Selective CO$_2$ Electroreduction to Ethylene and Multicarbon Alcohols via Electrolyte-Driven Nanostructuring

Dunfeng Gao, Ilya Sinev, Fabian Scholten, Rosa M. Arán-Ais, Nuria J. Divins, Kristina Kvashnina, Janis Timoshenko, and Beatriz Roldan Cuenya*

Abstract: Production of multicarbon products (C$_n$H$_m$) from CO$_2$ electroreduction reaction (CO$_2$RR) is highly desirable for storing renewable energy and reducing carbon emission. The electrochemical synthesis of CO$_2$RR catalysts that are highly selective for C$_2$ products via electrolyte-driven nanostructuring is presented. Nanostructured Cu catalysts synthesized in the presence of specific anions selectively convert CO$_2$ into ethylene and multicarbon alcohols in aqueous 0.1 M KHCO$_3$ solution, with the iodine-modified catalyst displaying the highest Faradaic efficiency of 80% and a partial geometric current density of ca. 31.2 mA cm$^{-2}$ for C$_2$ products at $-0.9$ V vs. RHE. Operating X-ray absorption spectroscopy and quasi in situ X-ray photoelectron spectroscopy measurements revealed that the high C$_2$ selectivity of these nanostructured Cu catalysts can be attributed to the highly roughened surface morphology induced by the synthesis, presence of subsurface oxygen and Cu$^{+}$ species, and the adsorbed halides.

Introduction

The electrochemical production of fuels and chemical feedstocks from CO$_2$ and water using the electricity derived from renewable energy holds promise as a sustainable process that might help to mitigate some of our current energy and climate challenges. CO$_2$ electroreduction reaction (CO$_2$RR) to multicarbon hydrocarbons and oxygenates (C$_n$H$_m$) with high energy density is highly desirable, but is severely limited by the slow kinetics of multiple proton and electron transfer steps during C=C coupling$^{[1,6–8]}$. Cu, among the studied metals, is the only one producing hydrocarbons and alcohols in considerable amounts. However, polycrystalline Cu usually suffers from high overpotential and low C$_2$ selectivity.$^{[5]}$ The formation of C$_2$ products during CO$_2$RR has been found to be extremely sensitive to the catalyst structure.$^{[1,6–8]}$ Therefore, nanostructured electrocatalysts capable of efficient generation of multicarbon products from CO$_2$RR might be developed through rational design.

It is well-known that the activity and selectivity of CO$_2$RR catalysts strongly depend on the precise control of their structure, such as the content of defects$^{[9]}$, subsurface oxygen or Cu$^{+}$ species$^{[10–15]}$ the specific shape of the nanocrystals$^{[16–18]}$ or the surface composition and atomic ordering in bimetallic nanostructures$^{[19,20]}$. Previous experimental and theoretical studies demonstrated that Cu(100) is the most favorable crystal orientation for the C=C coupling process$^{[21–23]}$. However, the surface of Cu electrodes under electrochemical environments often undergoes reconstructions induced by applied potentials$^{[24–26]}$. The intermediates formed during CO$_2$RR$^{[27]}$ as well as specifically adsorbed anions$^{[28–30]}$ on the other hand, some anions either present in the electrolyte$^{[32]}$ or adsorbed on the electrode surface$^{[33]}$ have been shown to play a vital role in the dynamic evolution of the catalyst structure under reaction conditions as well as the activity and selectivity of CO$_2$RR. These important findings might be used in the design and development of new electrodes via electrochemical modifications.

The morphology and composition of electrochemically synthesized catalysts is strongly affected by the applied potential and electrolyte employed.$^{[34]}$ Herein we report an electrolyte-driven nanostructuring strategy for the facile synthesis of highly selective CO$_2$RR catalysts. The nanostructured Cu catalysts synthesized in the presence of specific anions can selectively convert CO$_2$ to ethylene and multicarbon alcohols in aqueous 0.1 M KHCO$_3$ solution, with the KI-treated catalyst displaying the highest FE of about 80% and partial current density of about 31.2 mA cm$^{-2}$ for C$_2$ products at $-0.9$ V vs. RHE. The high C$_2$ selectivity of these nanostructured Cu catalysts is attributed to their rough morphology, the presence of subsurface oxygen, Cu$^{+}$ species, and adsorbed halides on the surface.
Results and Discussion

Nanostructured Cu catalysts were synthesized by cycling electropolished Cu foils in different 0.1 m potassium salt solutions (between 0.3 and 2.2 V vs. RHE) and were denoted by Cu_X (X = Cl, Br, I) and Cu_CO_3, respectively. Additional details on the synthesis parameters are shown in the Supporting Information, Table S1. Figure 1 and the Supporting Information, Figure S1 show scanning electron microscopy (SEM) images of these samples as-prepared, after immersion in 0.1 m KHCO_3 solution, as well as after 1 h of CO_2 RR at −1.0 V vs. RHE. Cu nanocubes with an edge size of 250–300 nm are formed on the surface of the Cu_Cl (Figure 1A) sample as we discussed previously. In clear contrast, the Cu_Br and Cu_I samples show a faceted crystal morphology characterized by flatter larger structures for Cu_Br (Figure 1B) and needle-like shapes for Cu_I (Figure 1C).

