Investigating the Role of Copper Oxide in Electrochemical CO₂ Reduction in Real Time

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ABSTRACT: Copper oxides have been of considerable interest as electrocatalysts for CO₂ reduction (CO₂R) in aqueous electrolytes. However, their role as an active catalyst in reducing the required overpotential and improving the selectivity of reaction compared with that of polycrystalline copper remains controversial. Here, we introduce the use of selected-ion flow tube mass spectrometry, in concert with chronopotentiometry, in situ Raman spectroscopy, and computational modeling, to investigate CO₂R on Cu₂O nanoneedles, Cu₂O nanocrystals, and Cu₂O nanoparticles. We show experimentally that the selective formation of gaseous C₂ products (i.e., ethylene) in CO₂R is preceded by the reduction of the copper oxide (Cu₂OR) surface to metallic copper. On the basis of density functional theory modeling, CO₂R products are not formed as long as Cu₂O is present at the surface because Cu₂OR is kinetically and energetically more favorable than CO₂R.

KEYWORDS: electrochemical CO₂ reduction, CO adsorption, chronopotentiometry, Raman spectroscopy, Cu₂O reduction, DFT modeling

1. INTRODUCTION
Conversion of carbon dioxide (CO₂), an important greenhouse gas, into energy-rich chemicals is a viable approach to reducing the global carbon footprint.¹ Electrochemical CO₂ conversion (CO₂R) using renewable electricity is envisaged as a promising technology to achieve this end.² Among the many catalysts studied for CO₂R, copper is unique because it is the only metal that reduces CO₂ to significant amounts of C₂ and higher-order hydrocarbons and alcohols.³,⁴ Nanostructuring copper into cubes and needles can enhance the selectivity toward C-C coupled products.⁵-⁷ Alternatively, copper oxides can be employed as precursors for making high-surface-area structures.⁸,⁹ When operated under CO₂R conditions (typically -0.8 to -1.1 V vs RHE), the oxides would be reduced to metallic copper (Cu⁰) in accordance with the Pourbaix diagram, producing nanostructured Cu.¹⁰ In the literature, the improved performance of such oxide-derived copper nanostructures toward C₂ products has been attributed to a number of factors: (1) a higher local pH at the catalyst surface, favoring the pH-independent C-C coupling pathway over the formation of methane,¹¹ (2) a higher density of grain boundaries and defect sites, optimizing the binding energy of reaction intermediates such as CO,¹²,¹³ and (3) the presence of oxides and subsurface oxygen alongside the metal, which provides Cu sites with multiple valences to increase catalytic activity.¹⁴,¹⁵,¹⁶,¹⁷,¹⁸,¹⁹,²⁰,²¹ Studies on copper oxide as a CO₂R electrocatalyst showed transient changes in the product distribution attributed to the temporary presence of surface oxide species.²²,²³ Recently, Li et
al. found that thermally oxidized copper showed stable and improved product generation to CO and HCOOH at a lower overpotential compared to that for polycrystalline copper; however, this performance was not attributed to the oxide itself. This is reasonable given the Pourbaix diagram for Cu and was confirmed in their ex situ X-ray diffraction (XRD) study. Kas et al. investigated electrodeposited Cu2O of different orientation and thickness and found that the selectivity depended on the initial oxide thickness and not on the orientation of the starting copper oxide. By performing cyclic voltammetry and employing online electrochemical mass spectrometry, they concluded that CO2R starts only after Cu2O is reduced into Cu. However, this study did not employ an in situ characterization of the catalyst surface. Using in situ Raman spectroscopy, Ren et al. found that in aqueous, CO2-saturated 0.1 M KHCO3 the surface of a Cu2O film reduces within a few minutes to Cu0 at negative potentials. Interestingly, in this same study, it was found that when all signals belonging to copper oxide had disappeared, adsorbed CO2, the pertinent reaction intermediate in CO2R, is detected. All of these studies suggest that surface Cu0 and not copper oxide is the active catalyst species.

In contrast, Lee et al. and Mistry et al. used in situ X-ray absorption near-edge structure (XANES) spectroscopy to show the presence of Cu0 even after CO2R begins. They proposed that residual Cu0 is responsible for the improved selectivity to C2 products found with oxide-derived (OD) copper. Similarly, Eilert et al. using in situ ambient pressure X-ray photoelectron spectroscopy (XPS), reported the existence of subsurface oxygen during CO2R. They proposed that the enhanced C2 selectivity is due to subsurface oxygen, which changes the electronic structure of the Cu and enhances the binding of CO.

