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Electrochemically scrambled nanocrystals are catalytically active for CO_2-to-multicarbons

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Author Contributions

Y.L. and D.K. designed and performed experiments with assistance from S.L., C.X., Q.K., S.Y., S.F., and T.L.. Y.L. and D.K. analyzed data with assistance from S.L., C.X., S.F., and S.A. P.Y. supervised the project and experimental design. All authors wrote the manuscript.

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Main Text
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Abstract

Promotion of C-C bonds is one of the key fundamental questions in the field of CO_2 electroreduction. Much progress has occurred in developing bulk-derived Cu-based electrodes for CO_2-to-multicarbons (CO_2-to-C_{2+}), especially in the widely-studied class of high surface area "oxide-derived" copper. However, fundamental understanding into the structural characteristics responsible for efficient C-C formation is restricted by the intrinsic activity of these catalysts often being comparable to polycrystalline copper foil. By closely probing a Cu nanoparticle (NP) ensemble catalyst active for CO_2-to-C_{2+}, we show that bias-induced rapid fusion or "electrochemical scrambling" of Cu NPs creates disordered structures intrinsically active for low overpotential C_{2+} formation, exhibiting around 7-fold enhancement in C_{2+} turnover over crystalline Cu. Integrating *ex situ*, passivated *ex situ*, and *in situ* analyses reveals that the scrambled state exhibits several structural signatures: a distinct transition to single crystal Cu_2O cubes upon air exposure, low crystallinity upon passivation, and high mobility under bias. These findings suggest that disordered copper structures facilitate C-C bond formation from CO_2, and that electrochemical nanocrystal scrambling is an avenue towards creating such catalysts.

Significance Statement

The electrocatalytic conversion of CO_2 to value-added products, especially valuable multi-carbon products, is a pathway towards sustainable formation of chemicals and fuels typically derived from fossil fuels, while mitigating CO_2 emissions. Fundamental understanding and development of more efficient catalysts for this reaction require deep investigation into structures with high intrinsic activity, which are limited at present. This work comprehensively investigates a dynamic copper nanoparticle ensemble catalyst that significantly improves intrinsic activity of copper for multicarbon formation. Through concerted *ex situ* and *in situ* characterization techniques, it illustrates an electrochemically-induced fusion of copper nanoparticles that result in a catalytically active disordered structure, motivating closer study of disordered metal nanostructures for C-C coupling electrocatalysis.

Main Text

Introduction

Structural evolution of materials under operation is a topic of emergent importance in the field of heterogeneous catalysis (1). Since nanoscale catalysts are highly susceptible to structural changes due to their high surface area and energetics, growing awareness of this phenomenon has led to deeper understanding of catalysis from a spectrum of works in both gas and liquid phase (1–4). The catalytic relevance of such dynamics to CO_2 electrocatalysis has recently been highlighted in copper-based systems (5–8).

Understanding the structural requirements of copper to promote CO_2 electroconversion to multicarbon products (CO_2-to-C_{2+}) is crucial for the development of catalyst materials in the field. With copper as the sole material to demonstrate CO_2-to-C_{2+} at reasonable rate and efficiency (9), a host of high-activity copper catalysts have shown promise in achieving high C_{2+} activity/selectivity in bulk product formation rates (10–17). However, the intrinsic CO_2-to-C_{2+} activity (*e.g.* $\mu A_{C2+}/cm^2{}_{Cu}$) of many of these catalysts only marginally improves against a typical copper foil surface thus far, suggesting that nominal activity enhancements are inextricable from the modulation of extrinsic factors, such as local pH or mass transport, through catalyst microstructure (9). Hence, despite many investigations into the structural and/or compositional origin of CO_2-to-C_{2+} (14, 15, 18–21), only few reports identify a core structural variable that correlates with and directly influences the intrinsic CO_2-to-C_{2+} activity (22). We ascribe this discrepancy largely to two difficulties: 1) enriching the active surface on bulk-processed copper catalysts, and 2) the tendency for materials to transform under electrochemical conditions.

Recently, we reported the structural transformation of a copper nanoparticle (Cu NP) ensemble into cuboidal structures, coupled with selective electroconversion of CO_2 to multicarbons at lowered overpotentials (23). The observed coalescence of NPs towards distinct shape formation and desirable catalytic performance, in contrast to conventional sintering and deactivation, warrants a close study of the electrochemical evolution process. In light of both the prevalence of structural dynamics on copper nanocatalysts and the importance of understanding structural effects on intrinsic activity, such work may enable directed evolution strategies as new avenues to electrocatalyst development for CO_2 utilization.

