Abstract: Oxide-derived copper catalysts have been shown to enhance CO₂ reduction reaction (CO₂RR) activity with high selectivity toward hydrocarbon products. However, the chemical state of oxide-derived copper during the CO₂RR has remained elusive and is lacking in situ observations. Herein, a two-step process was developed to synthesize Ag nanowires coated with various thicknesses of a CuOₓ layer for the CO₂RR. By employing in situ X-ray absorption spectroscopy, a strong correlation between the chemical state under reaction conditions and the CO₂RR product profile can be revealed to validate another competing reaction (i.e., the spontaneous oxidation of Cu(0) in aqueous electrolyte) that significantly governs the chemical state of active centers of Cu. In situ Raman spectroscopy reveals the existence of reoxidation behavior under cathodic potential, and the quantification analysis of reoxidized behavior is revealed to indicate that the reoxidation rate is independent of surface morphology and strongly proportional to the electrochemically surface area. The steady oxidation state of Cu in an in situ condition is the paramount key and dominates the products’ profile of the CO₂RR rather than other factors (e.g., crystal facets, atomic arrangements, morphology, elements) that have been investigated in numerous reports.

Introduction

The emission of carbon dioxide (CO₂) into the atmosphere has attracted much attention in recent years because CO₂ has a significant impact on climate change.¹² The electrochemical CO₂ reduction reaction (CO₂RR) has been regarded as a promising way to convert carbon dioxide into chemical fuels under ambient pressure/temperature conditions, which can potentially provide a perfect carbon cycle with carbon capture and storage techniques and renewable energy.³ In the 1980s, Hori’s group pioneered an electrochemical CO₂RR in aqueous solution,⁴ and the catalysts used for this reaction can be divided into several groups according to their product selectivity. For instance, catalysts with a major product of hydrogen gas, such as Pt, favor the reduction of protons instead of CO₂, whereas Sn and Ag are able to convert CO₂ into HCOO⁻ and CO, respectively. Among various metal catalysts, only copper-based catalysts have inherent selectivity toward CO₂ reduction to form hydrocarbons and/or alcohols.⁵ This CO₂ reduction selectivity toward the hydrocarbon products has been found to be governed by the binding energy of a key intermediate (i.e., CO) on various metal surfaces. Once a strong bond forms between CO and the metal surface, leading to CO poisoning, the hydrogen evolution reaction (HER) proceeds. In contrast, metals with weakly bound CO are going to yield CO as a major product because the weak binding results in CO desorbing before further reduction can occur. Copper metal, with inherently moderate binding energy with CO, is considered to be the key reason for selective generation of hydrocarbon products via electrochemical CO₂ reduction.⁶ This phenomenon is the well-known Sabatier principle, which relies on an optimum bond strength between the catalyst and the reactant. Nevertheless, the high-energy transition state resulting from multiple electron transfer steps and low selectivity toward particular products still plagues the development of copper-based catalysts.

In recent years, because of the intrinsic excellence of electrochemical production of hydrocarbon on metallic copper, modified copper catalysts have been developed to enhance the selectivity as well as the efficiency of the CO₂RR.¹⁰⁻¹⁶ Among numerous catalysts, a so-called oxide-derived Cu catalyst derived from copper oxide that could exhibit significant selectivity toward interesting products from the CO₂RR was developed by Kanan’s group.¹⁷ Since then, several groups have been devoted to manipulating the oxide-derived Cu catalyst by changing its structural morphology as well as the oxidation state of Cu.¹¹,²² Generally, this imperative activity is attributed to grain boundaries with undercoordinated atoms,²³,²⁴ while the presence of Cu(I) oxide species or residual oxygen is also speculated to play a vital role in the
catalytic performance.\textsuperscript{18,25,26} Nonetheless, regardless of the high activity of the oxide-derived Cu catalyst, the mechanism behind the imperative activity is still under debate.

To consider the products of CO\textsubscript{2} reduction, for most oxide-derived Cu catalysts, the selectivity toward ethylene is more favored than that toward ethanol, and this phenomenon has been studied by using density function theory, with the conclusion that the energy barrier of the reaction to produce ethylene is lower than that of producing ethanol.\textsuperscript{27,28} Although it was found that electrochemically reducing CO\textsubscript{2} to ethanol could not reach a high efficiency by using oxide-derived Cu, by reducing the intermediate (i.e., CO) instead of CO\textsubscript{2}, a Faradaic efficiency (FE) of 42.9\% for the production of ethanol can be achieved through the same Cu catalyst.\textsuperscript{29} However, a low current density as a consequence of the poor solubility of CO in an aqueous electrolyte (\textsim\ 1 mM) plagues the practical use of electrochemical CO reduction. To overcome this limitation and achieve a higher selectivity toward ethanol, an alternative strategy is to introduce a secondary catalyst that can selectively catalyze the CO\textsubscript{2}RR toward CO formation, and a few studies have reported tunable selectivity toward ethanol.\textsuperscript{30,31} The mechanism behind the imperative selectivity is, however, debatable. The dynamic surface states are receiving increasing attention because they subtly govern the reaction pathway of the electrochemical CO\textsubscript{2} reduction, especially from an in situ point of view.

