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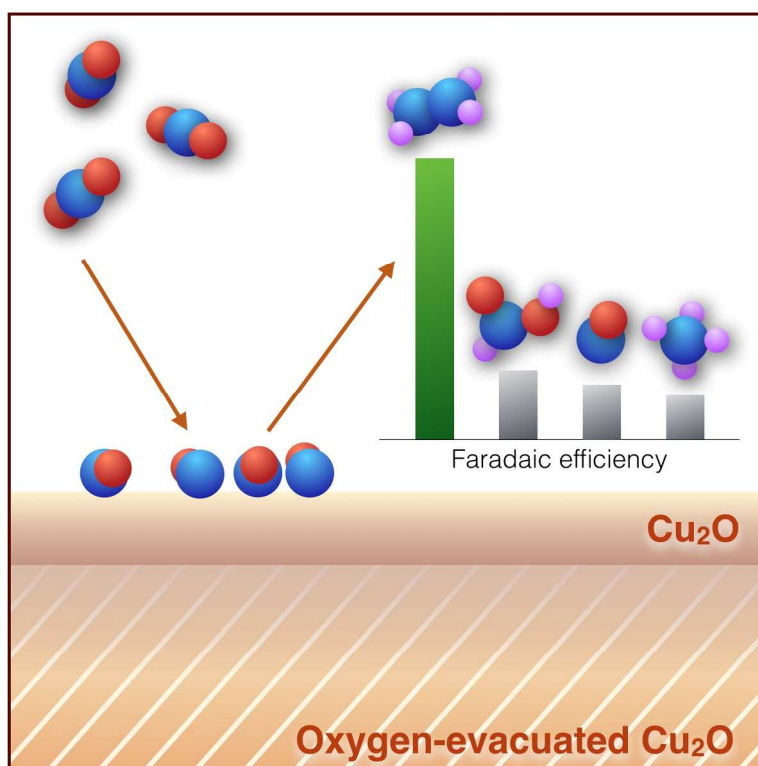
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Graphical Abstract

Insights into autonomously formed oxygen-evacuated Cu_2O electrode for the selective production of C_2H_4 from CO_2

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In-situ transformation of bulk Cu_2O to a Cu_2O -derived bulk structure with oxygen-vacated sites, with the oxide layer still on the surface, resulted to highly active, stable, and selective production of ethylene from carbon dioxide.

Insights into autonomously formed oxygen-evacuated Cu₂O electrode for the selective production of C₂H₄ from CO₂

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Electrochemical conversion of carbon dioxide (CO₂) to small organic fuels (*e.g.* formate, methanol, ethylene, ethanol) is touted as one of the most promising approaches in solving the problems of climate change and energy security. In this study, we report the highly efficient electrochemical reduction of CO₂ using cuprous oxide (Cu₂O) electrodes to produce ethylene (C₂H₄) primarily. During CO₂ electrolysis with an electrodeposited Cu₂O on a carbon electrode, we observe the transformation of compact metal oxide layer to a metal oxide structure with oxygen-vacated sites at the bulk region, where the notable electrocatalytic process towards selective production of C₂H₄ occurs. In contrast with previous studies, our results clearly indicate that the Cu₂O remains at the surface of the catalyst and it efficiently catalyzes the conversion process of CO₂ at low overpotential, exhibiting high selective faradaic efficiency of over 20 % towards C₂H₄ formation even in long-term electrolysis.

Introduction

Of late, the control of greenhouse gas emissions in the atmosphere is critical in averting the myriad of issues surrounding global warming. While carbon dioxide (CO₂) from fossil fuel combustion is one of the primary greenhouse gases, it has the potential also to be a feed for the production of hydrocarbons. To this end, researchers are still exploring for ways to solve the climatic CO₂ challenge and utilize its abundance to synthesize valuable chemicals *via* different conversion technologies (*e.g.* thermo-, photo-, electrochemical).¹⁻³

In particular, the electrocatalytic reduction of CO₂ to useful organic compounds has received great attention due to the relatively simpler process, with highly controllable operation.^{3,4} By passing current on an electroactive surface (*e.g.* metals, metal oxides), it is possible to break the strong carbon-oxygen bonds in CO₂ to form various small organic molecules. The process requires a considerable amount of electrical energy because of its non-spontaneous tendency and thus, the development of a highly efficient electrocatalyst is needed to overcome this drawback.⁵

In the electrolytic CO₂ reduction, superior catalytic activity and product selectivity are strongly dependent of the type of catalyst used.³ For instance, formate (HCOO⁻) is primarily formed on electrocatalysts such as Sn, Pb, and Hg, which exhibit negligible carbon monoxide (CO) adsorption.⁶⁻⁸ The Au and Ag electrodes mainly convert CO₂ to CO.⁹⁻¹² Cu is

analogous to the metals with weak CO adsorption, but is considered to be an unique catalyst for production of monovalent and divalent hydrocarbons.⁹⁻¹² Based on the above observations in previous studies, CO adsorption is undoubtedly an important step, since CO molecules are considered as key intermediates during CO₂ electroreduction.¹¹