In this work, we probe the structural transformation process of the previously reported Cu NP ensembles under CO_2 electroreducing conditions. By closely tracking the material state over electrolysis, an *ex situ* structural signature (*i.e.* single crystalline oxide nanocubes) is identified and confirmed to be unique to the C_{2+} active catalyst. This signature is determined to result from oxidation after removal of bias; hence, a chemical passivation technique is employed to impede this oxidation. Subsequent passivated *ex situ* characterization reveals a second signature: low crystallinity or enriched disorder, boosting the intrinsic C_{2+} activity by 7-fold over crystalline counterparts. Further *in situ* characterization suggests that the disordered state arises in part due to a high mobility of the initial state, resulting in a rapid transformation on a time scale of seconds. Together, these three lines of characterization illustrate a phenomenon we term “electrochemical scrambling,” in which cathodic bias induces the rapid fusion of nanocrystals into an active disordered state, highly susceptible to concurrent oxidation and crystallization upon exposure to ambient conditions. These findings motivate the closer study of disordered surfaces as structural characteristics responsible for enhancing CO_2-to-C_{2+} turnover, and raise the prospect of structural dynamics as an approach to catalyst design.

Results and Discussion

Colloidally synthesized Cu NPs (7 nm) were spread on carbon paper and biased in CO_2 electroreducing conditions for multicarbon production in an aqueous H-cell environment (0.1 M $KHCO_3$). The observed change by *ex situ* characterization is rapid and striking, with the appearance of cubic structures on the order of seconds and the predominance of these structures on the order of minutes (Fig. 1a and SI Appendix, Fig. S1). More negative potentials resulted in a more rapid evolution process (SI Appendix, Fig. S2). Regardless, the evolution of NPs under these biases eventually resulted in identical catalysts by both their morphology and catalytic activity (SI Appendix, Fig. S3).

Qualitatively, the evolution is described by the loss of original nanoparticles, being gradually replaced by cubic and cuboidal structures (Fig. 1b). The formation of cubes (Fig. 1c) is surprising given that the original NPs are spherical and exhibit 5-fold twinned Cu (SI Appendix, Fig. S4). Furthermore, high-resolution transmission electron microscopy (HRTEM) reveals that these cubes are single-crystalline Cu_2O (Fig. 1d). These observations are beyond the irregularly shaped structures typically expected from nanoparticle coalescence (24, 25). The copper appears to redistribute over the course of evolution, such that at intermediary time points when many particles have transformed, the resultant cubes are smaller and more uniformly spread. Indeed, the 10-20 nm particles at later times are characterized as monocrystalline Cu_2O cuboids as well (SI Appendix, Fig. S5). The prevalence of these structures with high crystallinity is confirmed on the ensemble by X-ray diffraction, most clearly seen at early time points (SI Appendix, Fig. S6). The Cu_2O cubes grow with no preferred orientation on the graphitic support (SI Appendix, Fig. S7), suggesting the absence of interaction with the support as part of the process.

To quantitatively assess the evolution of metal/oxide phase distribution, *ex situ* Cu K-edge X-ray absorption near-edge structure (XANES) experimental spectra were least-square linear combination fitted (LCF) using component phases. The XANES of the original Cu NPs was used alongside Cu^0 and Cu_2O standards for a 3-component LCF at early time points (Fig. 2a). The Cu NPs are suitable as a phase component as they are observed at those times by microscopy, and their XANES exhibits unique features poorly accounted for by other standard Cu phases (SI Appendix, Fig. S8). The relative phase portions were extracted from the XANES spectra as the evolution proceeds (SI Appendix, Fig. S9).

Cursory analysis of the time series (Fig. 2b) shows a rapid increase in intensity of the rising edge $1s \rightarrow 4p_{x,y}$ shake-down feature (~8984 eV) and a fingerprint crest (~9015 eV) indicative of Cu_2O (26). Quantitative tracking by LCF more visibly demonstrates that the early loss of Cu NPs is counterbalanced by a rapid growth of Cu_2O cubes (Fig. 2c). Beyond this critical period of Cu_2O formation ending around 600s, most of the steady state structure is characterized by the retention of cuboidal Cu_2O crystals. At more negative potentials, the phase evolution is accelerated but results in a similar final phase distribution (SI Appendix, Fig. S10). The minor metallic Cu phase is mainly found at the junctions of aggregates of Cu_2O cubes and less frequently in polycrystalline particles with no distinct morphology (SI Appendix, Fig. S11). Thus, *ex situ* XANES further confirms that the evolution of Cu NPs results in Cu_2O cuboidal rich structures as first identified using *ex situ* electron microscopy.