However, they concluded that the catalyst is present only in the Cu0 state. This contradiction in the results can be explained by the difference in the surface sensitivity of the techniques. XANES is a bulk material characterization technique in contrast to XPS which is a surface-sensitive technique. Mistry et al. and Eilert et al. both performed further analysis on the subsurface of the catalyst utilizing transmission electron microscopy energy-dispersive X-ray (TEM-EDX) and transmission electron microscopy electron energy loss spectroscopy (TEM-EELS), respectively, with conflicting conclusions. Mistry et al. claimed that an oxide phase exists, whereas Eilert et al. claimed the presence of a pure metallic phase with small subsurface oxide.

Summarizing the current literature, there are conflicting reports regarding the possible role of copper oxide in CO2R, especially relating to the role of surface copper oxide as the active catalyst. The question remains whether copper oxide itself can be a catalyst, if it only acts as the precursor for the formation of nanostructured copper, or if it could be a catalyst. Here, we investigate whether surface copper oxide itself plays any role as a catalyst in CO2R.

Because copper oxides are quickly reduced under cathodic conditions and quickly reoxidized upon the removal of that condition (see Figure S18, Supporting Information (SI) for details), it is difficult to determine with ex situ techniques if the periodically measured products are formed on the oxide or on the (largely) metallic surfaces. In operando, surface-sensitive techniques can help to clarify this. Previously, real-time product detection and in operando surface spectroscopy have not been combined to investigate the role of copper oxide.

Herein, we combine Raman spectroscopy with selected-ion flow tube mass spectrometry (SIFT-MS) to study in real time both the surface and the products generated during electrochemical CO2R. Density functional theory (DFT) calculations were employed to model the system and could rationalize the results very successfully. SIFT-MS can detect and quantify gaseous products such as methane, ethane, and ethylene as well as higher-order hydrocarbons, like propene, in a time scale of 0.1–10 s (depending on the number of masses scanned). This enables the capture of reaction dynamics. In this way, it overcomes the classic problem faced in much of the literature where the gaseous products of CO2R are analyzed by gas chromatography (GC) with analysis times in the range of minutes. In addition, liquid products, typically detected by high-pressure liquid chromatography (HPLC) or nuclear magnetic resonance spectroscopy (NMR), are only measured once at the end of an experiment by sampling aliquots of the electrolyte.

SIFT-MS allows the simultaneous detection of liquid products with finite vapor pressure (this aspect of the technique will be presented in another paper). SIFT-MS is able to provide this real-time analysis of complex multicomponent mixtures because of its use of gentle chemical ionization reactions. These reactions, such as proton addition, avoid the fragmentation of molecules typical of electron ionization mass spectrometry (MS), which results in an extremely low limit of detection of the parent ion. SIFT-MS has been well reviewed in the literature, and we point the reader to these works for a deeper understanding of the advantages of this technique. We have published technical details of SIFT-MS applied to CO2R elsewhere.

Here, three different forms of Cu2O were synthesized by electrochemical and thermal methods, yielding oxide-derived catalysts of different surface structures and different CO2R activities. These catalysts were subsequently evaluated in real time, using an electrochemical cell previously detailed, to determine the onset of CO2R after switching on a constant cathodic current. By combining DFT study and in situ Raman spectroscopy with real-time product detection, we show that Cu2O reduction (Cu0OR) typically occurs before CO2R begins because Cu0OR is energetically more favorable. Interestingly, Cu0 with certain exposed surfaces could be active catalysts for CO2R if not poisoned by reaction intermediates.

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalyst. Three types of copper oxides were prepared for this study. The first was synthesized by thermally annealing copper foils in a tube furnace at 450 °C for 3 h (Cu NP). Copper oxide nanocrystals (Cu NCs) were synthesized by a method previously reported. Copper oxide nanoneedles (Cu NN) were synthesized by anodizing the Cu foil in 2 M KOH solution in a two-electrode setup using graphite as the counter electrode. The electrode anodization was carried out at a constant current density of 7 mA/cm2 for 5 min for synthesizing Cu(OH)2 after which it was annealed in vacuum at 700 °C to convert Cu(OH)2 into Cu2O nanoneedles.

2.2. In Situ Raman Spectroscopy. In situ Raman spectroscopy was carried out with a confocal Raman microscope (modular system from HORIBA Jobin Yvon) in an epi-illumination mode (top-down). A He–Ne laser with 633 nm wavelength (CVI Melles Griot) was used as the excitation source. A water immersion objective lens (LUMFL, Olympus, 60×, numerical aperture: 1.10) covered with a 0.013 mm thin Teflon film (American Durafilm) was used to focus and collect the laser beam onto the sample. A liquid nitrogen-cooled charge-coupled device (CCD) camera (Princeton Instruments, PI-Max3, 2048 × 2048) was used to monitor the Raman signal. The laser power on the sample was kept below 10 mW to avoid any photothermal effects. The Raman spectra were recorded in the backscattering geometry using a 50× objective (numerical aperture: 0.85) and collected through a 1200 grooves/mm grating at a scattering angle of 180°. The spectra were recorded with a spectral resolution of 2 cm−1.

