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Adapted cell design for the operando X-ray absorption study of a structurally evolving Cu nanoparticle ensemble during the CO₂ electroconversion to multicarbon products

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ABSTRACT

An improved understanding of the materials that will sustain the future of energy production, storage, and delivery, calls for better characterization tools. *Operando* characterization methods have thus become essential for investigating electrocatalytic materials. Without their resulting insights, the study of highly performing catalysts post-mortem cannot viably facilitate the further development of functional catalysts. Herein, we present an *operando* electrochemical cell designed for hard X-ray absorption spectroscopy (XAS) and specifically adapted to the study of an electrocatalytically active Cu nanoparticle ensemble. So far, this nanocatalyst has proven to pose quite a challenge to characterize due to its unique structural dynamics. Adopting a design comparable to the H-cell employed for all activity testing, we report the excellent translation of the active site formation into an XAS-compatible cell. The simultaneous collection of CO₂-derived products during XAS characterization enabled the *operando* characterization of this CO₂-reducing active structure. We report a Cu-Cu coordination number of the first scattering path higher than suggested in our previous studies, highlighting the importance of monitoring metastable nano-electrocatalysts *operando*. This study illustrates important caveats for the electrocatalysis community when considering the application of *operando* XAS. Our results highlight that the sample size, homogeneity, and stability determine how to interpret the measured signal. Considering these parameters carefully, the *operando* EXAFS results confirm the exceptional undercoordinated character of the Cu nanoparticle ensemble during CO₂ reduction to C₂₊ products.

Introduction

The surface structure of heterogeneous catalysts determines their selectivity and turnover frequency during an electrocatalytic reaction.¹⁻³ Although this principle applies to all reactions, it becomes increasingly more complex with an increasing number of steps involving electron transfer. The CO₂ reduction reaction (CO₂RR) on Cu, for example, can produce more than 10 different products through mechanisms involving up to 18 electrons.⁴ The more electrons, the larger the produced molecule, and thus, the more energetically dense. Consequently, great interest lies in optimizing the selectivity and activity towards CO₂-derived products containing 2 to 3 carbon atoms. As such, the field of electrocatalysis has invested considerable effort in the study of material designs toward improved CO₂RR electrocatalyst.⁵⁻¹⁰ This focus has been especially pronounced on the conversion of CO₂ to higher-order products such as ethylene (C₂H₄) and ethanol (EtOH). They are, in fact, considered some of the most coveted products of CO₂-revalorization into energy-dense compounds, i.e., fuel. Through the effort to optimize such revalorization, several works have attempted to identify the structural descriptors associated with greater CO₂ to multicarbon (C₂₊) products. While single crystal studies have identified favorable facets toward CH₄, i.e., {111}, and others toward CO and C₂H₄, i.e., {100},¹¹ it is clear that nanocatalysts have pushed the realm of possibilities further when modulating reaction selectivity.^{5,12,13} This is partly due to the greater diversity of co-existing domains, which can help further lower the energy barrier toward C-C coupling.¹⁴ On the practical aspect of this, several studies have demonstrated how defects, structural disorder, and grain boundaries at the nanoscale can contribute to the selectivity and activity enhancement observed in nanocatalysts.^{8,9,15} Here, we refer to an activity enhancement as a higher turnover frequency of product per electrocatalyst active surface area.

An important caveat when studying those structures is the discontinuity between the structure responsible for the measured electrocatalytic activity and the structure measured spectroscopically. The CO₂RR activity reported for most nanomaterials results from measurements carried out in an H-cell configuration.^{5,16–18} However, this geometry is not always compatible with the techniques most insightful regarding morphology (electron microscopy), atomic structure (X-ray diffraction), or chemical composition (X-ray absorption spectroscopy). As a result, the true structure or composition of the active catalyst, whose performance is recorded, remains elusive. So far, correlations between the operating structure and its activity have been principally made indirectly by studying the morphology or chemical structure *ex-situ* after electrolysis. To achieve the characterization of the true active structure, the field has since seen a tremendous increase in *operando* cell designs, each adapted to the needs of not only the type of electrocatalyst but also the reaction and the limitations of the characterization technique itself.^{19,20} Unfortunately, the common challenge that comes with transferring an electrocatalytic system from one configuration to another is the unseen impact (such as X-ray and electron beam damage during *operando* characterization) that could have on the active structure itself and its corresponding electrocatalytic performance. In particular, the study of nanocatalysts is inherently challenged by the high surface energy of nanomaterials, which makes them especially dynamic under an applied potential.²¹ This implies that small changes in their environment, i.e., support, electrolyte turbulence, or bubble dissipation, can dramatically impact their ability to undergo structural phenomena such as migration, aggregation, coalescence, and dissolution-redeposition, all known to take place under electrocatalytic conditions.^{21–23}

In this work, we describe the translation of a well-studied nanocatalyst for the CO₂RR, known to exhibit excellent CO₂-to-C₂₊ conversion into an H-cell configuration, to an *operando*

cell. The structural evolution of this Cu nanoparticle (NP) ensemble during CO₂RR has been thoroughly studied *ex-situ*, first revealing the highly dynamic nature of this system.²⁴ Further efforts to identify a structural descriptor responsible for this high C₂₊-activity led us to apply X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) *ex-situ* and quasi *in situ*.¹⁶ Most recently, we successfully identified the morphological changes and corresponding formation of nanograins using electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM).⁹ Overall, studying the translation of this thoroughly studied nanocatalytic system is valuable for several reasons: (1) its excellent performance for CO₂RR in H-cells makes it an especially electrocatalytically-relevant system to study, (2) as it is well-documented, there are pre-existing standards for this system to refer to when evaluating the morphological and/or structural changes from the H-cell to the *operando* configuration, and (3) the determination of the coordination environment of Cu atoms in this nanocatalyst has not yet been determined with *operando* EXAFS. The adaptation of this well-studied electrocatalytic system into an XAS-compatible configuration is critically discussed here. We highlight the limitations and achievements possible through our cell design. We also demonstrate how the transfer into an *operando*-compatible system was not only successful but also adapted to complement our understanding of the active structure of this remarkable nanocatalyst.

