

# Dynamic structural changes of Cu electrode under CO<sub>2</sub> or CO reduction conditions from in-situ X-ray characterization

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## Abstract:

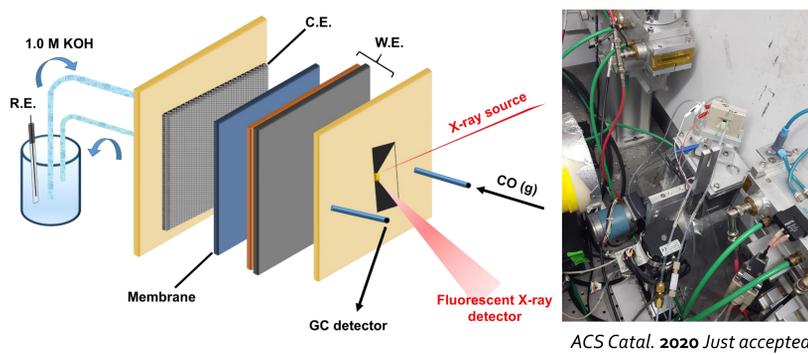
We conducted a time-resolved *operando* study on the effect of oxidation states on carbon monoxide reduction reaction (CORR) performance by X-ray absorption spectroscopy (XAS) and online gas chromatography (GC), which allows simultaneous monitoring of chemical valence state and ethylene (C<sub>2</sub>H<sub>4</sub>) selectivity. In addition, we studied the changes in the valence state and crystallographic structure in the near-surface region of polycrystalline Cu thin-films under realistic CO<sub>2</sub> reduction conditions by using an electrochemical flow cell that allows for in-situ grazing incidence XAS and XRD with improved CO<sub>2</sub> mass transfer.

## Introduction

- Investigating the direct relationship between oxidation states and CORR performance using an *operando* XAS cell is required to understand the exact roles of oxide phases.
- To more fully understand the structural dynamics of Cu surfaces, it is imperative to elucidate both the local atomic structure and long-range order under realistic CO<sub>2</sub>RR conditions.

## Results, Highlights, and Accomplishments

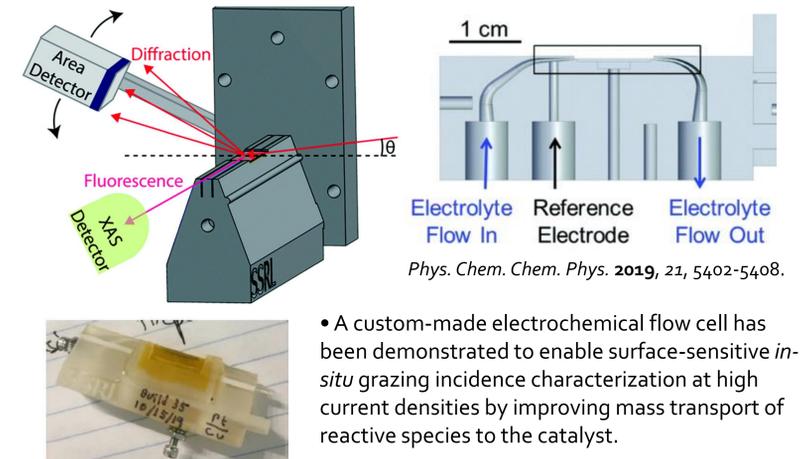
### Operando XAS Cell Design



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- Time-resolved XAS was coupled with simultaneous measurements of catalyst activity and selectivity by GC (6 min measurements for both XAS and GC).

### Electrochemical flow cell for GIXRD/GIXAS



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- A custom-made electrochemical flow cell has been demonstrated to enable surface-sensitive *in-situ* grazing incidence characterization at high current densities by improving mass transport of reactive species to the catalyst.