To evaluate the catalytic relevance of the appearance of Cu_2O cuboids, we considered two methods of varying the original evolved Cu NP system (Sample O). First, larger 14 nm Cu NPs (Sample L) were synthesized to controllably change the starting state of the material (SI Appendix, Fig. S12). The characteristic cube formation is absent for these larger particles under similar electrochemical conditions (SI Appendix, Fig. S13). Furthermore, the phase distribution remains mostly metallic throughout electrolysis (SI Appendix, Fig. S14). Secondly, we also aimed to disrupt the evolution process of the original nanoparticles by applying a voltammetric pulse perturbation program. The perturbation is applied at frequent intervals throughout the critical period of evolution, interrupting the transformation with a mild oxidation pulse (SI Appendix, Fig. S15). As a result, despite beginning with the same NPs, the pulsed electrode (Sample P) consists of larger, more irregular morphologies compared to Sample O (SI Appendix, Fig. S16).

A substantial reduction of C_{2+} formation is observed for Samples L and P relative to O (Fig. 2d and SI Appendix, Fig. S17), in conjunction with a more metallic composition by XANES (Fig. 2e and SI Appendix, Figs. S14 and S18) and more polycrystalline aggregates of Cu as opposed to cuboidal oxides (SI Appendix, Fig. S19). As such, we find that the catalytic variants lacking C_{2+} selectivity also have lower Cu_2O signature in their *ex situ* composition (Fig. 2e inset and SI Appendix, Table S1). These *ex situ* single-crystalline cuboidal Cu_2O structures are therefore a signature for catalytically enhanced C_{2+} formation. Variations of the evolution pathway, either by modifying the initial state or by perturbing the evolution process, shift the distribution of catalyst structures towards polycrystalline nanoparticles with a high proportion of metallic Cu post-reaction, correlated with lower activity for C_{2+} formation (Fig. 2f).

However, formation of Cu_2O is thermodynamically disfavored under CO_2 reducing conditions (27, 28), suggesting that the Cu_2O cubes should not have formed *in situ*. Indeed, when Cu_2O nanocubes are directly grown on the carbon support, activity is strictly limited to hydrogen evolution and C_1 formation at potentials where Sample O makes majority multicarbons (SI Appendix, Fig. S20). Furthermore, Cu_2O electrochemically grown on carbon, after CO_2 electrolysis, is dominated by metallic Cu consisting of small particles and broken cubes with their facets destroyed (SI Appendix, Fig. S21). Hence, neither crystalline cubic Cu_2O itself nor its reduced equivalent is the active phase in the transformed Cu NP ensemble, despite the above *ex situ* observations. These findings suggest that a different structure, most likely metallic, is formed *in situ* and is uniquely active for CO_2-to-C_{2+}. Moreover, the structure readily and distinctively oxidizes to the single crystal Cu_2O cubic signature at open circuit. To identify this structure, we employed a chemical immersion passivation method using benzotriazole (BTA), which is known to prevent copper oxidation (Fig. 3a) (29). Immersion into a BTA solution immediately post-electrolysis coordinates BTA to the surface, preventing the formation of Cu_2O single crystals and preserving more of the underlying metallic portion as characterized by XANES, XRD, STEM-EELS, and XPS (SI Appendix, Figs. S22-25).

Cu K-edge EXAFS was then used to probe the difference between the three catalysts when oxidation is inhibited by BTA (O-BTA, L-BTA, and P-BTA). A clear feature of O-BTA is the lower scattering amplitude from the first Cu shell of the metallic phase at 2.1 Å, with its subsequent shells following a similar trend (Fig. 3b). These EXAFS spectra were then fit in *q*-space to derive a numerical description of the coordination environment (SI Appendix, Fig. S26). The EXAFS-derived fitting parameter $N_{Cu\text{-}Cu1}$ is used here as a quantitative descriptor of this empirical scattering amplitude difference. According to the fits (SI Appendix, Table S2), O-BTA exhibits a considerably lower $N_{Cu\text{-}Cu1}$ (3.0) compared to the other catalysts L-BTA ($N_{Cu\text{-}Cu1}$ = 6.8) and P-BTA ($N_{Cu\text{-}Cu1}$ = 6.5). To contextualize this trend, a series of nanoparticles with varying size and well-defined crystallinity were employed as standards (SI Appendix, Fig. S27). The EXAFS-derived $N_{Cu\text{-}Cu1}$ is expected to decrease for smaller sized nanoparticles (SI Appendix, Figs. S28 and S29) by the rise in the surface area to volume ratio (SA/Vol); however, $N_{Cu\text{-}Cu1}$ for O-BTA is unexpectedly low given its size of structures (~20 nm). Furthermore, all three BTA-passivated samples are composed of similarly sized nanostructures (SI Appendix, Fig. S30) and therefore, the difference in SA/Vol does not sufficiently explain the difference in $N_{Cu\text{-}Cu1}$ between O-BTA and L/P-BTA.

