



# Controlling the Oxidation State of Cu Electrode and Reaction Intermediates for Electrochemical CO<sub>2</sub> Reduction to Ethylene

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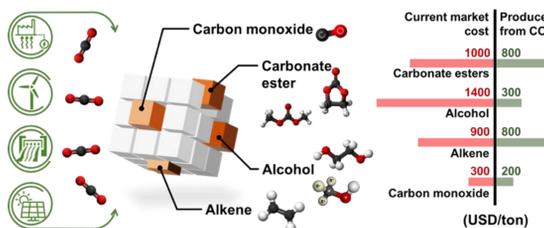


## ABSTRACT

Electrochemical CO<sub>2</sub> reduction has been considered as a potential route to convert harmful CO<sub>2</sub> to valuable hydrocarbons for sustainable carbon cycles. However, the poor selectivity obstructs the applications. According to DFT calculations, CO is the most common and important intermediate during CO<sub>2</sub> reduction reaction, but further reaction mechanisms are still unclear. In this work, we used *in situ* surface enhanced infrared absorption spectroscopy (SEIRAS), *in situ* X-ray absorption spectroscopy (XAS, Cu L-edge) and on-line gas chromatography to study the electrochemical CO<sub>2</sub> reduction mechanism occurred in different copper catalysts. We observed various CO intermediates such as CO<sub>atop</sub> and CO<sub>bridge</sub>, on copper surface during electrochemical CO<sub>2</sub> reduction and the formation of CO<sub>atop</sub>/CO<sub>bridge</sub> can be correlated to the existence of Cu(I) and Cu(0) oxidation state. The existence of CO<sub>atop</sub> results in the formation of methane during further reduction. In addition, ethylene can be produced in the presence of CO<sub>atop</sub> and CO<sub>bridge</sub>. Our results suggest the electrochemical CO<sub>2</sub> reduction mechanism by controlling the oxidation state of Cu electrode and reaction intermediates.

## Introduction

➤ Converting CO<sub>2</sub> to valuable products by renewable energy

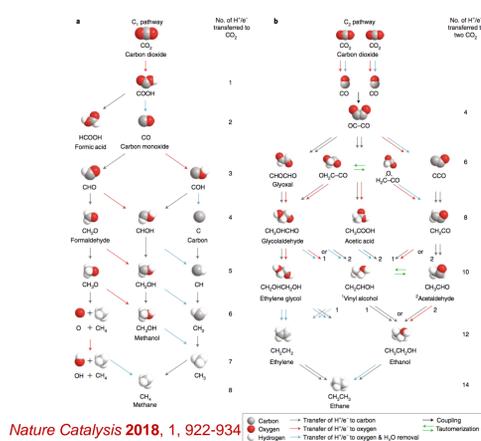


➤ Challenges

- Poor selectivity to desired products.
- Low productivity.
- Cu is still the best catalyst toward organic products.

**What is the key factor to result in different reaction pathway?**

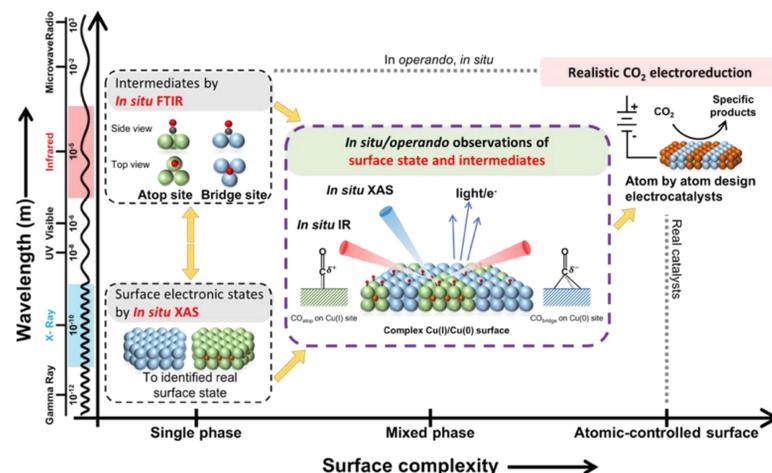
➤ Proposed CO<sub>2</sub> reduction pathway