The Raman microscope was integrated with a cryo-chamber to study the sample under cryogenic conditions (−150 °C). The cryo-chamber was equipped with a variable temperature stage (VCT-77, Oxford Instruments) enabling temperature-controlled experiments from room temperature to liquid nitrogen temperature. The sample preparation was carried out on electrical conducting Cu foils (Cu foil). The sample was placed on an electrical conducting Cu foil and placed on the sample holder. The sample was annealed in vacuum at 700 °C to convert Cu(OH)2 into Cu2O nanoneedles.
the incident and scattered laser light. The backscattered light was filtered through a 633 nm edge filter, before being directed into a spectrograph (iHR320)/charge-coupled device detector (Synapse CCD). The electrochemical Raman cell was a round Teflon dish with the detachable Cu electrode mounted in the middle. The acquisition time for each spectrum was 10 s.

2.3. Computational Details. We used the Vienna ab initio simulation package (VASP) for all periodic boundary calculations. The projector augmented wave (PAW) method together with the PBE exchange-correlation functional was employed to describe the electron–ion interactions. A cutoff of 450 eV was chosen for the plane wave basis set in all calculations. A Monkhorst–Pack type k-point grid was chosen for the optimization of bulk Cu and Cu2O. The Gaussian smear method was used for Cu2O and Cu. The value was chosen to be 0.1 eV for both cases. The energy convergence criterion was set to be $10^{-6}$ eV per unit cell, and the force convergence criterion of 0.03 eV/Å was used for all structure optimizations. We noted that sometimes the geometry optimization converges to stationary structures rather than energy-minimum structures (Figure S8). Therefore, we optimized all intermediate structures without symmetry constraints and always did frequency calculations to confirm that the optimized structures are energy-minimum structures. For the calculation of transition states (TSs), a tighter convergence criterion of $10^{-8}$ eV per unit cell was used. We used the nudged elastic band (NEB) method to locate the proper guess TS geometries, which were then optimized to saddle points with the improved dimer method. Frequency calculations were performed to confirm the nature of located transition states. A Monkhorst–Pack type k-point grid was chosen for slab calculations. Slab models were chosen to have 4 unit cells, which corresponds a coverage of $\theta = 1/4$. Seven layers of Cu were used to construct the Cu(111) slab model, whereas six atomic layers (three layers of Cu and three layers of O) were used to construct the Cu2O(111) and Cu2O(200) slab models. The sizes of slab modes were chosen to be $5.13 \times 5.13 \times 33.86$ Å, $6.084 \times 6.084 \times 22.452$ Å, and $6.084 \times 6.084 \times 23.605$ Å for the Cu (111), Cu2O(111), and Cu2O (200) surfaces, respectively. During the geometry optimization of the slab models, bottom five layers of Cu(111) slabs and bottom two layers (one layer of Cu and one layer of O) of Cu2O(111) and Cu2O (200) slabs were fixed at the bulk position.

The relative energies of intermediates of CO2 reduction (CO2R), hydrogen evolution reaction (HER), and Cu2O reduction (Cu2OR) were calculated relative to CO2, H2, and bare surfaces. For reactions involving the release of H2O, e.g., *COOH to *CO, the energy of isolated H2O was used in the calculations. A supercell of $15.0 \times 15.0 \times 15.0$ Å, the Gaussian smear method and a value of 0.1 eV were used in the calculations of small molecules. For reaction steps involving H+ and e−, the computational hydrogen electrode technique developed by Nørskov et al. was used to consider the dependence of relative energies on pH and applied bias potential and the detailed calculation approach is shown in Scheme S1 (see computational details in SI). The dispersion interactions were considered with Grimme’s D3 correction and the solvation effects were considered with the implicit solvation model as implemented in VASPsol. A dielectric constant of 80.0 was used to represent bulk water solvent. The effects of dispersion and solvation are shown in Figures S9–S11. Frequency

Figure 1. SEM images (scale 1 μm) of as-prepared copper oxides before CO2R: (a) nanoneedles (NNs), (b) nanocrystals (NCs), and (c) nanoparticles (NPs) and after CO2R: (d) nanoneedles (NNs), (e) nanocrystals (NCs), and (f) nanoparticles (NPs).
analysis was performed for both absorbates and surface atoms, which are allowed to relax to calculate thermal correction to the free energies, which are listed in Tables S4–S7. Please refer to the Supporting Information for more computational details.

