Probing the *In Situ* Electrochemical Reduction of Hierarchical Oxide-Derived Inverse Opals during the Conversion of CO_2 into Fuels

Thuy-Duong Nguyen-Phan[1,2*], Yunyun Zhou[1], Congjun Wang[1,2], Christopher M. Marin[1,2], Eli Stavitski[3], Eric J. Popczun[1], Yang Yu[1], Wenqian Xu[4], Bret H. Howard[1], Mengling Y. Stuckman[1,2], Iradwikanari Waluyo[3], Paul R. Ohodnicki Jr.[1], and Douglas R. Kauffman[1*]

[1] National Energy Technology Laboratory, Pittsburgh, PA 15236
[2] Leidos Research Support Team, Pittsburgh, PA 15236
[3] Photon Sciences Division, National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973
[4] X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

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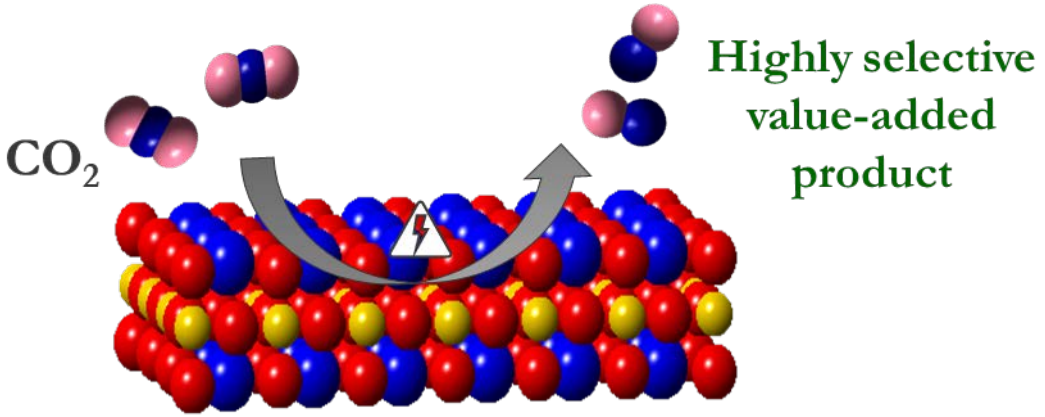
Outline of Talk

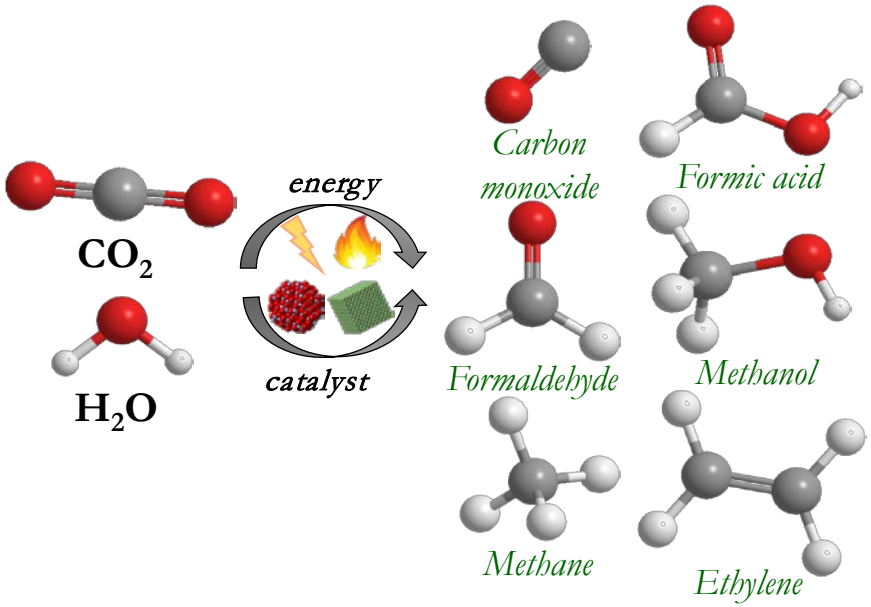
1. **Research motivation**
2. **Materials properties and activity**
   - How to fabricate and test hierarchical CuO-IO?
   - Structural and electronic properties
   - Electrochemical CO_2 reduction performance
3. **Understand structure-property relations**
4. **Conclusions**



1. Introduction

CO_2 Utilization Technologies program

: key contributions to the U.S. Department of Energy's carbon management portfolio



Industrially-relevant chemicals and fuels

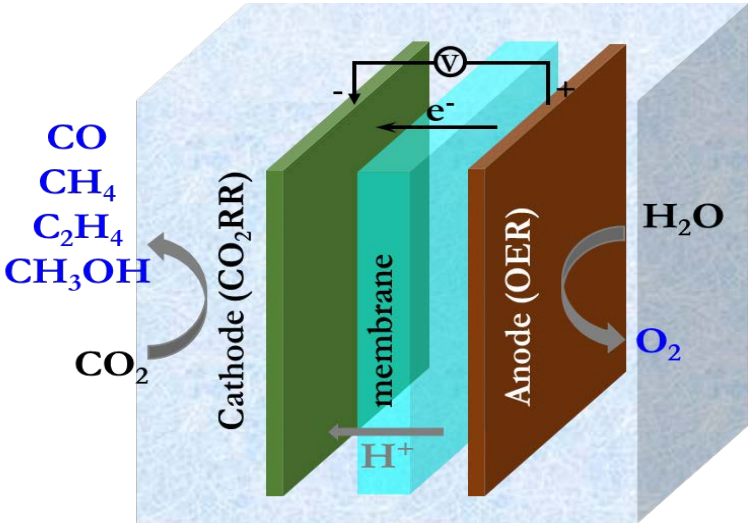
- Lower overall costs of CO_2 capture, transport, and sequestration
- Reduce carbon footprint of traditionally fossil fuel-powered processes

- Increase energy security + domestic employment
- New and expanded markets for domestic products
- Broader acceptance of fossil resource utilization

Develop technologies to utilize CO_2 for beneficial uses that store and/or offset CO_2 emissions

1. Solution – Energy & fuel production

Electrochemically converting CO_2 into value-added chemicals and fuels

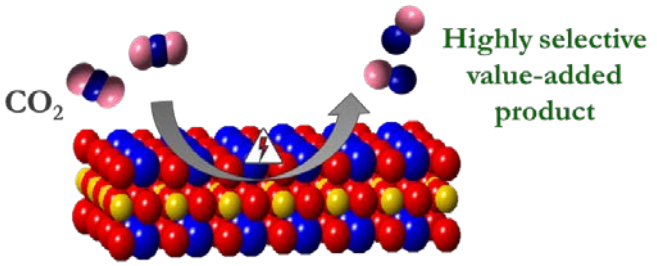


Cathode reaction	*E_0 (V vs. RHE)*
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.106
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.250
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.070
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+0.016
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	+0.080
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.169
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	+0.064
$2H^+ + 2e^- \rightarrow H_2$	0

- Competitive hydrogen evolution reaction
- Multi-electron transfer pathway
- Low selectivity & Faradaic efficiency
- Large overpotential
- Poor electrochemical stability
- Abundance + cost + scalability

EC-CO_2RR - Key challenges

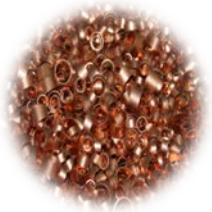
1. Materials challenge: What is important?



- **Active** - increase total amount of CO_2 converted
- **Selective** - decrease downstream processing
- **Robust and less expensive** - increase economic viability

Metal	H_2	CO	CH_4	C_{2-3}+	CH_3OH	HCOOH
Cu	+	+	+	+	*	+
Zn	+	+	*	-	*	+
Ni	+	-	*	+	*	+
Fe	+	-	+	-	-	-
Sn	+	*	-	-	-	+

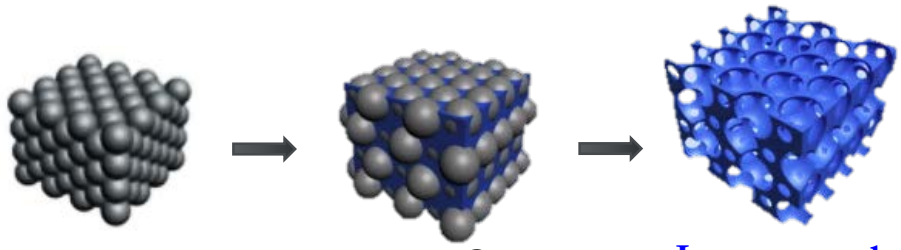
+ Major product + Minor product * Novel product - No product



- Earth-abundant element
- Broad product distribution!

Develop a new copper oxide catalyst that is more active, selective, and stable than traditional and state-of-the-art catalysts

1. Why inverse opal?

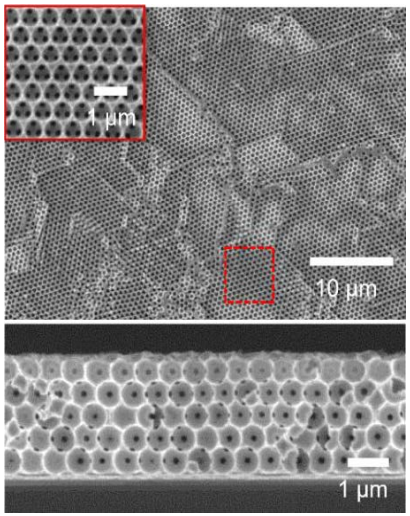


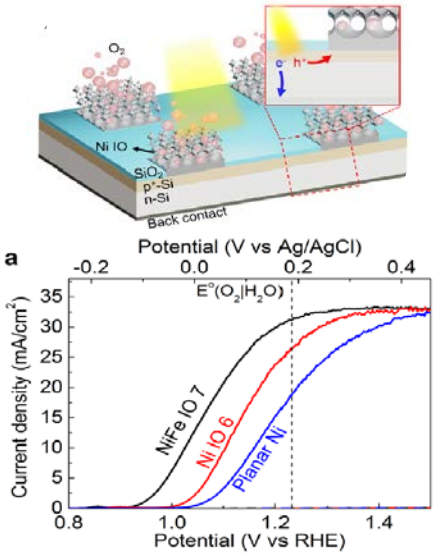
3D opal template (PMMA, PS, SiO_2)

Precursor@opal heterostructure

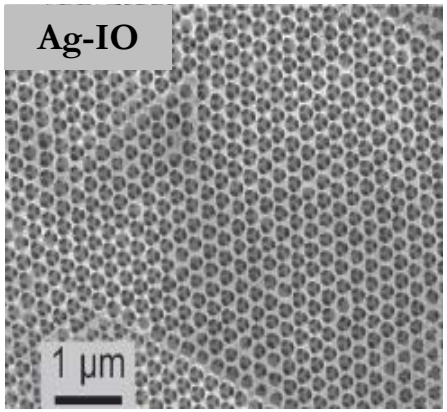
Inverse opal (3DOM)

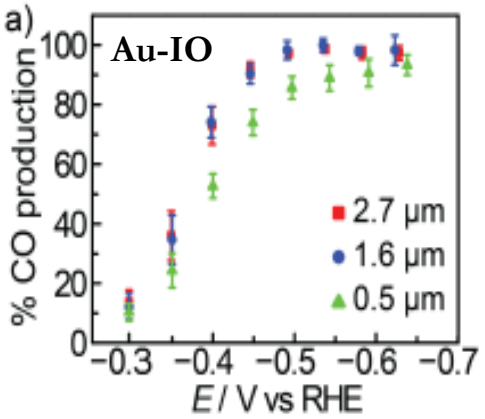
Hexagonal close packed arrangement stemming from *fcc* lattice of host template





