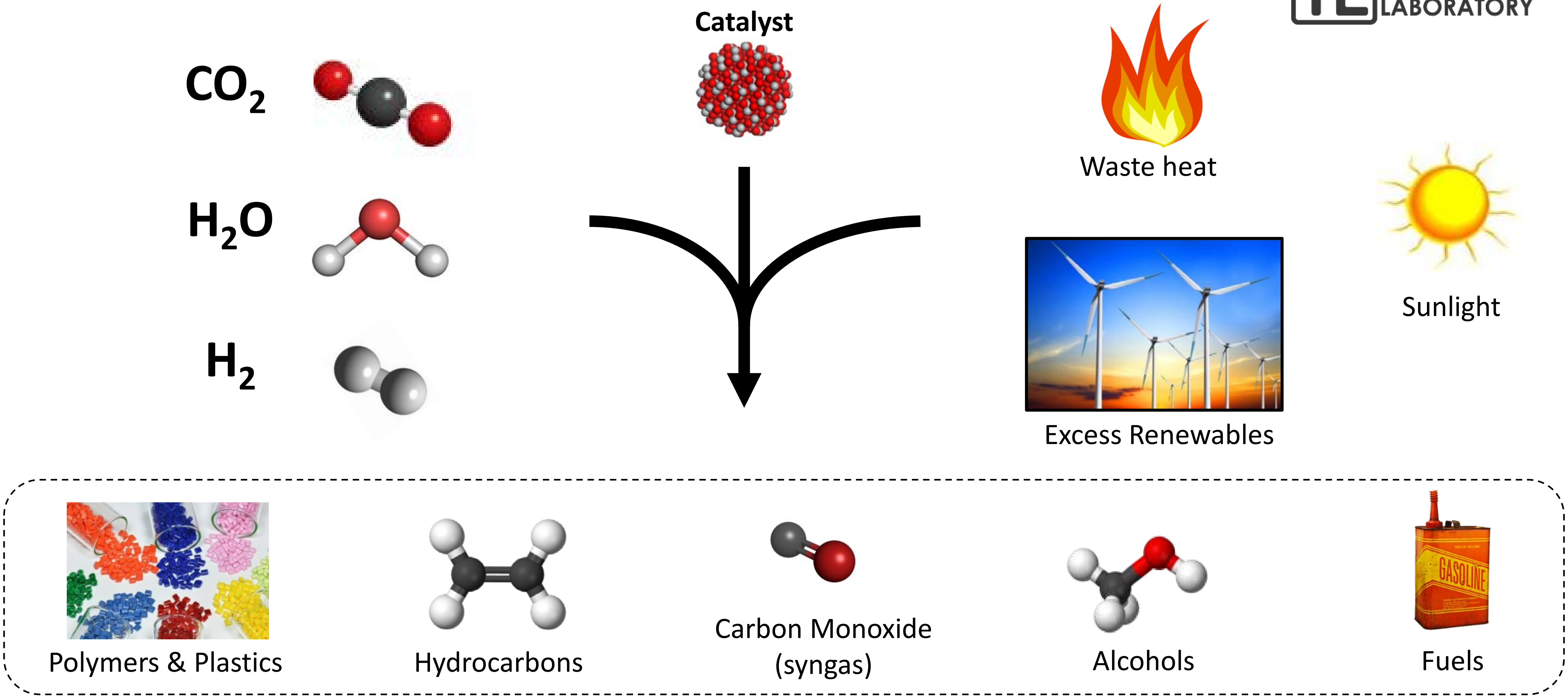
Catalytic Conversion of CO_2 into Value Added Products