A composition of CuBr and CuI was confirmed by energy-dispersive X-ray spectroscopy (EDX; Supporting Information, Table S2). The Cu_CO_3 sample shows particles dispersed on the underlying Cu surface (Figure 1D). After the former electrolyte-driven surface nanostructuring, when the different samples are subsequently immersed in the same 0.1 m KHCO_3 solution for 30 min before applying any potential, the edges of CuBr and CuI samples show a faceted crystal morphology characterized by flatter larger structures for Cu_Br (Figure 1B) and needle-like shapes for Cu_I (Figure 1C). A composition of CuBr and CuI was confirmed by energy-dispersive X-ray spectroscopy (EDX; Supporting Information, Table S2). The Cu_CO_3 sample shows particles dispersed on the underlying Cu surface (Figure 1D). After the former electrolyte-driven surface nanostructuring, when the different samples are subsequently immersed in the same 0.1 m KHCO_3 solution for 30 min before applying any potential, the edges of CuBr and CuI samples show a faceted crystal morphology characterized by flatter larger structures for Cu_Br (Figure 1B) and needle-like shapes for Cu_I (Figure 1C).

To monitor the evolution of the chemical state and local environment of Cu during CO_2 RR we conducted operando X-ray absorption spectroscopy (XAS) measurements. While extended X-ray absorption fine-structure spectroscopy (EXAFS) data measured in total fluorescence yield mode did not show any significant difference from the metallic structure apart from a highly defective structure (Supporting Information, Figures S3–S7, Table S4), high-energy resolution fluorescence detected X-ray near edge structure (HERFD-XANES) spectra are more sensitive to the chemical state and coordination environment of Cu under reaction conditions. Figure 2 shows the Cu K-edge HERFD-XANES spectra of the as-prepared Cu_X samples as well as data from the same samples obtained during CO_2 RR at −1.0 V vs. RHE along with the reference spectra of bulk Cu, Cu_2O, CuI, and CuBr. The spectra suffer from significant self-absorption effects, but a normalization was used here to have equal self-absorption in the reference spectra and halide- and carbonate-modified samples. The spectra of the as-prepared Cu_I and Cu_Br samples show distinctive features of CuI (Figure 2A; Supporting Information, Figure S8) and CuBr (Fig-
Figure 2. HERFD-XANES spectra of the Cu_I (A) and Cu.Br (B) samples in the as-prepared state and measured under operando CO\textsubscript{2}RR conditions in 0.1 m KHCO\textsubscript{3} after 1 h of CO\textsubscript{2}RR at -1.0 V vs. RHE. Reference spectra of bulk Cu, CuI, CuBr, and CuO are also plotted. Linear combination analysis (LCA) of operando HERFD-XANES spectra of the Cu_I sample measured in the as-prepared state (C) and during CO\textsubscript{2}RR at -1.0 V vs. RHE (D) are shown. The corresponding subspectral components necessary to fit the data (metallic Cu, CuI, and CuO) are scaled according to their weighting parameters.
The Cu_X and Cu_CO$_3$ samples were measured with XPS in the as-prepared state and after 1h of CO$_2$RR at $\eta=1.0$ V vs. RHE as shown in Figure 3 and the Supporting Information, Figures S12 and S13. Among the Cu_X samples, the Cu_I sample shows an almost pure CuI surface in its as prepared state, while the surface of the Cu_Br is composed of Cu$_2$O (65 at %) and CuBr (35 at %), and that of Cu_Cl is composed of Cu$_2$O (31 at %), CuCl (56 at %) and CuCl$_2$ (12 at %). The composition difference is also consistent with the relative stability of the three Cu halides.[33] However, the Cu_CO$_3$ sample has a starting Cu oxidation state of Cu$^{2+}$ in the form of CuO and CuCO$_3$. After CO$_2$RR, most of the Cu$^{+}$ and Cu$^{2+}$ species in the as prepared samples were reduced to metallic Cu. However, a small amount of CuBr still survived (Figure 3B). Moreover, considerable amounts of halides (Figure 3C,D) were observed on the Cu surface before but also after the reaction and subsequent in situ rinsing in water. The metallic Cu surface of the Cu_I sample seen by XPS, together with the Cu$_2$O and CuI species revealed by the more bulk-sensitive XANES measurements (Figure 2), indicate the presence of subsurface oxygen and Cu$^+$ species in the halide-derived CO$_2$RR Cu catalysts.