Results

The 7 nm diameter Cu NP ensemble used in this study has been thoroughly studied and reported as an excellent nanocatalyst for CO₂ electroconversion to C₂₊ products, with a faradaic efficiency (FE) of up to 50% at -0.8 V vs. RHE.²⁴ This Cu NP ensemble was shown to undergo dramatic structural evolution once exposed to CO₂-reducing conditions. We previously identified NP migration, agglomeration, coalescence, and surface atom dissolution/redeposition as

mechanisms leading to the formation of a metastable structure active towards CO₂-to-C₂⁺ electroconversion.¹⁶ Interestingly, while we confirmed the active structure to be metallic Cu using X-ray absorption spectroscopy (XAS), we also found that this metastable structure was especially susceptible to oxygen insertion. Hence, the surface of the nanocatalyst readily oxidized and crystallized into Cu₂O once returned to open circuit potential (OCP) and exposed to air. The rapid insertion of oxygen atoms in the Cu lattice was postulated to correlate with the degree of nanograin boundaries observed with EC-STEM, and thus, undercoordinated sites formed during the CO₂RR. Despite the insights so far acquired on this catalytic system, our tools were not adapted to measure simultaneously the electrocatalytic activity and the coordination environment of the catalyst. Our previous use of benzotriazole (BTA), a surface passivating agent, only allowed us to approximate the undercoordinated nature of the active structure.¹⁶ The former cell design employed at the time (**Figure S1**) was insufficient to not only maintain a sufficiently stable signal to acquire statistically meaningful data necessary for EXAFS but also ensure the Cu NP ensemble structurally evolved into its active state. Our initial work on this ensemble identified the initial assembly, support, and environment of this Cu NP ensemble to dramatically impact their properties as CO₂-reducing nanocatalyst.²⁴ Here, we report the design of a cell that enables the Cu NP ensemble to structurally transform into a CO₂-to-C₂⁺ converting nanocatalyst while allowing the acquisition of the Cu K-edge XAS of the system and monitoring the gas products during measurements. The liquid products can be collected post-measurements similarly to typical H-cell studies.

The adapted *operando* cell was designed to resemble as closely as possible the custom-made H-cell employed for electrocatalytic measurements (**Figure 1a**). That is, we maintained the same cell volume filled with the same amount of electrolyte and the same headspace volume. We preserved the same separation between the cathodic and anodic compartments with an anion

exchange membrane to prevent the oxidation of cathodic products at the anode. However, unlike the carbon paper-based electrode submerged by 1 cm² in the middle of the cathodic compartment of the traditional H-cell, the carbon paper electrode is affixed to a PEEK window with a customized PEEK part (**Figure S2**).