3. RESULTS AND DISCUSSION

3.1. Characterization of Electrocatalysts. Scanning electron microscopy (SEM) images of catalyst precursor structures formed from nanoneedles (NNs), cubic nanocrystals (NCs), and nanoparticles (NPs) before and after CO2R are shown in Figure 1a–f. Clearly, the morphology of all catalysts after reduction is different and different from that of the pristine Cu2O state (also distinct from planer electropolished Cu; Figure S2). In particular, we note that the reduced catalysts appeared to be composed of small particles, which could increase the effective catalytic area and provide a variety of defects and step-edge sites. Figure 2a,c,e shows the XRD patterns of the copper oxide samples before and after CO2R. In all samples before CO2R, we can identify peaks corresponding to Cu2O and the underlying Cu substrate in accordance with database patterns extracted from the International Center for Diffraction Data (ICDD No-01-077-0199 for Cu2O and 00-004-0836 for Cu). The Cu2O samples have different preferential orientations, shown by the higher intensities of the (200) peak of NCs versus those of the (111) peak of NPs. Interestingly, all three catalysts showed different preferential orientations after reduction as well; NCs and NNs showed higher intensities of the Cu (200) peak versus those of the Cu (111) peak of NPs.

The Raman spectra collected under ambient conditions before and after CO2R are shown in Figure 2b,d,f, and the identified Raman peaks are listed in Table S1. Interestingly, NN and NP samples show Cu2O peaks slightly below \( \Gamma_{12}^{\pm} \) at 109 cm\(^{-1}\) and \( \Gamma_{15}^{(1)} \) at 154 cm\(^{-1}\) possibly due to defect formation or strain. In contrast, the NC sample shows Cu2O peaks close to the expected values and with low Raman intensity. In perfect crystals, \( \Gamma_{12}^{\pm} \) and \( \Gamma_{15}^{(1)} \) phonon modes are IR-active and Raman-inactive.46

In the following sections, we investigate the initial period of Cu-oxide reduction in more detail employing in situ spectroscopic methods and DFT modeling.

3.2. In Situ Measurement of CO2R Products. A benchmark study was performed to validate that the CO2R production measurements made by SIFT-MS agree with those performed with traditional techniques such as GC (see Figure S1 for the experimental setup). The products from copper oxide NNs operated at a constant current density of \(-10\) mA/cm\(^{2}\) were measured. Figure 3a shows the GC data and overlaid SIFT-MS data for methane, ethylene, and propene (SIFT-MS detects all hydrocarbons but cannot detect H\(_2\) and CO). The extracted Faradaic efficiency (FEs) of both methods coincided within experimental uncertainties. Additional comparative data for SIFT and GC are provided in the SI (Figure S4). Figure 3b shows the real-time measurement of FEs for methane (C\(_1\)), ethylene (C\(_2\)), and propene (C\(_3\)). As explained below, during the first few minutes, Cu2O reduction predominates, and we do not observe the CO2R product in SIFT-MS. The sensitivity of the SIFT-MS technique is evident from the detection of the C\(_3\) product with only 0.1% FE. Detailed FEs of the products are listed in SI (Table S2).

Once a current is applied to a Cu2O cathode, three reduction processes are possible, namely, CO2R, hydrogen evolution reaction (HER), and Cu2OR to metallic copper. To identify the dominant reaction in the initial phase, we take advantage of the real-time sensitivity of SIFT-MS. Figure 4 shows the
chronopotentiometry (CP) and online SIFT-MS data of the different samples (the liquid products are shown in Figure S5). In a CP measurement, constant current is applied to an electrochemical cell and the change in voltage is measured as a function of time. Different current densities are chosen for different samples such that the long-term potential for all samples is approximately −0.8 V versus the reversible hydrogen electrode (RHE), a good operational condition for CO2R.14,15 The CP curve for all samples possesses a slightly negative initial potential ($V_i \approx −0.2$ V vs RHE) up to a time ($t_i$) when the potential steeply increases to stabilize at a final potential ($V_f \approx −0.8$ V). The observed change in potential from $V_i$ to $V_f$ is due to the change in the surface reaction at the cathode from copper oxide reduction during $V_i$, $t_i$ to CO2R after that and is explained in detail in SI-V. Time traces for NC samples run at different current densities are shown in the SI (Figure S6). In all cases, CO2R products are detected only after the increase in the overpotential measured in CP. This provides strong evidence that at the beginning Cu2OR is kinetically favored relative to CO2R. Only when Cu-oxide is essentially completely reduced to metal does CO2R begin.

