

Center for Atomic-level Catalyst Design

Lead institution: LSU (\$12M/5 year)

Team members: Clemson, Ga. Tech, Tech. U. Vienna, Texas A&M, Penn State, U. Utrecht, U. Florida, ORNL, La. Tech/Grambling

Energy Frontier Research Center

- The Energy Frontier Research Centers (EFRC) program aims to accelerate energy related transformative discovery understanding, and manipulating matter on the atomic and molecular scales.
- In August 2009, DOE established 46 EFRC's
- These integrated, multi-investigator Centers conduct fundamental research focusing on “grand challenges” ...
- The purpose of these Centers is to integrate the talents and expertise of leading scientists in a setting designed to accelerate research toward meeting our critical energy challenges.

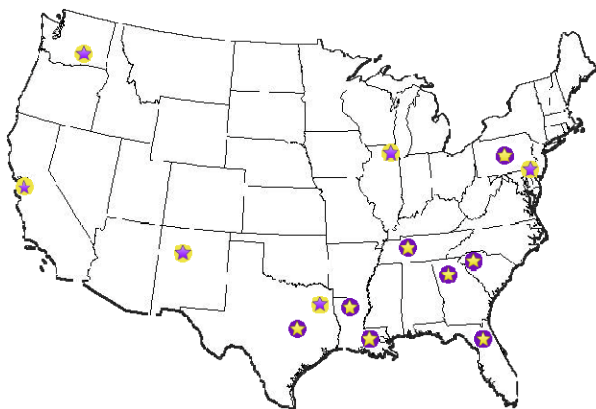
Center for Atomic-level Catalyst Design

Goal/Objective of our EFRC

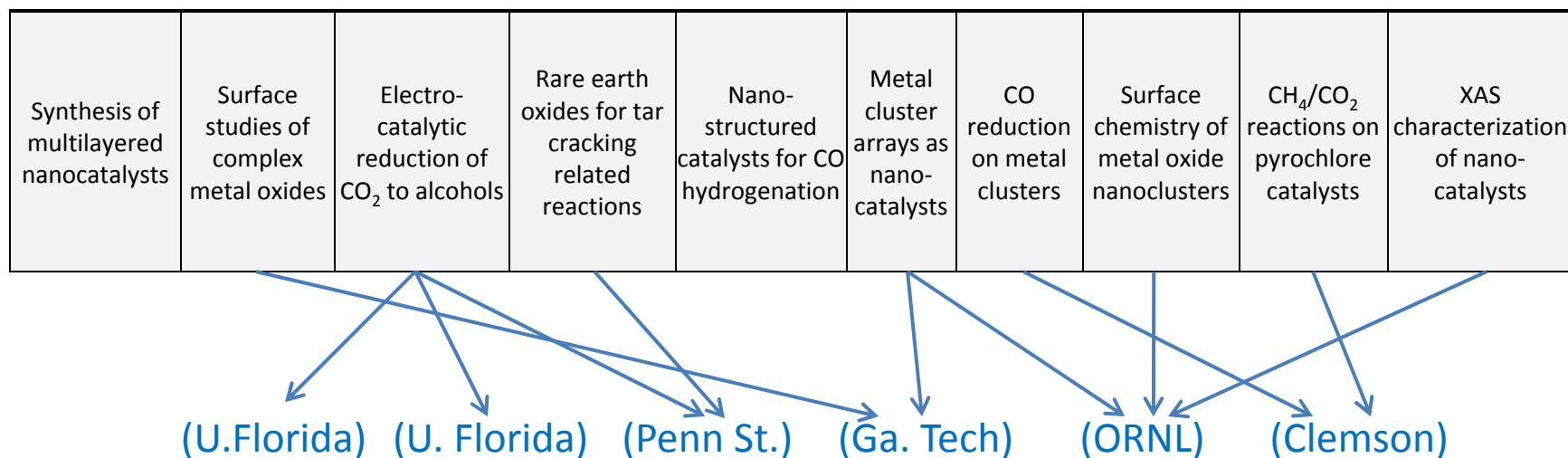
- to develop next-generation tools of catalyst computation, synthesis, and characterization so that the design of a catalyst at the computer, synthesis of this atomic-level design in the lab, and unambiguous characterization of the resulting material is entirely seamless.