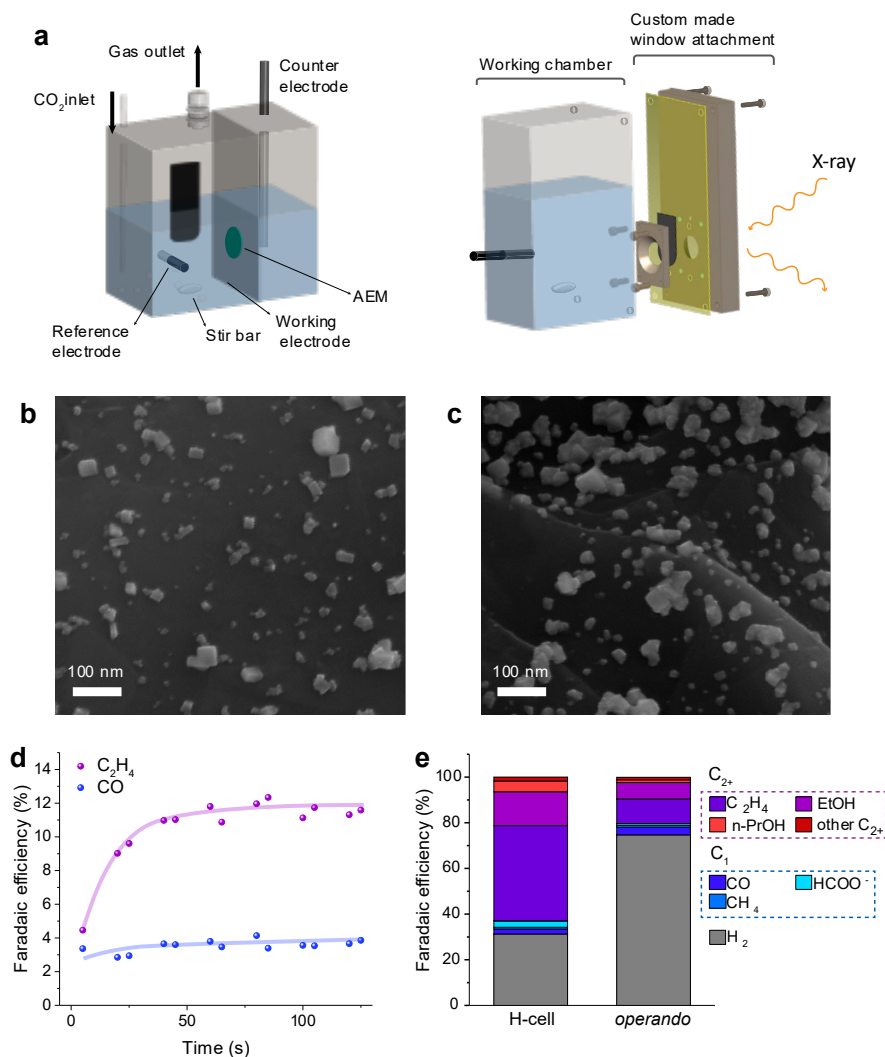


Figure 1. Translating CO₂RR into a XAS compatible *operando* electrochemical cell. **a.** 3-D schematic of the H-cell like *operando* electrochemical cell. An X-ray transparent PEEK window is attached to the original H-cell body part. The nanocatalyst is deposited on a carbon paper electrode affixed against the PEEK window. This configuration optimizes the nanocatalyst exposure to the incoming X-ray and maximizes the outgoing fluorescence signal. **b.** Post-electrolysis Cu₂O structure formed after CO₂RR in the H-cell are partially reproduced in **c.** the *operando* cell. **d.** The faradaic efficiency of two of the main CO₂RR gas products in the *operando* cell exhibits satisfactory stability over 2 h at -0.8 V vs RHE. Trend lines are drawn as a guide to the eye. **e.** The faradaic efficiency of gaseous products, i.e., C₂H₄ and CO, measured over 2 hours using GC-FID indicate stable CO₂RR in the *operando* cell at -0.8 V vs RHE.

In this configuration, the electrode is accessible to the incoming X-ray while maximizing the outgoing fluorescence signal to the detector. Given the porosity of the carbon paper, all of the Cu NPs deposited on the electrode will eventually be wetted by the electrolyte, allowing for its entire surface to participate in the electrocatalytic reaction (**Figure S2b**). Although a large area of the carbon paper, nanocatalyst-free, is also exposed to the electrolyte, we only observe wetting of the electrode where NPs are deposited. This indicates that the CO₂RR draws water to the desired area of the electrode, which in turn contributes most to the measured electrochemical current.

To confirm this cell was suitable to recreate the conditions necessary for the structural transformation of the ensemble into its most active form, we first checked the state of the post-electrolysis Cu NP ensemble. Our earlier work has demonstrated that the “sharpness”, size, and density of post-CO₂RR Cu₂O cubes observed with *ex-situ* SEM can serve as a qualitative estimation of the electrocatalytic quality of the nanocatalyst formed *operando*.²⁴ Indeed, the sharper features of the Cu₂O nanocubes indicative of enhanced C₂₊ selectivity that form in the H-cell (**Figure 1b**) were also found in the *operando* cell (**Figure 1c**). SEM images were obtained from both sides of the *operando* cell electrode to verify the homogeneity of this transformation. It is expected that the different degrees to which water can reach the substrate and catalyst on either side of the carbon paper could affect the migration, agglomeration, and other key evolution mechanisms of the ensemble structural changes. While we observe a different degree of agglomeration (**Figure S3**), the differences were small enough to conclude, at first approximation, that the system evolves similarly to the H-cell conditions. Additionally, we observe a stable gaseous faradaic efficiency (FE) for CO₂-derived products, i.e., CO and C₂H₄ (**Figure 1d**). The system appears to reach a steady state after 30 minutes and remains stable for 2 hours at -0.8 V vs the reversible hydrogen electrode (RHE).

Despite this rather successful translation of structural transformation from H-cell to *operando* cell, the overall product distribution is affected by the change in cell configuration (**Figure 1e**). At -0.8 V vs RHE, the hydrogen evolution reaction (HER), increases from ~30% in the H-cell to ~70% in the *operando* cell. The mass transport of CO₂ appears to be significantly affected by the absence of direct electrolyte contact with the surface pressed against the PEEK window (despite vigorous electrolyte stirring with a magnetic stir bar). Therefore, while the Cu NP ensemble can achieve the expected structural transformation, the CO₂ access to this surface impedes the measured activity. Yet, we retain a similar C₂₊/C₁ ratio in both cells (**Figure S4**), suggesting the surface available for CO₂ reduction maintains the surface sites active for C-C coupling. In other words, despite its overall depressed CO₂RR activity (likely resulting from CO₂ mass transport limitations), we appear to be forming an electrocatalyst whose structure and corresponding activity remain relevant for X-ray absorption spectroscopic investigation. Because the current and gas products can be directly measured in this cell configuration, and because of the sample homogeneity observed microscopically, it becomes possible to associate the XAS measurements with the truly catalytically active structure of this catalyst. Therefore, this *operando* cell was employed to measure the Cu K-edge XAS of our system. We focused more specifically on the EXAFS, considering this Cu NP ensemble has now been extensively studied with XANES.^{9,16,25}

To evaluate more quantitatively the structural differences expected from carrying out electrolysis in the two different cell configurations, we measured the 7 nm Cu NP ensemble post-CO₂RR. In our previous works, we had identified mixtures of metallic Cu and Cu₂O in different ratios depending on the structural evolution of this NP ensemble. Using Cu K-edge EXAFS, we can therefore focus on the peaks resulting from the scattering paths specific to those phases.

Comparison of the two *ex-situ* samples (**Figure 2a**) indicates that the first (Cu-Cu1) scattering path at $R = 2.2 \text{ \AA}$ is distinctively more intense in the sample produced in the *operando* cell in comparison to when formed inside the traditional H-cell. Whether this is due to a higher coordination number or a change in structural disorder must be carefully interpreted, taking into account the type of samples evaluated (see **Discussion S1**). Based on the morphology obtained with post-CO₂RR *ex-situ* SEM, the individual particles observed on the carbon paper appear to all be about the same size, ~40-60 nm edged-blocks, in the H-cell (**Figure 2b** and **S3**). However, the individual blocks vary significantly more in size in the *operando* cell, with a greater number of agglomerates (**Figure 2c-d** and **S3**). Taking these observations into consideration and knowing that $N_{\text{Cu-Cu1}}$ increases with particle size,²⁶ the average $N_{\text{Cu-Cu1}}$ is expected to be larger in the *operando* cell. Meanwhile, the larger surface area-to-volume (SA/Vol) ratio observed post-electrolysis in the H-cell must facilitate the oxidation of the active structures formed during the reaction, thus favoring the Cu-O1 path at $\sim 1.5 \text{ \AA}$ from the oxide phase at the expense of the Cu-Cu1 peak at $\sim 2.2 \text{ \AA}$, more representative of a metallic phase.