Herein, we synthesized a series of catalysts composed of ultrathin silver nanowires with the desired oxide-derived Cu catalyst over the surface, in which a highly CO-activated Ag nanowire was utilized because of the abundance of low-coordinate edge sites on ultrathin nanowires that can serve as active sites.\textsuperscript{32} In addition, the (100) facet of Ag nanowires can offer well-defined facets to suppress the atomic fluctuation from the substrate, while the oxide-derived Cu catalysts were coated onto Ag nanowires under the desired conditions to optimize the production of ethanol over ethylene. Most importantly, to validate the dynamic surface states as well as the local structure of the Cu during the CO\textsubscript{2}RR, we adopted in situ X-ray absorption spectroscopy (XAS) to investigate the effects of target cations (i.e., Cu) under cathodic potentials. This powerful analytical technique revealed the evident correlation between the chemical states/local structure of Cu...
and the resulting CO₂RR products of ethanol and ethylene. The result revealed the evident correlation between the chemical states of Cu under CO₂RR conditions and provided a new direction of designing CO₂ reduction catalysts through a rational chemical state.

**RESULTS AND DISCUSSION**

An ultrathin Ag nanowire with an average width of ~80 nm was prepared by means of a polyol process through a reduction of silver nitrate with a capping agent in EG. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were carried out to characterize the morphology of the Ag nanowires (Figure S1a). Figure S1a illustrates the SEM image of the as-prepared nanowires with a resulting product composed of a large quantity of nanowires. TEM and HRTEM images show a uniform surface of Ag nanowires with a d-spacing of 2.36 Å in the lattice fringe, as illustrated in the HRTEM image (Figure S1b−c), which can be assigned as the (111) plane of Ag (JCPDS no. 04-0783).

Following the synthesis of Ag nanowires, various thicknesses of oxide-derived Cu catalysts were obtained by successively reducing copper(II) acetate on the Ag nanowire (Figure 1a−d). As revealed in the HRTEM images, the outer shells of the samples were polycrystalline in nature, and the corresponding d-spacings of the lattice fringes were consistent with the bulk value of Cu₂O (JCPDS no. 05-0667) (Figure 1e−h). To gain further information regarding the structure as well as the composition profile, scanning transmission electron microscopy with energy-dispersive X-ray (STEM-EDS) spectroscopy was utilized through a cross-section line scan to reveal the elemental profiles of Cu and Ag, confirming the core−shell nanostructure and the existence of an outermost copper layer (Figure 1i−j). To verify the situation of the oxide-derived Cu layer, because of the significant Z-contrast between Ag (Z = 47) and Cu (Z = 29), scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) images confirmed the obvious contrast between the core Ag nanowire and the outer layer of Cu (Figure S2a−d). The average thickness of the oxide-derived Cu layer was 4.3 nm (denoted as Ag@CuO₂−4), 9.6 nm (denoted as Ag@CuO₂−10), 23.9 nm (denoted as Ag@CuO₂−24), and 32.3 nm (denoted as Ag@CuO₂−32) as shown in Figure 1m−p.

In terms of the crystal structure and chemical/physical states of the as-prepared catalysts, X-ray diffraction (XRD) measurements were carried out to clarify the crystal structure, showing that the characteristic peaks are consistent with the Cu₂O and metallic Ag phases, while the absence of the Cu–Ag alloy phase indicated the phase-separated nature of these catalysts (Figure S3a). Moreover, the intensity of the characteristic Cu₂O peaks intensified with increasing thickness, which was in accordance with the aforementioned TEM results. To reveal the oxidation state and the local structure of Ag and Cu in the as-prepared samples, XAS including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was conducted in the present study. The oxidation state of the catalysts can be determined via XANES, while the local structures are obtained by Fourier transformation of the corresponding K-space spectra of EXAFS. The XANES results of the Ag K-edge imply that the position of the main absorption edge corresponding to a transition from the 1s to the empty 5p state retains the initial feature when modifying the oxide-derived Cu catalysts, indicating the metallic silver property for all samples (Figure S3b). Note that even if the oxide-derived Cu catalysts were modified onto the Ag nanowires, the local structural feature extracted from the EXAFS results revealed that there was no significant Ag–Cu scattering path except for the metallic Ag–Ag bond feature (Figure S3c). This phenomenon clarifies that no remarkable interdiffusion between Ag and Cu atoms occurred at the interface, which corroborates our XRD results in the absence of alloy formation features. On the other hand, the Cu K-edge XANES spectrum of all the as-prepared samples exhibited the characteristic feature of Cu₂O with two distinctive peaks at 8982 and 8995 eV, which could be assigned as the transitions of the 1s-4pₓ, 4pᵧ, and 1s-4p_z states, respectively (Figure S3d). This result implied that the oxidation states of all samples were similar to the Cu(I) state. This result is further confirmed by EXAFS spectra at the Cu K-edge (as depicted in Figure S3e), which further describes the local environment of Cu cations. As indicated by the atomic radial distribution of the metal center of Cu, the first peak at apparent distances of ~1.5 Å and the second peak at 2.7 Å are attributed to the single scattering path of the closest oxygen (that is, Cu−O(Cu₂O)) and the second neighboring copper metals (that is, Cu−Cu(Cu₂O)) surrounding the Cu cations, respectively.