Douglas R. Kauffman

08/17/2018

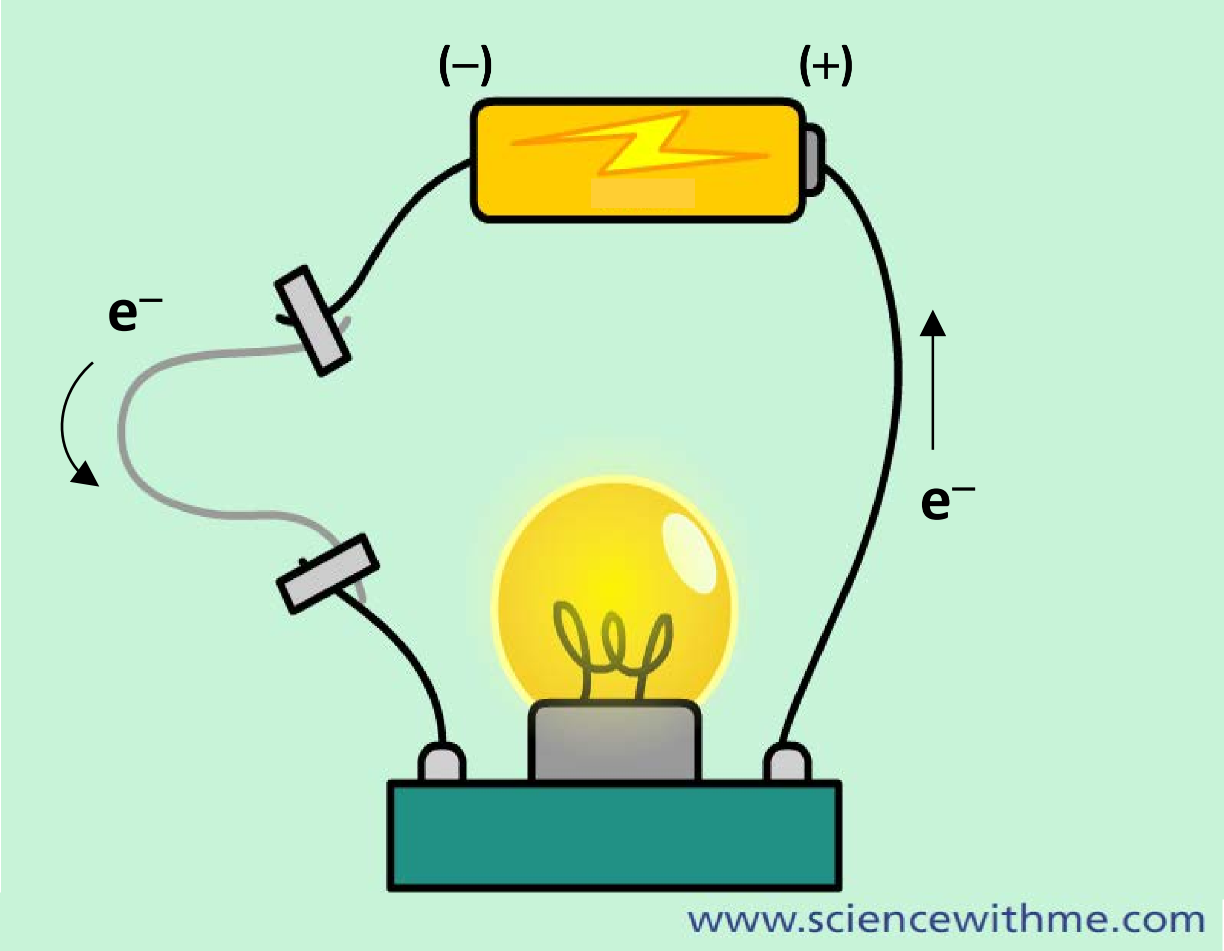
NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL Materials Research: Creating Value from Waste CO_2



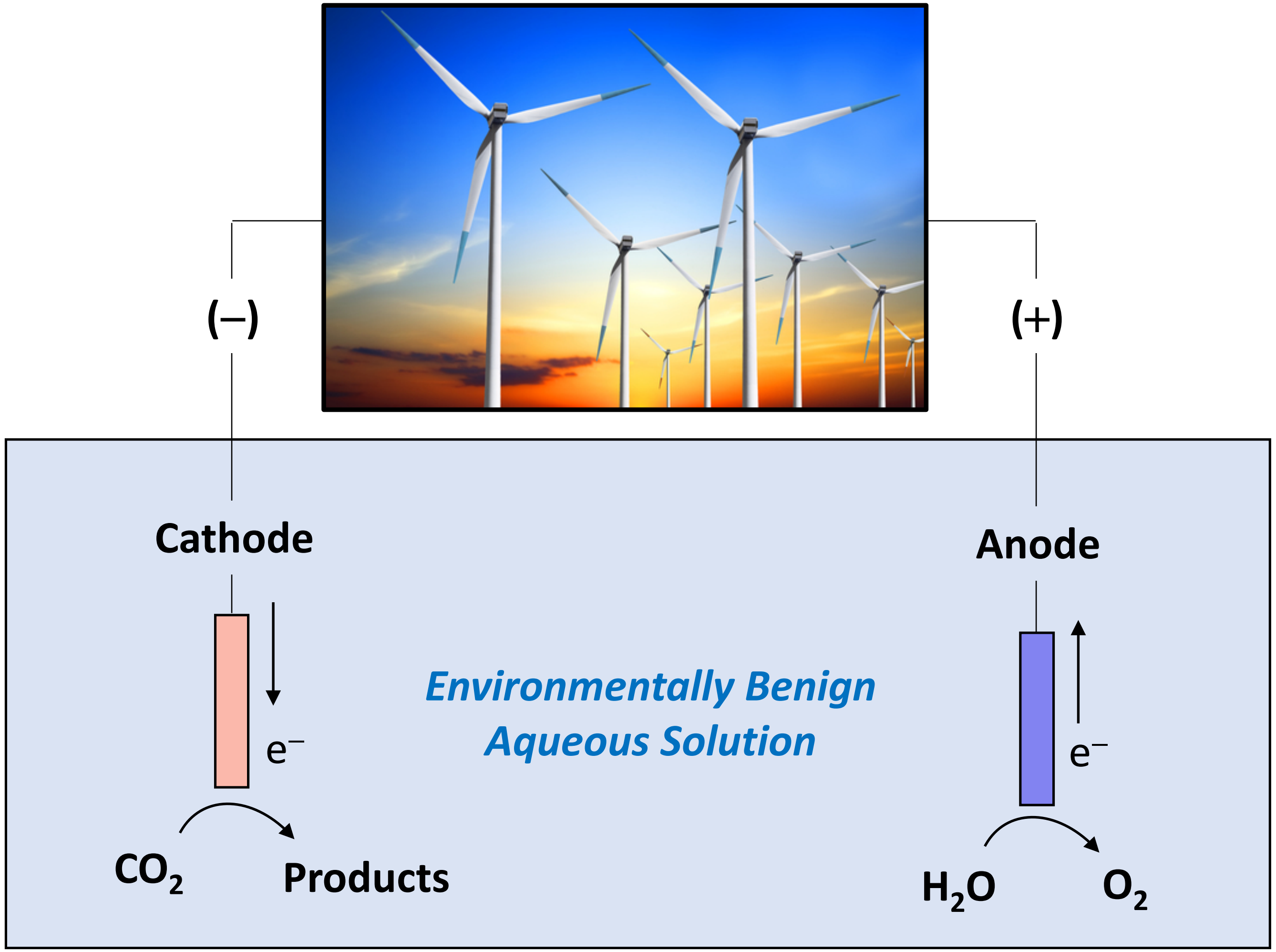
General Approach: Electrochemical CO_2 Conversion