Our previous work, carried out exclusively in an H-cell, also indicated that the cube-like structures observed after electrolysis are principally single-crystalline Cu₂O.¹⁶ This suggests that an increase in disorder in the H-cell is less likely than a change in N . Altogether, the comprehensive evaluation of EXAFS and post-mortem SEM images strongly supports the greater agglomeration of Cu NPs in the *operando* cell, thus leading to the formation of structures with a more prominent disordered Cu⁰ phase. This different degree of NPs agglomeration could be due to the limited wetting of the carbon paper facing the PEEK window. Fewer agglomerates are indeed observed on the carbon paper facing the electrolyte (**Figure 2c**) than on the side facing the PEEK window (**Figure 2d**). Nevertheless, it is interesting to note that the intensity of the Cu-O1 scattering path

is of comparable intensity for both samples. Likely, the 7 nm Cu NP ensemble evolves to overall similar features with an overall slightly lower SA/Vol in the *operando* cell. Despite the unavoidable changes in device configuration and thus structural evolution, our cell design enabled us to closely recreate the structure most active for C_{2+} formation, formerly studied in a H-cell.

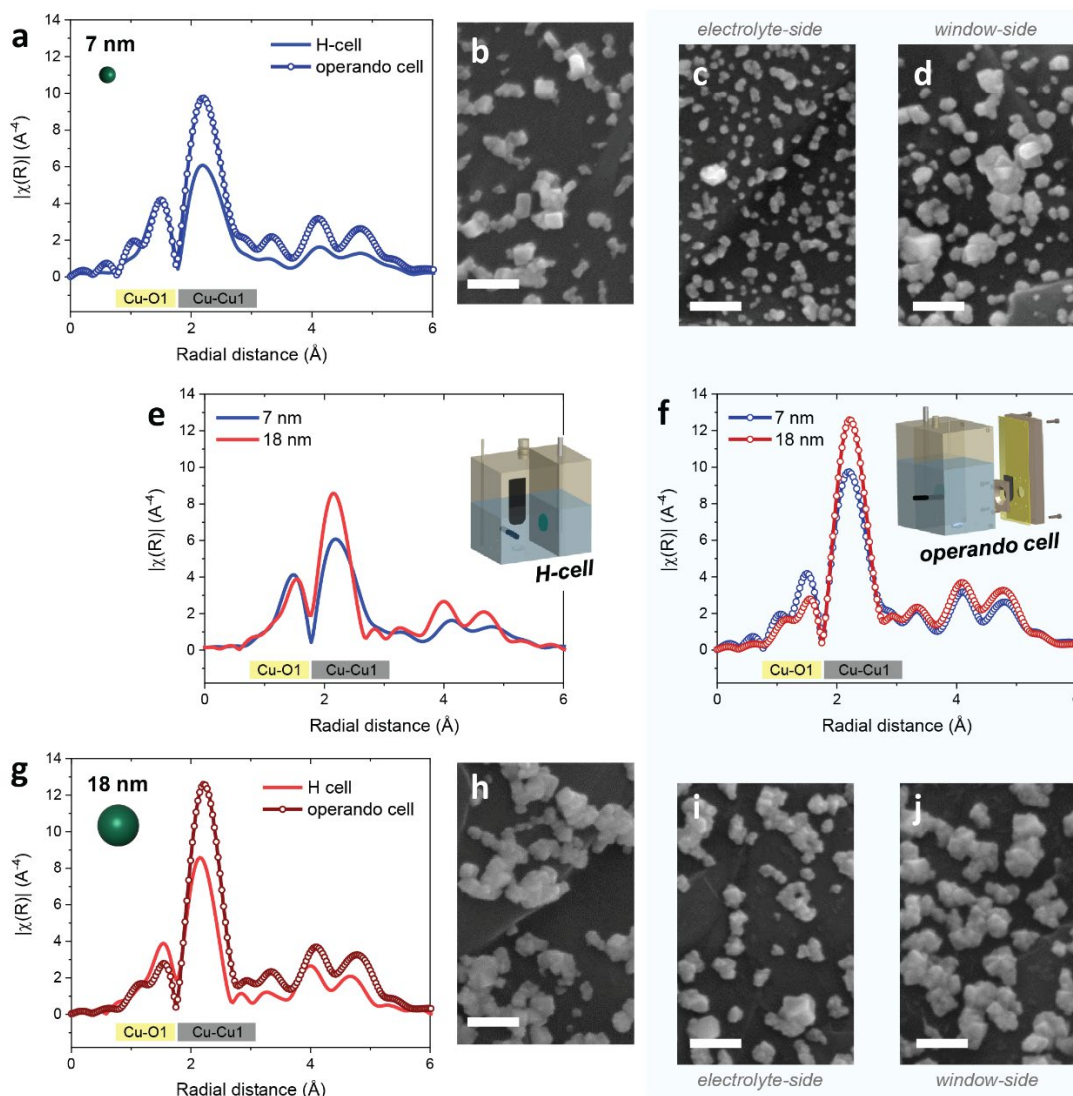


Figure 2. Comparison of the post-CO₂RR *ex-situ* nanocatalyst in a H-cell and *operando* design. **a.** k^3 -weighted R-spectra of the Cu K-edge EXAFS ($3 < k < 12$) for the 7 nm Cu NP ensemble measured *ex-situ* after running CO₂RR in the H- and *operando* cells. Corresponding *ex-situ* SEM images of the post-CO₂RR nanocatalyst used in **(b)** a H-cell, in the *operando* cell on the **(c)** electrolyte, and **(d)** on the PEEK window side (scale bar = 100 nm). Comparison of the Cu K-edge EXAFS for the 7 and 18 nm Cu NP ensemble after running CO₂RR in **(e)** a H-cell and **(f)** the *operando* cell. **g.** Cu K-edge EXAFS of the 18 nm Cu NP ensemble measured *ex-situ* after running CO₂RR in the H- and *operando* cells. Corresponding *ex-situ* SEM images of the post-CO₂RR nanocatalyst used in **(h)** a H-cell, in the *operando* cell on the **(i)** electrolyte, and **(j)** on the PEEK window side (scale bar = 100 nm). CO₂RR was run at -0.85 ± 0.05 V vs RHE for 1 h (SI).

Furthermore, we previously employed the comparison between ensembles of different Cu NP diameters to identify the structural origin of the enhanced C-C coupling observed with the 7 nm Cu NP ensemble.¹⁶ Concretely, we identified a structure-to-activity correlation by comparing the more active 7 nm to the ≥ 14 nm Cu NP ensemble.^{9,16} We were able to assign the increased CO₂-to-C₂⁺ conversion rate observed in the 7 nm Cu NP ensemble to a larger density of undercoordinated sites. Therefore, we compare the effect of the *operando* cell design on the structural transformation of a 7 nm and an 18 nm Cu NP ensemble (**Figure 2**). First, we observed that just like the 7 nm Cu NP, a more intense Cu-Cu1 peak is observed for the 18 nm Cu NP ensemble after the CO₂RR is carried out in the *operando* cell in comparison to the H-cell (**Figure 2g**). Second, we confirmed that the increase in the Cu-Cu1 peak intensity previously observed in the H-cell between the two size NP ensembles (**Figure 2e**) is still present when comparing them after operation in the *operando* cell (**Figure 2f**). Despite the larger agglomeration observed for the 7 nm Cu NP ensemble in the *operando* cell, they seem to retain their structural distinction from the 18 nm Cu NP ensemble in both types of cells (**Figure 2 a,g**). Qualitatively, it also appears the 18 nm Cu NP ensemble evolves to the same degree of agglomeration regardless of the cell (**Figure 2 h-j**), with perhaps slightly larger aggregates on the window-side as previously observed for the 7 nm Cu NPs.

