the phase information 105
 (Figure S6). We obtained similar results in the Ar-purged 106
 phosphate and bicarbonate electrolytes, suggesting that the 107
 reduction of oxide is primarily driven by the polarization to 108
 negative potential (Figure S7). As the GIXAS is highly 109
 sensitive to the disordered and local surface structure, our 110
 results demonstrate that an oxide phase in the near-surface 111
 region was either not present or below our ability to measure. 112

To elucidate the crystalline structure during CO₂RR, we 113
 performed *in situ* GIXRD as a function of probe depth and 114
 applied potential in CO₂- and Ar-purged electrolytes (Figure 115
 S8). The obtained diffraction measurements were corrected for 116
 refraction at the electrode–electrolyte interface (Figure S9a,b) 117
 and fit with a pseudo-Voigt function without contribution from 118
 electrolytes (Figure S9c). To estimate the uncertainty in 119
 determining the Cu(111) peak position, we calculate errors 120
 based on the peak asymmetry and sample variations (Figure 121
 S10). In the case of the as-synthesized Cu thin film, the *d*- 122
 spacing of Cu(111) showed a 0.15% expansion near the surface 123
 compared to that of bulk, possibly originating from the 124
 existence of the oxide phase (Figure S11). However, at 125
 potentials where the CO₂RR occurs, no changes larger than the 126
 estimated error in the Cu(111) *d*-spacing values were observed 127
 depending on the applied potential and probe depth (Figure 128
 S12a). The result with Ar-purged electrolytes is quite similar, 129
 except for 0.14% surface expansion at -1.1 V, possibly through 130
 hydrogen-induced expansion (Figure S12b).²² We note that 131
 the metallic Cu surface rapidly oxidized into Cu₂O after 132
 releasing the applied potential (Figure 2). The Cu₂O phase 133

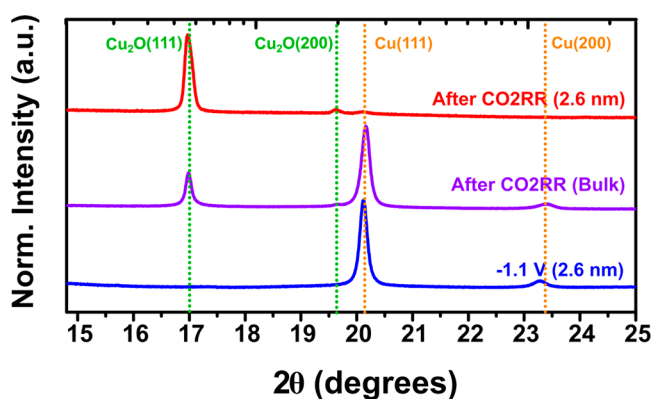


Figure 2. GIXRD of Cu(pc) at a probe depth of 2.6 nm and bulk before and after releasing the applied potential.

was even detected in the bulk within 5 min, demonstrating that 134
 the metallic Cu electrode can easily reoxidize at the OCP 135
 (generally ~ 0.55 V in our case). This result suggests that *ex* 136
situ or *quasi in situ* characterization could contain Cu(I) 137
 artifacts on the sample surfaces even without exposure to 138
 ambient conditions. 139

While we observe that the valence state and *d*-spacing of the 140
 Cu surface remain unchanged, we do find evidence for surface 141
 reconstruction as a function of applied potential. We calculate 142
 the area ratio of Cu(200) to Cu(111) Bragg peaks at a probe 143