The catalytic activity and selectivity of the nanostructured Cu catalysts were obtained by performing chronoamperometry measurements in a CO$_2$-saturated 0.1m KHCO$_3$ solution. All the nanostructured Cu catalysts show significantly higher geometric current density than an electropolished Cu foil (EP_Cu), and Cu_I shows the highest current density in the measured potential range (Figure 4A). However, when the current densities were normalized by the electrochemically active surface area (ECSA), the three halide-modified Cu catalysts show similar specific activity (Supporting Information, Figure S17A). Therefore, the high surface area (thus high density of surface reactive sites) of the roughened Cu catalysts plays a very important role in the significantly improved apparent activity compared to a flat Cu surface.

Figure 3. Quasi in situ Cu Auger LMM XPS spectra of Cu_CO$_3$, Cu_Br, and Cu_I before (A) and after (B) 1h of CO$_2$RR at $-1.0$ V vs. RHE in a CO$_2$-saturated 0.1 m KHCO$_3$ solution. Br 3p and I 3d XPS spectra of the Cu_Br (C) and Cu_I (D) measured before and after CO$_2$RR are also shown.

Figure 4. Total geometric current density (A), total Faradaic efficiency and geometric partial current density of (B) C$_2$H$_4$, C$_2$H$_5$OH, C$_3$H$_7$OH, and CH$_4$ as a function of the applied potential after 1h of CO$_2$RR in a CO$_2$-saturated 0.1 m KHCO$_3$ solution.
Nevertheless, apart from the roughness, the increased activity over the nanostructured Cu catalysts versus EP_Cu could also be ascribed to defects, their porous structures, and the presence of adsorbed halide species, Cu+ or subsurface oxygen species, as we observed by XPS (Figure 3) and XANES (Figure 2).

The total FEs of C2+ products are shown in Figure 4B and the Supporting Information, Figure S14, and FEs for each individual product are shown in the Supporting Information, Figure S15. The highest C2+ FE of about 80% was achieved at @0.9 V vs. RHE over Cu_I, while the C2+ FEs of about 66–73% at −1.0 V vs. RHE were obtained over Cu_Cl, Cu_Br, and Cu_CO3. The C2+ FEs of all nanostructured Cu catalysts were 3-fold higher than those of the EP_Cu sample (ca. 20 %) at −0.9 V vs. RHE. At more negative potentials (<−1.0 V vs. RHE), all the catalysts show decreased C2+ FE and increased H2 FE, which is due to CO2 mass-transport limitations. The potential-dependent partial current densities of the various CO2RR products are shown in Figure 4C–F and the Supporting Information, Figures S16, S17. Cu_I showed the highest partial current densities for ethylene, ethanol, and n-propanol. Compared to the previously reported systems, where EP_Cu was studied in an electrolyte mixture containing KX (X = Cl, Br, I) and KHCO3, our new nanostructured catalytic systems (synthesized by cycling the Cu foil in KX followed by washing in water) avoided the complexity of the co-existence of structural and chemical electrolyte effects since all CO2RR measurements were done in KHCO3. Furthermore, higher activity, lower onset potential and higher C2+ selectivity were obtained for the present electrolyte pre-nanostructured catalysts as compared to the case where iodine was added to the electrolyte during the reaction (Supporting Information, Figure S18). Although the Cu_CO3 sample showed high partial current density for C2+, its methane partial current density was also higher, comparable to that of EP_Cu. The simultaneously favorable production of ethylene and methane over the porous Cu_CO3 is slightly different from that reported for Cu foam catalysts, which simultaneously favored the production of ethylene and ethane, which is probably due to the smaller pore size (430 nm) in our Cu_CO3. Overall, the iodine modified Cu catalyst (Cu_I) synthesized via electrolyte-driven nanostructuring showed a high C2+, geometric current density of about 31.2 mA cm−2 at −0.9 V vs. RHE (Supporting Information, Figure S19), superior to previously reported Cu catalysts (Supporting Information, Table S6).

Stability tests were carried out for the Cu_I and Cu_CO3 samples at potentials for which the highest C2+ FEs were detected (Figure 5). The current density of Cu_I remained almost stable within our 22 h test, while a 20% decrease was
observed for the Cu\_CO\_3 sample. Furthermore, a decrease in the C\_H\_4 FE was observed for both samples, although in the case of the Cu\_I this took place only during the first 5 h, becoming stable subsequently. The decrease in the C\_H\_4 FE was accompanied by an increase in methane for the Cu\_I sample (a fast decrease in C\_H\_4/CH\_3 FE ratio; Supporting Information, Figure S20) and of CO and H\_2 FE for Cu\_CO\_3. However, the morphology (inserts in Figure 5A) and roughness (Supporting Information, Table S3) of Cu\_I after the stability test were similar to those after 1 h of CO\_RR, suggesting that the increased production of CH\_3 (or CO) at the expense of C\_H\_4 was not caused by morphological changes, but most likely by the gradual depletion of subsurface oxygen species\[^{38-40}\] and Cu\(^+\) species as well as the loss of adsorbed iodine ions in the Cu\_I sample. In clear contrast, a large number of NPs were formed during CO\_RR on the surface of the Cu\_CO\_3 sample (inserts in Figure 5C) and the roughness increased accordingly (Supporting Information, Table S3). The presence of these new low-coordinated sites in the form of NPs is expected to favor the formation of CO and H\_2 [\(^{41}\)] and could also lead to the deactivation of the Cu\_CO\_3 sample.