Scientific approach

- Computational catalysis
→ *extend the time and length scales beyond DFT*
- Synthesis
→ *extend the length scales at which precise, computationally-specified catalytic surfaces can be prepared*
- Characterization
→ *determine the atomic-level structure of our catalytically active surfaces*



Research Projects and Computational Efforts



Goal: to develop new, advanced modeling technologies that will significantly increase the accuracy and speed of the simulation results so that computationally driven catalyst design becomes the preferred path for new catalyst development.

Surface Chemistry of Metal Oxide Nanoclusters

interacting with subgroups

Electrocatalytic Reduction of CO₂ to Alcohols

and

Surface Studies of Complex Metal Oxides

*From ultra-high vacuum synthesis/characterization to the electrochemical cell
– first principles to electrocatalysts “by design”.*

Motivation

- Questions: **Focus on electrolytic reduction of CO₂ to CH₃OH**
 - Why do oxide-supported metal clusters work as catalysts?
 - What is the role of: the support, defects, active sites... ?
 - What are the dynamics and how can they be controlled?
 - How can we provide an atomistic understanding, use surface science tools, and evaluate the performance in an electrochemical cell?

Example:

Cu → methane

Cu/ZnO → methanol (?)

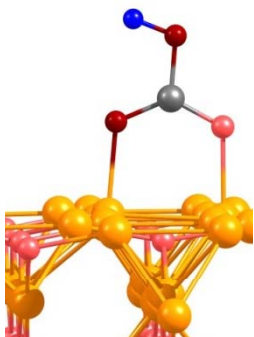
Cu₂O/ZnO → **4 times** more methanol than Cu/ZnO

Cu₂O nanoclusters/ZnO → **HIGHER** methanol than bulk Cu₂O

Why?

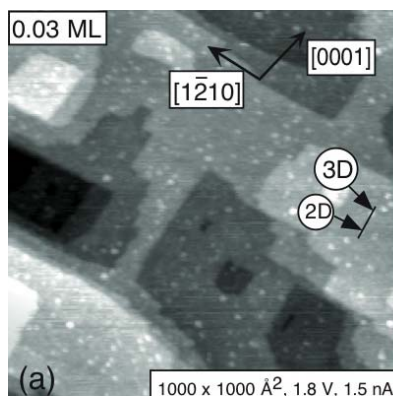
Current Work: Focuses on Cu deposited on single crystal ZnO substrates

Atomic-Level DFT



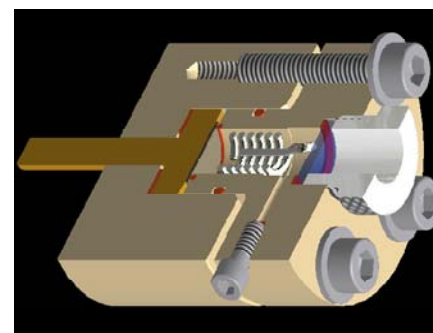
Fundamentals to Application

uhv nm-scale characterization (STM, synchrotron)



Clusters nucleate at hydroxyl groups. 2D and 3D clusters form. U. Diebold, TU Vienna

cm-scale Single Crystal Reactor



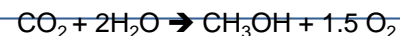
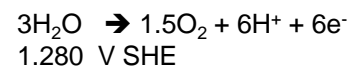
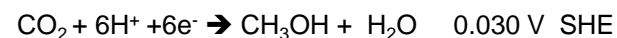
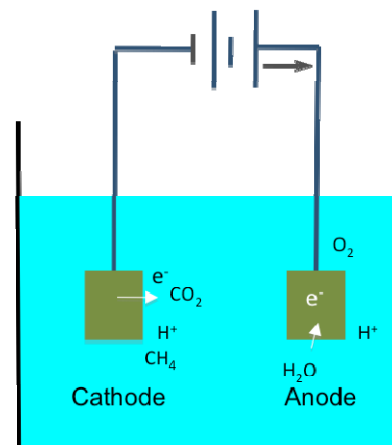
Experimental Results Drive Improved Models & Design

Common **single crystal platform** improves collaboration between simulation, characterization, and catalyst evaluations.