Low $N_{Cu\text{-}Cu1}$ can result not only from having a higher portion of atoms with missing neighbors, but also by local atomic disorder, which leads to destructive interference of the scattered X-rays (30). A chemical effect should also be considered – the imperfectly passivating effect of BTA results in some remnant oxide as evidenced by the rise in amplitude at 1.5 Å, which would partially contribute to a lower observed $N_{Cu\text{-}Cu1}$. Nevertheless, crystalline domains in O-BTA are difficult to detect by HRTEM (Fig. 3c), in contrast with L/P-BTA where extended metallic domains are easily identified (SI Appendix, Fig. S31). Nanobeam electron diffraction (SI Appendix, Fig. S32) suggests a relative lack of crystallinity in O-BTA as well. Meanwhile, control experiments on model Cu-based nanocrystal systems (*i.e.* single nanocrystals and the original 5-fold twinned nanoparticles) confirm that BTA coordination alone is insufficient to disrupt the inherent crystallinity of a Cu nanostructure (SI Appendix, Figs. S33 and S34). Therefore, despite some limitations of the BTA immersion technique, the overall implication of a disordered active structure is considered the most likely interpretation of these results.

These observations indicate that O-BTA achieves a unique state of structural disorder characterized by a low EXAFS-derived $N_{Cu\text{-}Cu1}$ at low SA/Vol (Fig. 3d, calculation details in SI Appendix, Discussion S1). L/P-BTA exhibit similarly low SA/Vol but higher $N_{Cu\text{-}Cu1}$, indicating that higher crystalline order is linked to their lower C_{2+} selectivity. Furthermore, low $N_{Cu\text{-}Cu1}$ achieved by high SA/Vol in a crystalline state is likewise insufficient to attain high C_{2+} selectivity at low overpotentials, as evidenced by the activity of isolated small Cu nanoparticles (Fig. 3d) (23). These findings strongly suggest that the electrochemical "scrambling" of the original nanoparticles creates a disordered active surface (low $N_{Cu\text{-}Cu1}$ with low SA/Vol) catalytically favorable for CO_2-to-multicarbons. Previous works have conjectured C_{2+}-boosting effects of tuning binding strength of key intermediates, especially *CO, on diverse and undercoordinated copper surfaces (15, 21, 31). Accordingly, a host of high-activity oxide-derived copper catalysts may present such disordered surface sites. However, the direct identification/quantitation of disorder in these catalysts and its effect on binding has not emerged, likely because the large volume involved of the necessary copper oxides as precursors (*e.g.* oxidized Cu foils) yields large proportion of bulk atoms that are catalytically irrelevant but spectroscopically obtrusive for ensemble characterization. Furthermore, because such OD-Cu catalysts tend to have high roughness factors, they may present a complex mix of disordered/undercoordinated active sites and catalytically inactive copper surfaces, one possible explanation for the lack of intrinsic activity increase previously observed (9).

To quantify the enhancement of intrinsic C-C activity owing to the disordered Cu resulting from electrochemical nanoparticle scrambling, we estimated the electrochemical surface area (ECSA)-normalized specific C_{2+} activity ($\mu A/cm^2_{Cu}$) of the catalysts using lead underpotential deposition (UPD) to measure Cu ECSA (SI Appendix, Fig. S35 and Discussion S2). Sample O exhibits a considerable 7-fold increase in C_{2+} activity to that of a Cu foil, whereas the polycrystalline Sample P exhibits only a minor increase (Fig. 3e). OD-Cu catalysts (10, 14–16) that show high performance by typically presented metrics such as F.E. (SI Appendix, Fig. S36) demonstrate similar or lower intrinsic activity to Sample P or Cu foil as well (9). In contrast, the enrichment of disorder on Sample O is directly responsible for a higher C-C dimerization activity per copper surface available, ranging from 6- to 40-fold enhancement over a representative spread of OD-Cu catalysts (Fig. 3e and SI Appendix, Fig. S37) at moderate overpotentials (-0.8 V vs. RHE).

