



## Research Highlight

# Structural evolution of oxide-/hydroxide-derived copper electrodes accounts for the enhanced C<sub>2+</sub> product selectivity during electrochemical CO<sub>2</sub> reduction

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Electrocatalytic CO<sub>2</sub> reduction reaction, namely CO<sub>2</sub>RR, provides a versatile way of storing energy in chemical bonds while simultaneously closing the anthropogenic carbon cycle. Producing valuable multicarbon products (C<sub>2+</sub>) from CO<sub>2</sub>RR is desirable yet challenging [1]. It has been noted that oxide-/hydroxide-derived copper electrodes exhibit excellent selectivity toward C<sub>2+</sub> products during CO<sub>2</sub>RR [2]. However, the origin of such enhanced selectivity remains unclear, and the existence of Cu oxide species on electrode surface or subsurface at CO<sub>2</sub>RR conditions is still under debate [3]. For example, Jiang et al. [4] used an electrodeposited Cu<sub>2</sub>O(100) electrode to obtain a Faradaic efficiency (FE) of 60% for C<sub>2+</sub> products, and no oxide species has been detected on the electrode surface during reaction. Whereas, Mistry et al. [5] evidenced the stability of Cu<sup>1+</sup> during CO<sub>2</sub>RR in their plasma-activated Cu electrode, and related it to the observed high C<sub>2</sub>H<sub>4</sub> selectivity (60% FE). Hence, the solid evidence to prove or exclude the presence of Cu oxide species on the oxide-/hydroxide-derived copper electrodes during CO<sub>2</sub>RR is urgently needed, as an effort to further investigate the mechanism behind the enhanced C<sub>2+</sub> selectivity.

Recently, Lei et al. [6] published a research article targeting to solve this problem. In this work, they studied the nature and distribution of Cu species, as well as their crystal evolution on both oxide-derived and hydroxide-derived copper electrodes during CO<sub>2</sub>RR. Two types of catalysts were prepared by successive heat and quench process (HQ-Cu) or anodization in alkaline solution (AN-Cu).