CO₂ Electrochemical Reduction

- Product selectivity is dependent on the electrocatalyst.
- Mechanism for selectivity (alcohols, hydrocarbons, CO) is ~unknown.
- Relationships between surface chemistry and catalyst performance are needed.

Cu vs CuO vs Cu₂O for methanol??



Initial Experimental Work

Electrocatalytic Reduction of CO₂ to CH₃OH

- Experimental

- Oxidized Copper Electrodes

- Air Oxidized

air oven at 130 °C for 17 hrs, followed by cleaning with 0.1 M HCl for 20 sec

- Electrochemically Anodized

anodize Cu at 1.25 V SCE in 0.5 M KHCO₃ for 3 minutes

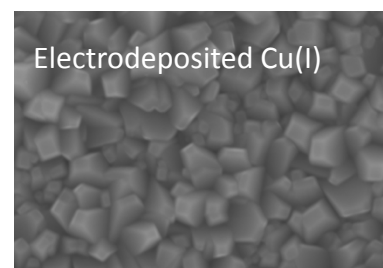
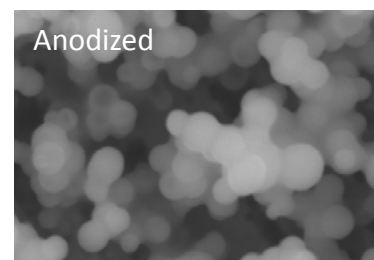
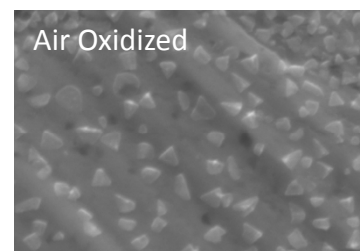
- Electrodeposited Cu(I)

reduction of Cu(II) lactate in alkaline solution for 30 minutes:

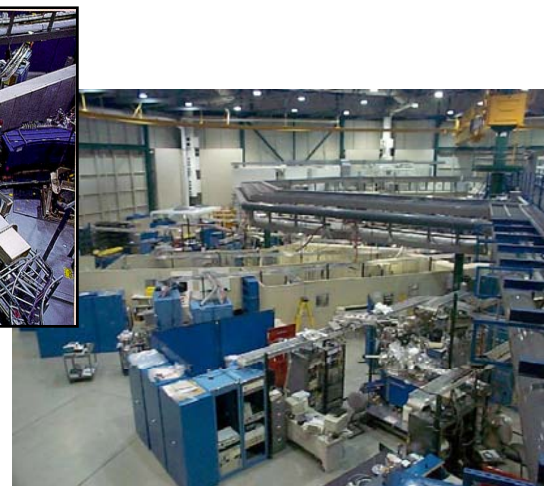
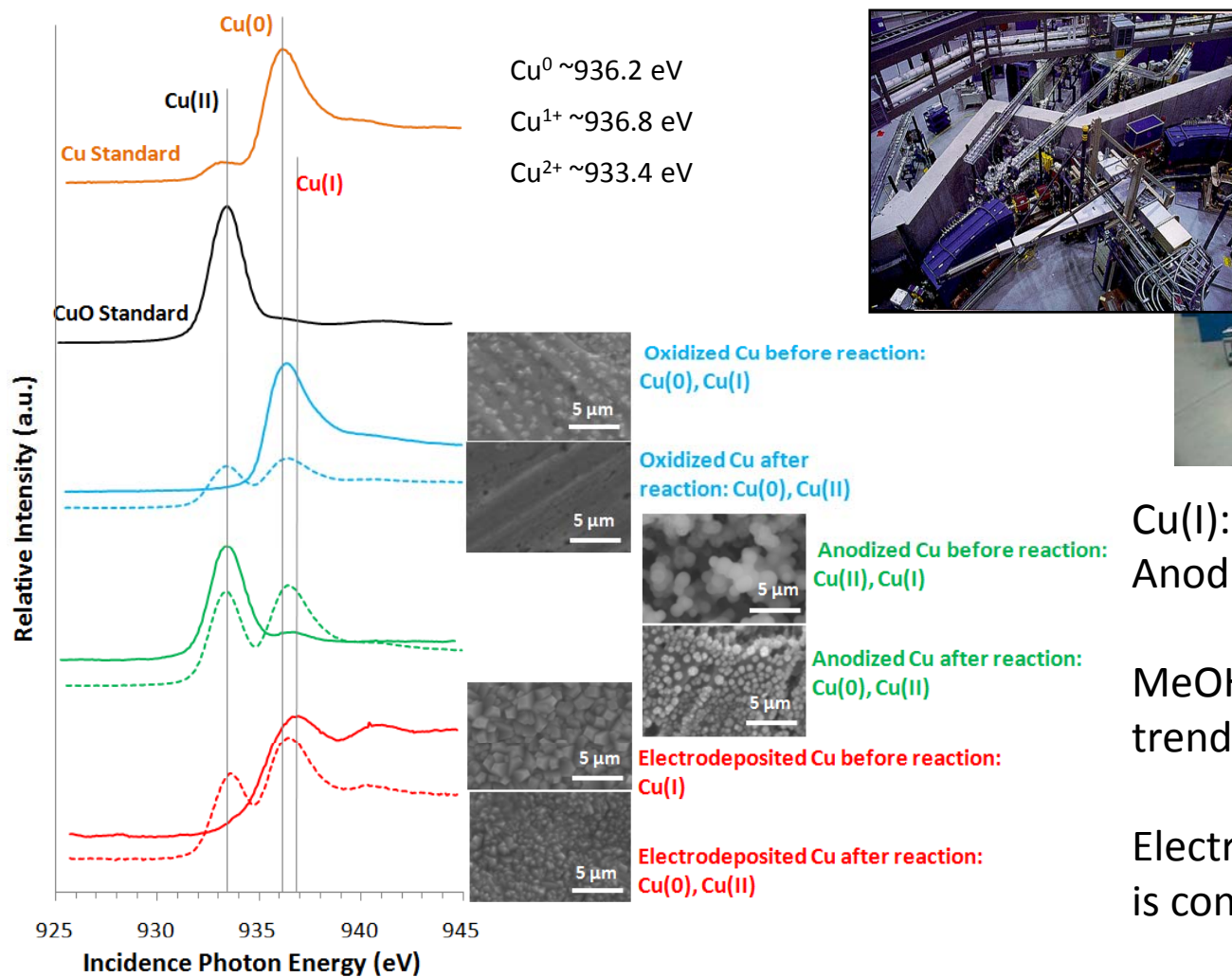
- Copper – Zinc Oxide Electrodes