Notably, no significant Cu−Cu scattering path of metallic Cu (that is, Cu−Cu(Cu₂O)) was obtained in any of the as-prepared samples, implying the initial oxidized state of Cu(I) catalysts. These results clearly reveal the local environment of Cu in all as-prepared samples, which are more similar to that of the Cu₂O phase, as opposed to the metallic Cu case.

The catalytic performance of the Ag nanowire and Ag@CuO₂-X samples was investigated in the presence of CO₂-saturated 0.1 M potassium hydrogen carbonate (KHCO₃). Figure S4a shows the LSV curves of each sample. The various modified Ag@CuO₂-X samples outperformed the Ag nanowire in geometric current density, which can be attributed to the higher surface area as a result of CuO₂ modification. The increase of surface area can be obtained from the ECSA double-layer capacitance of each catalyst, indicating that the double-layer capacitance is proportional to the increase in the thickness of CuO₂.

To investigate the Faradaic efficiency (FE) of each sample for CO₂ reduction, as shown in Figure S4b−f and Table S2, CO was the major CO₂RR product for Ag nanowires with a maximum FE of 78.21% at −1.04 V vs RHE. Ag nanowires merely produced trace amounts of hydrocarbons at relatively large cathodic potentials (above −1.30 V vs RHE). This high efficiency toward CO resulting from the weak binding energy between the Ag and CO* intermediate implied a rapid desorption of the CO* intermediate before further reduction. Once the Ag nanowire was modified with CuO₂, the modified catalysts had a tremendous effect not only on the activity but also on selectivity (Figure S4c−f). Generally, the FE toward hydrocarbon and alcohol products remarkably improved with increasing CuO₂ content. Note that a striking FE enhancement toward the alcohol product in the Ag@CuO₂−10 sample is revealed and declines slightly with further increases of CuO₂ catalysts, which apparently displays a different trend than those of typical Cu electrocatalysts that exhibited strong selectivity toward ethylene instead of ethanol. Most interestingly, with an increasing thickness of CuO₂, smaller overpotentials were required to drive the production of hydrocarbon and alcohol from the
CO\textsubscript{2}RR, which was similar to a study utilizing the oxide-derived copper for the CO\textsubscript{2}RR.\textsuperscript{17} These findings suggest that the surface states vastly influence the reduction pathway as well as the selectivity of corresponding products.

To further probe the selectivity toward ethylene and ethanol, the partial current density and FE of these C\textsubscript{2} products are shown in Figure 2a,b, respectively. The FE of ethylene was increased by increasing the thickness of CuO and reached a maximum value of 31.55% with a partial current density of ∼4.93 mA cm\textsuperscript{-2} in the Ag@CuO\textsubscript{-32} samples (at −1.06 V vs RHE). Additionally, the Ag@CuO\textsubscript{-32} sample required the lowest potential of ∼900 mV to reduce the CO\textsubscript{2} to ethylene compared to the rest of the samples. In comparison with the results for the ethylene product, the FE and the partial current density toward ethanol showed a different behavior: the Ag@CuO\textsubscript{-10} sample reached a maximum FE of 28.08% with a partial current density of 7.62 mA cm\textsuperscript{-2} (at −1.20 V vs RHE) with great suppression of ethylene (Figure 2b). Notably, contrary to that of ethylene production, the FE of ethanol production seems to decline once the thickness of CuO is further increased (in both cases of Ag@CuO\textsubscript{-24} and -32), with the absence of a remarkable correlation between the two, suggesting that there is an optimized thickness for producing ethanol. Notably, an evident feature in which smaller overpotentials are required to achieve the production of both ethylene and ethanol with more CuO\textsubscript{-}assistance can still be found in Figure 2a,b. To further clarify the correlation between ethylene and ethanol pathways, Figure 2c shows the production of ethanol over ethylene as a function of catalysts was prone to generate ethylene prior to producing ethanol (i.e., a lower overpotential was required to generate ethylene), and the Ag@CuO\textsubscript{-10} sample was verified to achieve a maximum value (more than 3 at −1.20 V vs RHE) of the ethanol-to-ethylene ratio. For the Ag@CuO\textsubscript{-4} sample, although the maximum C\textsubscript{2}H\textsubscript{5}OH/C\textsubscript{2}H\textsubscript{4} ratio is approximately ∼2.5, CO is still the major CO\textsubscript{2}RR product at all potentials, implying an Ag-like catalytic behavior. In contrast, in the case of thick CuO\textsubscript{x} samples (Ag@CuO\textsubscript{-24} and Ag@CuO\textsubscript{-32}), the maximum ethanol-to-ethylene ratio is only approximately ∼1, suggesting a typical Cu-like catalyst.\textsuperscript{26,36,39} The above-mentioned results, to a certain degree, have offered some insights into the disparity of surface states under operating conditions. To ascertain the fundamental issue with respect to the electrochemical CO\textsubscript{2} reduction, the in situ approach is indispensable for exploring the dynamic oxidation state and the local structure.