Overall, we were able to assess the impact of our cell designs on the morphological and structural characteristics of the Cu NP ensemble after running CO₂RR. Namely, the enhanced agglomeration of the 7 nm Cu NPs in the *operando* cell results in the formation of larger structures during their ensemble evolution. This effect is less pronounced for the larger Cu NPs. While we have previously shown that soft X-rays could impact the oxidation state of Cu NPs under reaction conditions,²⁷ the Cu K-edge XAS signal does not indicate any evidence of beam damage (**Figures**

S5-6). We can safely attribute the structural evolution disturbance from one cell to another to their respective configuration. Despite these changes, the structural differences previously observed between 7 nm and 18 nm Cu NP ensembles are conserved in the new cell design, thus confirming its suitability for investigating the structural characteristics of this dynamic nanoelectrocatalyst during CO₂RR.

Upon confirming the integrity of the sample studied from the H-cell to the *operando* cell, we can take a closer look at the measurements carried out *in operando*. Our new cell design enables us to achieve excellent signal intensity while applying the desired potentials for CO₂RR. The XAS signal remains unchanged after the current stabilizes, thus indicating we are measuring the steady state of the nano-electrocatalyst structure (**Fig. S6**). We first applied -0.7 V vs RHE for 1 hour to minimize the electrocatalytic current and thus, bubble formation, which would negatively impact the XAS measurement. Once the current stabilized, we measured Cu K-edge EXAFS. Previously, our principal challenge had been to obtain spectra with a sufficient *k*-range to provide enough parameters in the modeling, according to the restriction on the number of independent points, $2\Delta k\Delta R/\pi$, while applying a potential. The various reasons for this challenge are presented in further detail in **Discussion S2**. Our new *operando* cell enabled us to overcome this challenge by yielding spectra up to $k = 12 \text{ \AA}^{-1}$ (**Figure S7**). Such a *k*-range is necessary for meaningful fitting and interpretation of the Fourier-transformed Cu K-edge EXAFS spectra. After confirming the signal stability at -0.7 V, we applied -0.8 V vs RHE, where we observed the same signal stability (**Figure. S5**).

For a better overview of the structural transformation of the nanocatalysts, we compare their EXAFS fittings before, during, and after running CO₂RR (**Figure 3a-f, Figures S7-S9**). As previously reported, the as-synthesized 7 nm Cu NPs (**Figure S10**) present a more oxide-dominant

character than their 18 nm counterparts (**Figure 3a,d**). According to a linear combination analysis (LCA), the as-synthesized 7 nm and 18 nm Cu NP ensembles are composed of 15% and 85% Cu⁰, respectively (**Figure S11**). This is consistent with the high SA/Vol of the smaller 7 nm NPs, thus especially prone to air oxidation despite their passivating ligands. Meanwhile, although the 18 nm Cu NP ensemble exhibits a more prominent Cu-Cu₁ peak intensity (**Figure 3a**), the $N_{\text{Cu-Cu}_1}$ of 8.7 obtained from the EXAFS data fitting is lower than 12, the expected value for bulk fcc Cu⁰. It also involves no oxide phase as reflected in the absence of a Cu-O₁ peak around 1.8 Å. The 5-fold twinned structure of these NPs might induce strain, resulting in the measured surface coordination being lower than bulk Cu⁰ foil.