Enhances OER performance by increasing light absorption and by providing more electrochemically active sites





Interconnected porous network - dynamic diffusion and adsorption of reactants + increased local pH gradient

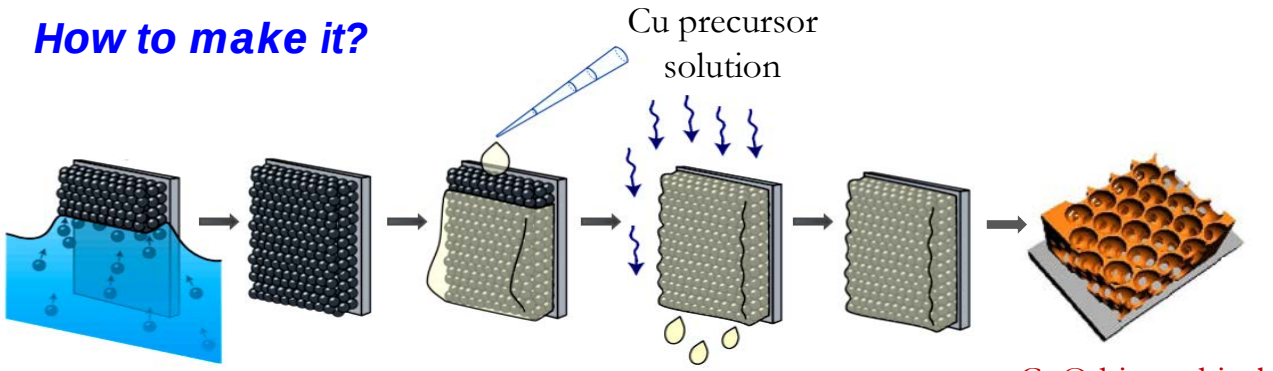
→ local proton depletion: strong H_2 suppression

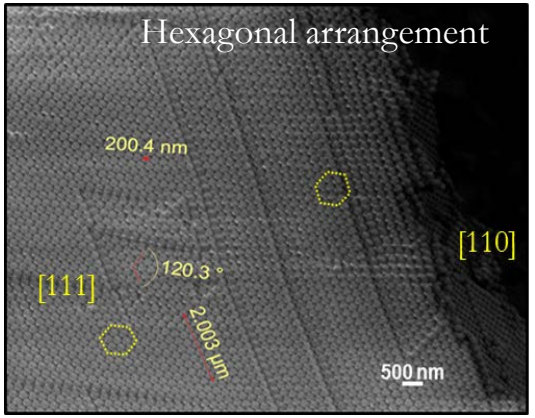
Oh et al., Nano Lett. 2017, 17, 5416

Hall et al., JACS 2015, 137, 14834
Yoon et al., Angew. Chem. Int. Ed. 2016, 55, 1

2. Synthesis & EC-CO_2RR test

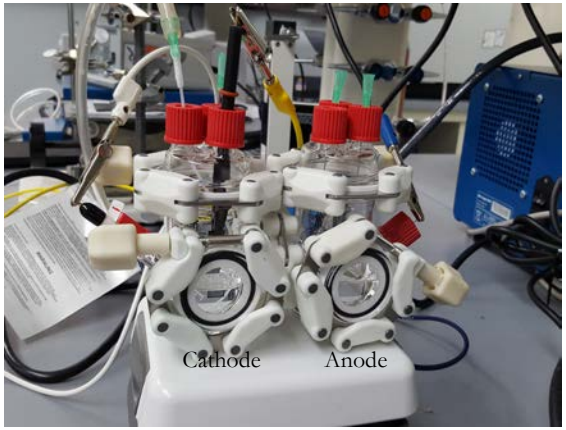
How to make it?





Close-packed (111) face-centered cubic dry opal

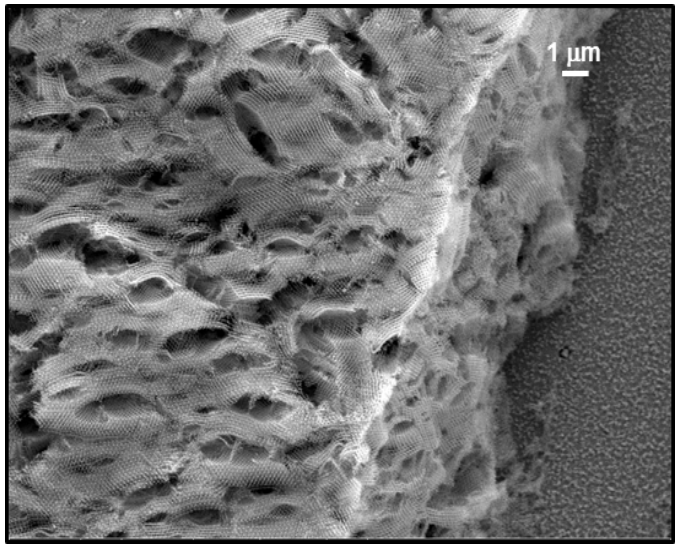
How to test it?

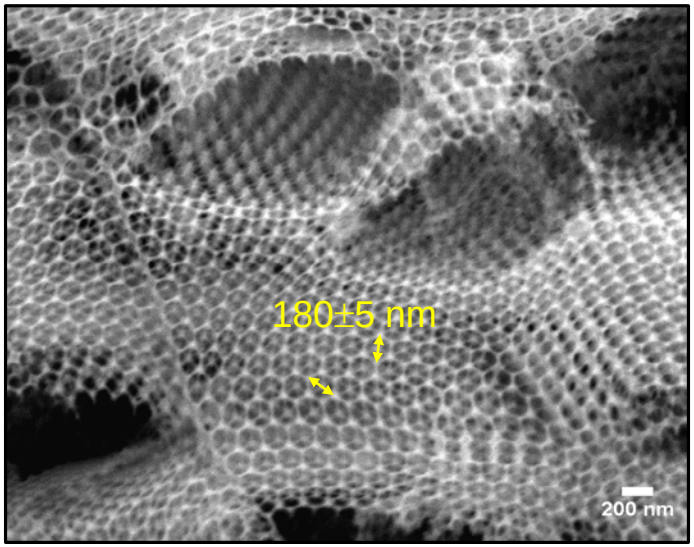


- 50 mL/50 mL $KHCO_3$ (0.1 M) catholyte and anolyte, 100 mL headspace/each compartment
- CO_2 flow rate = 20 mL min^{-1}
- Pt wire (CE), Ag/AgCl (RE), WE: CuO-HIO + Nafion (5%)/carbon paper
- 85% *i*R-compensation

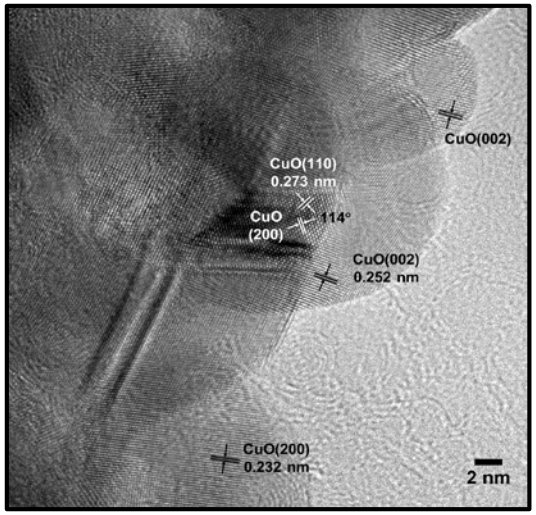
Cheng et al., Nat. Mater. 2006, 5, 830

2. Structural and electronic properties



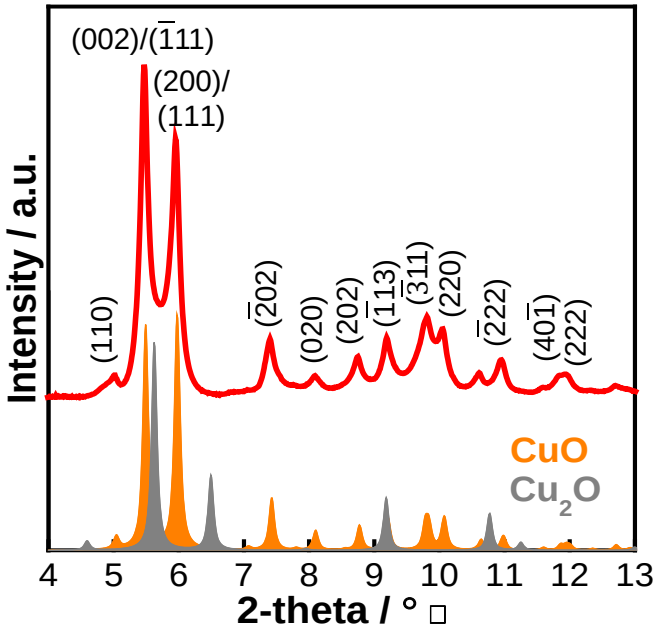


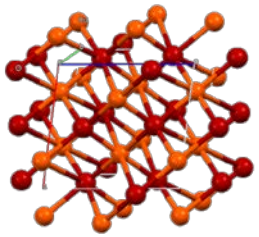
3D interconnected CuO backbone in a *fcc* lattice



Hierarhical CuO inverse opal composed of 15~20 nm nanoparticles

2. Structural and electronic properties

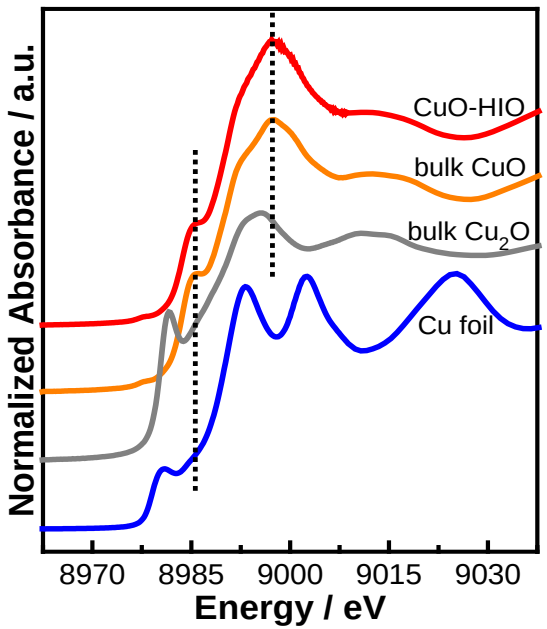


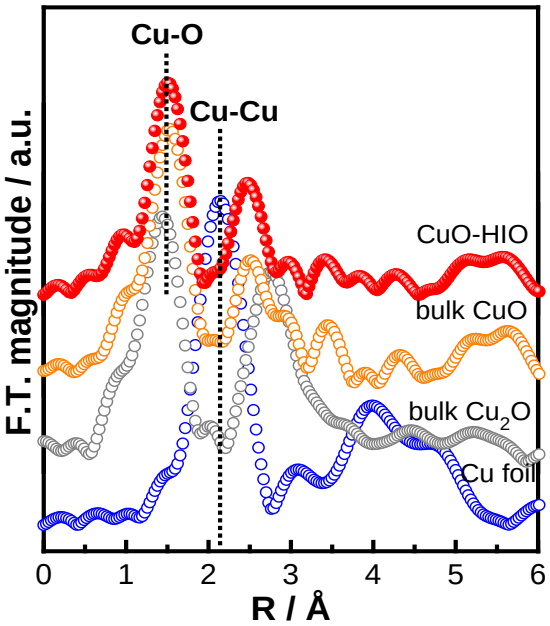


- Monoclinic symmetry unit cell
- Space group C2/c
- a = 4.71187 Å, b = 3.43496 Å, c = 5.11641 Å
- α = γ = 90, β = 98