The high degree of disorder exhibited by Sample O is expected to result in a large concentration of strong binding sites for the key intermediate *CO, thereby increasing the probability and rate of C-C dimerization. Desorption of underpotentially deposited Pb adatoms sheds some light into the Cu surface (Fig. 3f). Sample P and Cu foil both exhibit anodic stripping of Pb in the same potential region of around -0.27 V vs. Ag/AgCl. Meanwhile, Sample O exhibits Pb desorption peaks (-0.25 and -0.16 V vs. Ag/AgCl) that are quite anodically shifted compared to Sample P or Cu foil (-0.27 V vs. Ag/AgCl), resulting in a +28 mV shift in the centroid of the anodic stripping wave. In particular, the salient component at -0.16 V is not observed in the crystalline Cu samples in this work, nor in previous studies of Pb underpotential stripping on polycrystalline Cu surfaces composed of common low-index facets or on single-crystal Cu (32, 33). This indicates that Sample O contains a prevalence of Cu surfaces that should have stronger electrochemical binding to adsorbates, with a lower presence of the sites on the crystalline counterpart (*i.e.* Cu foil) that exhibit weaker binding. The anodic shift is drastically diminished when the catalyst oxidizes to the characteristic single-crystal Cu_2O cubes, where the reduced equivalent is not disordered as before (SI Appendix, Fig. S38). It is also observed in a greatly reduced manner on a representative OD-Cu catalyst (SI Appendix, Fig. S38), which explains the low intrinsic C_{2+} activity resulting from their large portion of inactive Cu surfaces. Hence, enhanced C-C activity in Sample O stems from the concentration of structural disorder, which creates surfaces of increased electrochemical binding strength to catalytic intermediates.

To determine whether any signature of the evolution can be observed *in situ*, we used liquid cell electrochemical (EC) XANES and (S)TEM to directly visualize their formation from the starting NP ensemble (Fig. 4a). Upon reductive bias, the EC-XANES shows a rapid (<40s) transition to metallic Cu (Fig. 4b), which develops its characteristic oxidized feature after exposure to ambient conditions (SI Appendix, Fig. S39). This confirms that the phase of the *in situ* active structure is Cu^0, formed almost immediately upon bias, and that Cu_2O only develops afterwards at open circuit.

NP evolution was also visually tracked by EC-HAADF-STEM (SI Appendix, Fig. S40). An electrochemical potential of -0.6 V vs. the internal reference electrode (C/Pt) was selected to induce electrochemical evolution and cathodic current, but without rupturing the cell from vigorous gas product formation. Based on water splitting cyclic voltammetry control experiments within the cell, this potential is negative of the onset potential for HER (SI Appendix, Fig. S41). Within a second of bias, ~20 nm structures appear to grow from the 7 nm NPs (Fig. 4c and SI Appendix, Movie S1 and Fig. S42). When the EC-TEM cell is then dried at ambient conditions, cubic structures are commonly found on the electrodes, which are characterized as single crystal Cu_2O (Fig. 4d and SI Appendix, Fig. S43), confirming that catalytically relevant structures have formed for the biasing period of EC-TEM. In contrast, larger (15-20 nm) nanoparticles do not undergo much structural change even after 60s of bias (SI Appendix, Movie S2 and Fig. S44), as expected from the post-electrolysis structures of Sample L that indicate minimal movement (SI Appendix, Fig. S13). These *in situ* results confirm that the evolution process unique to Sample O occurs rapidly, on the order of seconds. Further resolution of the structural details of these systems was limited due to the NPs' dynamic nature (see SI Appendix, Discussion S3 and Movies S3, S4).

In conjunction with our *ex situ* observations, we find that electrochemical bias induces rapid fusion of a NP ensemble into a disordered metallic steady-state (Sample O) with high C_{2+} selectivity and intrinsic C-C activity, which we term scrambling (Fig. 4e). This relative loss of atomic order is likely what triggers a complete "recrystallization" to a single crystalline Cu_2O nanocube on air exposure. The effect is largest for small nanocrystals, owing to their higher energy increasing the tendency for free atomic migration upon bias as represented by their high mobility. In contrast, larger NPs scramble to a lesser extent, while redox pulses allow periods of oxide crystallization to interrupt the scrambling process, resulting in Samples L/P exhibiting more typical polycrystalline Cu structures surrounded by oxide shells. The disorder-derived active surfaces arising from scrambling exhibits increased electrochemical binding strength, which potentially translates to a higher population of strongly-bound *CO. This effect may be related to previous reports of disorder-induced microstrain modulating electrocatalytic activity (34). Additionally, relaxing the geometric constraint of crystallinity may allow configurations that alleviate the undesired repulsive interactions of a high density of bound *CO (35), comparable to the creation of optimal geometries in enzymatic systems. The sum of these effects potentially contributes to the overpotential reduction towards C-C coupling in the scrambled nanocrystal system. Catalysts exhibiting a lower degree of disorder (*e.g.* Samples L/P) thus are only able to yield comparable C_{2+} activity at elevated potentials (-0.9 V and beyond) (SI Appendix, Fig. S45).