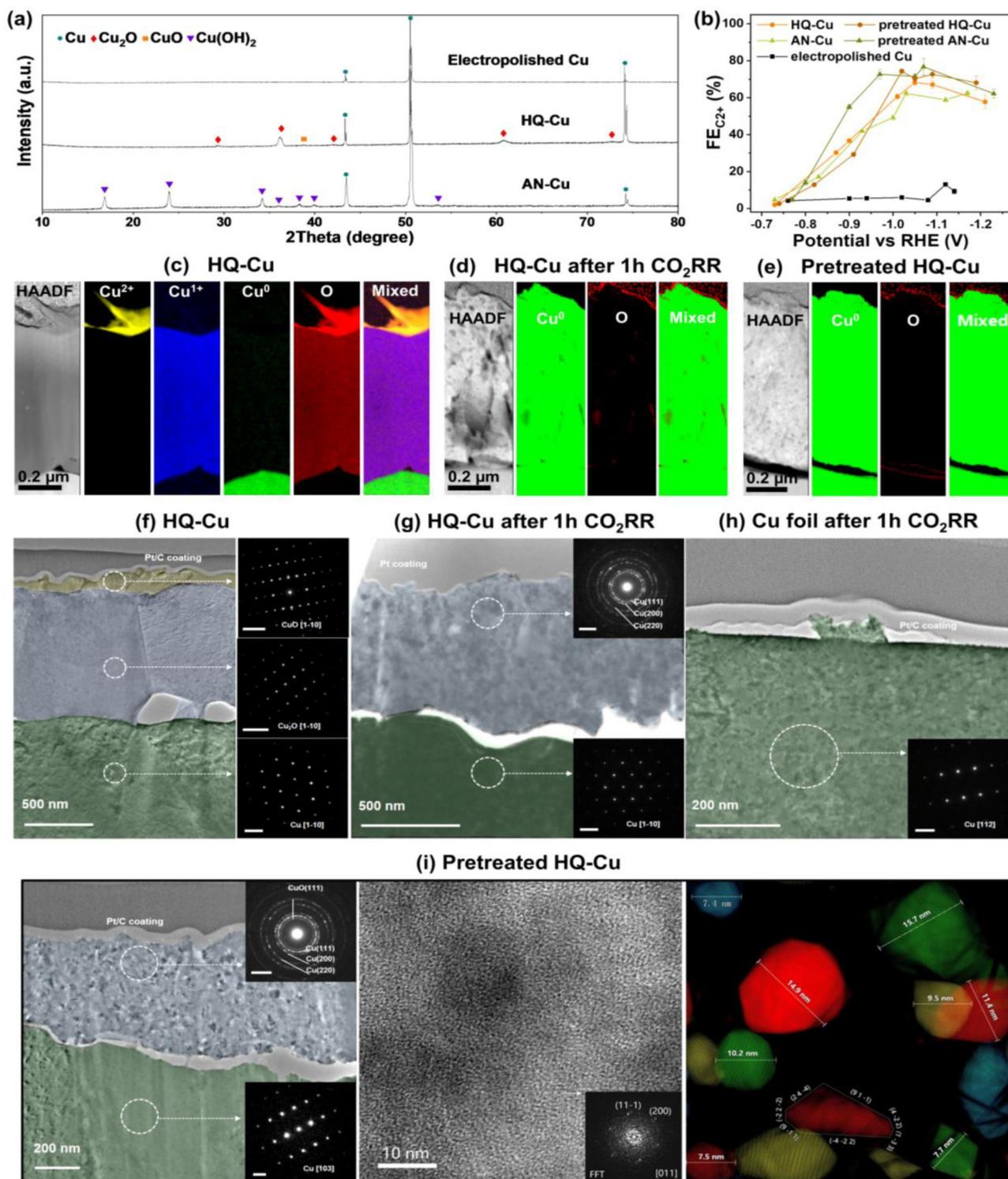
With the help of X-Ray diffraction (XRD) and X-ray photoelectron spectroscopy, HQ-Cu and AN-Cu were found to consist of CuO, Cu<sub>2</sub>O, Cu and Cu(OH)<sub>2</sub>, Cu, respectively (Fig. 1a). Both catalysts were directly submitted to CO<sub>2</sub>RR and exhibited high selectivity toward C<sub>2+</sub> products. Specifically, the peak FE(C<sub>2+</sub>) of HQ-Cu is 68.2% at -1.05 V<sub>RHE</sub> and that of AN-Cu is 62.3% at -1.03 V<sub>RHE</sub> (Fig. 1b). In addition, not only their partial current densities for C<sub>2+</sub> products were extensively improved in comparison with pure Cu foil, but also the catalytic stability was prolonged to more than seven hours.