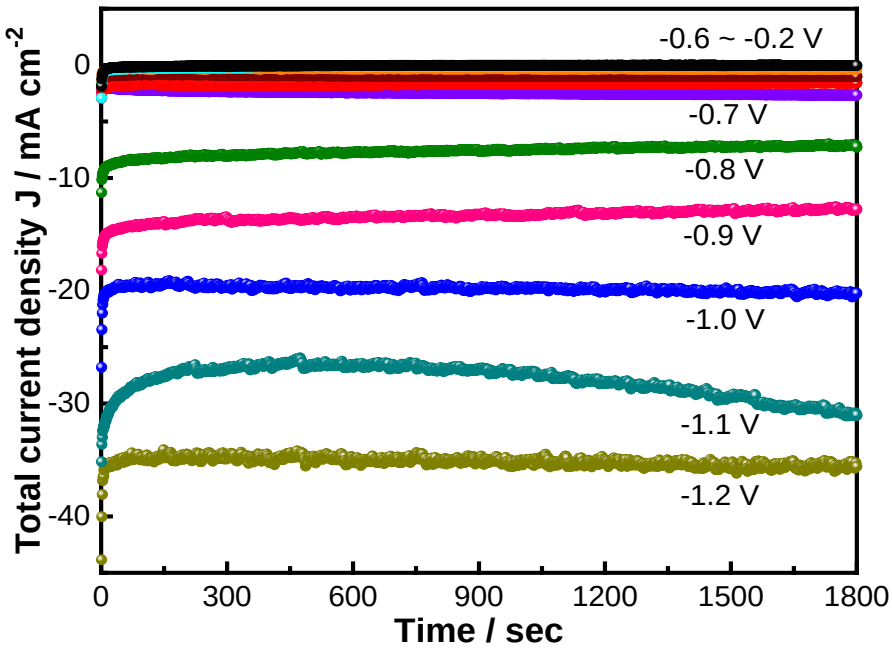
Mean crystallite size ~ 15 nm

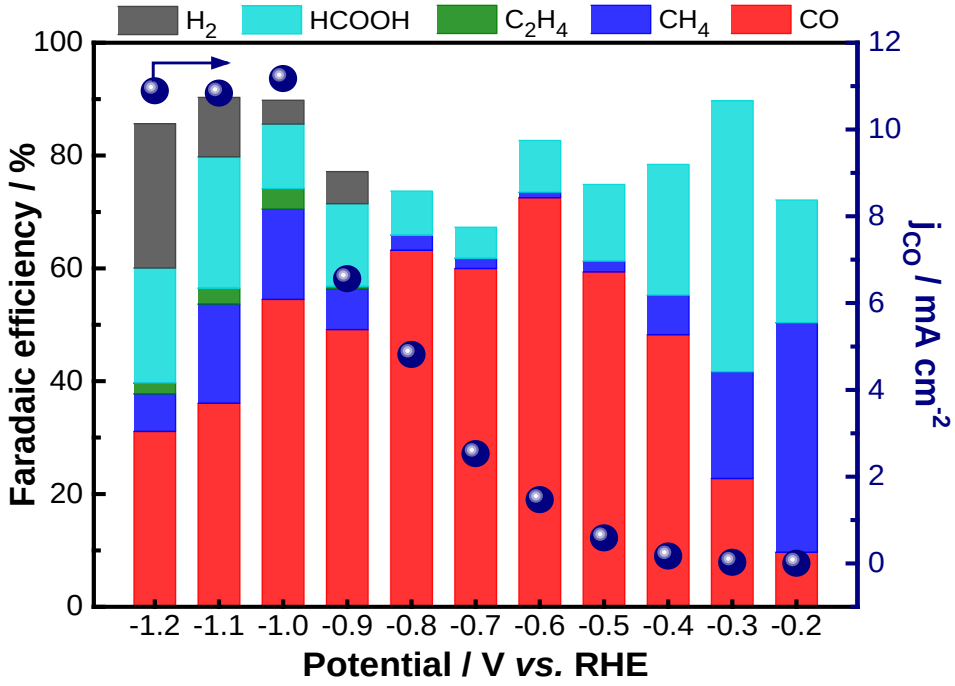
Confirmed Cu(II) oxidation state





2. How does it perform?





Chronoamperometry between -0.2 and -1.2 V *vs.* RHE

- Impressive C_1 selectivity
- Peak FE_{CO} of >70% at -0.6 V
- Significant HER suppression

2. How does it perform?

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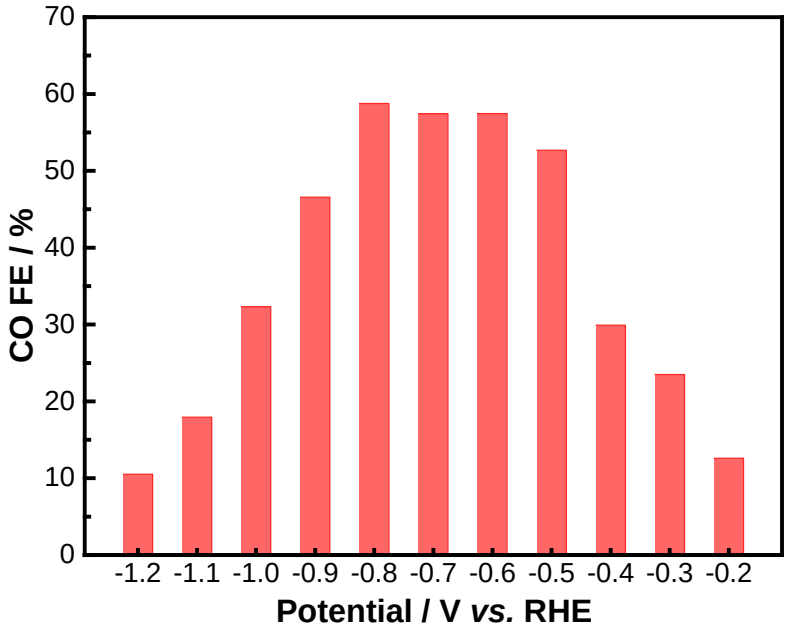
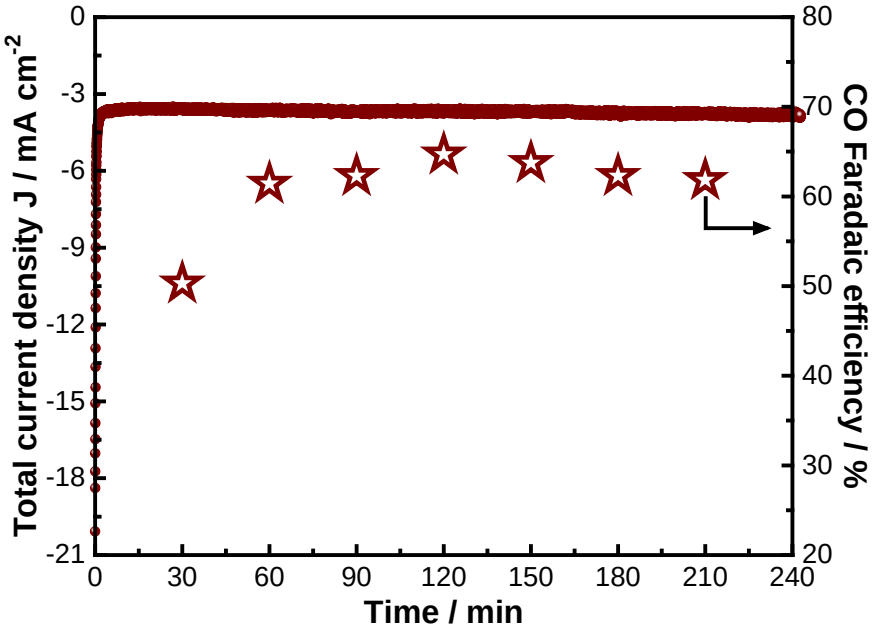
Control experiments



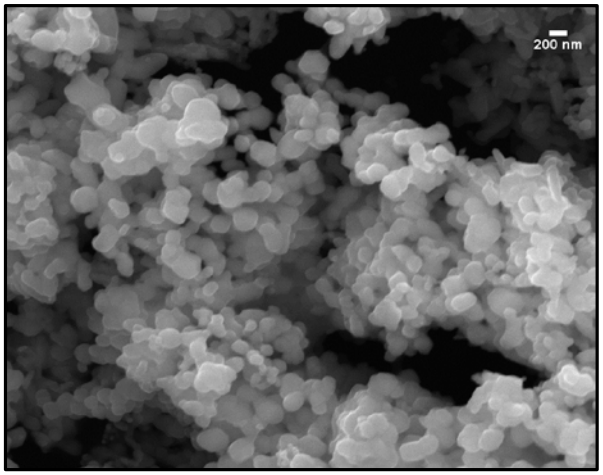
High CO yield at moderate potentials with higher catalyst loading



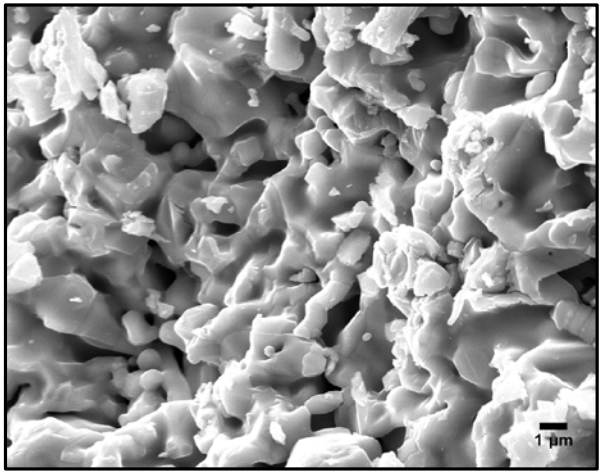
Use of graphite counter electrode: No Pt crossover artificially increases CO selectivity

2. How does it perform?

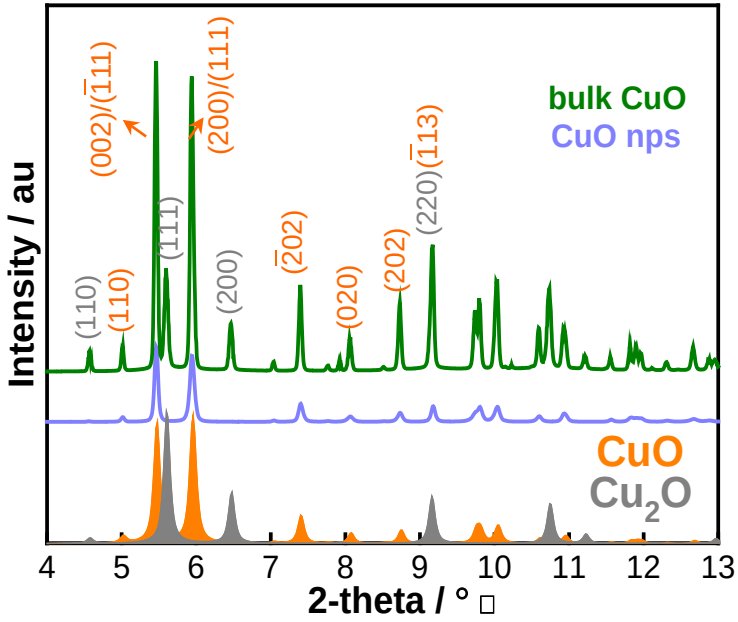
CuO-HIO vs. CuO standards



CuO nanoparticles (~50 nm)