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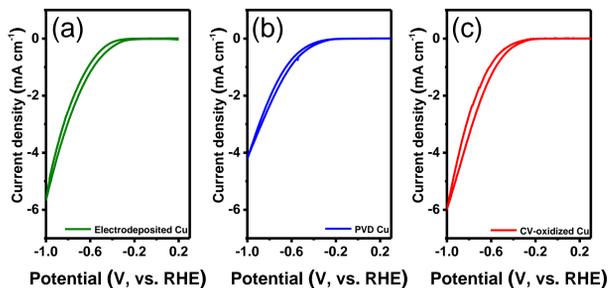
## Our strategies

➤ By using different *in situ* spectroscopy, we try to provide a catalyst design principle.



## Results and discussions

➤ Catalytic performance of copper-based catalysts

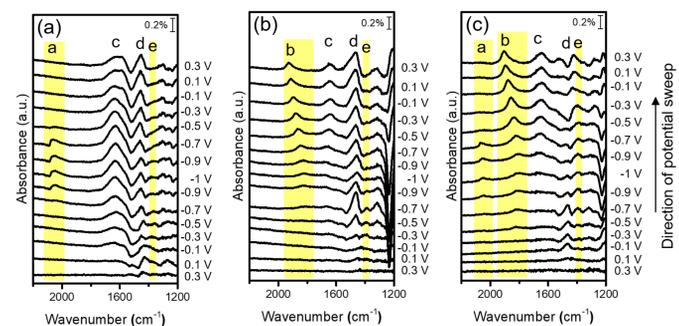


**Figure 1.** Cyclic voltammograms of (a) electrodeposited Cu, (b) as-prepared Cu and (c) CV-oxidized Cu in 0.1 M CO<sub>2</sub>-saturated KHCO<sub>3</sub> at a scan rate of 25 mV s<sup>-1</sup>.

### Experimental details

Electrolyte: 0.1 M CO<sub>2</sub>-saturated KHCO<sub>3</sub>  
Reference electrode: RHE  
Counter electrode: Pt mesh  
Scan rate: 25 mV s<sup>-1</sup>

➤ *In situ* SEIRAS to observe key intermediates during reaction



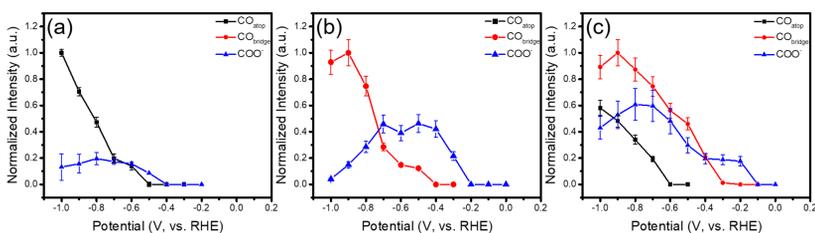
➤ Peaks assignment in left hand side figures.

Peak label	Peak position (cm <sup>-1</sup> )	Assignments	Literature reference
a	1951–2094	$\nu(\text{C-O})$ of atop adsorbed CO	1–6
b	1806–1907	$\nu(\text{C-O})$ of bridge adsorbed CO	4–6
c	1645	$\delta(\text{H-O-H})$ of H <sub>2</sub> O	2–3
d	1467	$\nu(\text{C-O})$ of HCO <sub>2</sub> <sup>-</sup>	7–9
e	1396	$\nu(\text{O-C-O})$ of COO <sup>-</sup>	10–12