Cu clusters deposited on Zn(10⁻¹⁰) in uhv
(the commercial syngas catalyst, CO to CH₃OH)

- Single Crystal Reactor



Surface Analysis NEXAFS - CAMD Synchrotron



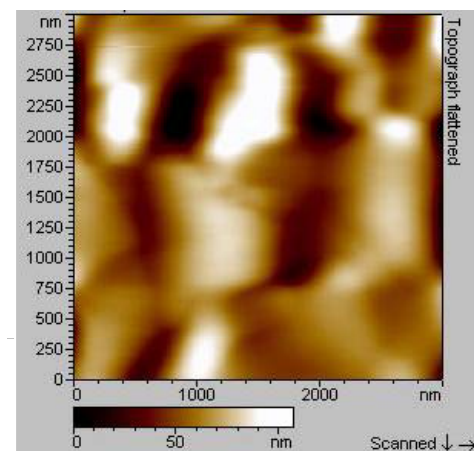
Cu(I): Electrodeposited Cu > Anodized Cu > Oxidized Cu

MeOH yield follows same trends (4x larger on Cu(I))

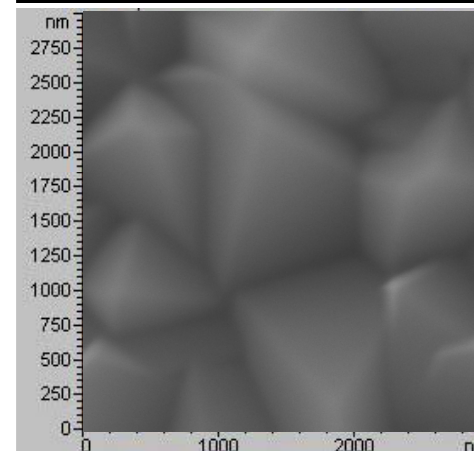
Electrodes are not stable Cu(I) is converted to Cu(0) and Cu(II).