Electrochemistry moves electrons

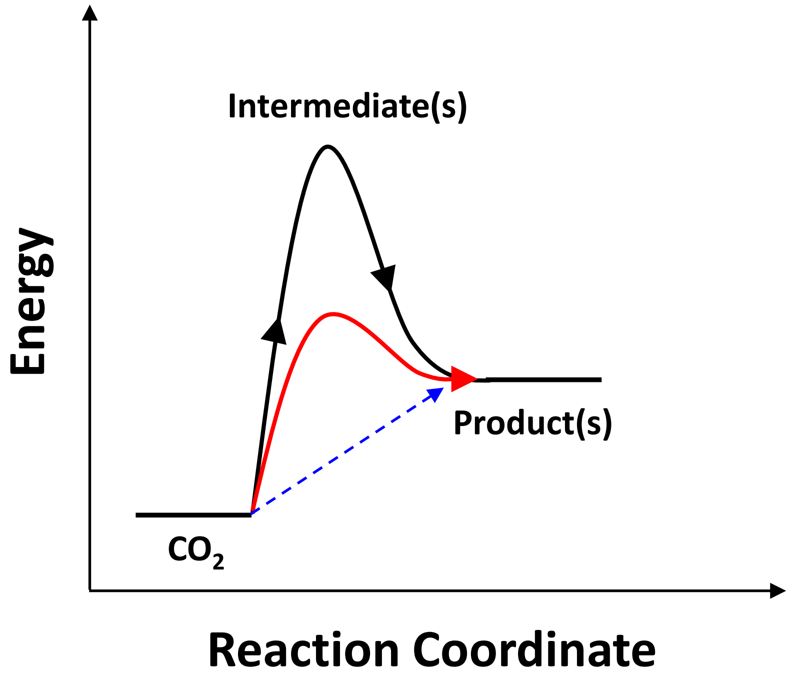


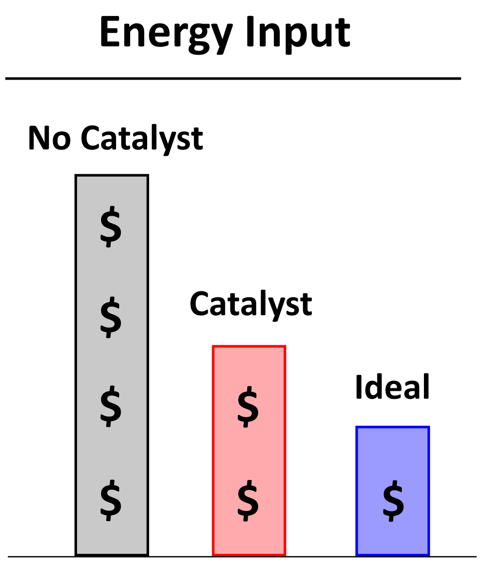
General Approach: Electrochemical CO_2 Conversion

Use carbon-free electrons to convert CO_2 !



Designing CO_2 Electrocatalysts





- **Large energy input or poor efficiency ...** <u>Wasted energy = $$$$!</u>
- **Large Product Distribution...** <u>Separation = $$$$!</u>

“Coinage” Metal Catalysts

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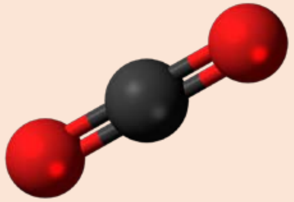
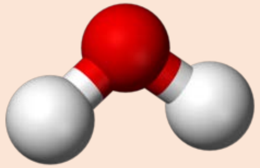
CO_2



Water



Gold

Synthesis gas
($CO + H_2$)