Among these metals, great effort has been recently focused on Cu electrodes because of its unique electrocatalytic behaviour in enabling adsorbed CO to further react to more reduced organic molecules, such as methane (CH₄), ethylene (C₂H₄), methanol (CH₃OH), and ethanol (C₂H₅OH).¹³

In addition, recent studies have shown that the oxidation state of Cu influences its electrocatalytic properties. For example, Chang *et al.* studied CO₂ electroreduction with Cu₂O-catalyzed carbon cloth, with CH₃OH as the only confirmed reaction product, while the Faradaic efficiency was not reported.¹⁴ In another study, Faradaic efficiencies of 7.5 % and 6.8% for CH₄ and C₂H₄, respectively, were observed using an electrode based on Cu₂O/Zn.¹⁵ Furthermore, Le and co-workers suggested that Cu (I) species might play a key role for the selective catalysis of CH₃OH from their experiments using Cu₂O electrodes.¹⁶ Of the latest studies on Cu₂O electrodes, a recent study reported that the Cu₂O layer could contribute to the fabrication of highly active Cu electrodes. Kanan's group suggested that Cu₂O layers formed by annealing are fully reduced to Cu particles during CO₂ electroreduction and these Cu particles efficiently catalyze the reduction process at relatively lower overpotentials.¹⁷ In addition, it was shown that

formate (HCOO^-) was produced at lower overpotentials on the Cu electrode, which was prepared by a combined process of high-temperature annealing and electroreduction.^{17,18} Summarizing previous reports on the usage of Cu_2O catalyst in an electrolytic reduction of CO_2 , the catalyst itself was completely covered into Cu metal during the reduction process.¹⁵⁻¹⁸

In this paper, we compared the activity of Cu and Cu_2O to figure out how the Cu_2O behaves as a catalyst for CO_2 conversion. We tried to understand the enhanced selectivity of in-situ formed specific structure of Cu_2O towards C_2H_4 formation. Finally, we provide new insights on the structural transformation of Cu_2O for CO_2 electrolysis.

Experimental

All electrochemical experiments were carried out using a three-electrode assembly, with a commercial Ag/AgCl electrode. Pt plate (1 cm^2) was used as counter electrode. The working electrode was fabricated by electrodepositing Cu or Cu_2O at room temperature on a GDE (TGPH-060, Toray). Deposition of metal catalysts on GDE was carried out by constant potential electrolysis using a potentiostat/galvanostat (PGSTAT-302N, Autolab). A polycrystalline copper electrode was prepared by applying -0.3 V (vs. Ag/AgCl) for 10 min in a 0.01 M CuSO_4 solution ($> 99\%$, Sigma-Aldrich) in diluted sulfuric acid. Additionally, Cu_2O nanoparticles were deposited at -0.5 V (vs. Ag/AgCl) for 10 min from a 0.5 M CuSO_4 -containing lactic acid and 5.0 M NaOH solution. An optimized procedure to fabricate the electrodes was used, following a previous study on the electrodeposition of Cu and Cu_2O .¹⁹

The H-type electrolytic cell used for CO_2 electrolysis is shown in Figure S1. A cation exchange membrane (Nafion N117, Dupont) separated the cathode compartment from the anode compartment, while a Pt mesh (4 cm^2) was used as the counter electrode. The electrolyte was made from ultrapure water and reagent-grade potassium bicarbonate (KHCO_3 , Sigma-Aldrich), with a catholyte volume of 300 mL . Further, the electrolyte was saturated using high purity CO_2 (99.999%) via bubbling for 40 min at 5°C . Linear sweep voltammetry (LSV) measurements were carried out to examine the catalytic activity for CO_2 electroreduction, while bubbling Ar and CO_2 on the electrodes. Subsequent CO_2 reduction experiments were performed at a chosen potential between -0.9 V and -2.5 V (vs. Ag/AgCl) for 30 min. After optimizing the operating conditions, long-term electrolysis was done at -1.9 V (vs. Ag/AgCl) for 2 h to ascertain the stability of the catalyst. In order to compare the relative surface roughness of Cu_2O and Cu electrode, Cyclic voltammetry (CV) was performed in 0.1 M HClO_4 with Ar gas bubbled. Chronopotentiometry experiment was also performed on Cu electrode at 80 mA for 1 h to check the dependence of current density which might cause higher local pH.