The mechanism of disorder development in the scrambled NP system should stem from the structural details of the original nanoparticle. For instance, the five-fold twinned 7 nm NP structure contains a high proportion of atoms at grain boundaries, where disorder-forming processes such as premelting are observed in model crystal systems (36). The disorder may also be intrinsic to the effect of reducing an oxide shell, as is present on the original NPs and has been suggested previously (18). However, since not every reduced oxide can achieve the same catalytic activity (as shown by the Cu_2O cubes as-grown), the NP fusion involved in the scrambled system is likely to be critical to preserving such characteristics. For example, as the fusion occurs within the NP ensemble, the presence of a high grain boundary density may result in pinned crystallite junctions that impede boundary migration and crystal growth as evolution proceeds (37). Additional factors not presently investigated, such as the behavior of surface ligands under bias, may also play a role. Eventually, unraveling the atomistic details of the electrochemical nanocrystal scrambling process will contend with the complex interplay among an ensemble of particles composed of nanoscale-twinned Cu cores, thin Cu_2O shells, and surrounding ligands, under biased conditions. Additionally, the question of how it is maintained raises an intriguing opportunity to understand the structural requirements for its sustenance, in the context of translating such insights to other materials. We expect more advanced *operando* techniques as well as cryo-XAS (38), may yield important new insights, presenting opportunities for designing catalysts with the necessary characteristics to attain similarly active states.

In conclusion, we have comprehensively probed the dynamic fusion of Cu NPs under CO_2 reducing conditions to form multicarbon-active scrambled nanocrystals. These structures are described by three distinct signatures: *ex situ* formation of single crystal oxide cubes, low coordination and crystallinity after passivation, and high mobility observed *in situ*. Together, these observations suggest an enriched disorder in the copper phase with substantially enhanced intrinsic CO_2-to-C_{2+} compared to crystalline Cu, motivating closer investigation into the atomic details of low-crystallinity Cu surface motifs and their preservation throughout. Moreover, we emphasize that a full understanding of active catalysts, which are more likely to be structurally unstable, will require *ex situ*, *quasi in situ*, and *operando* techniques explored in concert.

Materials and Methods

Nanoparticle synthesis and electrode fabrication

7 nm copper nanoparticles were synthesized as previous reported (23). For larger size nanoparticles, size was controlled by tuning the mole ratio of tetradecylphosphonic acid (TDPA) to copper(I) acetate (CuAc), where higher ratio resulted in larger particles. Specifically, to synthesize 7, 9, 14, and 20 nm nanoparticles, ratios of 0.5, 0.7, 1, and 1.25 respectively were used while maintaining the absolute concentration of CuAc (1 mmol).

Nanoparticle concentrations by mass of copper were measured by inductively-coupled plasma optical emission spectroscopy, after which 68.9 µg of copper was deposited on 1 cm^2 area of carbon paper (Sigracet 29AA, Fuel Cell Store) to make working electrodes. Larger nanoparticles were deposited in a similar manner with identical mass loading.

For electrochemically grown Cu_2O nanocubes, a square wave voltammetric pulse program was employed as reported previously. Cu_2O nanocubes were directly grown on carbon paper (Sigracet 29AA) (39).

For copper foil derived electrodes, copper foil (Alfa Aesar 99.9999%) was electropolished in 85% H_3PO_4 at 3 V for 3 minutes against a copper counter electrode. Electrochemically-cycled oxide-derived copper was then fabricated following the method previously reported for EC-Cu (14).

Electrochemical evolution of NPs and catalytic activity measurements

The customized electrochemical setup used to carry out bias-induced evolution of NPs and catalytic testing has been described previously (23). All electrochemical measurements were made against a 3 M KCl Ag/AgCl reference electrode (World Precision Instruments). For all biasing experiments, the bias was applied directly without a prior linear sweep. Evolution was typically carried out by directly applying -1.2 V vs. Ag/AgCl, while catalytic results were measured at -1.45 V vs. Ag/AgCl. These potentials were considered equivalent by the steady-state structure made, as elaborated upon in SI Appendix, Fig. S3. All chronoamperometry was corrected with 85% of the solution resistance (Biologic), with the remaining 15% corrected afterward. Gas and liquid products were measured by a gas chromatograph equipped with TCD and FID-methanizer (SRI) and NMR with water suppression (Bruker Avance 500), respectively.

For pulsed preparation of Sample P, the potential was varied between -1.2 V vs. Ag/AgCl and 0.0 V vs. Ag/AgCl with periods of 2.5 s each. This pulse program was repeated 240 times, for a total of 1200 s of bias, before the potential was immediately switched to -1.45 V vs. Ag/AgCl for catalytic testing.

Passivation with benzotriazole (BTA, Sigma-Aldrich 99%) was conducted after electrolysis by removing the electrode from the cell and, within a short period time, immersing the electrode in a pre-made 10 mL bath of BTA dissolved in CO_2-saturated 0.1 M $KHCO_3$. The amount of BTA was set to a mole ratio of 1000 mol BTA to 1 mol Cu (the maximum concentration shown in SI Appendix, Fig. S22).