Oxidized Cu Electrode versus CuO_x/ZnO Electrode

Cu(I) films



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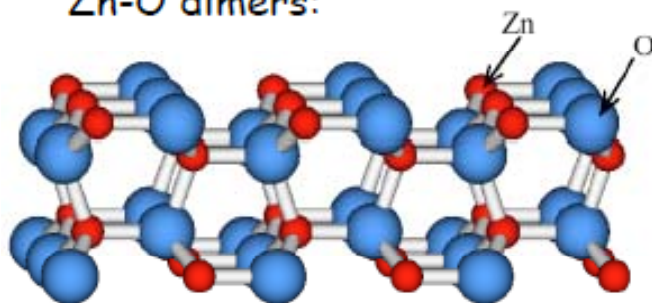


CH₃OH yield (μmol
cm⁻² hr⁻¹)

STM: Clean ZnO(10 $\bar{1}$ 0)

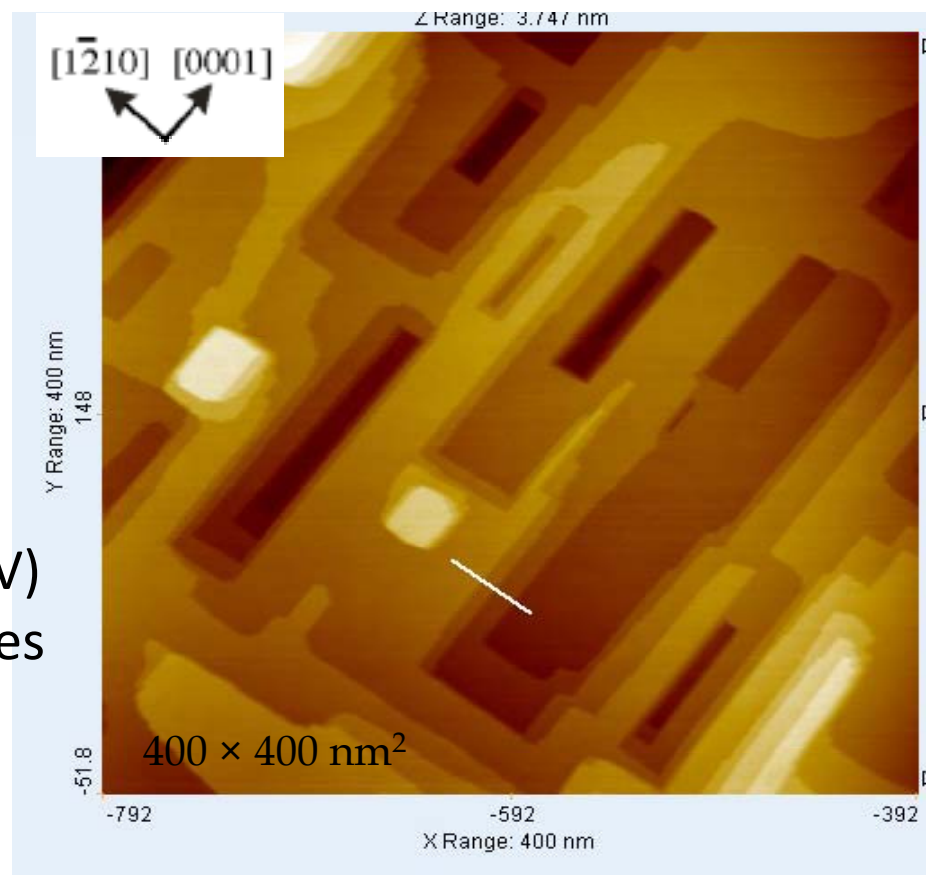
Wurtzite structure

Zn-O dimers:



Zn-Zn separation: 3.25 Å

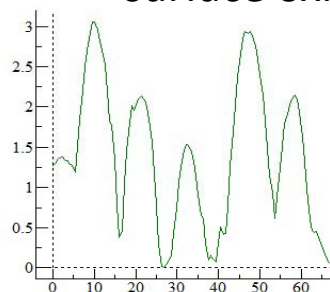
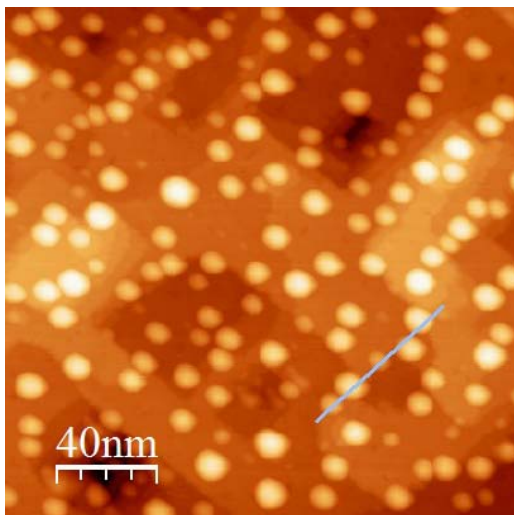
- Non-polar surface
- wide bandgap semiconductor (3.4eV)
- STM shows large, defect free terraces
- monatomic steps



STM: > ML Cu coverage: oxidized

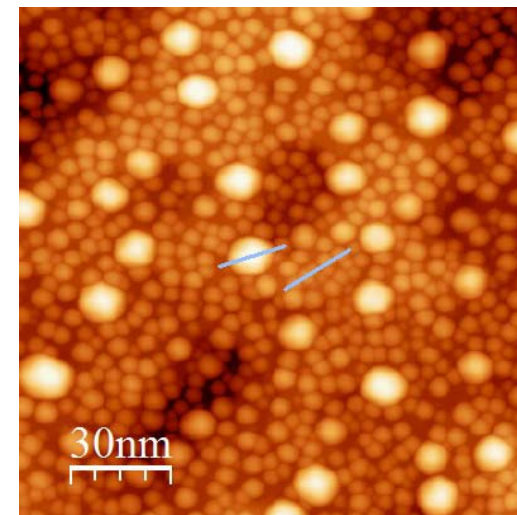
100L O₂ / 2ML Cu/ZnO at 400 C

- cluster size slightly larger
- surface oxide??

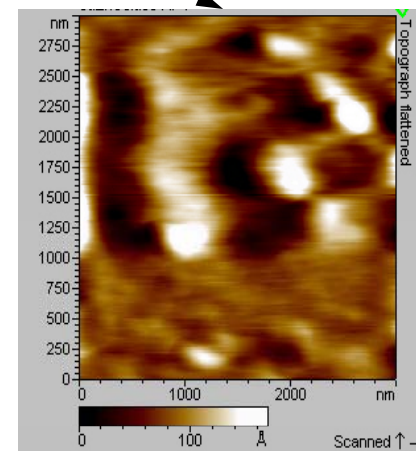
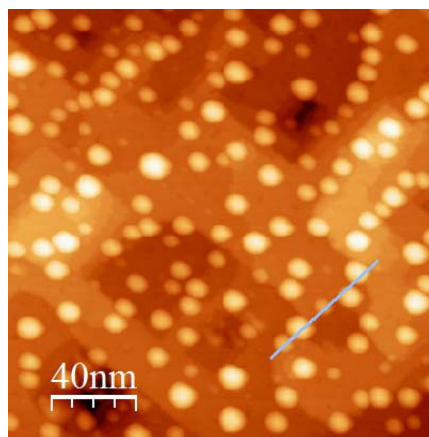
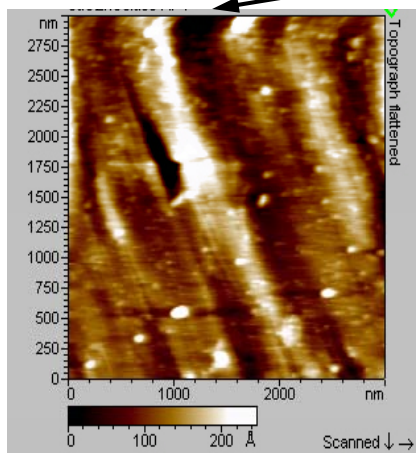