Industrial Chemicals

Fuels

Polymers and Plastics

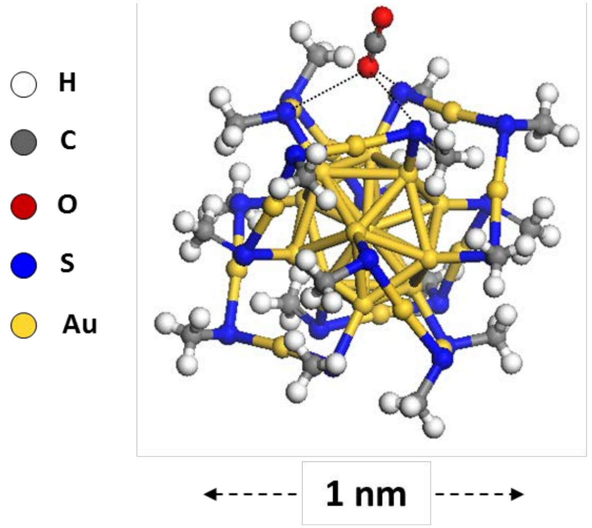
Copper

$H_2 + CO$
formic acid
methane
C_2+ hydrocarbons
alcohols

Purified product

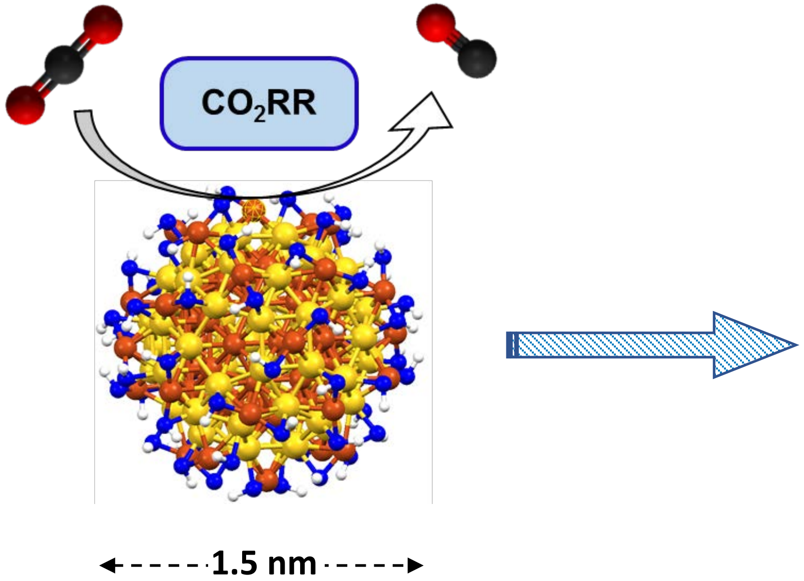
Previous Success with Ligand-Capped Nanocatalysts

$Au_{25}(SR)_{18}$ Nanocluster



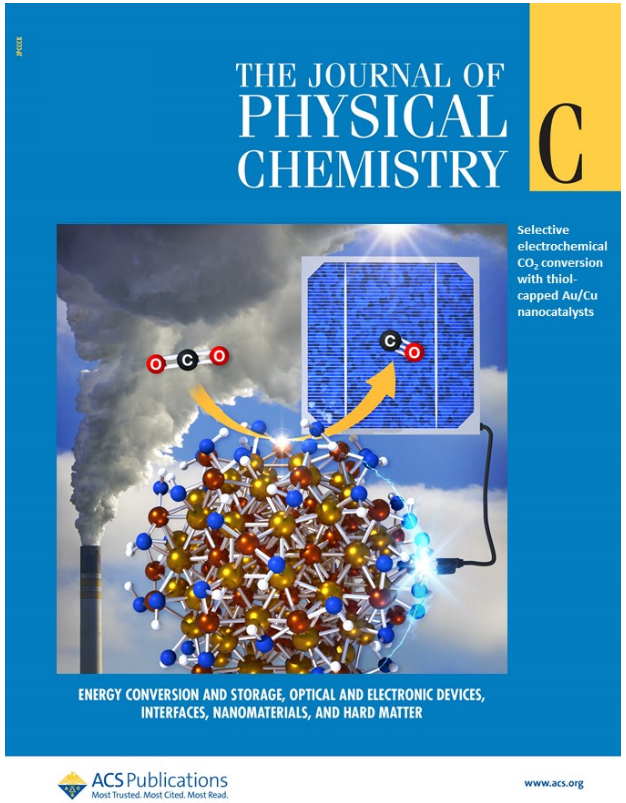
Extremely active for CO_2 → CO

Gold-Copper Nanocatalysts



Retained performance with ~50% reduction in gold

JPCC cover in December 2018



** Just accepted and chosen for JPCC Cover! **

DOI: 10.1021/acs.jpcc.8b06234

J. Am. Chem. Soc. 2012; J. Phys. Chem. Lett. 2013; Chemical Science 2014; ACS Applied Materials and Interfaces 2015; J. Chem. Phys. 2016; ACS Catalysis 2016; MRS Commun. 2017, J. Phys. Chem. C. 2018, US Patent 9,139,920.

Can We Eliminate Precious Metals?

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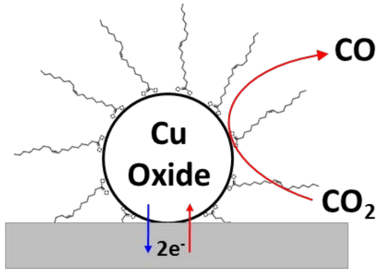
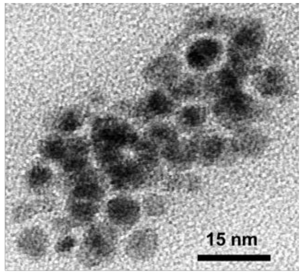
Nanostructured copper oxides as a starting point

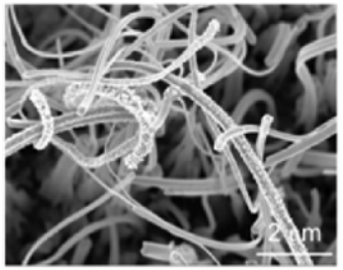
- Previously shown that surface oxides promote $CO_2 \rightarrow CO$

Kauffman *et. al.* JPCL 2011.