In situ XAS has been acknowledged to validate the dynamic oxidation state and the local structure under operating conditions, especially in liquid medium.\textsuperscript{40–45} Accordingly, a homemade in situ cell was utilized to carry out the observation (Figure S6). The initial oxidation state of Ag@CuO\textsubscript{-10} was consistent with the Cu\textsubscript{2}O reference, as illustrated in the in situ XANES data in Figure 3a. Once cathodic potentials were applied, the catalyst retained the initial situation within the region of −0.50 to −0.70 V (vs RHE). A shift of the absorption edge at −0.80 to −0.90 V (vs RHE) was observed, indicating the formation of metallic copper. This phenomenon was also confirmed by the appearance of a new absorption at ∼9000 eV, which could be ascribed to a transition from the 1s to 4p\textsubscript{σ} state (as indicated by arrow). With a further increase in the reduction potential (−0.90 to −1.30 V vs RHE), the XANES features were similar at these potentials and confirmed the metallic copper nature under such high cathodic potentials. The atomic radial distribution of the Ag@CuO\textsubscript{-10} sample is shown in Figure 3b. The FT-EXAFS peak at ∼1.5 Å could be attributed to the nearest oxygen atoms around the Cu atoms (Cu–O\textsubscript{Cu(O)}) while the peak at approximately 2.7 Å could be assigned as a single scattering Cu–Cu path of Cu\textsubscript{2}O. A drastic change in the local structure occurred at approximately −0.80 (vs RHE), with declining intensities of both the Cu–O\textsubscript{Cu(O)} and Cu–Cu\textsubscript{Cu(O)} peaks, the characteristic peak of the metallic

![Figure 2](image-url)  
Figure 2. Faradaic efficiency (FE) and partial current density toward (a) ethylene and (b) ethanol. (c) FE of ethanol over ethylene as a function of potential.
Cu−Cu(0) bond at ∼2.2 Å intensified. This result shows a clear phase transformation from Cu₂O to metallic copper without forming a Cu−Ag alloy under reduction potentials, which was consistent with the finding from the corresponding XANES data. For the Ag@CuO₂₋₁₀ sample, the XANES spectrum of the as-prepared sample was similar to that of Cu₂O (Figure 3c). The most interesting phenomenon of the Ag@CuO₂₋₃₂ sample during the reaction was that the Ag@CuO₂₋₃₂ sample required a smaller cathodic potential to trigger the structural transformation from Cu₂O to metallic Cu than that of the Ag@CuO₂₋₁₀ sample, as validated by the increase in the characteristic feature of the 4p₆ state (indicated by an arrow). Furthermore, the in situ EXAFS spectra of the Ag@CuO₂₋₃₂ sample in Figure 3d also demonstrated that the metallic Cu−Cu bond was formed at almost −0.60 V vs RHE, which was significantly smaller than the case of the Ag@CuO₂₋₁₀ sample (less than 200−300 mV). Following the formation of metallic Cu, a steady atomic arrangement was observed between −0.70 and −1.30 V. Note that the XRD and XAS analyses for the postcatalysts are conducted to clarify the local structure of the catalysts after the CO₂ reduction as illustrated in Figures S7 and S8, which clearly indicates that no surface alloy was formed during the reaction in present study. The results suggested that the thickness of the CuOₓ layer significantly affected the chemical state transition from Cu(I) to Cu(0), which may correlate with the CO₂RR product profile.

To further understand how the surface state-dependent trend correlates with the FE of the products, we obtained the Cu−Cu path from both Cu₄₋₃₋₁₀ and Cu(I) extracted from a standard fitting procedure (Table 1 and detailed results are shown in Tables S3−S4 and Figure S9−10). Quantification of the Cu surface state in each situation can be referred to as the percentage of both metallic Cu(0) and oxide-derived Cu(I) according to eqs 1 and 2,

\[
CN_{\text{metallic Cu}} = \text{metallic Cu(0)%}
\]

\[
CN_{\text{oxide derived Cu}} = \text{oxide derived Cu(I)%}
\]

where \( CN_{\text{metallic Cu}} \) and \( CN_{\text{oxide derived Cu}} \) represent the coordination numbers of the Cu−Cu path at 2.5 and 3.0 Å, respectively. \( CN_{\text{metallic Cu}} \) refers to the theoretical coordination number of the Cu−Cu path in metallic Cu (i.e., 12), and \( CN_{\text{oxide derived Cu}} \) represents the theoretical coordination number of the Cu−Cu path in the CuO₂ phase (i.e., 12).