Because SIFT-MS cannot detect CO and H2, we have conducted GC measurements to rule out HER during the initial phase. Because of the slow time evolution of GC, we slowed down the rate of Cu2O reduction to stretch the initial phase $t_i$. Hence, we have run the samples at a very low constant current density of $−1$ mA/cm2. Figure 5 shows the chronopotentiometry and GC data of NCs and NNs under such conditions, confirming that there are no HER and no CO2R products (including CO and H2) during the initial period, $t_i$. Cu NPs run at $−1$ mA/cm2 did not fully reduce during the 1 h reaction, and no products are observed by GC shown in the SI (Figure S7).

### 3.3. Density Functional Theory Modeling

To rationalize the distinct reactivity of Cu2O NCs, NNs, and NPs, we analyzed the reaction free energy profiles of CO2R at the density functional theory (DFT) level, using the Vienna ab initio simulation package.$^{34−37}$ Figure 2 shows that the dominant XRD peak of Cu2O NPs corresponds to the (111) surface and that of Cu2O NCs corresponds to the (200) surface, whereas those of Cu2O NNs exhibit both (111) and (200) surfaces. Therefore, we calculated the relative free energies of intermediates of CO2R, HER, and Cu2O on both Cu2O (111) and Cu2O (200) relative to CO2, H2, and bare surfaces. In addition, we computed the relative free energies of intermediates of HER and CO2R on Cu (111).

Figure 6a shows the DFT-optimized geometries of model surfaces of Cu (111), Cu2O (111), and Cu2O (200). The Cu–Cu distance on Cu (111) is 2.57 Å, similar to that of bulk Cu. In contrast, the Cu atoms on Cu2O (111) and Cu2O (200) are significantly spaced more due to their coordination to O atoms (Figure S8). In addition, the presence of subsurface O atoms creates different binding sites, leading to different binding modes and reactivity of molecular adsorbates. For example, with the PBE functional, CO prefers to bind at fcc sites on the Cu (111) surface, with a binding energy of $−0.79$ eV, consistent with previous studies.$^{1}$ However, as shown in Figure S8, on the
Cu$_2$O (111) surface, CO prefers to bind at the atop position of Cu atoms (−1.37 eV) and on the Cu$_2$O (200) surface, CO binds at the bridge site (−1.34 eV), forming stronger bonds than on Cu (111).

We first analyze the HER and CO$_2$R on Cu (111). Figure 6b shows the relative free energies of intermediates of HER and CO$_2$R. The reduction of protons to form surface-bound hydrogen atoms is energetically favorable, and the subsequent reduction to release H$_2$ requires only 0.12 eV, consistent with the experimental observation that hydrogen is the major product at low bias potentials. The reduction of CO$_2$ to CO needs to overcome the high-energy intermediate *COOH with a relative free energy of 0.52 eV, whereas further reduction of CO needs to overcome the high-energy intermediate *CHO with an energy increase of 0.76 eV. Both energy uphill steps involve redox processes, which can thus be driven by applying a potential. As shown in Figure S12, the total energy balance for CO reduction products becomes negative when applying a bias potential more negative than −0.07 V, it is possible to open a Cu$_2$OR pathway to reduce surface-bound hydroxyl groups to H$_2$O (Figure S13a). At an even more negative bias potential (< −0.78 V), the reduction of surface-bound CO is also possible, leading to hydrocarbon products (Figure S13c).