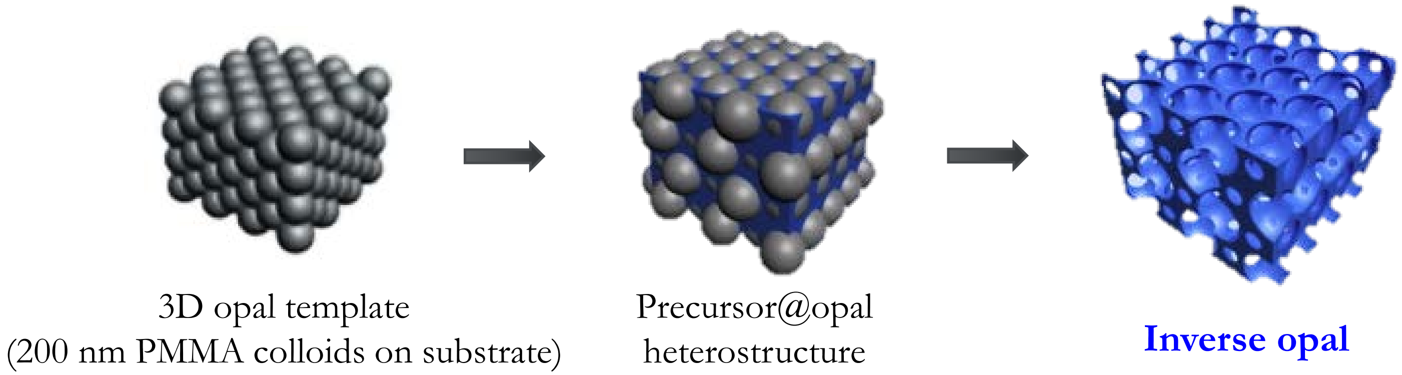
Li and Kannan JACS 2012

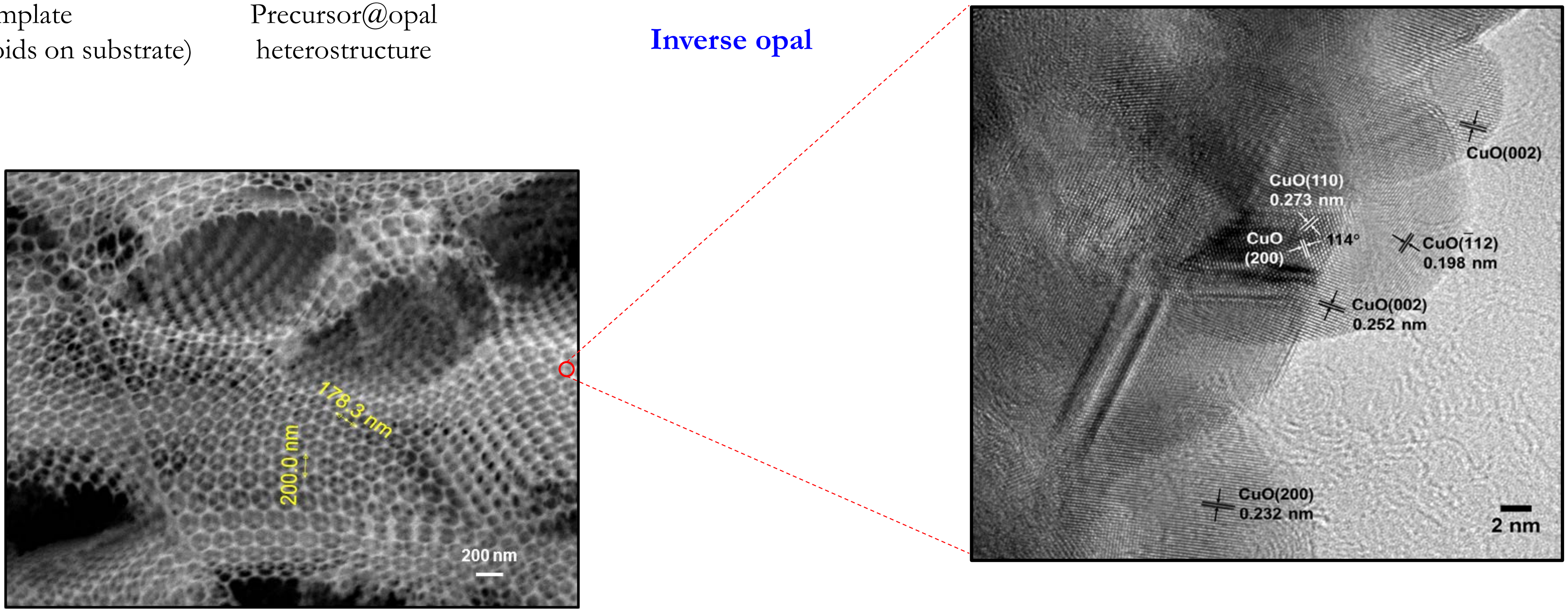


We want

- High surface area & large density of reactive sites
- High concentration of oxide groups
- High porosity for good mass transport