### References

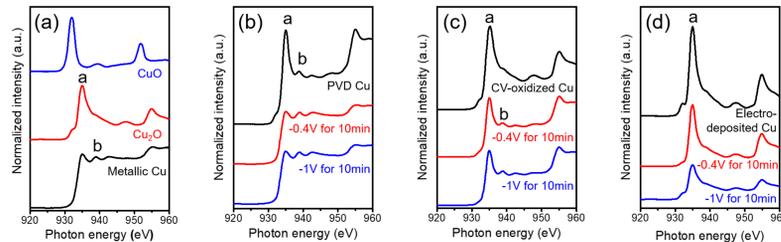
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**Figure 2.** *In situ* surface-enhanced infrared spectroscopy of (a) electrodeposited Cu, (b) as-prepared Cu and (c) CV-oxidized Cu during electrochemical CO<sub>2</sub> reduction in the potential range of 0.3–1 V (vs. RHE). The peak assignments were also listed.

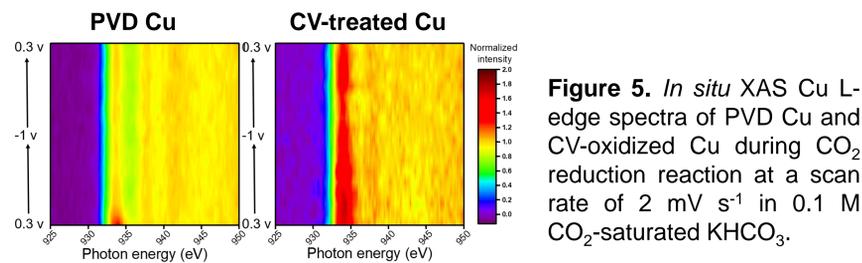


**Figure 3.** Potential-dependent intermediates intensities on electrodeposited Cu, as-prepared Cu and CV-oxidized Cu extracted from figure 2. The schematic illustrations of intermediates are also presented.

➤ X-ray absorption spectroscopy to monitor the surface electronic states during reaction

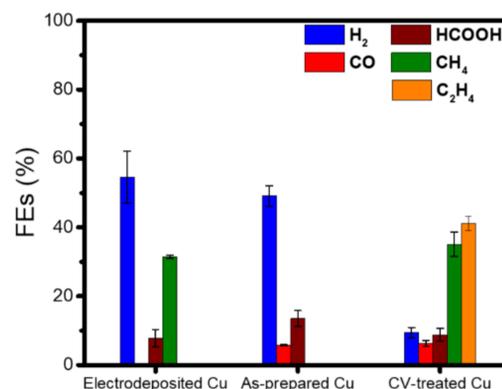


**Figure 4.** (a) Reference spectra of Cu L-edge. *Ex situ* XAS of (b) as-prepared Cu, (c) CV-oxidized Cu and (d) electrodeposited Cu before and after electrochemical CO<sub>2</sub> reduction reaction.



**Figure 5.** *In situ* XAS Cu L-edge spectra of PVD Cu and CV-oxidized Cu during CO<sub>2</sub> reduction reaction at a scan rate of 2 mV s<sup>-1</sup> in 0.1 M CO<sub>2</sub>-saturated KHCO<sub>3</sub>.

➤ Products analysis by on-line gas chromatography



**Figure 6.** Faradaic efficiencies (FEs) of major products catalyzed by electrodeposited Cu electrode, as-prepared Cu electrode and CV-treated Cu electrode (after 100 CV-treated cycles) at -1 V vs. RHE in CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> electrolyte.

## Conclusions

- The electrochemical CO<sub>2</sub> reduction mechanism was examined by *in situ* SEIRAS, *in situ* XAS and on-line gas chromatography.
- CO<sub>atop</sub> is observed on the electrodeposited Cu electrocatalyst which mainly has the Cu(I) oxidation state and CO<sub>bridge</sub> is observed on the as-prepared Cu electrocatalyst with oxidation state of Cu(0)
- The co-existence of CO<sub>atop</sub> and CO<sub>bridge</sub> is considered as the important intermediates to the formation of C<sub>2</sub> products.

➤ Schematic illustration of CO<sub>2</sub>RR mechanisms on Cu

The oxidation state of copper surface leads to the formation of different reduction intermediates, which result in different final products.