The surface states and the FE of both hydrocarbon and alcohol products as a function of applied potential are depicted in Figure 4. The major surface state is Cu₂O (Cu(I)) rather than metallic Cu(0) at smaller cathodic potentials, which is consistent with the observation from Figure S3. With increasing applied cathodic potential, the surface state of Cu(0) became dominant instead of Cu(I) for both Ag@CuO₂₋₁₀ and -₃₂, except for the required potential to reach a metallic Cu content above 90%. In both cases, a similar tendency for the production of hydrocarbons from the CO₂RR to be strongly correlated with the surface state of metallic Cu rather than Cu(I) is clearly observed. We also believe that the C−C coupling is unlikely to occur on the Cu₂O surface because of the larger distance of interatomic Cu−Cu in Cu₂O (approximately 3 Å), although several reports have suggested the critical roles of the formation of Cu(I) in the generation of ethylene or carbon monoxide. Notably, the required cathodic potential for the Ag@CuO₂₋₁₀ sample is larger than that of the Ag@CuO₂₋₃₂ case by approximately 200 mV. We speculate that a smaller CuOₙ layer at the Ag@CuO₂₋₁₀
sample would limit the reduction of Cu₂O to metallic Cu because of another competing reaction (i.e., the reoxidation of Cu⁰ in aqueous electrolyte). To ascertain the reoxidation during the reaction, in situ Raman spectroscopy was adopted to elucidate the behavior of the oxide catalysts. Ag nanowire could serve as a perfect substrate to improve the effect of surface-enhanced Raman spectroscopy (SERS) and thus enhance the sensitivity to identify the characteristic peaks of Cu₂O. Figure 5a,b indicates the in situ Raman results of Ag@CuOₓ₋₁₀ and Ag@CuOₓ₋₃₂, respectively. Prior to the reaction, as shown in Figure 5a, typical characteristic peaks of Cu₂O at 520 (T₂g) and 609 (T₁u) cm⁻¹ were observed under 0.1 M KHCO₃ condition.⁴⁷,⁴⁸ A constant potential of −0.55 V vs RHE that belonged to metallic Cu domain in the Pourbaix diagram was applied, and each spectrum took 10 s to acquire. The characteristic peaks of Cu₂O greatly declined once applying the cathodic potential in first 2 min as illustrated in Figure 5a. Note that the peaks remain steady under the cathodic potential of −0.55 V for 5 min, which evidently indicates a fact that the copper oxide cannot be entirely reduced even though a cathodic potential that can thermodynamically reduce Cu₂O to metallic Cu⁰ is employed. It seems that the finding clearly contradicts the Pourbaix diagram which predicts the Cu₂O should be reduced to metallic Cu under such potential.⁴⁹ This phenomenon may be attributed to a reason that the diagram is predicted according to the thermodynamic consideration without taking into account other conditions, such as overpotentials as well as kinetics behaviors.⁵⁰ Consequently, we suggest this stage may reach a dynamic equilibrium between Cu(0) and Cu(I) under mild conditions (i.e., a mild cathodic potential). This might be ascribed to the presence of reoxidation which was caused by a trace amount of oxidative species in the electrolyte, since it is unlikely to remove all undesired species. To further prove the presence of the reoxidation that may occur during the CO₂ reduction reaction, a constant flow of oxygen gas was introduced into the electrolyte system since oxygen gas is one of the major factors to oxidize Cu, while a trace amount of oxygen can be expected to exist.⁵¹ Under the constant flow of oxygen gas, the characteristic peaks of Cu₂O significantly intensified, which evidently implied the fact that Cu has been reoxidized even though a cathodic potential was applied as illustrated in Figure 5a. This finding clearly explicates that both the reduction of Cu₂O drove by the applied potential and the reoxidation of Cu caused by oxidative species can coexist, and the thermodynamic consideration cannot be the only one factor to realize the resulting phase under a specific condition. As shown in Figure 5a, once the cathodic potential was removed, the peaks of Cu₂O significantly intensify and further suggest the presence of reoxidation of Cu. A similar behavior could be observed when applying the same procedure on Ag@CuOₓ₋₃₂ sample (Figure 5b). By purging the oxygen gas into the system, all results vastly validated that the Cu₂O could be reoxidized under the cathodic potential and reductive environment. This phenomenon was also observed on various types of copper oxide-based materials, since many reports also

Figure 4. (a) Quantification of chemical state extracted from in situ XAS of Cu as a function of applied potential for the Ag@CuOₓ₋₁₀ and Ag@CuOₓ₋₃₂ samples. (b) FE toward hydrocarbon and alcohol products as a function of applied potential for the Ag@CuOₓ₋₁₀ and Ag@CuOₓ₋₃₂ samples.

Figure 5. In situ Raman spectroscopy of the catalysts under a constant potential of −0.55 V vs RHE for the Ag@CuOₓ₋₁₀ (a) and Ag@CuOₓ₋₃₂ (b) samples, respectively. (c) Previous reports indicated that Cu⁺ existed under cathodic potentials which is predicted by Pourbaix diagram with a metallic copper (for further details, see Table S5)
concluded that copper oxide-based materials could not be entirely reduced to Cu⁰ and thereby leading to a coexistence of metallic Cu and Cu oxides even though the Pourbaix diagram has suggested that, under such conditions, the thermodynamic phase should be metallic copper rather than copper oxide. As shown in Figure 5c and Table S5, we have summarized some reports that have revealed the chemical states of copper through in situ/ex situ approaches and suggested the presence of Cu oxide under a cathodic potential. For these reasons, we have to point out the effect of reoxidation behavior under a cathodic potential as illustrated through in situ Raman spectroscopy. The most important thing is that the reoxidation caused by a trace amount of oxidative species is evidently present under a cathodic potential and able to dominate the resulting chemical state of copper catalysts, which can be further expected to alter the nature of CO₂ reduction reaction onto the catalytic sites.