Nanostructured CuO Inverse Opals

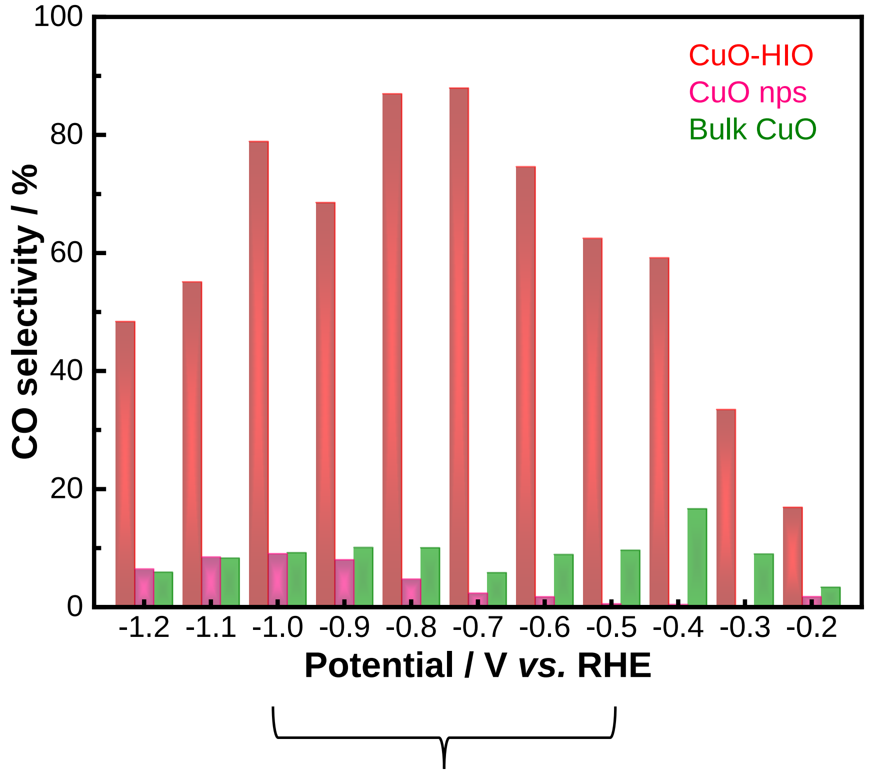


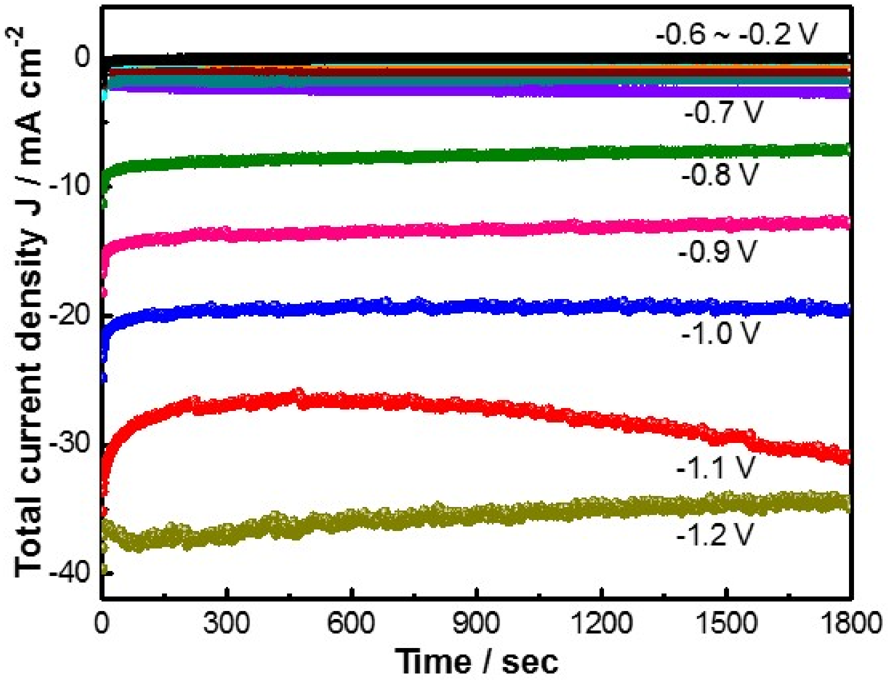


Phan & Kauffman, et al.; manuscript in preparation

Selective and Stable CO Formation

Almost no H_2 below -1V , minor CH_4 and HCOOH, trace C_2





- ~8x more selective than commercially available CuO powder
- ~10-60x more selective than commercially available CuO nanoparticles