Bulk CuO (1 ~ 5 µm)



Higher crystallinity and larger particle size

2. How does it perform?

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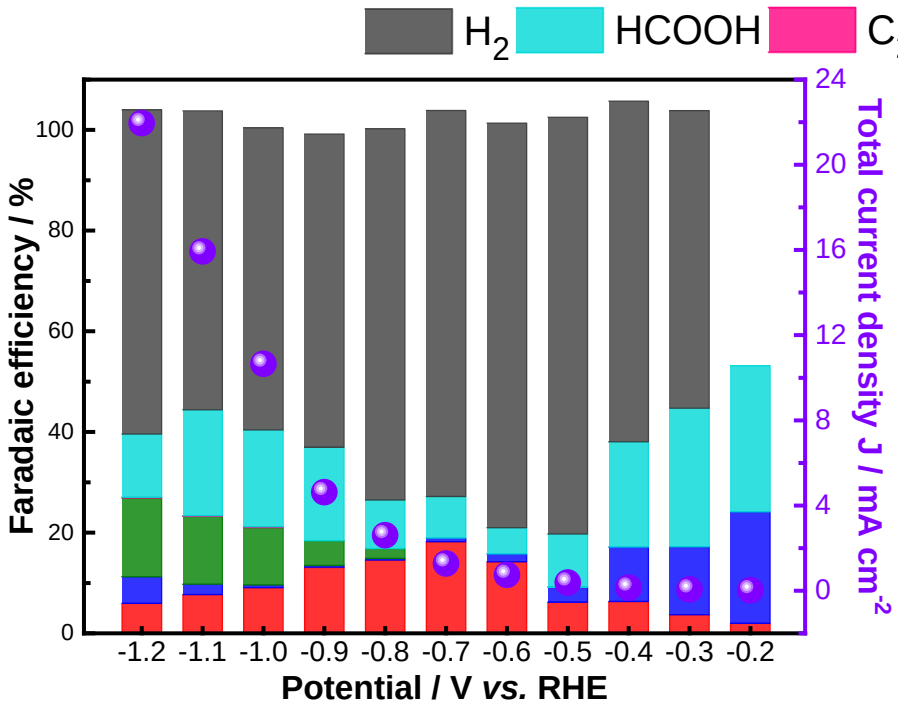
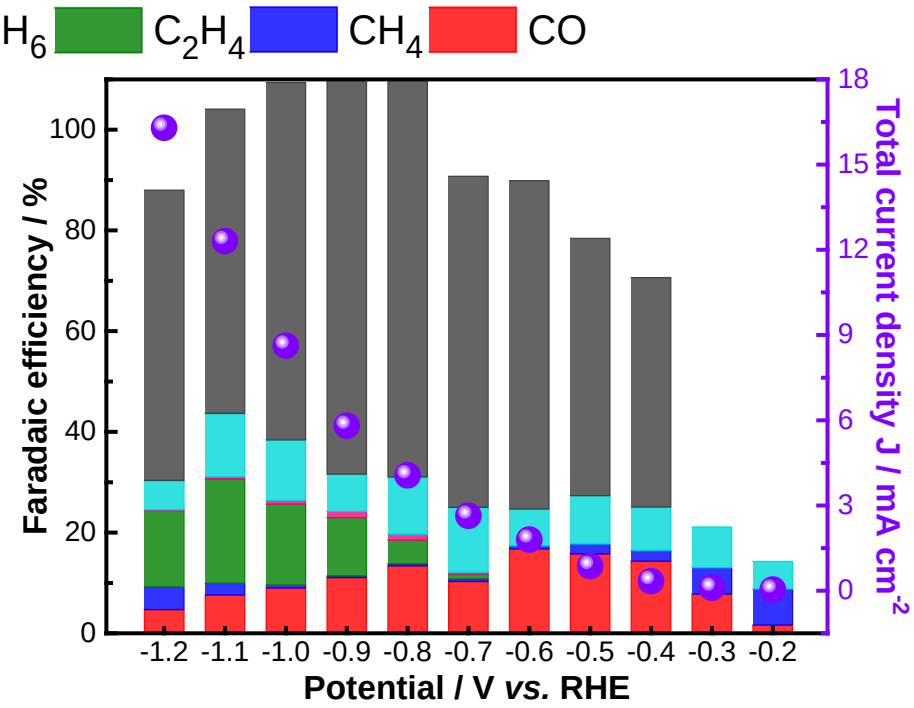
CuO-HIO vs. CuO standards



CuO nanoparticles



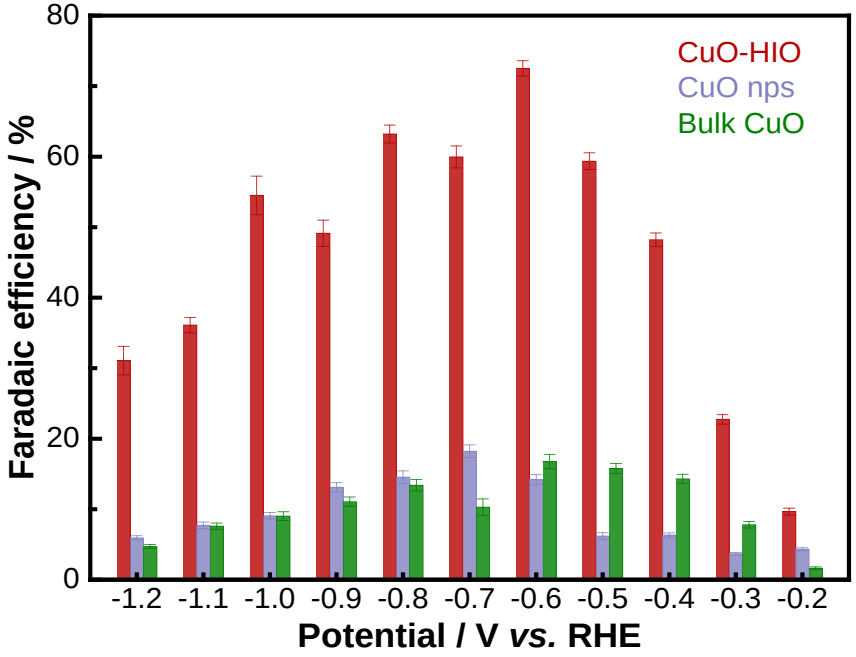
Bulk CuO

Favors H_2 and C_2 production

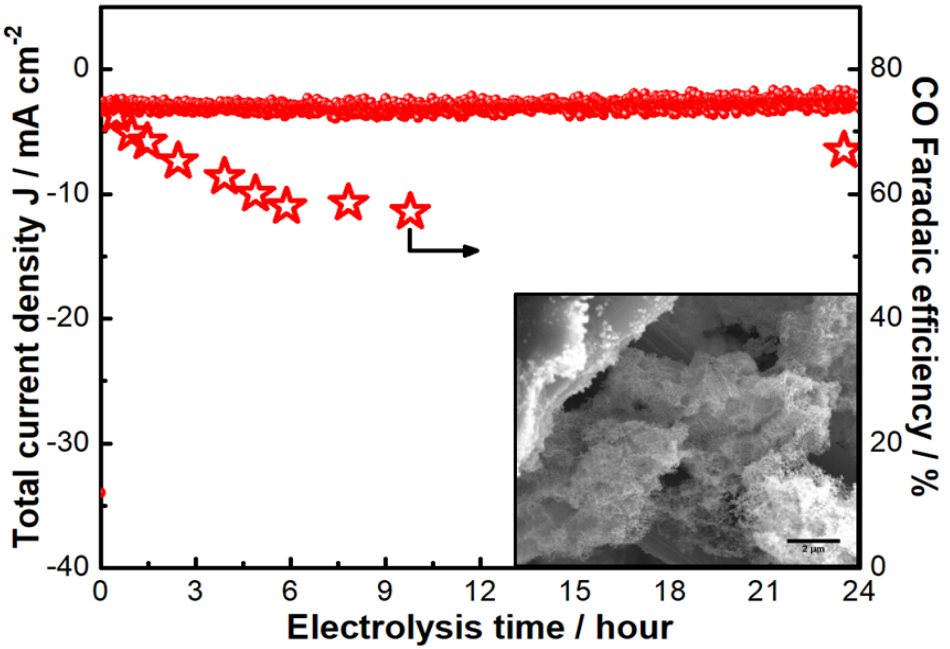
Broad product distribution

2. How does it perform?

CuO-HIO *vs.* CuO standards



Stability test @-0.6 V *vs.* RHE



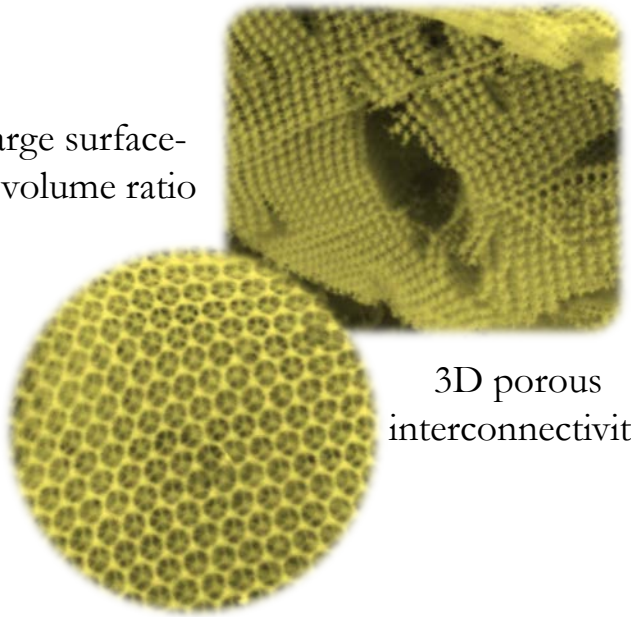
80 ~ 90% CO selectivity over CuO-HIO

Highly robust and active CO_2-to-CO catalyst

2. How does it perform?

Sample	Major product	CO FE / %	Potential / V vs. RHE	References
Cu_2O-derived Cu	CO HCOOH	45 38	-0.35 -0.55	Li et al., J. Am. Chem. Soc. 2012, 134, 7231-7234
CuO-derived Cu nanowire	CO HCOOH	50 40	-0.6 -0.7	Ma et al., Phys. Chem. Chem. Phys. 2015, 17, 20861-20867
Cu_2O-derived Cu inverse opal	CO HCOOH	45.3 34.5	-0.6 -0.8	Zheng et al., Nano Energy 2018, 48, 93-100
Electrochemically reduced CuO-derived Cu nanowire	CO HCOOH	62 25	-0.4 -0.5	Cao et al., ACS Catal. 2017, 7, 8578-8587
Electrochemically reduced CuO-derived Cu nanowire	CO HCOOH	61.8 30.7	-0.4 -0.6	Raciti et al., Nano Lett. 2015, 15, 6829-6835
3D CuO-derived Cu hierarchical nanostructures	CO HCOOH	60 30 ~ 40	-0.55 -0.55 ~ -0.7	Raciti et al., ACS Appl. Energy Mater. 2018, 1, 2392-2398
CuO-derived Cu inverse opal	CO HCOOH CH_4	72.5 48.0 40.7	-0.6 -0.3 -0.2	This work