Besides, to further quantitatively confirm the reoxidation of Cu in aqueous solution under a cathodic potential, an LSV investigation was carried out to quantitatively estimate the amount of reoxidized Cu based on the total coulombs of redox-active Cu centers obtained by integration of the Cu(0)/Cu(I) redox peak area of Ag@CuO_x-10 and Ag@CuO_x-32 samples. In the first place, LSV was applied, and a redox peak of Cu(I)/Cu(0) was extracted to estimate the total coulomb resulting from Cu(I) to Cu(0). Afterward, the electrode was left to stand for an hour under an open circuit potential, followed by another LSV integrating the total coulomb from the redox peak of Cu(I)/Cu(0) (Figure S11). Quantification of the reoxidized (SRO) Cu could be performed as follows:

\[
\frac{C(\text{redox peak at } t = X)}{C(\text{redox peak of the first scan})} = \text{SRO copper (%)}
\]

where \(C(\text{redox peak at } t = X)\) and \(C(\text{redox peak of the first scan})\) refer to the total coulombs for reducing Cu(I) to Cu(0), respectively. \(M\) represents the total amount of Cu in the electrode, which was determined by inductively coupled plasma mass spectrometry (ICP-MS) (0.1464 mg/cm² in Ag@CuO_x-10 and 0.4587 mg/cm² in Ag@CuO_x-32, respectively). Accordingly, the reoxidized (SRO) copper as a function of time is presented in Figure 6a. The reoxidized Cu amount of Ag@CuO_x-10 is obviously higher than that of Ag@CuO_x-32, which implies that the copper from Ag@CuO_x-10 is prone to reoxidize in aqueous solution. To further consider the effect of the surface area, SRO copper \(\left(\text{mg/cm}^2\right)\) was divided by the roughness factor (Table S1b). Note that the ECSA normalized quantification of reoxidized amount was revealed to be a similar value, indicating that the reoxidation rate is independent of surface morphology and strongly proportional to the electrochemically active surface area. The above observation confirmed that the spontaneous oxidation of Cu(0) would simultaneously compete with the CO₂RR, which is the key reason why Ag@CuO_x-10 and Ag@CuO_x-32 exhibited different overpotentials for the CO₂RR.

Several studies have proposed that the Cu oxide species is catalytically active for the CO₂RR. For instance, Kim et al. employed ex situ XRD and ex situ Auger electron spectroscopy to investigate the Cu₂O electrode after the CO₂RR and concluded that the oxide species were still present on the surface. Mistry et al. utilized ex situ STEM-EDS to clarify the cross-sectional profile of oxide-derived Cu catalysts after the CO₂RR, which implied that oxide-derived Cu catalysts seemed to sustain the oxide species during the reaction. However, these analytical approaches were conducted under ex situ rather than in situ conditions, in which the catalysts may be oxidized in water within a few minutes (as revealed in Figure 6a) or in air before further analysis. The in situ realization in the present study strikingly elucidates the interplay between the production of hydrocarbon from the CO₂RR and metallic Cu rather than the aforementioned Cu(I) subsurface oxide for CuO_x-based catalysts. Accordingly, the metallic Cu phase was suggested to be the active phase for the CO₂RR, which was corroborated by several reports. For instance, by utilizing simultaneous online electrochemical mass spectrometry (OLEMS), hydrocarbon formation appeared to occur only after the oxide was reduced. Another study also demonstrated via secondary ion mass spectrometry with isotopically labeled ¹⁸O on a Cu₂O electrocatalyst that only a trace amount of residual oxide was present during the CO₂RR. These studies also support our suggestion that forming metallic Cu is an imperative step in the formation of hydrocarbon/alcohol products under the CO₂RR. A schematic process was proposed in Figure 6b to illustrate the behavior of the Cu atom during the CO₂RR. Once the Cu(I) was reduced, the spontaneous oxidation would serve as a competing reaction with the CO₂RR. If the rate of SRO is higher than that of electroreduction, meaning that the reactive Cu cannot be stabilized in Cu(0), the major product of the CO₂RR is CO.
On the contrary, once the rate of SRO is slower than that of electroreduction, the stabilized Cu(0) could undergo further CO₂RR for the formation of hydrocarbon/alcohol products.