Next, we analyze the reduction of Cu$_2$O surfaces through Cu$_2$OR and CO$_2$R reaction pathways. Figure 6c,d shows the relative free energies of the intermediates of HER, CO$_2$R, and Cu$_2$OR on Cu$_2$O (111) and Cu$_2$O (200). As mentioned above, CO binds more strongly on Cu$_2$O surfaces than on Cu (111). In addition, all other intermediates of CO$_2$ reduction are more stabilized on Cu$_2$O surfaces. Furthermore, the reduction of a proton to form surface-bound hydrogen is energetically very favorable on Cu$_2$O (111), more favorable than CO$_2$R pathways. However, the reduction of the second proton to release H$_2$ requires an energy increase of 0.66 eV. The reduction of a subsurface O atom to form surface-bound OH on Cu$_2$O (111) is energetically very favorable, but the further reduction of surface-bound OH to H$_2$O is slightly energy uphill. With bias potentials more negative than −0.07 V, it is possible to open a Cu$_2$OR pathway to reduce surface-bound hydroxyl groups to H$_2$O (Figure S13a). At an even more negative bias potential (≪ −0.78 V), the reduction of surface-bound CO is also possible, leading to hydrocarbon products (Figure S13c). Similar energetics applies to Cu$_2$O (200) (Figure S14). Again, the reduction of subsurface O atoms to form surface-bound hydroxyl groups, and ultimately H$_2$O, is very favorable. We note that the binding location for H and OH differ (Figure S8), and consequently, the strong binding energy of H does not hinder Cu$_2$OR. Thus, Cu$_2$OR on Cu$_2$O (200) is more favorable than the HER or CO$_2$R and it is the expected reaction to proceed (for energy diagrams under bias, see Figure S14). We note that the reduction of surface-bound CO on Cu$_2$O (200) requires much less energy than on Cu$_2$O (111), suggesting that CO$_2$R on Cu$_2$O(200) is possible. However, the Cu$_2$OR is energetically favorable and expected to be the dominant reaction. For completeness, we also highlight that a surface oxygen atom is easily removed from Cu surfaces (Figure S15).

The calculated energetics suggests that Cu$_2$OR is thermodynamically more favorable than CO$_2$R on both Cu$_2$O(111) and Cu$_2$O(200). We also located transition states associated with Cu$_2$OR and CO$_2$R on both surfaces, and the results are given
in Figure S16. The barriers for Cu2OR are much lower than those for CO2R. Therefore, Cu2O is both energetically and kinetically more favorable than CO2R on both copper oxide surfaces.

3.4. In Situ Raman Spectroscopy. We now discuss in situ Raman spectra for the different copper oxide samples. Figure 7b shows the time-dependent Raman spectra of NCS (the corresponding CP curves are shown in Figure S17). The black curve was taken as reference and is measured in the original condition before the reaction has started (no current is applied). We can identify peaks at 144, 215, 528, and 623 cm$^{-1}$ corresponding to Cu2O.58 After application of current, the next Raman spectrum is taken at 10 s, and it shows a significant enhancement in intensity. The signal enhancement can be due to either surface-enhanced Raman spectroscopy (SERS)33 or inelastic light scattering by charge carrier excitations in the metal (i.e., by electron–hole pair excitations), which are made possible by the breakdown in momentum conservation caused by the submicroscopic surface roughness.51 Considering that enhancement in Raman spectra (RS) is observed, we conclude that a metal Cu layer forms as Cu2O reduction starts, whereas residual oxide remains present in the bulk. With enhancement in RS, there is a corresponding change in the background signal, making it hard to interpret the peaks in the range of 100–250 cm$^{-1}$. Hence, we focus on Cu2O peaks between 250 and 750 cm$^{-1}$. The Raman peaks attributed to Cu2O (528 and 623 cm$^{-1}$) show a sudden decrease in the intensity. Furthermore, there are indications of Cu defect-related peaks in the region of 100–250 cm$^{-1}$.53 These observations are consistent with an immediate formation of metallic Cu on Cu2O surfaces.57

The Raman spectra provide additional information on CO2R reaction intermediates. Figure 7b shows the instantaneous appearance of new peaks at 1074 and 2060 cm$^{-1}$ after the application of current. The 1074 cm$^{-1}$ peak is attributed to the stretching mode of adsorbed CO$_2$ (CO$_{ad}$)52,53 (the bicarbonate deprotonates after adsorption) consistent with the observation of Xu et al.54,55 Hori et al.56 and Wuttig et al.57 The adsorbed carbonate is the surface-absorbed species and does not participate in the CO2R. When electrochemical CO2R is performed in an Ar-purged bicarbonate solution, no CO2R products are generated; thus, there is no possibility of electroreduction of bicarbonate (i.e., bicarbonate as active species in CO2R). In a recent report, Dunwell et al.54 used in situ spectroscopy and isotopic labeling to show that bicarbonate increases the reducible CO$_2$ concentration (dissolved CO$_2$) in the solution through rapid equilibrium exchange between aqueous CO$_2$ and bicarbonate near the electrode surface. For Cu NC samples, we see the decrease in the concentration of CO$_2$ near the surface with time. This can be assigned to the increase in potential (see Figure S6a), as higher negative electrode potentials decrease the adsorption of anions. The peak at 2060 cm$^{-1}$ is attributed to adsorbed CO$_2$.57–60 Whereas Raman spectra show the appearance of CO on NCS within seconds after the application of current, the corresponding GC data shows only negligible production of CO, H$_2$, or any other hydrocarbons during the first 20 min (Figure 5a,b). The applied current density of −1 mA/cm$^2$ corresponds to a very low potential, which cannot reduce CO further. However, for Cu2O NCS, with dominant (200) surfaces exposed, Cu2OR can occur at a very low potential, as shown by our DFT calculation. Hori et al.56 have shown that adsorbed CO suppresses hydrogen generation and other electrochemical reductions. Indeed, the rate-determining step in CO2R is the step following CO adsorption.58–61 Thermodynamic analysis shows that high coverage of CO blocks hydrogen absorption sites, inhibiting C–H bond formation.62,63 Our DFT calculations show that Cu2OR is energetically the most favorable reaction pathway, but with the Cu site blocked by CO, CO2R and HER have also a dynamic disadvantage. Consequently, Cu2OR will dominate until almost all of the oxide is reduced.