3. Structure-property relations



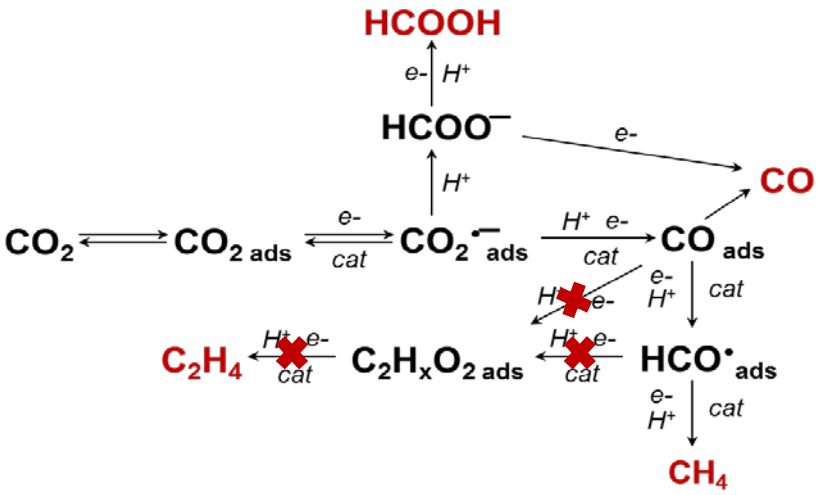
Large surface-to-volume ratio

3D porous interconnectivity

Sample	ECSA / cm^2	RF
CuO-HIO	2.962	30.79
Bulk CuO	0.372	5.27
CuO nps	0.548	7.76

High surface roughness allowed rapid consumption of both CO_2 and H^+ at the catalyst surface

- Reduction of available protons increased local pH and prevented further *CO protonation and HER
- CO_2 consumption may limit number of bound *CO intermediates close enough to undergo C-C coupling path



3. Structure-property relations

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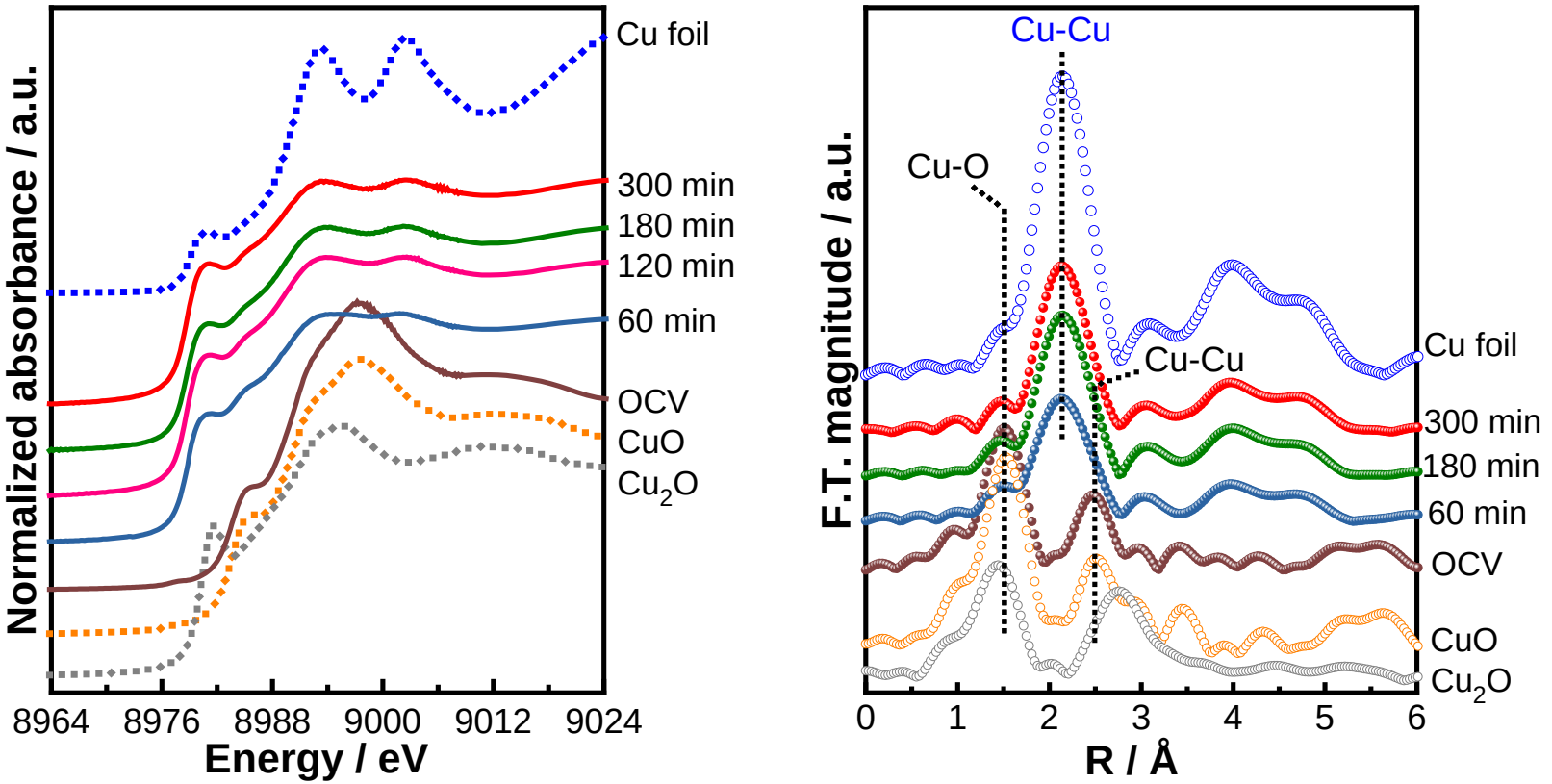
In situ XAFS at -0.6 V *vs.* RHE



XANES line shape and Cu-Cu first-nearest-neighbor distance in EXAFS

: confirmed Cu^0 oxidation state

3. Structure-property relations

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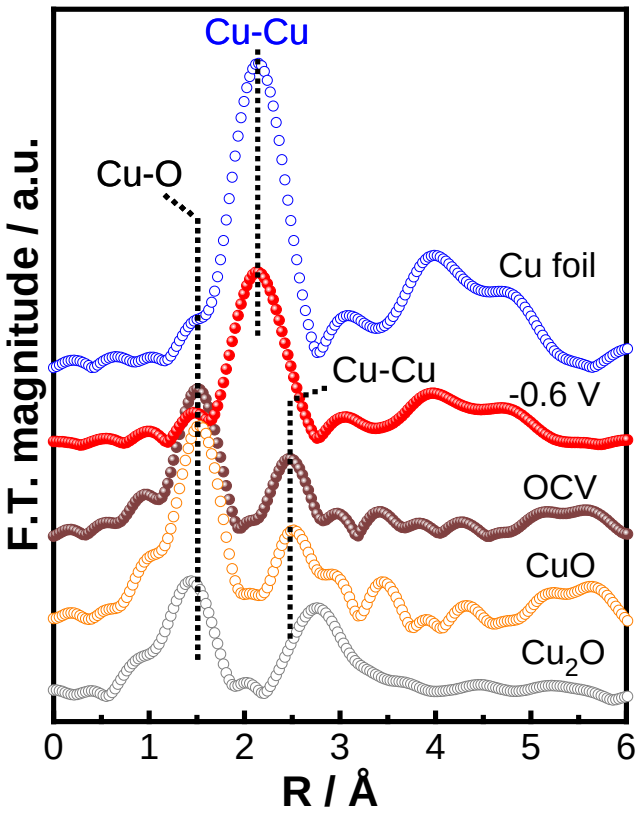
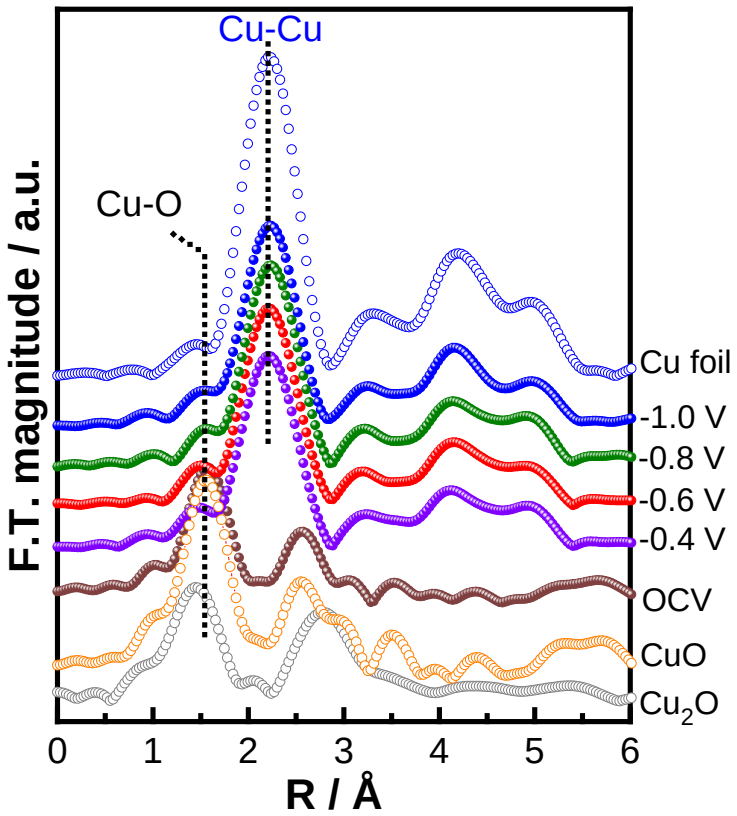
At -0.6 V *vs.* RHE



At various potentials



Metallic copper is likely to be electrochemically active sites

3. Structure-property relations

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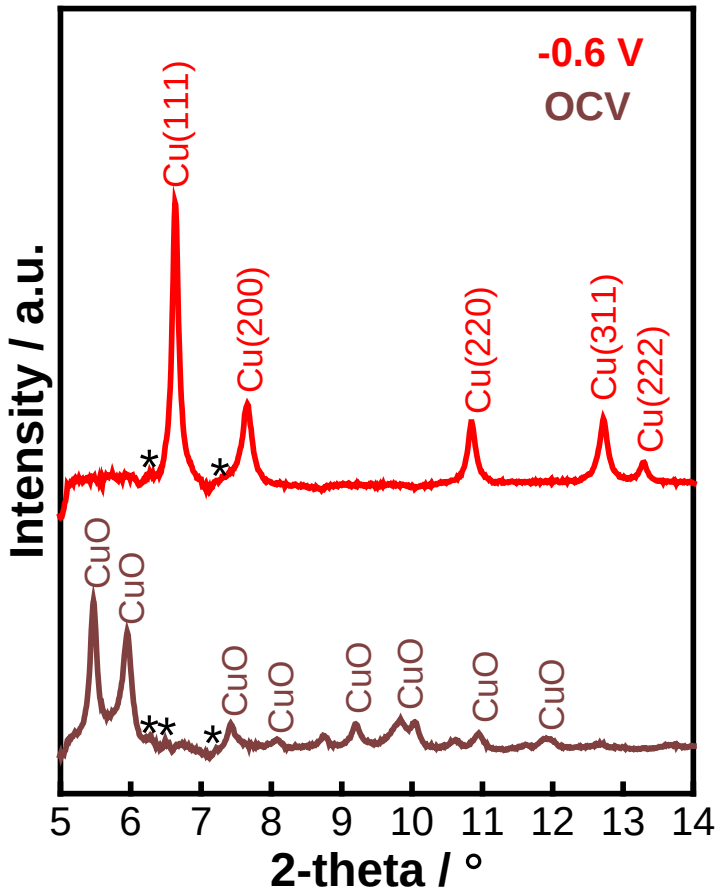
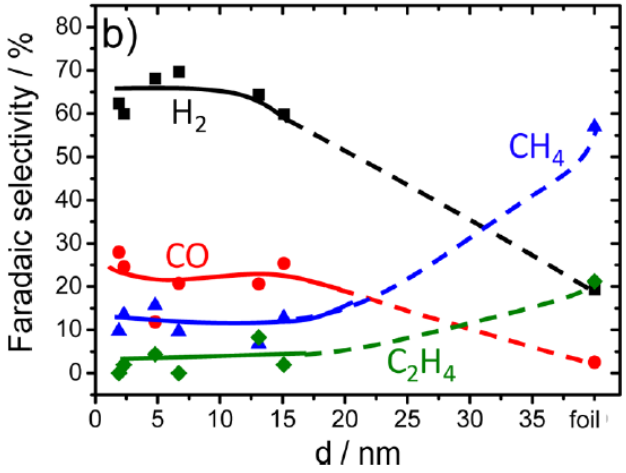
***In situ* SXRD at -0.6 V *vs.* RHE**