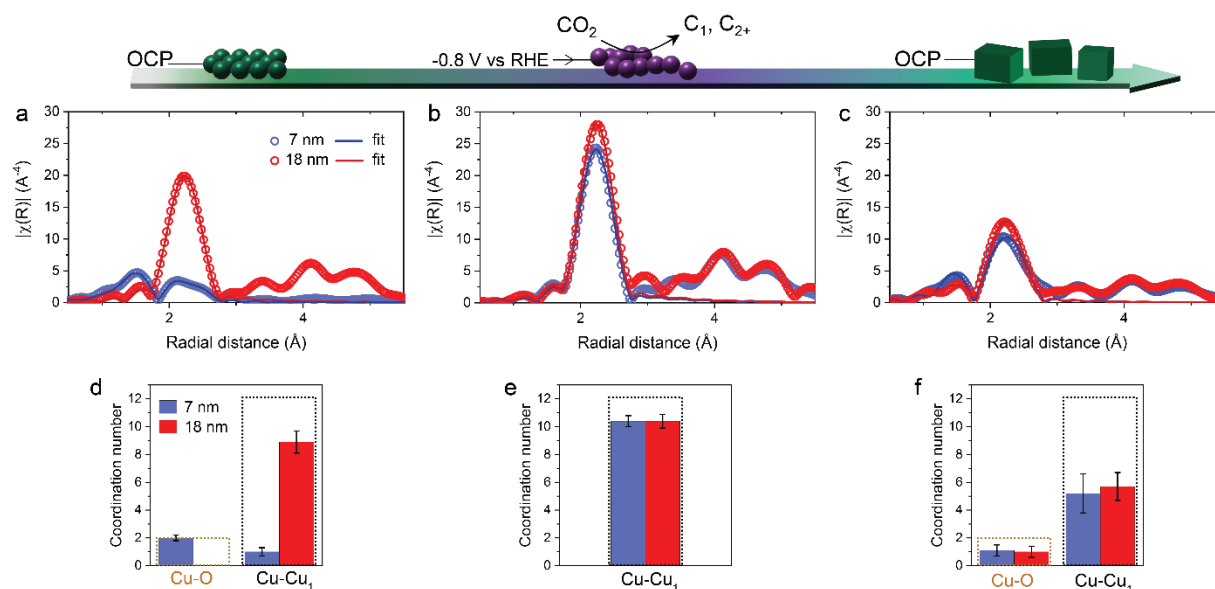


Figure 3. Operando EXAFS fittings of the 7 nm and 18 nm Cu NP ensembles before, during and after CO₂RR at -0.8 V vs RHE. k^3 weighted R spectra ($3 < k < 12$, $1 < R < 2.7$) of the 7 nm (blue) and 18 nm (red) Cu NP ensembles (a) before, (b) during CO₂RR at -0.8 V vs RHE, and (c) after. Pre- and post-electrolysis data is acquired at open circuit potential (OCP) while mounted inside the cell. All data is represented by circular symbols while fittings are solid lines. (d-f) The corresponding coordination numbers calculated from the fittings which employ a Cu₂O (encased in yellow) and a Cu (encased in black) crystal structure to generate the expected scattering path calculated with f_{eff} (see Methods and Table S1 for more details). The yellow and black dotted rectangles indicate the expected value of the coordination number for the bulk of each crystal structure, e.g., bulk fcc Cu has a $N_{\text{Cu-Cu}_1}$ value of 12. The error bars correspond to the fitting error associated with each of those coordination numbers.

Once exposed to CO₂-reducing conditions, the *operando* EXAFS reveals a larger $N_{\text{Cu-CuI}}$ for both nanocatalysts compared to their respective as-synthesized structures. This increase is more dramatic in the case of the 7 nm Cu NP ensemble that goes from a Cu₂O dominant character with nearly no metallic Cu-CuI contribution, to a $N_{\text{Cu-CuI}}$ of 10.1. Meanwhile, the 18 nm Cu NP ensemble already features a metallic $N_{\text{Cu-CuI}}$ of 8.7 before electrolysis, which increases to 10.1 during the reaction (**Figure 3b,e**). This is mostly due to the rapid and complete reduction of the NPs as reported in our previous works (**Figure S12**).^{9,16} While the transition from a more oxidized to a fully reduced structure was expected, its value of $N_{\text{Cu-CuI}} = 10$ is inferior to previous observations (**Figure 3e**). In earlier work, we had attempted to isolate the active structure of the 7 nm and 14 nm Cu NP ensembles with a quasi *in situ* method. The nanocatalysts were BTA-passivated immediately after electrolysis to “quench” their surface oxidation. The resulting $N_{\text{Cu-CuI}}$ measured with this approach were considerably lower, ~3 and ~7 for the 7 nm and 14 nm Cu NP ensembles, respectively. However, an imperfect passivation leaving traces of Cu₂O can impact the metallic $N_{\text{Cu-CuI}}$ extracted from fittings, leading to its underestimation (**Discussion S3**). Therefore, the *operando* CN values in this work which result from a metallic-only system are more reliable.