Figure 7a,c shows the Raman spectra of NNs and NPs, respectively. Consistent with our observations on NCS, we find quasi-instantaneous reduction of copper oxide-related peaks within the first few seconds, confirming the formation of copper. Interestingly, the three copper oxide samples differ in terms of the bicarbonate and adsorbed CO peaks. Compared with NCS, the NNs show a very weak CO peak, whereas NPs do not show any adsorbed CO peaks. As shown in Figure 1, all of the three catalysts on reduction generate different nanostructures with different defect densities and preferential
crystal orientations, as shown by the higher intensities of the (200) peak of NCs versus those of the (111) peak of NPs. Consequently, under-coordinated sites, such as defects and boundaries, are expected to be different in all three catalysts. The difference in the intensities of the CO peak can be related to the adsorption strength of CO on these different defects and crystal orientation. This is also evident by the difference in product distribution on the three catalysts shown in Table S2. A direct quantitative comparison of the selectivity and efficiency of these SERS-active Cu films (Cu NC, Cu NN, and Cu NP) relative to each other is not possible as the SERS intensity is convoluted with the different surface structures of the reduced Cu. We nonetheless observe that Cu NC and Cu NN samples are capable of producing higher-order C2–C3 products such as propylene (detected by SIFT-MS) and propanol (detected by head space GC) compared with the Cu NP sample (see Tables S2 and S3). This is consistent with the more intense absorbed CO peak in the Raman spectra shown in Figure 7a,b. For the Cu NC sample, we observed the inhibition of the catalyst surface to liberate the electrogenerated CO. This indicates that there could be a high population of surface-adsorbed CO, which is necessary for conversion to higher-order products.

To empirically validate the claim that essentially all Cu2O is reduced within the initial time, t, we estimate the effective thickness of reduced Cu2O on the basis of the partial current density for Cu2O reduction. On the basis of our experimental findings, we assume that all current goes to Cu2O reduction until CO2R or HER products are detected. Afterward, the measured CO2R and HER contributions are subtracted from the total current to find the current still going toward Cu2O reduction. For this estimate, we use NCs because of their simplified morphology (Figures 1b and S19a). Figure 3c shows that within the first 5 s there is no change in the SIFT background signal; thus, all applied current is assumed to be consumed by Cu2O. The calculated thickness of the reduced Cu2O layer is 1.1 ± 0.1 μm, which is consistent with the estimated thickness of Cu2O in the NC samples of 1.2 ± 0.1 μm, as determined by cross-sectional SEM (Figure S19a).

In a second estimation, we use data from the much lower current density experiments (Figure 4a,b). Within the initial time (t = 700 s), an estimated 860 nm of Cu2O is reduced, which is less than the estimated total thickness of the Cu2O layer from SEM images. However, we note that the Cu2O peaks disappear from the Raman spectra within 10 s of applying a potential; thus, the reduction must proceed from the surface deeper into the bulk of the catalyst. Therefore, the residual copper oxide yet to be reduced must be present in the bulk of the catalyst. This leaves open the possibility that Cu2O reduction continues at a lower rate in the bulk in parallel to CO2R and HER at the surface once the potential has increased (Figure S20). With this assumption, we calculate that all of the Cu2O is completely reduced to Cu within 20 min, similar to the observations by Lee et al. and Mistry et al. A similar calculation for the Cu NP sample is given in SI-X.

Oxide-derived Cu nanostructures can easily reoxidize under OCP conditions, as shown in Figure S17 and by Lum et al., compromising the ex situ measurement. From the reduction of Cu2O peaks and the apparent noise level in the after-CO2R XRD spectra, we can estimate an upper bound of residual crystalline Cu2O of 3%. By comparing the heights of residual Cu2O-related peaks in Raman spectra, we can estimate an upper bound of 6% of Cu2O. In contrast to XRD that measures the bulk, Raman spectroscopy is more surface-sensitive, which explains the larger estimate for residual Cu2O. Considering a typical thickness of 4 nm of natural Cu2O, we conclude that residual Cu2O is not more than 6%, consistent with recent studies.