- Steady state: cubic Cu (*Fm-3m*, *a* = 3.6102 Å)
- Dominance of Cu (111) (I_{111}/I_{200} = 3.58)
- Mean crystallite size of 10-11 nm

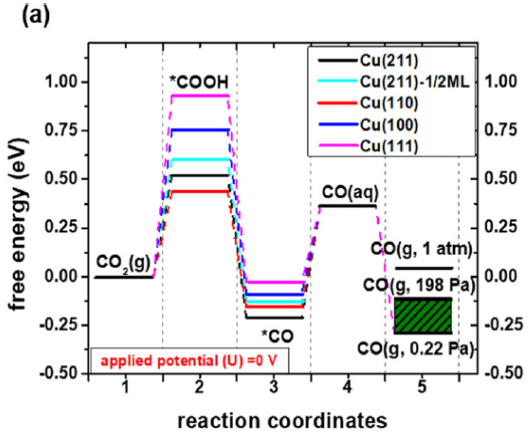
***In situ* works demonstrate metallic copper is electrochemically active site for selective CO formation over CuO-HIO**

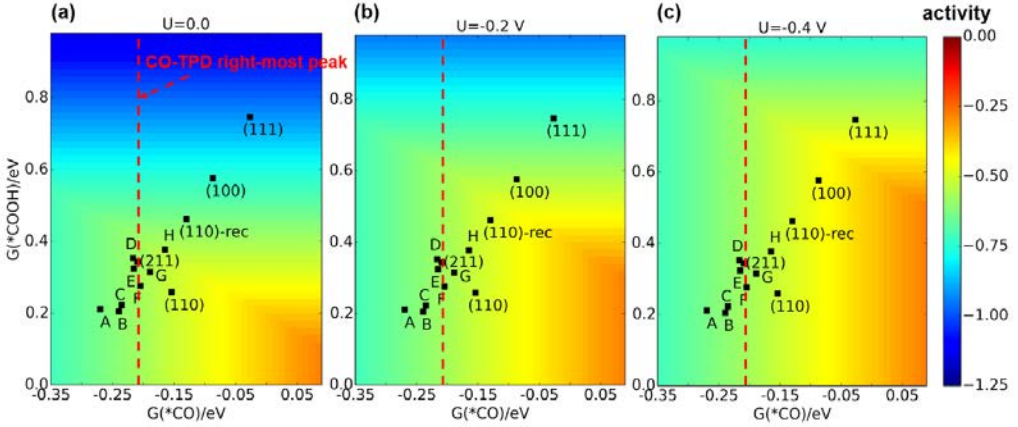


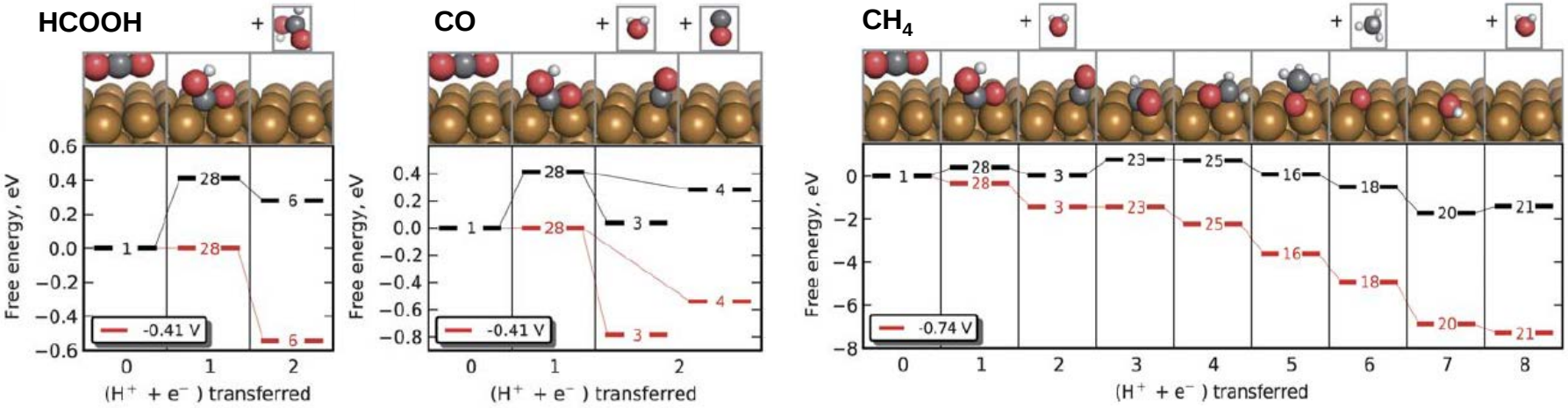
2-15 nm Cu nps could reduce intermediate mobility and facilitated CO and H_2 desorption

Reske et al., JACS 2014, 136, 6978

3. Structure-property relations



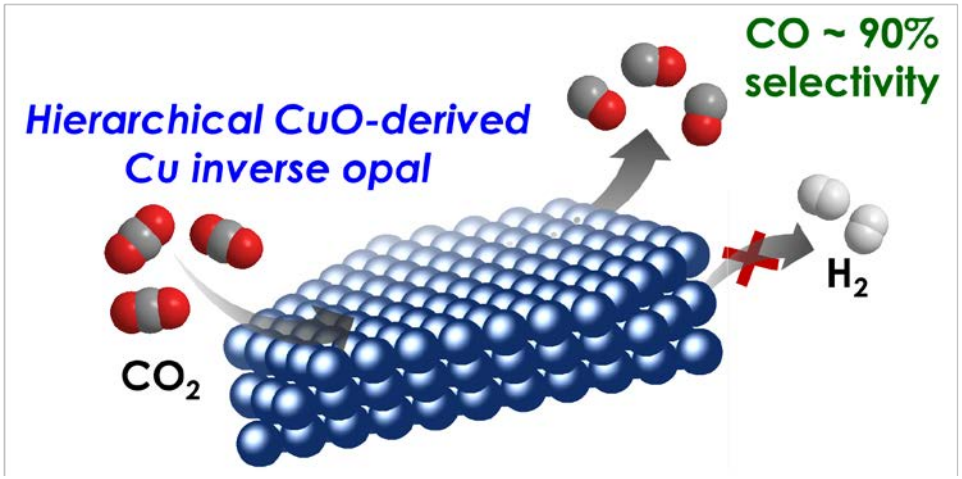




- Cu (111) - lowest binding energy for both *CO and *COOH intermediates
- Cu (100) facet - most active in C_2 production due to lower energetic barrier for hydrogenation step

Hori et al., J. Mol. Catal. A: Chem. 2003, 199, 39
Peterson et al., Energy Environ. Sci. 2010, 3, 1311
Reske et al., JACS 2014, 136, 6978
Dutta et al., ACS Catal. 2016, 6, 3804
Cao et al., ACS Catal. 2017, 7, 8578
Raciti et al., ACS Energy Lett. 2018, 3, 1545-1556

4. Conclusions



- Highly active, selective, robust oxide-derived Cu inverse opal catalyst outperforms CO_2-to-CO over commercially-available Cu catalysts
- Production of CO with 80~90% selectivity and >70% Faradaic efficiency at moderate potentials

- 3D interconnected porous structure - decrease in the local concentration of CO_2 and proton donors and local pH increment
- Small metallic Cu sites - electrochemically active sites promoting CO_2RR
- Highly roughened surface and dominance of Cu (111) surface site - weakly bind the intermediate species, lower adsorbate mobility and reduce reactant availability per active site

Acknowledgment

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Disclaimer

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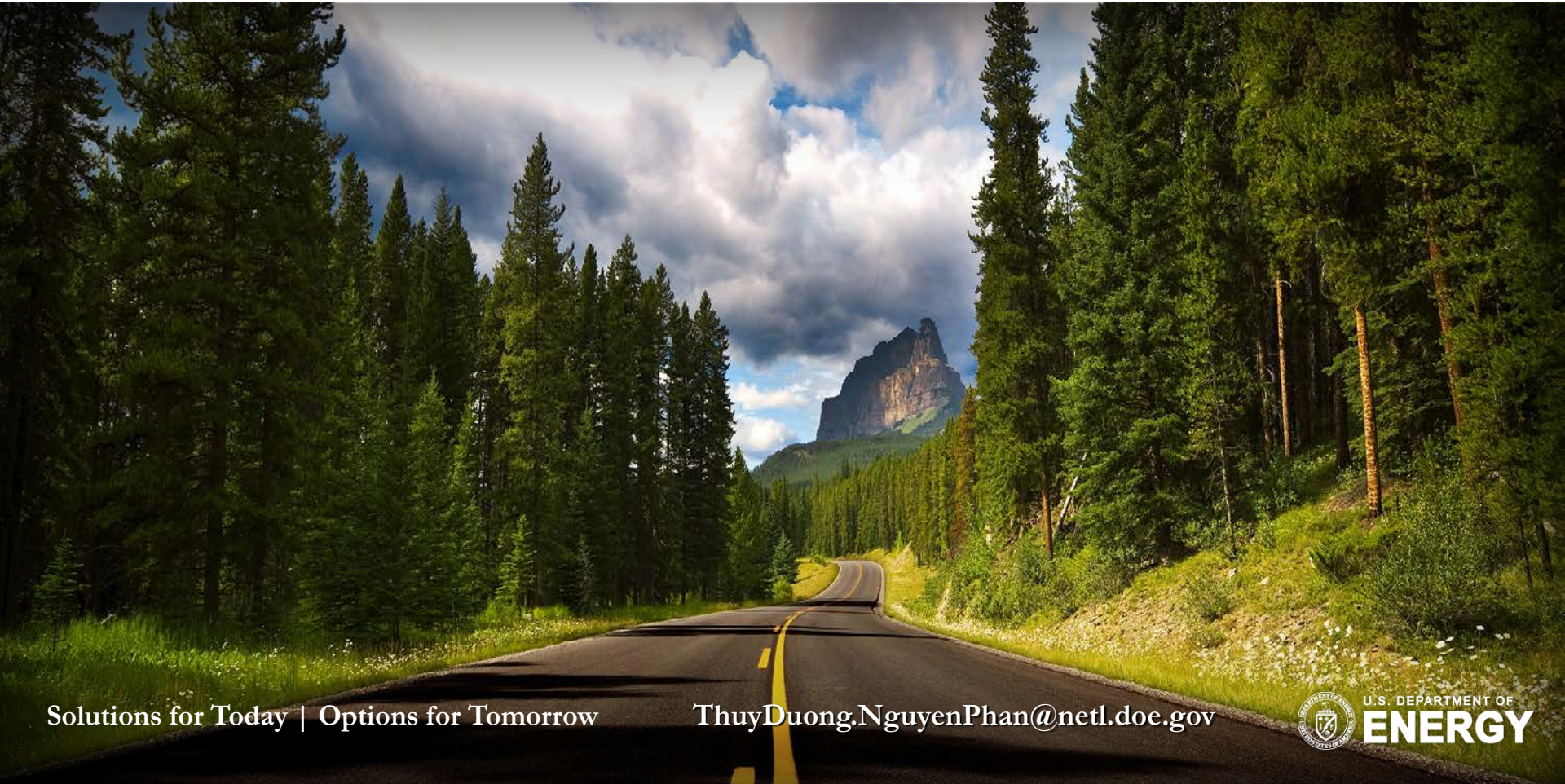
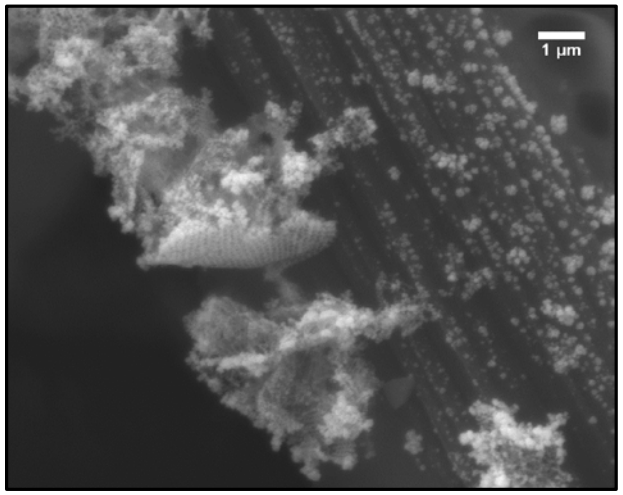
Thank you for your listening
Questions & Answers?