Discussion

The comparison of the 7 nm and 18 nm Cu NP ensembles' EXAFS during their respective life cycle further illustrates the complexity of these ensembles' dynamics. While they present clear structural differences before CO₂RR (**Figure 3a**), they qualitatively exhibit Cu-CuI peaks of slightly different intensity *in operando* (**Figure 3b**). Fitting the EXAFS data assuming the two systems are distinct reveals an $N_{\text{Cu-CuI}}$ of ~10 for both the 7 nm and 18 nm Cu NP ensembles. If the same degree of structural disorder, i.e., same σ^2 is assumed for both systems, the EXAFS fits

yield N_{Cu-CuI} of 9.9 and 10.9 for the 7 nm and 18 nm Cu NP ensembles, respectively (**Figure S13** and **Table S2**). While more pronounced, that difference remains very small. A similar observation is made for the systems post-electrolysis where their best fit N_{Cu-CuI} are both ~ 5 . Again, although the Cu-CuI peak intensity of both ensembles seems qualitatively to differ (**Figure 3c**), their N_{Cu-CuI} are the same within error and the LCA indicates only a $\sim 5\%$ larger contribution of the oxide phase in the 7 nm Cu NP ensemble post-electrolysis (**Figure 3f** and **Figure S14**). Overall, the structural differences initially observed become and remain less apparent after electrolysis. The lack of differences in the N_{Cu-CuI} of the 7 nm and 18 nm Cu NP ensembles during CO₂ electrolysis contradicts several previous observations. First, the fitting of the post-CO₂RR BTA-passivated ensembles presented apparent differences between the 7 nm and 14 nm NP ensembles (which are expected to be even greater for the 18 nm NPs). Second, the rate of the ensemble oxidation post-electrolysis was previously reported to be especially fast for the 7 nm Cu NP ensemble. Finally, we previously verified that the active surfaces of these two ensembles were electrochemically distinct using Pb underpotential deposition (UPD). In light of this information, we can formulate the following hypothesis.

Assuming the Cu NPs adopt a spherical shape with the fcc structure, metallic Cu NPs larger than 10 nm in diameter are expected to exhibit negligible differences in their average N_{Cu-CuI} (**Figure S15** and **Figure 4a**). Before electrolysis, Cu NPs are self-assembled into a monolayer of Cu NPs that retain a distinct size and average N_{Cu-CuI} . However, upon applying a potential, the Cu NPs structurally transform into larger structures, mostly greater than 10 nm in diameter or edges if rectangular, which clearly exceeds 1000 atoms per aggregate. As previously shown in several studies, irrespective of the size or shape, metallic clusters larger than 1000 atoms, or fcc spherical cluster of 3.5 nm in diameter, exhibit a N of the first and second shell close to their bulk value.^{26,28,29}

Consequently, little to no difference can be determined in the first coordination shell of the 7 nm and 18 nm Cu NP ensembles. However, as highlighted by Jentys et al. in their study of Pt clusters, the coordination numbers of the higher shells are more influenced by the size and shape of metallic clusters.²⁶ Unfortunately, here the fitting of other shells beyond the first was found to be limited by a necessary constraint on the second Cu-Cu2 path (see **Discussion S4**). Because of this constraint, the pertinence of the values obtained for paths at higher radial distances may be less reliable. Given the larger structures formed during the electrochemical scrambling of these Cu NP ensembles, Cu K-edge EXAFS becomes less sensitive to differences in the surface structure of the transformed nanocatalyst.

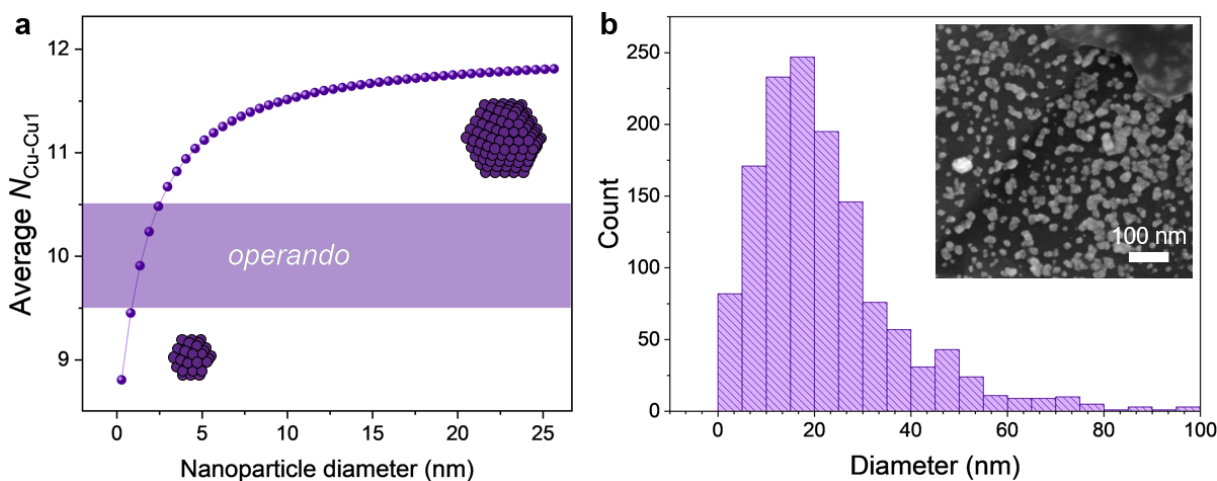


Figure 4. Average $N_{\text{Cu-Cu1}}$ calculated from a spherical fcc sphere geometry. (a) The $N_{\text{Cu-Cu1}}$ derived from EXAFS fittings (purple band indicates 10 ± 0.5) is distinctively lower than the average $N_{\text{Cu-Cu1}}$ estimated from fcc spheres larger than 5 nm in diameter. **(b)** Estimated diameter distribution of post-electrolysis features formed from the 7 nm Cu NP ensemble after 2 h CO_2RR in the *operando* cell at -0.8 V vs RHE. Diameter values are derived from the projected surface area of the features measured in an SEM image and extrapolated to assume a spherical shape. Inset of a representative SEM image (scale bar = 100 nm).