In addition to describing the surface state evolution of Cu, we further offer a point of view regarding the role of silver, as shown in Figure S12, that illustrates the ratio of ethanol to ethylene production as a function of CuOₓ thickness. The rational thickness of Cu₂O could substantially promote ethanol production to achieve a maximum ethanol/ethylene ratio of ∼3.5. As the CuOₓ thickness was further increased, the selectivity toward ethylene was increased, thereby leading to a decrease in the ethanol/ethylene production ratio to ∼1. This phenomenon may be attributed to the entire CuOₓ nature as a consequence of the thick CuOₓ layer with a rough surface. A fact has been demonstrated that the surface area of the oxide-derived layer is also another critical parameter affecting selectivity, indicating a strong relationship between surface roughness and CO₂ depletion and its effects on C₂ product selectivity. We can reveal that the Ag nanowire served as a substance that can synergistically promote the pathway toward ethanol. On the basis of the above observations and relevant ref S4, as shown in the Figure 7, a possible reaction pathway...
was proposed for thin CuO$_x$ cases in which the Ag nanowires were not entirely covered by CuO$_x$, thereby giving rise to a significant amount of reactive sites for generating CO from the CO$_2$RR. This proposed mechanism can be further confirmed by the results in Figure S4. The Ag nanowires can reach a nearly maximum CO evolution at a potential of $-0.90$ V vs RHE previous to the onset of ethanol production in both Ag@CuO$_{0.4}$ and Ag@CuO$_{0.2}$, which can greatly increase the local concentration of CO near the CuO$_x$ surface to successively produce ethanol. That is, the spilled-over CO desorbed from the Ag surface can trigger an insertion between the $^*$CH$_3$ intermediate and the Cu surface to complete the further production of ethanol (Figure 7). This suggestion is also consistent with some studies demonstrating that the production of ethanol versus ethylene could be promoted by introducing a CO-favored element or direct CO reduction, and the CO insertion can also form another critical intermediate, acetaldehyde, which has been proven to be the precursor of ethanol formation from both theoretical and experimental considerations. Note that the formation of ethanol through the insertion of CO can hinder dimerization of CO since it has been proposed to share a common pathway with ethylene, which benefits the ethanol pathway. As a consequence, we can suggest that a high local concentration of CO is the paramount factor to elevate the ethanol selectivity as well as its activity. The CO generation near the Cu particles is able to overcome the mass transport limit caused by its low solubility and reach a high FE of ethanol production. In contrast, in high-coverage cases without reactive Ag sites (Ag@CuO$_{0.24}$ and Ag@CuO$_{0.32}$), the observed behaviors are practically similar to those of pure Cu-like electrodes, rendering the major C$_2$ product of ethylene through the CO dimerization pathway.

**CONCLUSIONS**

In this work, we developed a two-step process to synthesize Ag nanowires coated with various thicknesses of the CuO$_x$ layer for electrochemical CO$_2$ reduction. The FE of ethanol production reached 28% and a partial current density of 10.38 mL of solution (3), and 10.38 mL of solution (4) were added into the EG solution. The mixed solution was then reacted for 6 h at 130 °C, and Ag nanowires were obtained. For the synthesis of Ag@CuO$_x$, 0.113 g of Cu(OAc)$_2$ in 10 mL of EG, 0.119 g of PVP in 27.5 mL of EG, and 17.5 mL of Ag nanowire solution without further purification were mixed in a three-neck bottle with magnetic stirring. After N$_2$ gas bubbling for 30 min, the reaction proceeded at 130 °C under oil bath conditions for 30, 40, 90, and 200 min. Each sample was cooled to room temperature and then centrifuged three times at 8000 rpm in ethanol for 5 min. Samples were stored in 5 mL of absolute ethanol. No unexpected or unusually high safety hazards were encountered.

**Structural Characterization.** The morphology of the samples was investigated using a TEM (JEOL JEM-2100F operated at 200 kV) and a JEOL JSM-7600F field emission scanning electron microscope (SEM). Energy-dispersive X-ray analysis (EDX) line scan was also observed in JEOL JEM-2100F FE-TEM. The crystalline structure characterization was revealed by X-ray diffraction (XRD, Bruker D2 Phaser) using Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å). The quantification of copper from the samples was quantized by using ICP-MS (Agilent 7700e).

**XAS Data Collection and Analysis.** X-ray absorption spectroscopy composed of X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) was carried out to obtain the oxidation state and local structure of each sample. A customized reaction cell was used to operate in situ X-ray absorption measurements of Cu K-edge (8979 eV) using synchrotron radiation in total-fluorescence-yield mode at ambient air/temperature. The energy of the incident beam was monochromatized using a Si(111) double crystal monochromator. The scan range was 8779–9879 eV for Cu K-edge. $E_0$ value with 8979 eV was used to calibrate all data with respect to the first inflection point of the absorption K-edge of copper foil. A customized reaction cell was used to operate in situ X-ray absorption measurements in total-fluorescence-yield mode at ambient air/temperature. The measurement with a typical three-electrode setup was performed in a specially designed Teflon container with a window sealed by Kapton tape. In this study, the edge-jump of each spectrum was carefully controlled in a range of approximately 1–2 to suppress the undesired affects from self-absorption. Prior to applying the potential, the sample was...
measured with/without the electrolyte. Subsequently, a constant-desired potential which started from lower over-potential (−0.5 to −1.3 V vs RHE) was applied during the measurement of XAS. Each spectrum takes about 40 min to collect the whole range spectrum for further analyzing, in which each potential was kept at the desired potential for the duration that allows acquiring the whole range spectrum. The above measurements were performed at the SP8 SP12B1 beamline at SPring-8, Japan, in which the electron storage ring was operated at 8.0 GeV with a constant current of ~100 mA.