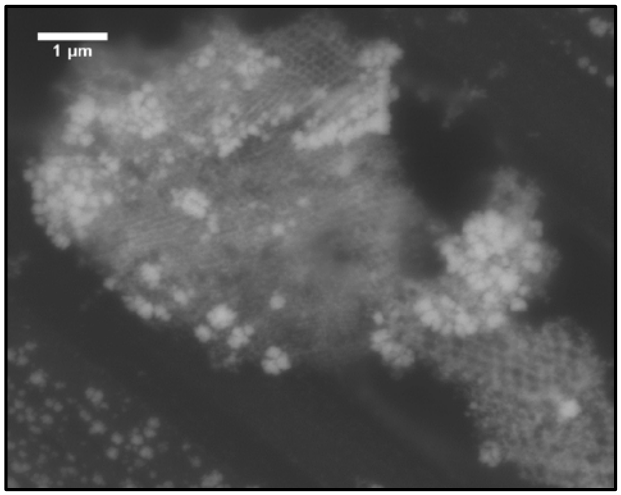


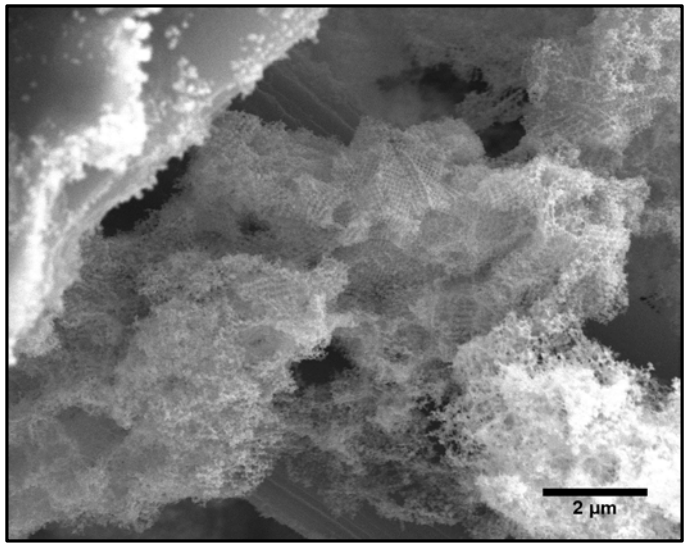
ThuyDuong.NguyenPhan@netl.doe.gov

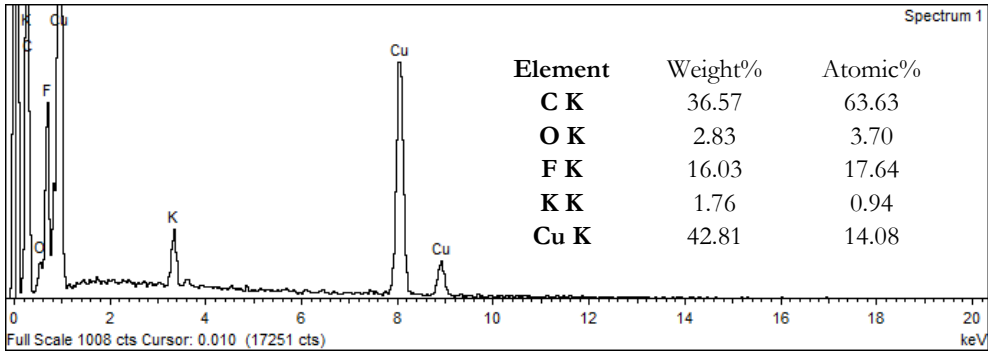
U.S. DEPARTMENT OF ENERGY

2. How does it perform?





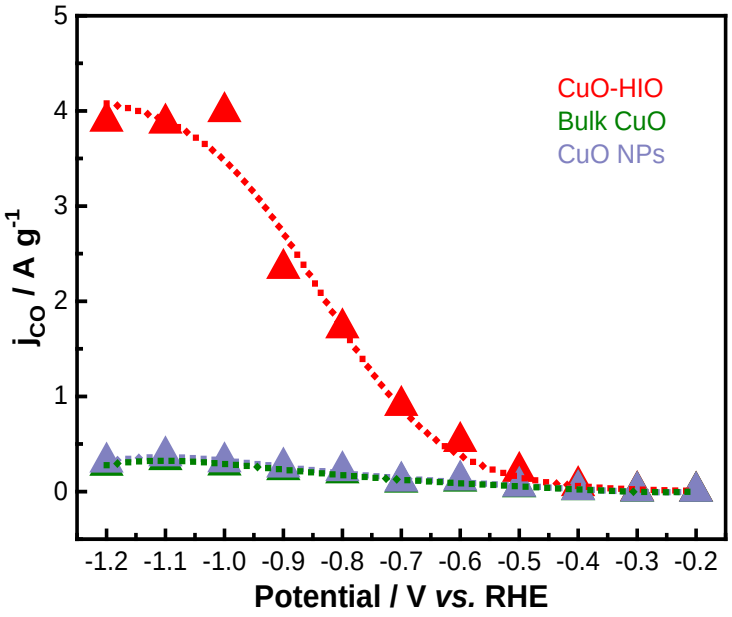




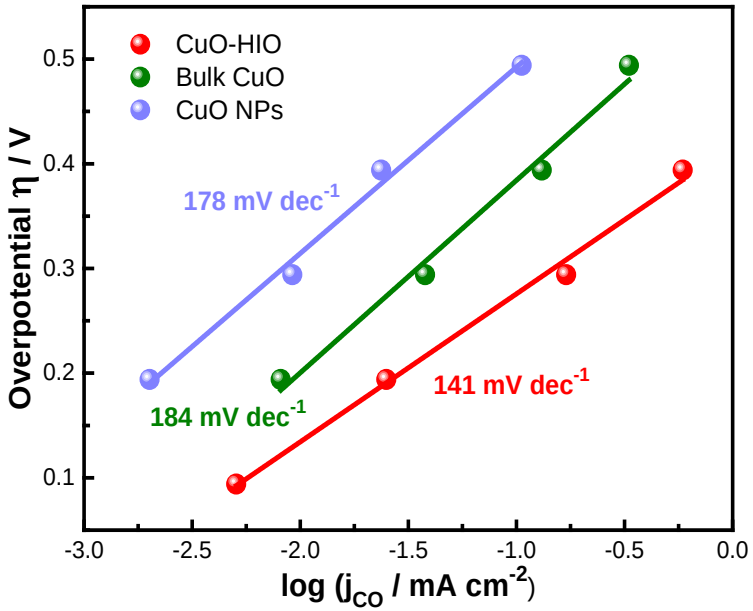
Element	Weight%	Atomic%
C K	36.57	63.63
O K	2.83	3.70
F K	16.03	17.64
K K	1.76	0.94
Cu K	42.81	14.08