Phan & Kauffman, et al.; manuscript in preparation

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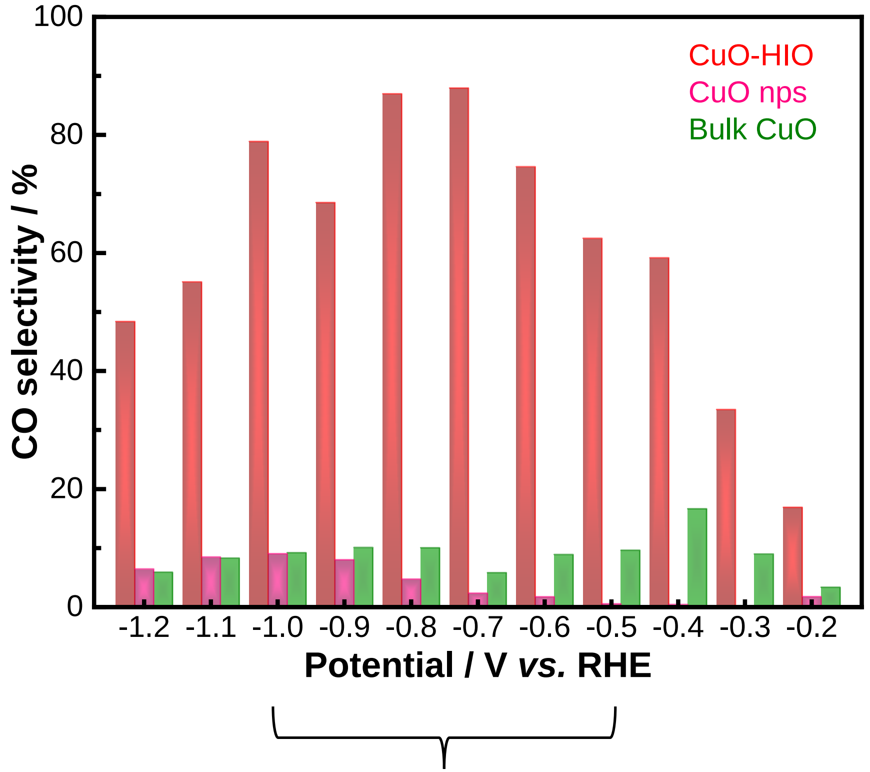
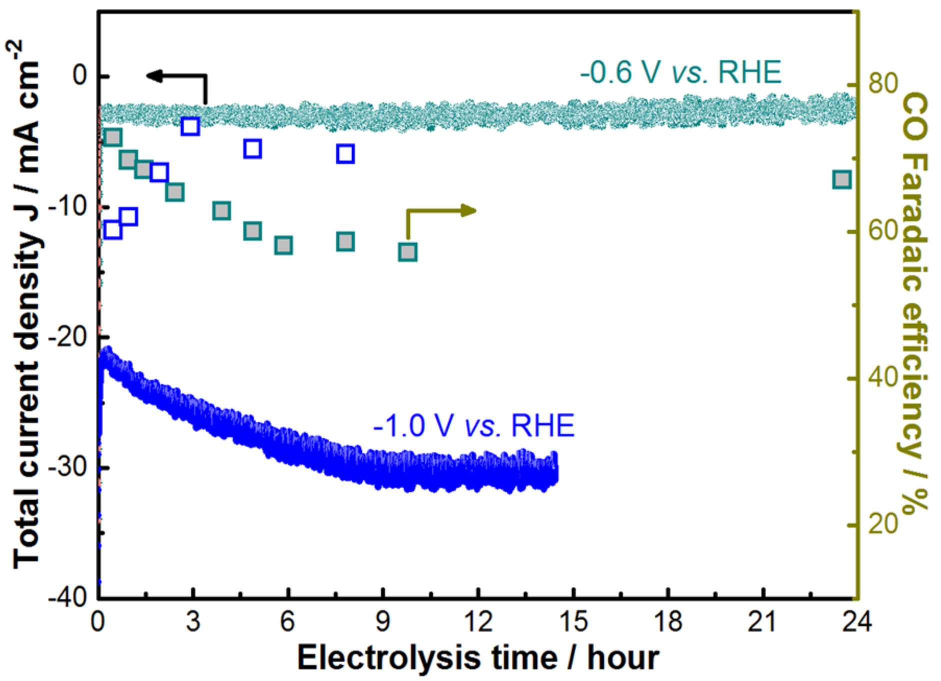


Excellent stability during 12-24 hour tests



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Quasi In-Situ XRD (ANL / APS Synchrotron)

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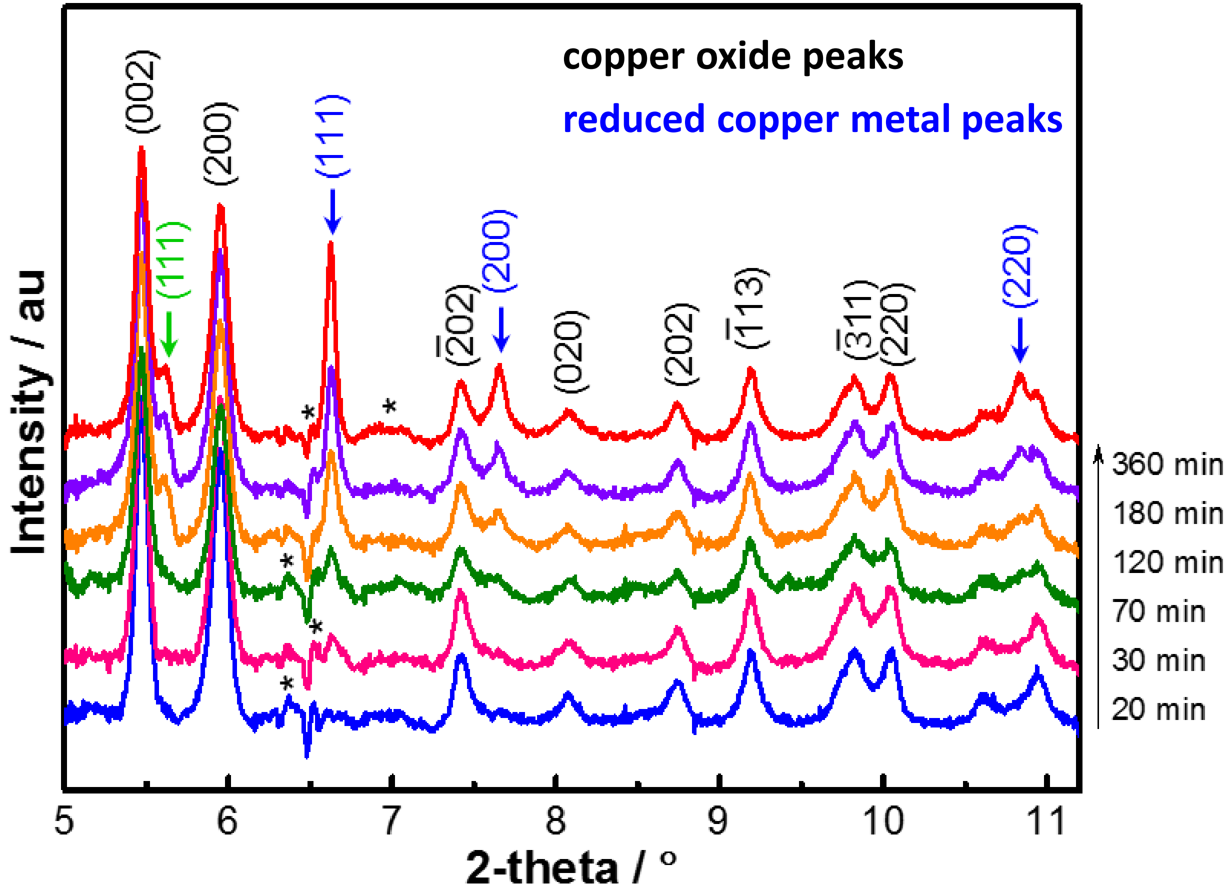
Catalyst retains significant fraction (~20-30%) of oxides during 6 hour CO_2 reduction