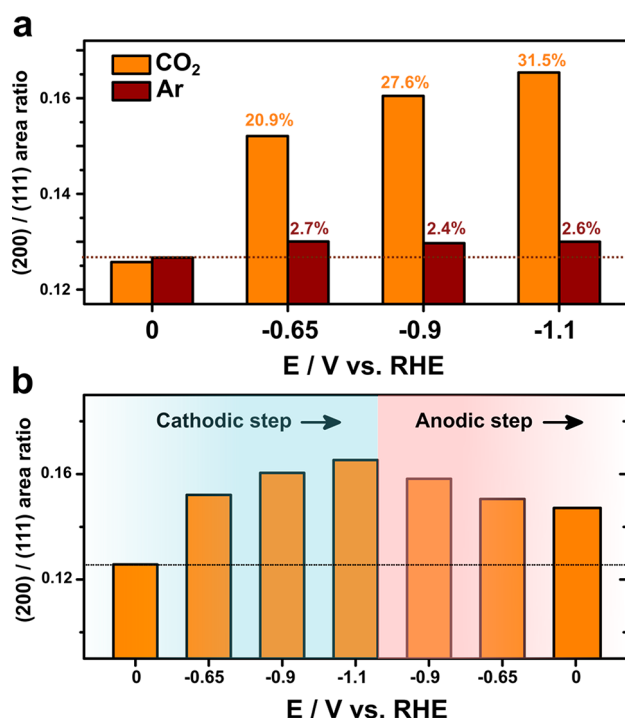


Figure 3. (a) Ratio of the area of Cu(200) to Cu(111) Bragg peaks at a probe depth of 2.6 nm in CO₂- and Ar-purged electrolytes as a function of the applied potentials. Each percentage above the bars indicates an increase of ratio compared to the value at 0 V. The dashed line indicates the ratio in Ar-purged electrolyte at 0 V. (b) Changes of Cu(200)/(111) area ratio at a probe depth of 2.6 nm in cathodic and anodic steps in CO₂-purged electrolyte. The dashed line indicates the ratio at 0 V.

144 depth of 2.6 nm according to the applied potentials under both
 145 CO₂ and Ar-purged electrolytes (Figure 3a). Although peak
 146 area is not a rigorously quantitative measure of the amount of
 147 specific facet, relative area ratios reflect changes in the
 148 preferentially exposed facets on the surface.²³ At 0 V, where
 149 no CO₂RR or hydrogen evolution reaction (HER) occurs on
 150 Cu(pc), the area ratio in the surface exhibited similar values in
 151 CO₂- and Ar-purged electrolytes. As the applied potential
 152 becomes more negative, the (200)/(111) area ratio in the
 153 surface increases (20.9–31.5%) under CO₂-purged electrolyte,
 154 while the area ratio in the Ar-purged electrolyte showed only a
 155 slight increase (2.4–2.7%) across the applied potentials. The
 156 increase in area ratio was only observed at the probe depth of
 157 2.6 nm, indicating the reconstruction is a surface phenomenon
 158 (Figure S13). Both the intensity and integral breadth of the
 159 (200)/(111) ratio also increase as a function of the applied
 160 potential under CO₂-purged electrolytes (Figure S14). The
 161 increase in the area ratio is significantly higher than that of the
 162 estimated errors (Figure S15), and the trend is reproduced in
 163 another Cu sample (Figure S16). Therefore, these results
 164 indicate that a surface reconstruction from Cu(pc) to
 165 Cu(100)-like surface occurs during CO₂RR. The differences
 166 in CO₂ and Ar-purged electrolytes suggest that surface
 167 hydrogen and hydroxide species generated from HER have a
 168 limited effect on surface reconstruction. Previous theoretical
 169 calculations and spectroscopic observations indicate that the
 170 dominant intermediate during CO₂RR is adsorbed CO
 171 (CO*^{24,25}). We found that the surface reconstruction is
 172 enhanced at more negative electrode potentials. Computa-
 173 tional results indicate that similar trends in the CO* coverage

at these potentials.²⁶ We also observed a similar reconstruction 174
 under CO reduction conditions under alkaline electrolytes in a 175
 previous study.²³ Considering that the local pH at the Cu 176
 surface increases due to the OH⁻ ions generated from CO₂RR, 177
 we conjecture that the microenvironment under CO₂-purged 178
 electrolytes could be similar to the situation under CO-purged 179
 alkaline electrolytes. This suggests that CO* is likely a key 180
 reaction intermediate in promoting surface reconstruction (see 181
 SI for a detailed discussion). 182