Lead underpotential deposition was conducted immediately post-electrolysis in a solution of 0.1 M $NaClO_4$, 10 mM $HClO_4$, and 3 mM Pb(II)$(ClO_4)_2$. Cyclic voltammetry in the Pb underpotential region was conducted at 10 mV/s six times, for which the cycles were confirmed consistent and the fifth scan was reported. The potentials are referenced against a 1.0 M KCl Ag/AgCl electrode.

Ex situ *structural characterization*

Electrodes were directly imaged by SEM (Ultra 55-FESEM), and samples were crushed into a fine powder for powder X-ray diffraction (Bruker D8). For TEM sample preparation, the carbon paper electrode was crushed into a fine powder and dropcast on a TEM grid, typically lacey carbon, from a dispersion in toluene. Low magnification TEM (Hitachi H-7650) was conducted at 100 kV, while HRTEM and STEM-EELS (Tecnai F20 UT) were conducted at 200 kV. NBED, along with additional HRTEM (JEOL 2100-F) were also conducted at 200 kV. XPS (Thermo Scientific K-Alpha) was measured using an Al Ka source with spectra collected at a pass energy of 20 eV and step size of 0.05 eV.

X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) experiments were conducted at ALS XFM beamline 10.3.2 following previously reported procedures for Cu NPs (40). All data were recorded in fluorescence mode in quick-XAS mode (where the Si(111) is scanned on the fly), using a 7 element Ge solid state fluorescence detector. Energy calibration was performed using a Cu foil (1^{st} derivative maximum set at 8980.48 eV) (41). For *ex situ* measurements, electrodes were biased in the typical manner and removed for measurement under ambient conditions. Cu K-edge XANES data processing (deadtime correction, deglitching, energy calibration, pre-edge background substraction and post-edge normalization), and least-square linear combination fits (LCF), were conducted with the LabVIEW custom software available at https://sites.google.com/lbl.gov/lbnl-als-1032/software-download/. In addition, LCFs were performed in Athena for corroboration; the variation of phase contributions between these two programs did not exceed 5% in all cases.

EXAFS data reduction was performed in Athena and EXAFS fitting was performed in Artemis according to previous procedures (40). Both programs are part of Demeter package 0.9.26 (42). For EXAFS data fitting of the various Cu samples, two FEFF models of Cu metal and Cu_2O were generated. They were made according to the well-known crystal structure (both face-centered cubic with respect to Cu) of the bulk materials. All Cu nanoparticles samples were fit using the first three single scattering paths and the collinear triple scattering path to the fourth shell from Cu metal, as well as the first O single scattering path in Cu_2O. Addition of the first Cu single scattering path in Cu_2O was required to fit the samples containing a more prominent oxide phase.

In situ XAS was conducted in a custom-designed PEEK electrochemical cell. A working electrode was fabricated by depositing Cu NPs over a $1cm^2$ area of carbon paper (Sigracet 29AA), which was pressed against a 300 µm Kapton window. The cell was filled and constantly purged at under 1 sccm with 0.1 M $KHCO_3$ kept under CO_2 saturation. Open circuit voltage was measured during purging, and XANES scans were taken after the cell was completely filled. To begin electrochemical evolution, -1.3 V vs. Ag/AgCl was applied vs. the 3 M KCl Ag/AgCl reference electrode with a glassy carbon counter electrode. Due to the rapid structure evolution under bias, the XANES spectral range was shortened so that each spectrum took only ~40 seconds, increasing temporal resolution for qualitative study. Depending on the desired duration of bias, 1-20 QXAS lines were measured before electrolysis was stopped and the cell disassembled under ambient conditions.

In situ *electron microscopy*

All *in situ* electron microscopy was conducted at 200 kV (JEOL 2100-F). Commercial electrochemical TEM chips (Hummingbird, XL P7 carbon electrochemical chip) were used with a 500 nm silicon nitride spacer (Hummingbird), such that the total assembly included 100 nm of silicon nitride and 500 nm of liquid volume. All biasing leads were carbon-coated Pt as supplied by the manufacturer.

To create working electrodes, a 2 µL droplet of a dilute (25 µg/mL) solution of Cu NPs in hexanes was spread over the viewing area of the chip. The droplet was allowed to evaporate, after which the full cell was assembled. 300 µL of ethanol were first purged through, after which 1-1.5 mL of 0.1 M $KHCO_3$ or pure H_2O were purged at 10 µL/min in order to wet and fill up the entire cell. Control experiments were conducted with Pt/C particles (20 wt% nominal, Alfa Aesar) using a similar loading strategy, without ethanol purging.