**EXAFS Fittings.** X-ray absorption spectroscopy composed of X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) was carried out to obtain the oxidation state and local structure of each sample. XANES was obtained with standard procedures, including pre-edge and postedge background subtraction, normalization with respect to the edge height, while EXAFS was obtained using Fourier transform on k^3-weighted oscillations to estimate the local environment of the Cu atom. The data were processed through Athena software from the IFEFFIT package for analyzing XANES and EXAFS. REX2000 software using ab initio-calculated phases and amplitudes from the program FEFF 8.2 was used for EXAFS fitting. The ab initio phases and amplitudes were used in the EXAFS eq 4:

$$\chi(k) = S_0^2 \sum_{i} \frac{N_i}{kR_{ij}^{eff}} f_{eff}(\pi, k, R_j) e^{-2n_i^2} e^{-2R_j/k} \sin(2kR_j + \phi_j(k))$$

(4)

The neighboring atoms with different distances are divided into j shells. N_j represents the coordination number of shell j at a distance of R_j relative to the central atom. f_{eff}(\pi, k, R_j) is the ab initio amplitude function for shell j, while the Debye–Waller factor $e^{-2n_i^2}$ accounts for the damping that results from static and thermal disorder in absorber–backscatterer distances. The mean free path term $e^{-2R_j/k}$ reflects losses due to inelastic scattering, where $\lambda(k)$ is the electron mean free path. The sinusoidal term $\sin(2kR_j + \phi_j(k))$, where $\phi_j(k)$ is the ab initio phase function for shell j defines the oscillations in the EXAFS. Shake-up/shake-off processes at the central atom(s) affects the amplitude reduction factor, $S_0^2$. CN, R, $\Delta E$, and the EXAFS Debye–Waller factor (DW; $\sigma^2$) are variable parameters of the EXAFS equation for fitting the experimental result.

**In Situ Raman Characterization.** UniNano UNIDRON was adopted to record in situ Raman results. A 60X objective lens was used to focus the laser with a wavelength of 785 nm on the sample, in which the size of the laser spot is 1 μm^2. The measurement was performed under an exposure time of 1 s with an accumulation number of 10 times by illuminating 2.5 mW laser power.

**Electrochemical Characterization.** Electrochemical measurements were carried out in our customized H-type cell with two compartments separated by an anion-exchange membrane (FuMA-Tech, Fumasep FAA-3-PK-130). The 0.1 M KHCO_3 electrolyte with saturated CO_2 (pH 6.8) was prepared by bubbling CO_2 for at least 30 min to ensure that the solution was saturated. The working electrode was prepared by drop-casting 5 μL of 5 wt % Nafion solution and 20 μL of each sample solution onto an L-type glassy carbon with a diameter of 1 cm. The current densities reported in this work were normalized against the geometric surface area (0.785 cm^2). Pt wire served as a counter electrode, and Ag/AgCl (3 M KCl) served as a reference electrode. All electrochemical measurements were performed using an Autolab PGSTAT302N potentiostat (Metrohm Autolab). Chronoamperometry was adopted to measure product distribution at various potentials. Linear sweep voltammetry (LSV) was performed at a scan rate of 10 mV s⁻¹, and potentiostatic electrochemical impedance spectroscopy (PEIS) was conducted to determine the uncompensated solution resistance (R_u). All potentials in this report were presented relative to a reversible hydrogen electrode (RHE) scaled by eq 5:

$$V_{vs \text{RHE}} = V_{\text{measured vs Ag/AgCl(3 M KCl)}} + 0.21 + 0.059 \times \Delta \text{pH (of electrolyte)} - \text{iR drop}$$

(5)

Since the electrochemically active surface area (ECSA) is proportional to the double-layer capacitance, we can compare the double-layer capacitance of each sample to estimate the effect of ECSA on activity. The double-layer capacitance could be determined via cyclic voltammetry (CV) at a non-Faradaic region with different scan rates in 0.1 M KHCO_3 with saturated CO_2.

$$i_c = \nu C_{DL}$$

(6)

where $i_c$ is the charging current and $\nu$ is the scan rate; thus, the double-layer capacitance is the slope of the above equation. A non-Faradaic potential region of −0.35 to −0.60 V vs RHE was chosen and was assumed to be due to double-layer charging. The anodic and cathodic charging currents at −0.475 V vs RHE were plotted as a function of scan rate. Double-layer capacitance was determined by averaging the absolute values of the slopes.

**Analysis of the CO2 Reduction Product.** After collecting more than 8 coulombs under constant potential, product distribution was analyzed. Gas products were analyzed by gas chromatography (GC, Agilent 7890A, Agilent Technologies) with a thermal conductivity detector (for H_2 and CO) and a flame ionization detector (for CH_4 and C_2H_6). Liquid products (for C_3H_8, C_2H_6, and C_3H_7OH) were detected by gas chromatography–mass spectrometry. The FE of each product was calculated by eq 7:

$$\text{FE(\%)} = \frac{\text{quantity of the product} \times n \times F}{C} \times 100\%$$

(7)

where $n$ is the number of electrons transferred, $F$ refers to Faraday’s constant (96 485 C mol⁻¹), and C represents the total amount of charge passed through the working electrode.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.9b01142.

Figures S1–S12 and Tables S1–S5 (PDF)

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