Gas-phase products generated during CO_2 electrolysis were analysed using gas chromatography (GC) with thermal conductivity detector (TCD) and gas chromatography-mass spectrometry (GC-MS). The dissolved products in the

electrolyte were quantified by high performance liquid chromatography (HPLC, Alliance 2690) analysis of the electrolyte after the electrolysis. The crystallinity and morphology of the electrodes were analyzed by X-ray diffraction (XRD, Rigaku Miniflex II), a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4700) and high resolution transmission electron microscope (HR-TEM, Tecnai-F20 Ultra twin). The surface composition was identified via the Auger electron spectra obtained using an X-ray photoelectron spectroscopy (XPS, VG Multilab 2000). During the XPS sample preparation, the electrodes were rinsed with deionized water and dried immediately by blowing air to prevent the formation of copper hydroxide on the surface. The electrodes were then instantly vacuum-packed and placed in an Ar-filled glove box.

Depth profiling of Cu_2O and Cu electrodes were performed using Auger electron spectroscopy (AES, Perkin Elmer, SAM 4300) with differentially pumped ion source controller (Physical Electronics, model 11-065). The surface of electrodes was sputtered by Ar ions of 3 keV energy with a starting pressure of 10^{-9} bar. The base pressure was increased to 1.2×10^{-7} bar during the sputtering. For the excitation Auger electrons, an 5 keV electron beam was irradiated on the surface of samples and monitored beam current was 300 nA .

Results and discussion

After preparing the electrodes, the surface morphology and the crystal structures were characterized. Figure 1 shows the X-ray diffractograms of as-prepared Cu_2O and Cu electrodes before applying the cathodic potential. Several dominant Cu_2O and Cu phases on the electrode were observed. Inset images display the surface structure showing nano-sized Cu_2O and Cu catalyst particles uniformly placed on the GDE surface. Hence, the two different electrodes were prepared as desired.

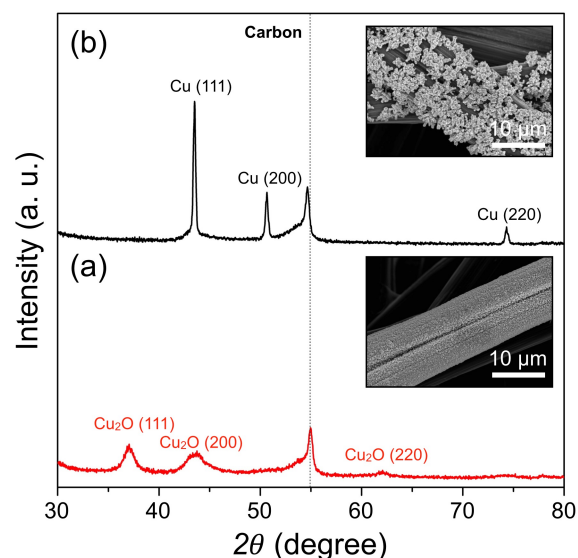


Figure 1. X-ray diffractograms of the electrodeposited Cu (black) and Cu_2O (red) electrocatalysts on GDE. Insets show the SEM images of (a) Cu_2O and (b) Cu catalyst.

In order to compare the electrocatalytic activity between Cu_2O and Cu, LSV curves were obtained. The electrode potential was swept at 10 mV s^{-1} with an initial open-circuit voltage in the 0.5 M KHCO_3 electrolyte saturated with Ar and CO_2 . As shown in Figure 2, hydrogen evolution reaction (HER) slowly begins at around -0.9 V at Cu_2O and -1.1 V at Cu under the Ar-saturated condition (inset of Figure 2). The cathodic currents in the sufficient CO_2 condition were notably smaller than in Ar gas, in potentials ranging from HER through -2.1 V . Suppression of HER during CO_2 electroreduction was generally attributed to the adsorbed CO molecules on the electrode surface.^{11,13} The difference in the reduction current measured in Ar-purged electrolyte and the current measured in CO_2 -saturated electrolyte should be considered as the indication of CO_2 reduction. This transition could be confirmed by product analysis, which will be discussed in the next paragraphs. With the Cu_2O reduction to Cu taking place simultaneously during CO_2 electrolysis, moreover, further detailed understanding is needed to determine the Faradaic efficiencies at given potentials.