Although the activity, selectivity, and stability of CO\_RR catalysts are determined by multiple complex factors such as roughness, defects, shape, and oxidation state, the present data feature that the C–C coupling process over the Cu\_X samples, especially Cu\_I, is strongly related to the presence and stabilization of Cu\(^+\) species as well as of the adsorbed halides, as confirmed by operando HERFD-XANES (bulk-sensitive) and quasi in situ XPS measurements (surface-sensitive). We found a positive correlation between the production of C\_2 and the amount of Cu\(^+\) species in the halide-modified Cu catalysts in the following order: Cu\_I > Cu\_Br > Cu\_Cl. Previous theoretical studies predicted that subsurface oxygen as well as the presence of a Cu\(^+\)/Cu\(^0\) interface plays a crucial role in CO\_2 activation and CO dimerization, ultimately resulting in higher C\_2 selectivity [\(^{11,42}\)]. Interestingly, the adsorbed halides are known to bind more strongly to the oxidized Cu surface [\(^{12,31}\)] and to facilitate the formation and stabilization of the intermediates during CO\_RR required to obtain C\_2 products. On the other hand, the Cu\_CO\_3 sample with only metallic Cu species under reaction conditions, showed higher CH\_3 selectivity than all Cu\_X samples. The latter is probably attributed to its nanoporous structure [\(^{43}\)]. At the end, we should also highlight the role of the high ECSA of the present nanostructured Cu catalysts [\(^{44}\)]. Apart from having a higher surface area, a drastic increase in the ECSA during nanostructuring a flat Cu surface is usually coupled with the creation of highly reactive surface sites such as defects and low-coordinated sites. These surface sites might be more favorable for C–C coupling during CO\_RR [\(^{14,45}\)]. Not only improving the apparent activity but also helping to tune the selectivity towards multicarbon products. In this work we were able to modify the surface morphology and its composition and chemical state (Cu\(^+\)) via an electrolyte-driven nanostructuring pre-treatment strategy, which was found to lead to enhanced C\_2 selectivity.

**Conclusion**

We have presented an electrolyte-driven nanostructuring strategy for the facile synthesis of CO\_RR electrocatalysts highly selective to C\_2 products. The proposed synthesis not only leads to strong morphological modifications of the sample surface, but also to the presence of residual halides and cationic Cu species. These Cu electrocatalysts can selectively convert CO\_2 into ethylene and multicarbon alcohols in a KHCO\_3 solution, with the iodine-modified catalysts showing the highest FE for C\_2\_gas of about 80% and partial geometrical current density of about 31.2 mA cm\(^{-2}\) at −0.9 V vs. RHE. The superior C\_2 selectivity of the halide-modified Cu catalysts was attributed to their rough surface morphology combined with electronic and chemical effects arising from the stabilization of subsurface oxygen as well as Cu\(^+\) species and adsorbed halides on the surface. Cu\_CO\_3 shows both high C\_2\_gas and methane selectivity, which is attributed to its particular nanoporous structure. Stability tests suggested that the gradual depletion of subsurface oxygen/Cu\(^+\) species and the increased number of low-coordinated sites formed under reaction conditions are behind the distinct catalytic performance of the halide- and carbonate-modified Cu catalysts, respectively. This work provides new insights required for the design of highly active C\_2\_gas-selective CO\_RR catalysts.

**Experimental Section**

Cu\_Cl, Cu\_Br, Cu\_I, and Cu\_CO\_3 catalysts were prepared by electrochemically cycling an electropolished Cu foil in 0.1 M KCl, KBr, KI, and K\_2CO\_3 solutions with triangular potential scans at a rate of 500 mV s\(^{-1}\), respectively. During each cycle, the potential was held at the negative (E\(_{\text{IL}}\)) and positive (E\(_{\text{PI}}\)) limits for 5 and 10 s, respectively. The cycled Cu catalysts were prepared with the indicated potential ranges and number of cycles as shown in the Supporting Information, Table S1. For other experimental details, including operando and ex situ characterizations and electrochemical measurements, see the Supporting Information.

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