The larger gap between the 7 nm and 18 nm Cu NP ensembles, as well as the especially low $N_{\text{Cu-Cu1}}$ of the 7 nm ensemble, which were observed in the previous quasi-*in situ* measurements, may result from the imperfect passivation of the catalyst and the persistence of Cu_2O . Although we had demonstrated with high-resolution TEM (HR-TEM) and Cu K-edge

XANES that there was a lesser degree of post-electrolysis oxidation after BTA-passivation, thoroughly quenching those oxidation-prone nanograins outside of an inert atmosphere remains evidently imperfect. In addition, even if the apparent SA/Vol of the structures formed during CO₂RR were found to be of comparable values from both the 7 nm and 14 nm Cu NP ensembles, the smaller NPs can form a larger number of nanograins. This is corroborated by the presence of more extended crystalline domains found for larger NP ensembles after BTA-passivation.¹⁶ A higher density of nanograins increases vulnerability to rapid surface oxidation, which in turn would lead to a greater underestimation of $N_{\text{Cu-CuI}}$ from the metallic phase for the 7 nm than the ≥ 14 nm Cu NP ensemble.

Overall, the successful transition of this nanocatalyst into an *operando* configuration, adapted to reproduce its dynamic reconstruction toward its inherently active state for CO₂-to-C₂₊, has allowed us to improve our understanding of the previously incomplete insights obtained in our previous studies. Namely, the 7 nm Cu NP ensemble undoubtedly forms an active structure with an especially high density of active nanograins that correlate with enhanced CO₂-to-C₂₊ conversion. However, once subject to electroreduction conditions, both the 7 nm and the 18 nm Cu NPs migrate and agglomerate into larger structures, which are structurally more difficult to deconvolute only from first shell Cu K-edge EXAFS fittings. The agglomerates larger than 10 nm in diameter or edge feature coordination numbers are significantly less sensitive to any shape or size differences. Yet, if the Cu NPs assume metallic Cu fcc structures during electrolysis, the electrocatalytically active surface of the microscopic features observed by *ex situ* SEM must be composed of several grains equivalent to Cu clusters between 200 and 600 atoms, i.e., spherical 2 and 3.5 nm diameter, to achieve the persistent $N_{\text{Cu-CuI}}$ of 10 fitted for both the 7 nm and 18 nm Cu NP ensembles.³⁰ This is relatively coherent with the Cu grains in the 5-10 nm range previously

observed with EC-STEM.⁹ In this case scenario, EXAFS analysis is not suitable to distinguish the nanograins' density between the two studied ensembles. Only the qualitatively persistent difference in the Cu-Cu1 peak intensity and the slightly larger degree of oxidation observed in the 7 nm Cu NP ensemble post-electrolysis corroborate the hypothesis that a higher density of nanograins is formed in the nanocatalyst formed from smaller Cu NPs.²¹ It is important to note that the estimation made from our model can only be considered insightful in the case of a homogeneous distribution for the nanocatalyst features' size and shape. Thus, the importance of monitoring and reporting post-electrolysis images with morphological information. In this study, the size distribution of post-electrolysis features reveals a mean diameter of 23 nm with a standard deviation of 10.5 nm (**Figure 4b**). This estimation doesn't take the larger aggregates into account. Given that the latter is expected to exhibit a much larger average $N_{\text{Cu-Cu1}}$, this implies that the undercoordinated sites present on the structurally transformed Cu NP ensemble must be especially low to amount to the *operando* $N_{\text{Cu-Cu1}}$ 10.

Conclusion

The careful adaptation of the dynamic structural transformation of a CO₂RR performant Cu nanocatalyst from an H-cell to an XAS-compatible *operando* cell has allowed us to confirm the undercoordinated character of the electrocatalyst surface active for C-C coupling. The *operando* cell design preserves the support and reaction environment necessary for the sensitive structural evolution of a 7 nm Cu NP ensemble toward their active form, especially performant for the CO₂ electroconversion to C₂₊ products. Like studies carried out in a H-cell, the distinct transformation and resulting CO₂RR activity of an 18 nm Cu NP ensemble is also reproduced in our *operando* cell. The *operando* EXAFS results uncover surprising similarities between the otherwise electrocatalytically different nanocatalysts. Concretely, we measure a $N_{\text{Cu-Cu1}}$ of 10 for both Cu NP

ensembles while running CO₂RR at -0.8 V vs RHE. Given the structural homogeneity observed for the Cu NP ensembles, we can attribute this $N_{\text{Cu-CuI}}$ value to a high degree of surface undercoordination present *operando*. In fact, most structures formed during the Cu NP ensemble electrochemical scrambling exhibit sizes too large to explain their average $N_{\text{Cu-CuI}}$. Those results corroborate the hypothesis that a high density of nanograins made of 2-3 nm diameter clusters form during CO₂RR and serve as support for undercoordinated sites of superior electrocatalytic activity. Most importantly, given the real-time measurements of C₂⁺-products captured during the EXAFS measurements, we can confirm that those undercoordinated sites are essential to the C-C coupling step.

ASSOCIATED CONTENT

Supporting Information.

Additional experimental details, methods, and data analysis (PDF)

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ABBREVIATIONS

XAS, X-ray absorption spectroscopy (XAS); CO₂RR, CO₂ reduction reaction; C₂H₄, ethylene; EtOH, ethanol; C₂₊, multicarbon; NP, nanoparticle; XANES, X-ray absorption near-edge spectroscopy; EXAFS, extended X-ray absorption fine structure; EC-STEM, electrochemical liquid-cell scanning transmission electron microscopy; FE, faradaic efficiency; OCP, open circuit potential; RHE, reversible hydrogen electrode; HER, hydrogen evolution reaction (HER); SA/Vol, surface area-to-volume (SA/Vol); LCA, linear combination analysis (LCA); BTA, benzotriazole; UPD underpotential deposition.

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