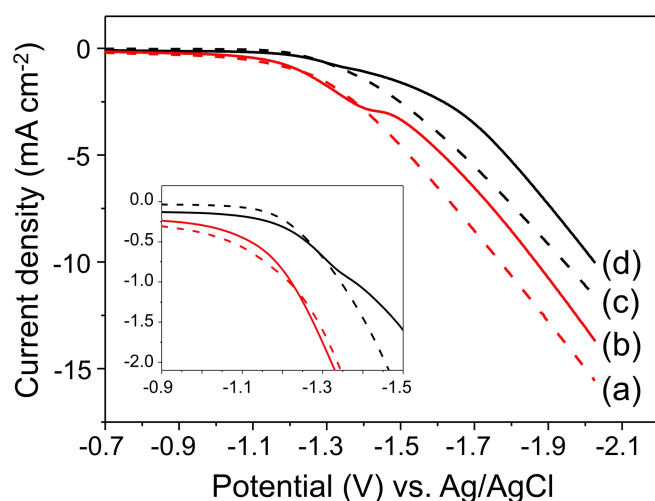


Figure 2. Linear sweep voltammograms for the electrodeposited Cu_2O (red) and Cu (black) electrode in 0.5 M KHCO_3 purged with Ar (dashed line) and CO_2 (solid line). Electrocatalytic CO_2 reduction began on Cu_2O at around -0.9 V with (a) Ar and (b) CO_2 gas purging, while CO_2 reduction in Cu were observed at around -1.1 V with (c) Ar and (d) CO_2 gas purging. Inset graph focuses on the potential region where the reactions occurred and the overpotential difference between the two electrodes. The scan rate was set at 10 mV s^{-1} in all the experiments.

The Faradaic efficiencies of the reaction products during the CO_2 electroreduction were used to evaluate and compare the electrocatalytic activity between Cu_2O and Cu electrodes at a fixed potential for 30 min. Various electrolysis products from CO_2 electroreduction were observed and the product distribution is displayed in Figure S2. It was observed that the Cu_2O electrode required less overpotential of $\sim 0.2 \text{ V}$ to convert CO_2 to its reduction products than that of metallic Cu electrode, in good agreement with a previous study.¹⁷ As shown in Figure S2, both Cu_2O and Cu electrodes showed similar trends in the oxygenate formation in the less negative potential region. CO and HCOO^- were the dominant species, when excluding the hydrogen, which is predominantly produced during CO_2

electrolysis in the potential ranges.^{11,13} In addition, the remainder of faradaic efficiency was allotted for the reduction of Cu_2O to Cu in the less negative potential ranges where applied potential for activation of CO_2 electrolysis was deficient.

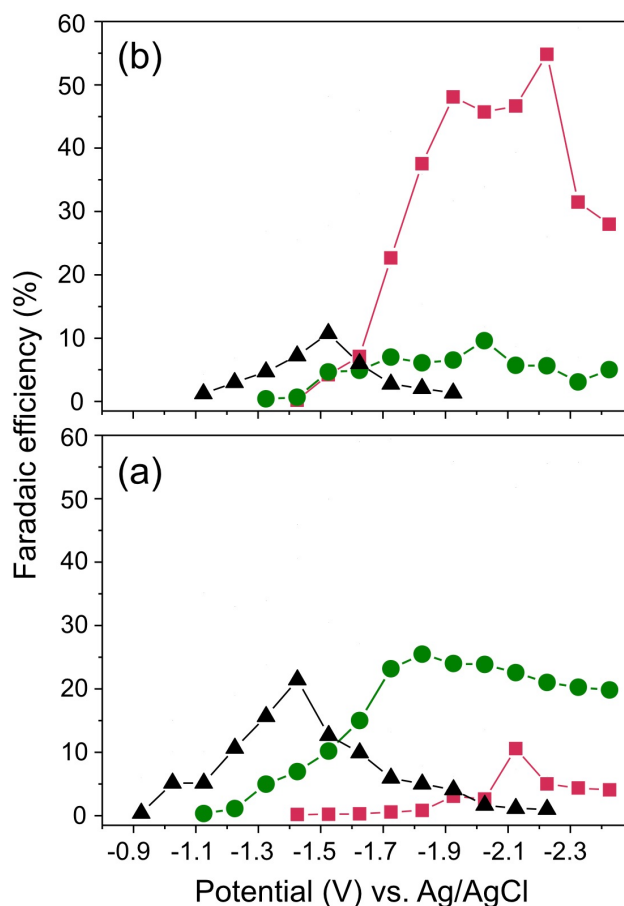


Figure 3. Faradaic efficiencies for the production of CH_4 (■), C_2H_4 (●), and CO (▲) Cu_2O and (b) Cu at different reduction potentials. CO_2 electrolysis was performed for 30 min at each potential in a CO_2 saturated 0.5 M KHCO_3 solution. Relatively lower overpotentials were required for CO_2 electrolysis on Cu_2O than at Cu and each electrode has varying selectivities for the production of hydrocarbons.