Almost retain inverse opal structure

2. How does it perform?

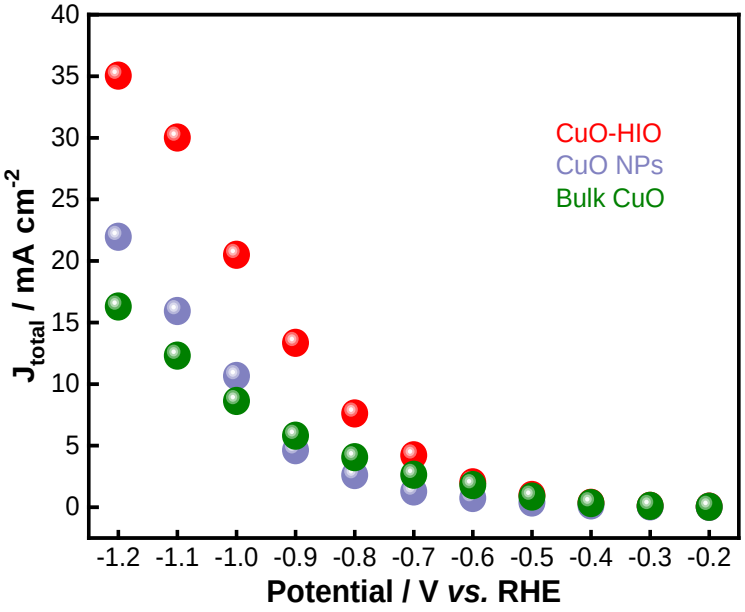


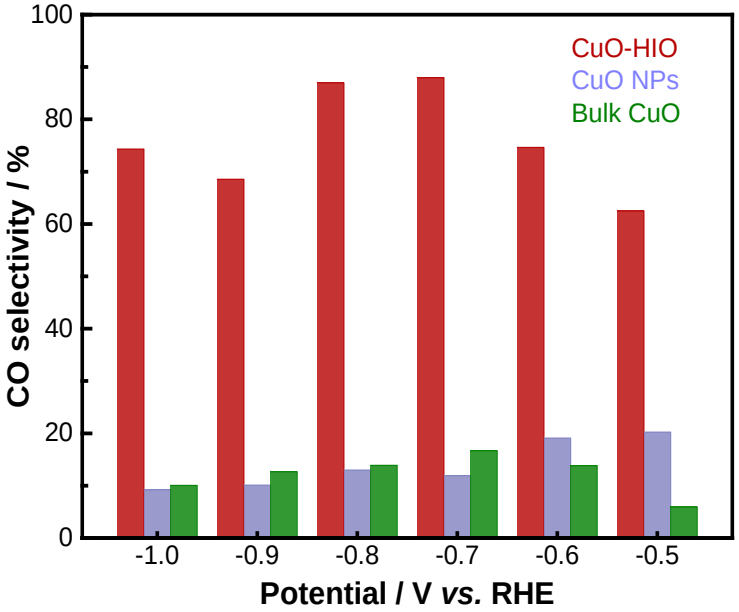
High mass current density of CuO-HIO



Rate determining step involving the initial electron transfer to CO_2

2. How does it perform?

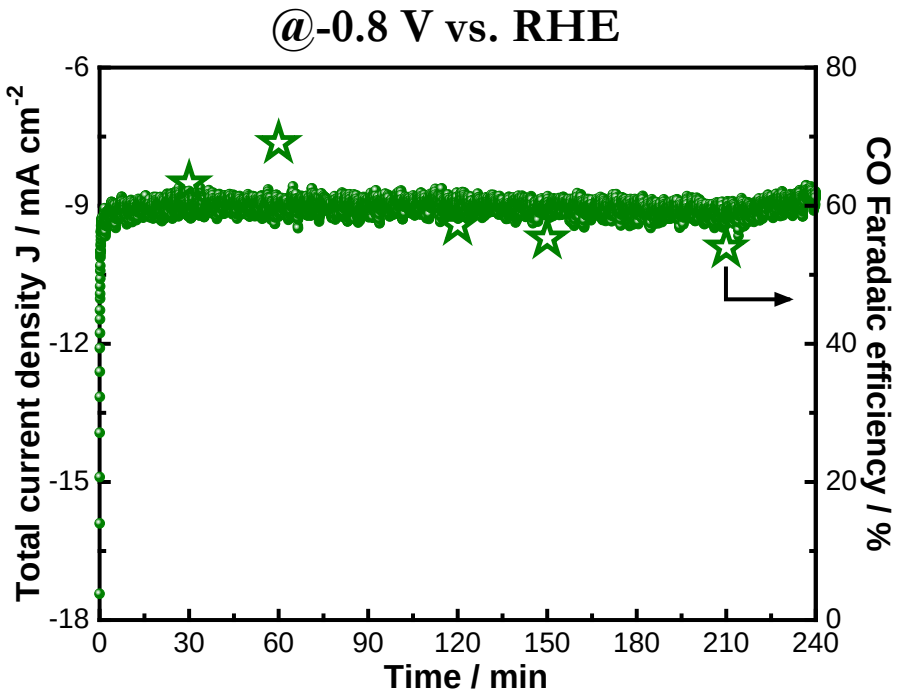


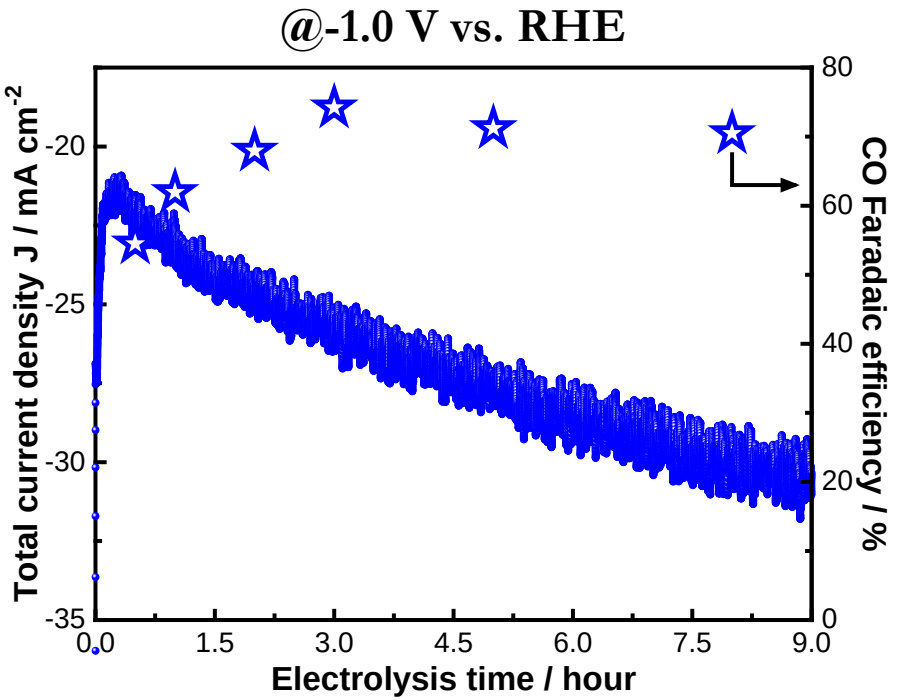


80 ~ 90% CO selectivity over CuO-HIO

5X ~ 9X higher than those for bulk and nanostructured CuO

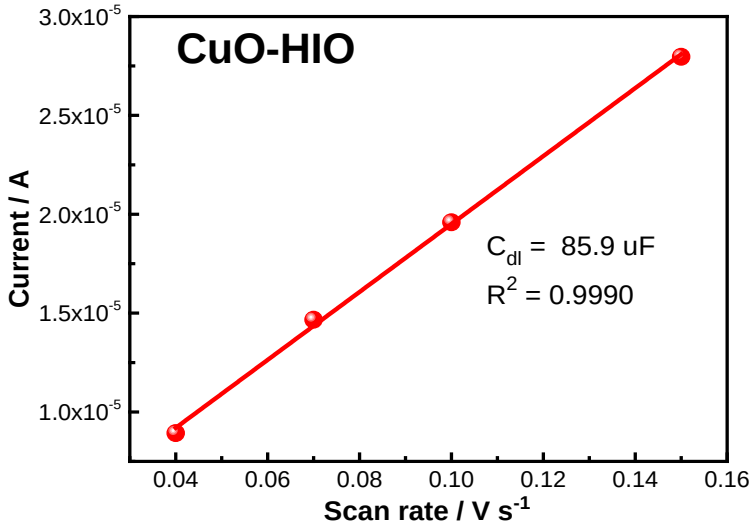
2. How does it perform?

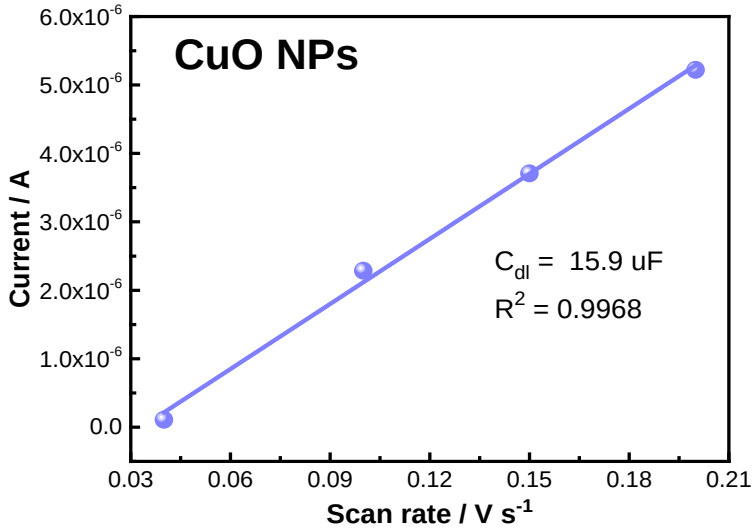


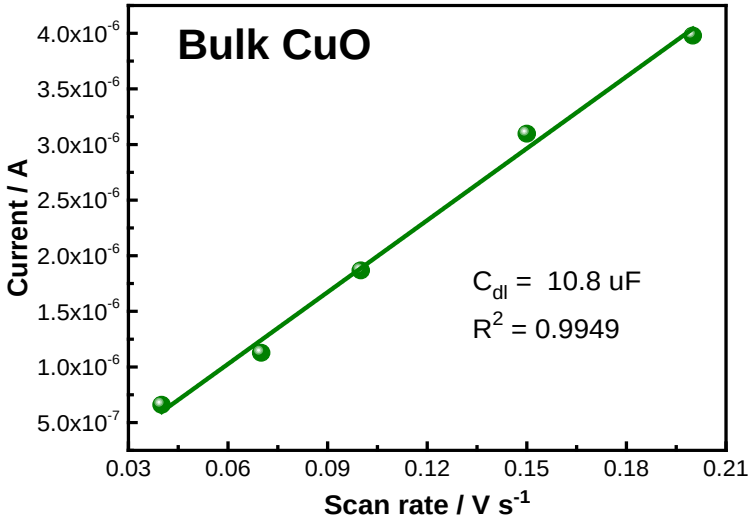


3. Structure-property relations

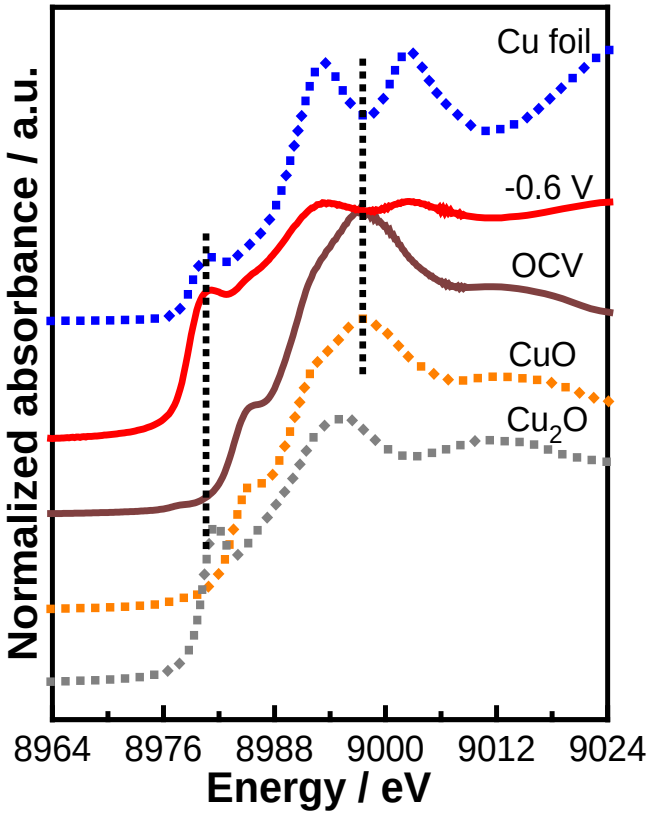
Double layer capacitance measurement

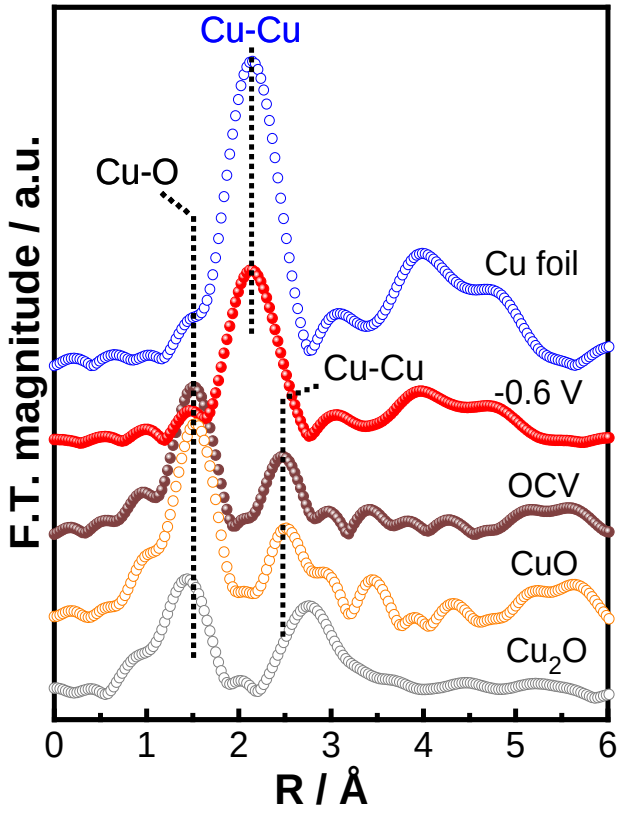






3. Structure-property relations





3. Structure-property relations