Electrochemical testing was conducted in a specially-designed biasing holder (Hummingbird) with a floating potentiostat (Gamry Interface 1000), using a three-electrode configuration. The biasing potential was set at -0.6 V vs. the carbon pseudo-reference electrode, at which chronoamperometry using a typical cell produced ~500 nA of reductive current. Higher currents/potentials (*e.g.* >1 µA at -0.8 V vs. Ref) were deemed unsuitable due to violent ruptures of the electrochemical cell, while significantly lower currents (*i.e.* order of 10-100 nA) failed to reproduce the cubic oxide structures post-electrolysis in favor of adventitious side reactions such as the growth of polycrystalline copper.

During bias, electrolyte purging was halted. Real-time videos were recorded using a screen capture program at 5 frames per second, matching both the raster rate of the STEM beam over the viewing frame and the exposure time of the camera during BF-TEM. After electrochemical imaging experiments, the holder was disconnected from the potentiostat. The cell was then directly disassembled and the working chip rinsed gently with H_2O before drying under N_2. The chip was then imaged by TEM and NBED (JEOL 2100-F) under vacuum conditions.

Data availability

All data analyzed in this work are included in the main text and SI Appendix.

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Figures and Tables

Figure 1. *Ex situ* electron microscopy of the Cu NP ensemble evolution timeline. (a) SEM after removing the electrode at various time points of bias (scale bars 100 nm). (b) Schematic of the structural evolution. (c) TEM (scale bars 50 nm) after 50 seconds (left) and 3600 seconds (right) of bias. (d) HRTEM (scale bar 10 nm) of a single Cu_2O cube at 50s with FFT showing Cu_2O reflections (scale bar 2 nm^{-1}) and a selected region at higher magnification (scale bar 2 nm). Electrochemical conditions are -0.6 V vs. RHE in 0.1 M $KHCO_3$ at 1 atm CO_2.

Figure 2. *Ex situ* Cu K-edge XANES spectroscopy of catalysts. (a) Three standards used in this work: Cu, Cu_2O, and 7 nm Cu NPs. (b) XANES time series over electrolysis (-0.6 V vs. RHE) time *ex situ* with arrows indicating Cu_2O features. (c) Shift in composition tracked by LCF. (d) Catalytic selectivity for C_1 and C_{2+} products in samples O, L, and P (error bars 1 SD, n = 3) at -0.8 V vs. RHE. (e) XANES of O, L, and P after 1 hr at -0.8 V vs. RHE, with inset showing the correlation of phase composition and C_{2+} selectivity. (f) Scheme summarizing the catalytic relevance of the Cu_2O structures observed uniquely in Sample O.

Figure 3. *Ex situ* elucidation of the disordered C-C active surface. (a) BTA passivation diverts oxidation of the active catalyst for characterization. (b) R-space EXAFS of BTA-passivated O, L, and P after 1 hr at -0.8 V vs. RHE. (c) HRTEMs of O-BTA (scale bar 5 nm). (d) Relationship between SA/Vol and $N_{Cu\text{-}Cu1}$, showing unusually low coordination of O-BTA. Error bars are 1 SD (see SI Appendix, Discussion S1 for details on SA/Vol and SI Appendix, Figs. S26 and S28 for EXAFS fit details). Isolated 7 nm NPs catalytic activity from previous work at -0.8 V vs. RHE (23). (e) Specific ECSA-normalized C_{2+} partial current density at -0.8 V vs. RHE for foil (14), high-performance oxide-derived catalysts from literature (see SI Appendix, Fig. S36 for details), P, and O. (f) Desorption of underpotentially deposited Pb as an indicator for adsorbate binding strength, where Sample O exhibits anodic shifts (peaks at -0.25 and -0.16 V vs. Ag/AgCl) associated with its disordered surface. Dashed lines represent centroids for each anodic stripping voltammogram.

Figure 4. *In situ* characterization of the Cu NP ensemble evolution under bias. (a) Configurations used for *in situ* EC-XANES and EC-(S)TEM. (b) EC-XANES with the initial (top) scan at open circuit and the remainder during bias at -0.6 V vs. RHE. (c) EC-HAADF-STEM of the 7 nm Cu NP system taken over a 10s biasing period (frames from SI Appendix, Movie S1, scale bars 100 nm). (d) *Ex situ* TEM of the EC-STEM electrode after biasing, showing the expected NP-to-cube evolution (scale bar 100 nm), with NBED showing single-crystal Cu_2O (scale bar 2 nm^{-1}). (e) Unified description of electrochemically scrambled nanocrystals with disordered surfaces that enhance CO_2-to-C_{2+}, vs. relatively inactive polycrystalline Cu nanocrystals.