CO formation in the highly negative potential region suppressed the HER (Figure S2), as noted in the rise in Faradaic efficiencies of CH_4 and C_2H_4 and simultaneous decrease in CO as it was further converted to hydrocarbons (Figure 3).^{11,13} This observation supports the proposed mechanism for the formation of hydrocarbons *via* CO molecules as intermediate species.^{11,20} When the selectivity for C_2H_4 production was compared between two electrodes, the Faradaic efficiency in Cu_2O electrode was more than twice higher than that of Cu electrode. As discussed previously, earlier studies on CO_2 reduction have demonstrated only favorable CH_3OH production with Cu_2O electrode.¹⁴⁻¹⁶ On the other hand, a notable selectivity towards C_2H_4 formation was observed on Cu_2O electrodes in our

experimental results. Hence, it was expected that a transformation of Cu_2O electrode during the electrolytic process could lead to different CO_2 conversion routes such as results of Li *et al.* and Qiao *et al.*, showing the favorable HCOO^- production.^{17,18}

Long-term CO_2 electroreduction was carried out to fully confirm the electrocatalytic activity trends of Cu_2O and Cu electrodes in C_2H_4 production. Following the above results, the electrolysis was performed at the optimal potential of -1.9 V for 2 h. During long-term electrolysis, the Cu electrode exhibited an average current density of 8.5 mA cm^{-2} , while Cu_2O electrode demonstrated an average current density of 10 mA cm^{-2} (Figure S3). As seen in Figure 4, the Faradaic efficiency of CH_4 for Cu electrode changed from 52 % to 25 %, while the Faradaic efficiency of C_2H_4 decreased from 7 % to 3 %. In contrast, electrocatalytic activity for hydrocarbon formation over Cu_2O electrocatalysts remained high even after the 2 h electrolysis, with the Faradaic efficiencies towards CH_4 and C_2H_4 production at 2.5 % and 22 %, respectively. Furthermore, by multiplying the total current density in Figure S3 at a given potential by the faradaic efficiency towards each product, the distribution of partial current density can be plotted with respect to the electrolysis time (Figure S4). Considering other state of the art catalysts such as copper nanofoams showing faradaic efficiency for HCOOH of around 35 % and nanocrystalline copper for the production of liquid fuels with a faradaic efficiency of around 40 %, our catalyst's activity and selectivity are comparable with these previous studies.^{21,22} In addition, R. Reske *et al.* analyzed the particle size effects of Cu nanoparticles and their results showed a maximum Faradaic efficiency for CH_4 and C_2H_4 at 55 % and 20 %.²³

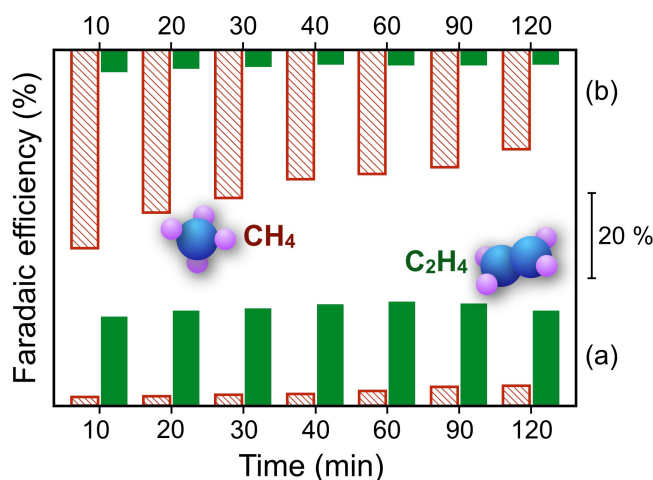


Figure 4. Faradaic efficiencies for the production of C_2H_4 (■) and CH_4 (▨) on (a) Cu_2O (bottom) and (b) Cu catalyst (top) during CO_2 with respect to the electrolysis time. Both of two gas phase products were collected and analyzed at each marked time.

From these experimental observations, one can assume that Cu_2O does not enhance all CO_2 reduction reactions, but only the reactions that form the heavier hydrocarbons in the more cathodic potential region. For a better understanding of the electrocatalytic behavior depending on the type of electrode, additional experiments were performed. First, CV was obtained

on both of two electrodes following the procedure in previous reports to measure their capacitance (Figure S5).^{17,22} In order to quantify the surface roughness of Cu_2O relative to Cu, we have assigned a surface roughness factor of 1.0 for the Cu electrode. As seen in Figure S5, Cu_2O has higher surface roughness factor than Cu at almost three times the latter's value. Although the electrode property based on the difference of particle size could increase the current efficiency at low overpotential region, surface area is not considered as the main contributor in the product distribution such as a $\text{C}_2\text{H}_4/\text{CH}_4$ ratio during CO_2 electrolysis.^{17,22,23} Previous reports have also suggested that the enhanced selectivity for C_2H_4 might have been a result of the increased total current density causing higher local pH in the vicinity of the electrode.^{11,13}

Hence, further experiment was carried out to investigate the dependence of current density, which might cause higher local pH. CO_2 electrolysis was performed on the Cu electrode at a constant current of 10 mA cm^{-2} , same as that of Cu_2O at -1.9 V (Figure S3). This should verify if the relationship between high current density and product selectivity is correct, with the same product distribution expected from both Cu and Cu_2O electrodes at high current densities. However, Figure S6 showed that a significant difference in the products was not observed, compared with that of Cu electrode at constant potential of -1.9 V in Figure 4. As the above results support our earlier hypothesis on the maintained selectivity of the Cu_2O electrode, we then characterized and analyzed the structure and morphology of the two cathodes by SEM, TEM, XRD, XPS, and AES.