Sequential: 100L O₂ / 2ML
Cu/ZnO at 400 C

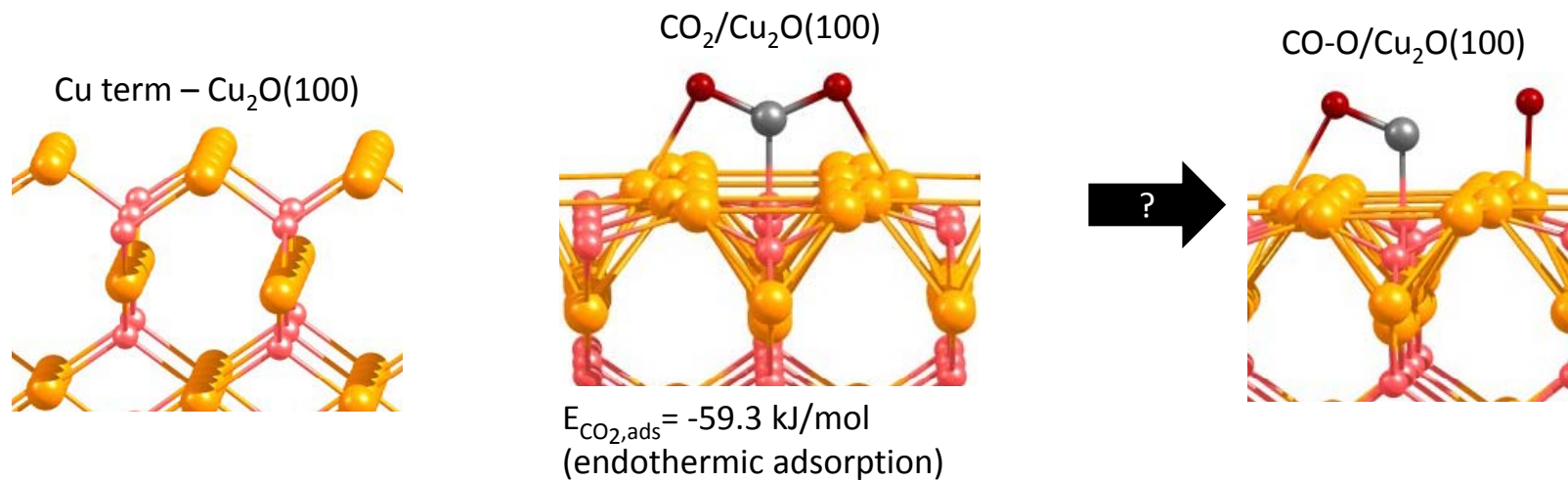
- 5×[0.4ML Cu + 20L O₂@ 400C]
followed by 2ML Cu at 200 C
- larger cluster ~15nm across x 4nm high
- fully Cu oxidized clusters ????



	3 ML (CuO _x /ZnO)	3 ML (Cu/ZnO)
Potential (V vs Ag/AgCl)	-1.4	-1.4
Current density (mA cm ⁻²)	2.70	1.30
Reaction time (min)	15	35
Diameter (nm)	<100	~500
Height (nm)	~20	~20
CH ₃ OH yield (μmol cm ⁻² hr ⁻²)	86.7	15.2
F _{CH₃OH} (%)	516	188
H ₂ yield (μmol cm ⁻² hr ⁻²)	0.22	0.29
F _{H₂} (%)	0.43	1.20



Knowledge gaps: DFT to address atomistic pathways

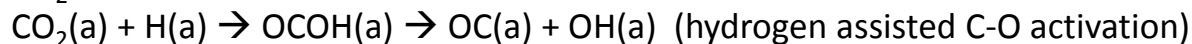


- Use DFT to examine reaction mechanisms for CO₂ reduction to CH₃OH & relevant side paths (e.g. methane)
- Surfaces are initially chosen based on experimental results
- Examining both a vacuum and electrochemical environment

How do the reaction mechanisms depend on the surface?

Can we promote/suppress certain reaction steps by the choice of surface structure?

- Pathways for activation for C-O bond in CO₂



Summary

- CH_3OH directly related to Cu(I)
- CuO_x nanoclusters / $\text{Zn(10}\underline{1}\underline{0})$ has higher CH_3OH Yields (2- 4 \times) in spite of small coverage
- Experimental results reveals ~ 5 nm CuO_x clusters are primarily Cu_2O that are stable!
- The role of the substrate, as well as the intermediate pathways to the formation of methanol are yet unknown (carbonate, formate, formaldehyde, methoxy ???)
- Theoretical input has started....