For a more quantitative description of the surface 183
 reconstruction, we analyzed the relative changes of the area 184
 ratio depending on the applied potential. The area ratio at a 185
 probe depth of 2.6 nm increases by 20.9% at -0.65 V 186
 compared to the value at 0 V. It is reported that the CO 187
 adsorption starts to appear at -0.5 V in a CO₂-saturated 0.1 M 188
 KHCO₃ electrolyte, and its coverage gradually increases with 189
 increasingly negative applied potentials.²⁵ This accumulated 190
 CO* on the surfaces could reconstruct Cu(pc) to Cu(100) 191
 before CO₂RR occurs. At -0.9 V, where the C₂₊ products 192
 begin to emerge on Cu(pc), the area ratio shows an increase of 193
 27.6% and this change helps to explain why the hydrocarbon 194
 formation on Cu(pc) is invariant to that on Cu(100).²⁷ The 195
 area ratio further increases to 31.5% at -1.1 V, where the 196
 selectivity toward HER has been reported to surpass the 197
 CO₂RR products due to the concentration polarization for 198
 CO₂ (i.e., mass transport limitation) in the H-cell config- 199
 uration.²⁰ This result implies that enhanced mass transport in 200
 our cell allows a higher degree of surface reconstruction to 201
 (100) at -1.1 V, possibly through an increase of CO* coverage 202
 on the surface. We collected the GIXRD data after reaching a 203
 steady state; however, further work is needed to understand 204
 the kinetics of surface reconstruction which has been observed 205
 on various time scales previously.^{17,28} We expect that the high 206
 mass transport rates and current densities in our cell translate 207
 to fast reconstruction kinetics. We also found that the surface 208
 reconstruction is only partially reversible. When the applied 209
 potential returns to more positive values, at 0 V the surface 210
 displays more (100) faceting than the original surface at 0 V 211
 (Figure 3b). The irreversible change of surface morphology has 212
 been observed during HER on the Cu(100), leaving behind 213
 structural defects such as small holes and clusters.²⁹ This 214
 observation likely explains the previously reported hysteresis of 215
 product distribution during cyclic voltammetry.^{27,30} In these 216
 reports, the enhanced generation of multi-carbon products 217
 during cyclic voltammetry has been observed only during the 218
 anodic sweep. Our results suggest this may be because the 219
 applied potential during the cathodic sweep leads to a 220
 significant surface reconstruction to a Cu(100)-like surface 221
 that can steer the CO₂RR selectivity toward hydrocarbon 222
 formation. During the anodic sweep, the surface is already 223
 reconstructed to be more Cu(100)-like, enabling the increased 224
 production of C₂₊ products. These results can provide 225
 fundamental insights into the previously observed processes 226
 that did not take account of the surface reconstruction during 227
 CO₂RR. 228

In summary, we investigated the changes in the valence state 229
 and crystallographic structure in the near-surface region of 230
 Cu(pc) thin films under realistic CO₂RR conditions. By using 231
 an electrochemical flow cell that allows for *in situ* GIXAS and 232
 GIXRD with improved CO₂ mass transfer, we successfully 233
 demonstrated that the surface copper oxide is reduced to 234
 metallic Cu prior to the onset of CO₂RR and that metallic Cu 235
 is the only detectable phase during CO₂RR. We also showed 236

237 that the surface reconstruction from Cu(pc) to Cu(100) takes
238 place only in the presence of CO₂ molecules, suggesting it is a
239 CO-driven phenomenon. The surface reconstruction increases
240 as the applied potential becomes more negative, and the
241 reconstructed surface partially persists in the anodic steps. Our
242 *in situ* measurements of surface oxidation state and
243 reconstruction behavior provide new insights for the atomic-
244 scale understanding of Cu-based electrocatalysts.

245 ■ ASSOCIATED CONTENT

246 **SI** Supporting Information

247 The Supporting Information is available free of charge at
248 <https://pubs.acs.org/doi/10.1021/jacs.0c10017>.

- 249 Experimental details, detailed *in situ* GIXAS and GIXRD
250 supplementary figures, and estimation of error margins
251 (PDF)
252 Raw data in .txt format for all figures (ZIP)

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<https://pubs.acs.org/10.1021/jacs.0c10017> 318

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Notes 321

The authors declare no competing financial interest. 322

323 ■ ACKNOWLEDGMENTS

The material for synthesis of Cu thin films, electrochemical 324
flow cell assembly, and GIXAS and GIXRD measurements is 325
based on work performed by the Joint Center for Artificial 326
Photosynthesis, a DOE Energy Innovation Hub, supported 327
through the Office of Science of the U.S. Department of 328
Energy, under Award No. DE-SC0004993. The material for 329
electrochemistry experiments with product analysis is based on 330
work performed by the Liquid Sunlight Alliance, which is 331
supported by the U.S. Department of Energy, Office of 332
Science, Office of Basic Energy Sciences, Fuels from Sunlight 333
Hub under Award No. DE-SC0021266. Use of the Stanford 334
Synchrotron Radiation Lightsource, SLAC National Accel- 335
erator Laboratory, is supported by the U.S. Department of 336
Energy, Office of Science, Office of Basic Energy Sciences 337
under Contract No. DE-AC02-76SF00515. Part of this work 338
was performed at the Stanford Nano Shared Facilities (SNSF) 339
and the Stanford Nanofabrication Facility (SNF), supported by 340
the National Science Foundation under Award ECCS- 341
1542152. 342

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