Figure S7 shows the SEM images of Cu_2O and Cu electrodes, before and after CO_2 electrolysis. In the case of as-deposited Cu electrode, Cu nanoparticles with individual particle sizes of up to 160 nm were formed on the carbon substrate (Figure S7a). CO_2 electrolysis on the Cu electrode, however, could lead to deactivation of the surface active sites.^{12,20,24} Previous studies have reported that adsorption of amorphous carbon and impurities in the electrolyte might have caused the catalytic activity degradation in Cu electrodes.^{12,24-27} Interestingly, the Faradaic efficiency of ca. 20% for the CH_4 production at Cu electrode in this study was kept for longer than 2 h, suggesting that another factor should have been accounted for the decline in activity. As observed in SEM (Figure S7b), Cu nanoparticles agglomerated into larger particles after CO_2 electrolysis up to $5 \mu\text{m}$, possibly explaining the catalyst deactivation as suggested by other researchers as well.^{20,24}

In contrast, the morphological structure Cu_2O nanoparticles were almost unchanged after electrolysis, as seen in Figure S7c-d. This structural feature in Cu_2O , which prevents the decrease of catalytic active sites, supports the superior electrocatalytic stability of Cu_2O than that of Cu during CO_2 electroreduction. In addition, we observed the electrode materials using HR-TEM before and after CO_2 electrolysis. Our observations from HR-TEM, however, showed that there is not much difference between the particle morphology of the two electrodes. As

shown in Figure S8, the particles seem to agglomerate, in agreement with our observation in SEM.

The Cu₂O electrode's structural durability was identified, we observed that after applying reduction potential for a few minutes, characteristic Cu peaks appeared in the X-ray diffractograms, indicating simultaneous reduction of Cu₂O during CO₂ electrolysis. As already introduced in previous studies, Cu₂O phases were changed into metallic Cu under the electrolytic reduction condition.¹⁵⁻¹⁸ Moreover, the superior electrocatalysis was specifically attributed to the Cu₂O-derived Cu electrode upon application of cathodic potential.^{17,18}

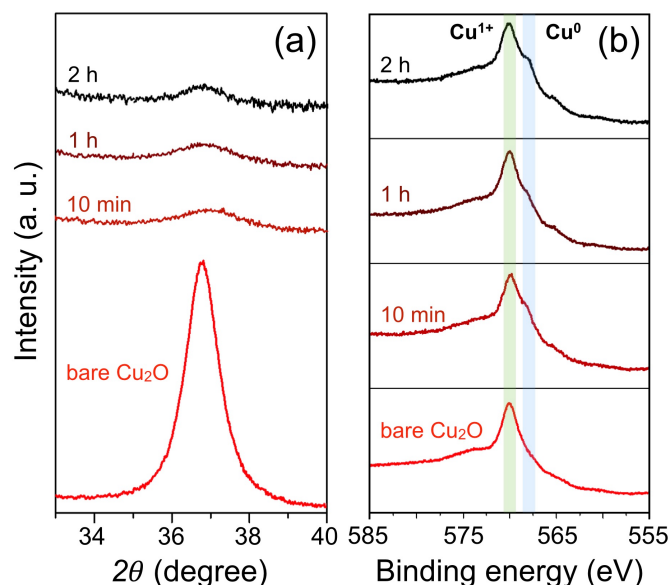


Figure 5. (a) X-ray diffraction patterns and (b) Auger spectra of Cu₂O electrocatalysts in as-prepared Cu₂O, and in 10 min, 1 h, and 2 h after electrolysis. Shaded areas in the Auger spectra indicate the binding energies of the most intense components of the Auger peaks (Cu¹⁺ and Cu⁰).