Focused ion beam (FIB) was then utilized to prepare ultrathin samples from the electrodes to identify the Cu oxidation states and their spatial distribution and evolution along CO<sub>2</sub>RR by electron energy loss spectroscopy (EELS). It was found that the three Cu species in HQ-Cu co-exist layer by layer, where a discontinuous CuO layer (0–200 nm thick) lies on the top surface and Cu<sub>2</sub>O layer (300–1000 nm thick) was sandwiched by the Cu substrate and the CuO layer (Fig. 1c). After 1 h of CO<sub>2</sub>RR, the C<sub>2+</sub> products selectivity of HQ-Cu reached the steady stage and only metallic Cu was detected on the electrode according to their XRD and EELS characterization (Fig. 1d), suggesting that Cu<sup>0</sup> is the key oxidation state to promote the observed high C<sub>2+</sub> selectivity. As a control experiment, the harsh electrochemical method was used to reduce the oxide and hydroxide species in HQ-Cu and AN-Cu, respectively, prior to CO<sub>2</sub>RR (Fig. 1e). Interestingly, these fully reduced electrodes (only contains Cu<sup>0</sup>) provided even slightly higher FE(C<sub>2+</sub>) (Fig. 1b), further confirming the unique and critical role of Cu<sup>0</sup> for the enhanced C<sub>2+</sub> selectivity. These observations agree well with previous reports on *in-situ* characterizations by Cu K-edge X-ray absorption spectroscopy [7], grazing incidence XRD [3], or Raman spectroscopy [8] which support the argument that Cu oxides are reduced prior to CO<sub>2</sub> reduction. Moreover, the CO<sub>2</sub>RR performance of electropolished Cu with and without such electrochemical reduction procedure has been compared. They applied a highly negative potential for shortened time to obtain the pretreated electrodes, which were denoted as pretreated HQ-Cu (PHQ-Cu) and pretreated AN-Cu (PAN-Cu), respectively. No obvious difference in catalytic selectivity nor activity has been found, indicating a negligible influence induced by this pretreatment. These results support the argument that the Cu oxide or hydroxide species will all be reduced to metallic Cu under CO<sub>2</sub>RR conditions and therefore the initial oxidation states of the oxidized Cu precursors are less important to determine product selectivity.

With high-resolution transmission electron microscopy (HRTEM) imaging and selected area electron diffraction (SAED), the crystal evolution in HQ-Cu under CO<sub>2</sub>RR or pretreatment conditions was visualized. The initial oxide layers show clear single crystalline patterns of CuO or Cu<sub>2</sub>O (Fig. 1f), whereas the oxide-derived layer exhibits Cu polycrystalline pattern (Fig. 1g, i), indicating that the initial oxide crystals got reduced and fragmented

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**Fig. 1.** (Color online) (a) Indexed XRD patterns of electropolished Cu, HQ-Cu, and AN-Cu. (b) FE for C<sub>2</sub><sup>+</sup> of the electrodes involved in this study. (c) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding EELS mapping of the FIB-prepared cross-section of (c) HQ-Cu, (d) HQ-Cu after 1 h of CO<sub>2</sub>RR, and (e) pretreated HQ-Cu. TEM images of the FIB-prepared cross-section of (f) HQ-Cu, (g) HQ-Cu after 1 h of CO<sub>2</sub>RR, (h) Cu foil after 1 h of CO<sub>2</sub>RR, and (i) pretreated HQ-Cu. Inserted SAED patterns were extracted from the circled area (160 nm in diameter) and all scale bars represent 5 1/nm. In (i), the middle panel is the HRTEM image representing the oxide-derived layer in PHQ-Cu, and the right panel is the processed crystal isolation image based on the raw HRTEM image. Adapted from Lei et al. [6] with permission. Copyright 2020, American Chemical Society.

into smaller Cu grains under the negative potential of CO<sub>2</sub>RR or electroreduction pretreatment. Using a self-developed image processing technique, they even enabled the isolation of individual Cu grains from HRTEM raw images, where the results clearly show that the fragmented grains have a dimension range of 5 to 15 nm

with irregular shape and many high-index facets exposed (Fig. 1i, right). Given that the crystal fragmentation process only occurs in oxide-/hydroxide-derived Cu, which gives high C<sub>2</sub><sup>+</sup> selectivity, and not in electropolished Cu (Fig. 1h), which gives low C<sub>2</sub><sup>+</sup> selectivity, they have concluded that: (1) an oxidation-reduction cycle is

requisite for crystal fragmentation and (2) crystal fragmentation is responsible for the enhanced  $C_{2+}$  selectivity by generating numbers of grain boundaries and high-index facets which favor the C–C coupling during  $CO_2$ RR [9,10]. Their work demonstrates the utilization of advanced techniques for detailed characterization of chemical states and crystal evolution within bulk catalyst system, and should attract general attention from the chemistry (electrochemistry in particular) community.

### Declaration of competing Interest

The authors declare that they have no conflict of interest.

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