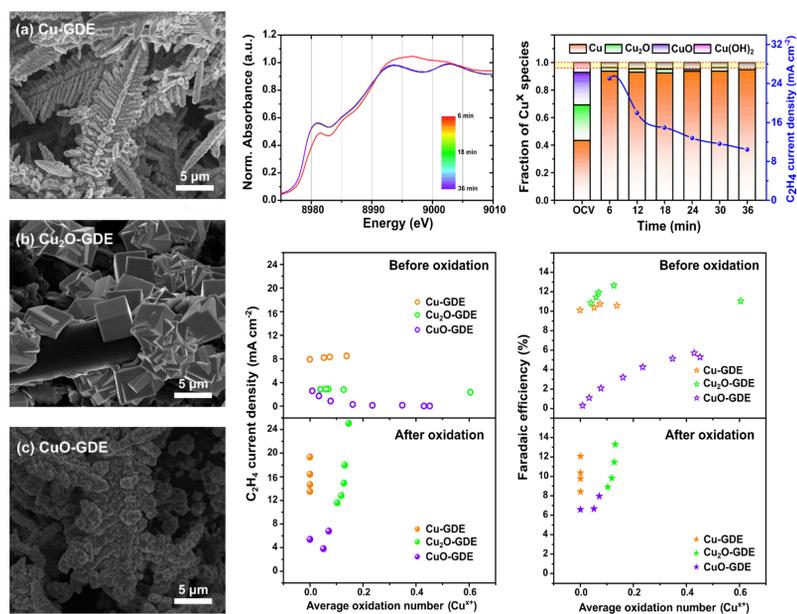
## Team



## Outlook

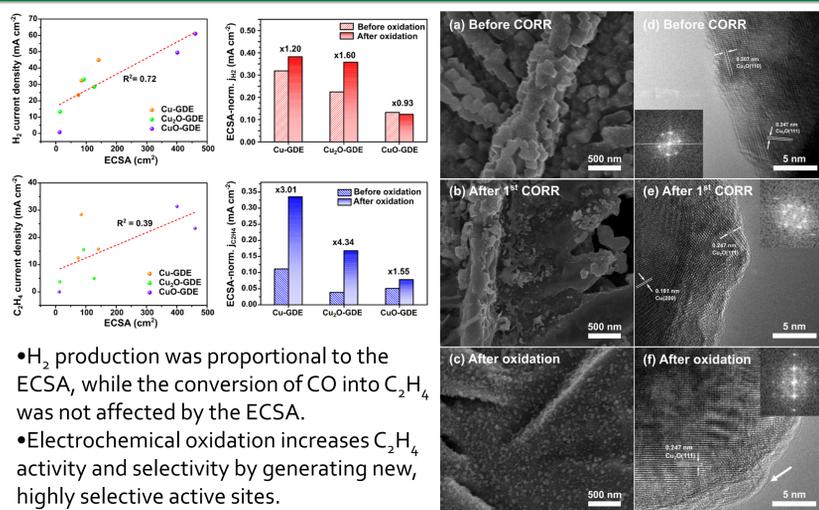
- Our study establishes a basis for the rational design of highly active electrocatalysts for broad-range reactions in a gas-fed device
- Our *in-situ* measurements of surface oxidation state and reconstruction behavior provides new insights for the atomic-scale understanding of Cu-based electrocatalysts.

## Relationship between oxidation and C<sub>2</sub>H<sub>4</sub>



- We synthesized three catalysts with three different oxidation states of Cu and deposited on the GDE.
- By using linear combination fitting, we correlated oxidation state and C<sub>2</sub>H<sub>4</sub> formation → No correlation between them

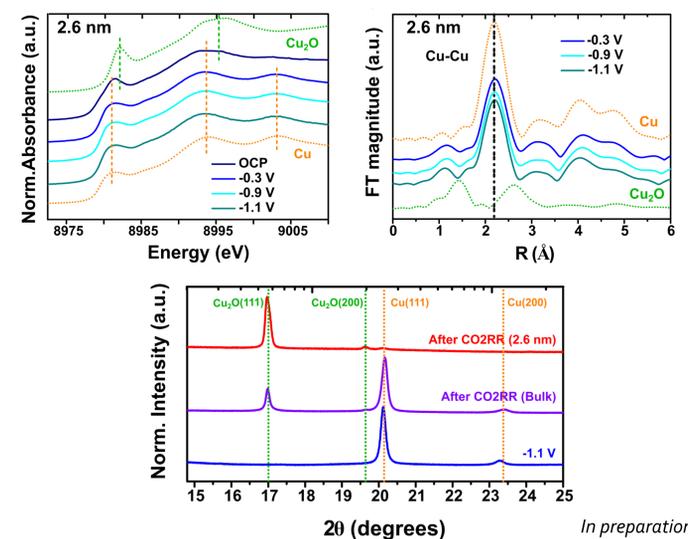
## ECSA and morphological changes



- H<sub>2</sub> production was proportional to the ECSA, while the conversion of CO into C<sub>2</sub>H<sub>4</sub> was not affected by the ECSA.
- Electrochemical oxidation increases C<sub>2</sub>H<sub>4</sub> activity and selectivity by generating new, highly selective active sites.

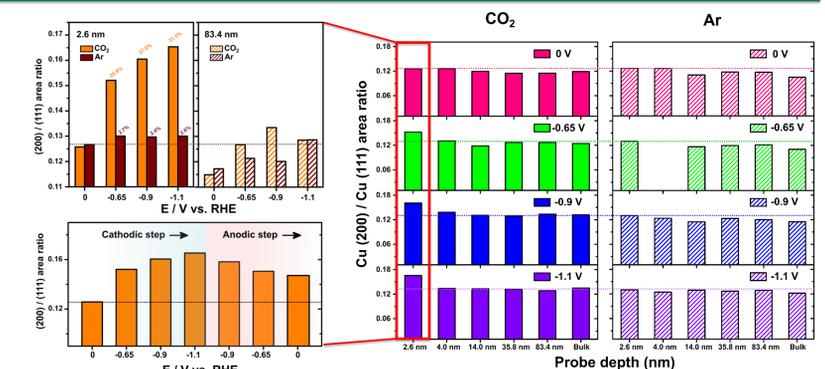
## In-situ XAS/XRD at Cu(pc) near-surface

Cu(pc) thin-film (50 nm) in a 0.1 M KHCO<sub>3</sub> electrolyte saturated with CO<sub>2</sub>/Ar



- Cu(I) features at OCV disappeared at -0.3 V, which is before the onset potential of CO<sub>2</sub>RR on the Cu(pc). And over the applied potential range relevant to the CO<sub>2</sub>RR, we observed only metallic Cu at the surface.
- The metallic Cu surface rapidly oxidized into Cu<sub>2</sub>O after releasing the applied potential and returned to OCV (~0.55 V vs. RHE)

## Surface reconstruction to Cu(100)



- The increase in Cu(200) / (111) area ratio was only observed at the probe depth of 2.6 nm, indicating the reconstruction is a surface phenomenon.
- The degree of reconstruction increases as the applied potential becomes more negative, and it persists when the applied potential returns to more positive.

## Acknowledgments

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