In our case, despite the electrochemical reduction of Cu₂O to Cu, SEM and TEM images did not show any noticeable surface morphological changes while the Faradaic efficiency towards C₂H₄ production was favorably kept high even after 2 h. This could be attributed to a particular characteristic of the transformed Cu₂O electrode during electrolysis. According to the XRD patterns of Cu₂O with respect to the electrolysis time (Figure 5a), Cu₂O (111) peak is barely visible on the as-used electrodes. The ex-situ X-ray diffractograms indicate that Cu₂O catalysts were not totally converted to Cu but obviously remained even after the phase changes caused by the applied cathodic potential for CO₂ electroreduction. The peak intensity decrease is most likely a result of increasing oxygen vacancy in the Cu₂O structure as the electrolysis occurs.²⁸

Figure 5b shows the Cu LMM Auger spectra indicating the oxidation state of the electrode surface up to 10 nm of depth.²⁹ The intense peak of Cu₂O was observed at 570.05 eV, together with a less intense peak corresponding to Cu at 568.15 eV (Figure S9).³⁰ The Auger spectra confirmed the presence of

Cu₂O on the electrode surface after the electrolysis and that the oxide layer was unchanged during electrolysis. This provides evidence to the fact that the surface layer of the as-used Cu₂O remained while the bulk Cu₂O was reduced to Cu. The structure remained Cu₂O on the outmost surface more densely might be possible because bulk phase reduction occurs easier than surface reduction in energy level calculations.^{31,32}

To further study the structural transformation of Cu₂O during CO₂ electrolysis, elemental depth profiling of the electrodes was performed using AES. Figure 6 exhibits the relative atomic concentration of O to Cu of each electrode as a function of the electrode depth. As already explained from the XRD and Auger spectra analyses above (Figure 5), complete reduction of the Cu₂O to metallic Cu did not occur. As shown in the concentration profile of oxygen in the as-deposited Cu (Figure 6a), a native oxide layer with a thickness of almost 2.5 nm is present.³³⁻³⁵ Identifying the thickness of the oxide in the Cu₂O electrode at the onset of electrolysis.

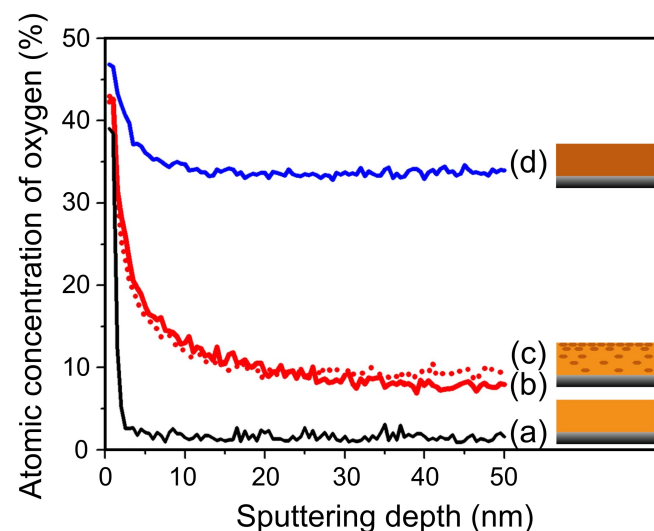


Figure 6. Auger depth profiles showing the atomic content of oxygen in Cu₂O of (a) as-deposited Cu electrode, Cu₂O electrodes after CO₂ electrolysis for (b) 10 min (dotted line) and (c) 2 h (solid line), and (d) as-deposited Cu₂O electrode.

For instance, the oxygen depth profile of as-deposited Cu₂O in Figure 6d demonstrates a decreasing amount of oxygen and then an almost constant oxygen amount at a depth around 20 nm. The oxygen concentration profile indicates that electrode structure is that of Cu₂O before electrolysis. Upon applying the cathodic potential, however, the oxygen depth profile changed, showing a decrease in the oxygen content for samples under electrolysis for 10 min and 2 h (Figure 6b-c). This provides another evidence on the partial conversion of Cu₂O nanoparticles to metallic Cu nanoparticles. Nevertheless, an oxide layer thicker than the native oxide still exists in the surface of the catalyst. In addition, both as-used Cu₂O electrodes exhibited similar depth profiles, regardless of the length of exposure in the reducing conditions of CO₂

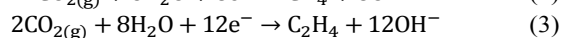
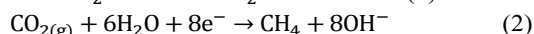
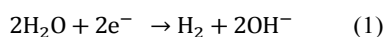
electrolysis. For these reasons, it is believed that the Cu₂O electrode partially maintained its initial structure, especially in the bulk phase, and the transformed structures were built with sites where oxygen atoms were removed. The new catalyst structure, with the oxide layer on top of the sub-surface Cu₂O-derived Cu at the bottom, contributed greatly to the sustained high activity and good selectivity for C₂H₄ formation. The structural transformation of the Cu₂O electrode, as ascertained in AES depth profiling is crucial in the high conversion rates for the production of Cu₂O from CO₂.