The high C2 (ethylene)/C3 (propane, propenol) product selectivity exhibited by these catalysts is due to the higher defect density in these catalysts supporting adsorption of CO, as shown by Ren et al. and Li et al. Furthermore, the OD Cu has high geometrical surface area (because of the nanostructure), leading to high local current density. During CO2R and HER, protons from water are consumed and OH− ions are released at the electrode surface, increasing the local pH near the electrode surface. The high local pH favors C−C coupling at low overpotential versus RHE, as shown by Koper et al. and Lum et al. The high local pH on the catalyst surface favors the CO dimerization pathway for ethylene formation. It should be noted that in situ SIFT-MS and the limits of detection of our Raman spectroscopy measurements do not allow us to determine if there could be trace amounts of residual O atoms embedded in the catalysts, as reported earlier by Nilsson et al. and Favaro et al. We highlight here though that copper oxides are extremely prone to be reduced to Cu metal at the potentials used in this work. Hence, we believe that if there is any residual O it should be in the bulk rather than on the surface.

4. CONCLUSIONS

In summary, by operando SIFT-MS, computational modeling, and Raman spectroscopy, we show that in three oxide-derived Cu electrocatalysts, with differing surface morphologies and crystal orientations, surface copper oxide reduces prior to CO2R into gaseous products. Even though Cu2O (200) seems to be a possible catalyst for CO2R based on our DFT modeling, CO2R products are not formed as long as Cu2O is present at the surface because Cu2O is kinetically and energetically more favorable than CO2R. Although we cannot exclude a small percentage of residual oxygen (as has been claimed by Favaro et al.), it is unlikely that it will be present in the form of Cu2O. Looking forward, the exceptional performance of SIFT-MS for real-time electrochemical CO2R can offer new applications in time-resolved monitoring of reaction intermediates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b15418.

Experimental procedures; computational details; schematic of the whole setup; dead time of the SIFT-MS; chronopotentiometry in operando SIFT-MS data on electropolished Cu; SEM images of electropolished Cu before and after CO2R; Raman peaks of copper oxide samples; comparative data for SIFT and GC for polycrystalline copper; Cu2O NPs, NCs, and NPs; FE of the product measured using GC, head space GC, and HPLC; Cu2O NCs run in SIFT-MS at different current densities; FE of CO2R products measured using GC, head space GC, and HPLC for nanoneedles and nanocrystalline Cu2O NPs run at −1 mA/cm2; chronopotentiometry and GC data of Cu2O NCs; binding geometries and energies of H, CO, and H− for Cu2O NCs on Cu2O surfaces; binding energies of intermediates on Cu.
and Cu2O surfaces; thermal corrections of intermediates; relative free energies at different bias potentials; free energy to remove O atoms on Cu(111); geometries of transition states for Cu2OR and CO2R on Cu2O surfaces and associated barrier height; chronopotentiometry curve for in operando Raman spectroscopy; in situ Raman spectra of Cu2O NCs; cross-sectional SEM image of Cu2O NCs; thickness calculation for Cu2O NCs; coordinates of all intermediates in the VASP format (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. K.R.Y. and M.R.M. contributed equally.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This work was supported by the Singapore National Research Foundation under its Campus for Research Excellence and Technological Enterprise (CREATE) program through the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE). M.M. is supported by NUSNNI-Nanocore, J.M. is supported by the Centre for Advanced 2D Materials supported by the National Research Foundation, Prime Minister’s Office, Singapore, under its Medium Size Centre program. B.S.Y. and D.R. are supported by an academic research grant from National University of Singapore (R-143-000-683-112). D.R. acknowledges the PhD Research Scholarship from Ministry of Education, Singapore. K.R.Y. and V.S.B. acknowledge computer time from National Energy Research Supercomputing Center (NERSC) and funding from Air Force Office of Scientific Research Grant FA9550-17-0198.

**ABBREVIATIONS**
- CO2R, carbon dioxide reduction
- Cu2OR, copper oxide reduction
- CP, chronopotentiometry
- GC, gas chromatography
- SIFT-MS, selected-ion flow tube mass spectrometry
- HER, hydrogen evolution reaction
- FE, Faradaic efficiency

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■ NOTE ADDED AFTER ASAP PUBLICATION
This paper was published on the Web on February 26, 2018. A new Supporting Information file with additional content was added, and the corrected version was reposted on March 1, 2018.