To summarize the discussions above, bulk and surface-sensitive techniques (i.e. XRD, AES) demonstrated the partial reduction of Cu₂O to metallic Cu. In addition, there is a strikingly similar structural feature between the two as-used Cu₂O electrodes after electrolysis in terms of their oxygen concentration profiles. Thus, giving us an insight on the possible role of Cu₂O catalysts for the selective C₂H₄ production from CO₂ electrolysis. On the basis of these experimental results, the Cu₂O electrode during electrolysis can be pictured as having an oxide layer on top of metallic Cu with a lot of oxygen-vacated sites from the restructuring of the crystal structure during CO₂ reduction. With the formation of the oxygen-vacated sites on the metallic Cu layer, along with the presence of the oxide layer, the electrode is able to maintain its high turn-over rate for C₂H₄ formation. Our results strongly suggest a new role of the Cu₂O layer, not only as a starting material for making an oxide-derived Cu catalysts, but as the active layer during CO₂ electrolysis, a view that is in stark contrast with previous works.^{17,18}

A key question in the structural transformation of Cu₂O is how the Cu₂O particles maintained its activity during CO₂ electrolysis. This interesting situation could be explained from first-principle calculations using density functional theory (DFT) on copper oxide reduction.^{31,32,36} Furthermore, in some cases of reduction of CuO and Cu₂O with H₂, not all Cu₂O powders were completely reduced to metallic Cu, leaving a residue of the starting oxide material when exposed to H₂ for more than 60 min.³¹ They reported that the partial reduction of Cu₂O grains was attributed to the coating protection by the Cu film, which was quickly reduced, leaving oxygen trapped within the structure.³¹

Maimaiti *et al.* found that loss of the subsurface oxygen is initially thermodynamically favorable in copper oxide reduction and showed that the reduction of CuO to Cu at the surface is more energetically difficult than in the bulk phase.³² Oxygen-vacancy structures in Cu₂O (111) were also studied and their usefulness for CO₂ adsorption as active sites was demonstrated.³⁶

In addition, the partial depletion of Cu₂O electrode might have resulted from following reactions:



Hydroxide ions (OH⁻) are generated at the electrode surface during CO₂ electroreduction. There is an instantaneous pH rise in the local region just close to the surface layer as active

sites.^{24,25,37} Under the electrolytic conditions, the reduction of Cu₂O to metallic Cu can be suppressed.^{14,38,39} Recent literature suggested that Cu₂O shows prominent stability even after applying the cathodic potential in alkaline media for oxygen reduction reaction.^{40,41} As a result, the uniquely structured Cu₂O electrodes leads to selective C₂H₄ formation - but not CH₄ formation - and the structure is maintained during CO₂ electrolysis owing to the hydroxide molecules (equation 1-3) promoting the locally alkaline state.

Conclusions

The superior electrocatalytic behaviour in CO₂ electrolysis of the electrodeposited Cu₂O electrode was demonstrated, with the catalyst exhibiting low overpotential and high selectivity towards C₂H₄ formation over other reaction products. Contrary to a number of earlier studies, Cu₂O was only partially reduced, leaving an oxide layer on top of the bulk Cu₂O-derived Cu layer. Using bulk and surface-sensitive analytical techniques, we demonstrated the decrease in the oxygen concentration of the Cu₂O electrode during electrolysis, resulting to the formation of oxygen-vacated structures, which are randomly distributed in the Cu₂O structure-derived bulk layer. The in-situ formed structures play a critical role in maintaining the high reactivity of the electrode for C₂H₄ production. Hence, the surface oxide coverage and the oxide-derived metallic layer are both key in the selective CO₂ catalysis towards large oxygenate molecules. While we have provided in-depth analysis on the oxide transformation during CO₂ reduction, more fundamental studies are needed to elucidate the atomic reorganization of the surface and bulk oxide layers and to understand its role in forming the CO₂-active sites. Our route to providing a highly active and stable CO₂ catalyst, however, is highly advantageous, because the extra oxide reduction step in preparing the electrode is no longer necessary. This will be important in preparing industrially-relevant catalysts for converting CO₂ into high value chemicals using renewable energy sources.

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Notes and References

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Schematic diagram of the H-type cell, Faradaic efficiencies for all products at different applied potentials, Current density profiles of Cu₂O and Cu during electrolysis for 2 h, Partial current densities during CO₂ electrolysis of Cu₂O and Cu, Cyclic voltammograms for the measurement of the surface roughness factor, Potential profile during CO₂ electrolysis on Cu electrode at a constant current density of 10 mA cm⁻² for 1 h, SEM images of Cu₂O and Cu electrodes before and after CO₂ electrolysis, TEM images of Cu₂O and Cu electrodes before and after CO₂ electrolysis, Auger spectra of Cu₂O and Cu electrodes before and after CO₂ electrolysis for 2 h. . See DOI: 10.1039/b000000x/

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