- Ongoing DFT calculations for CO_2 reduction on Cu-oxide vs Cu
- Provide atomic level details on product selectivity

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Phan & Kauffman, et al.; manuscript in preparation

Transitioning from H-Cell into Gas Diffusion Electrolyzers

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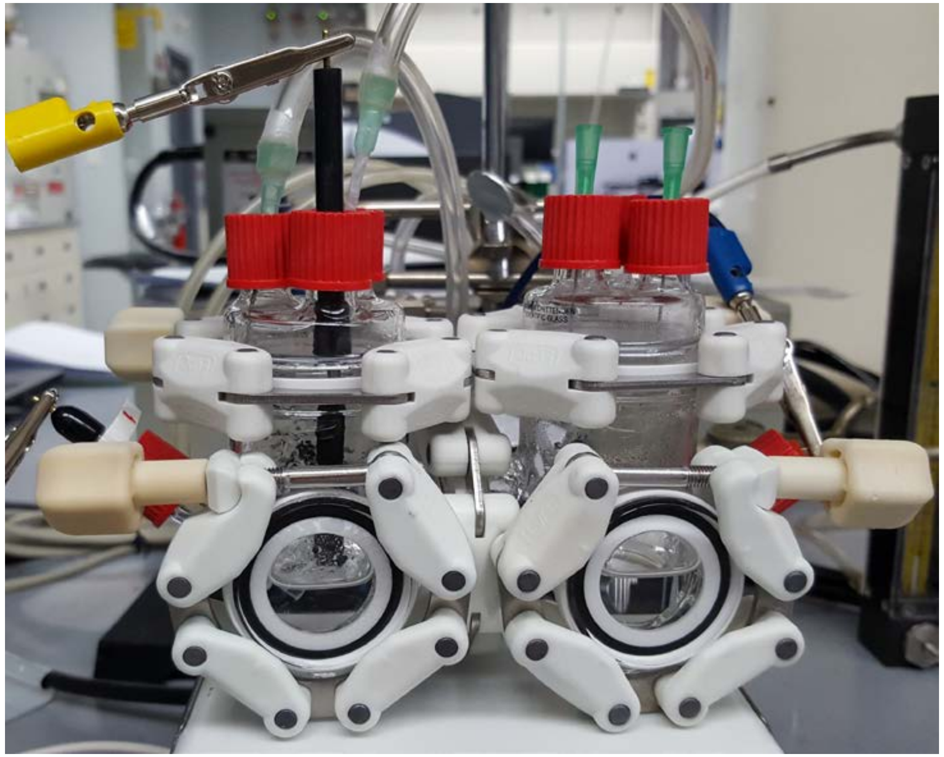
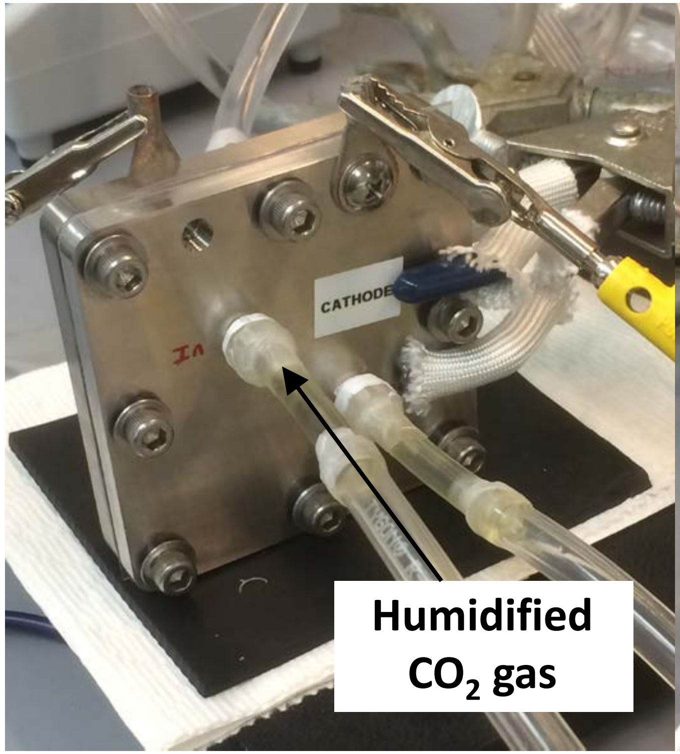
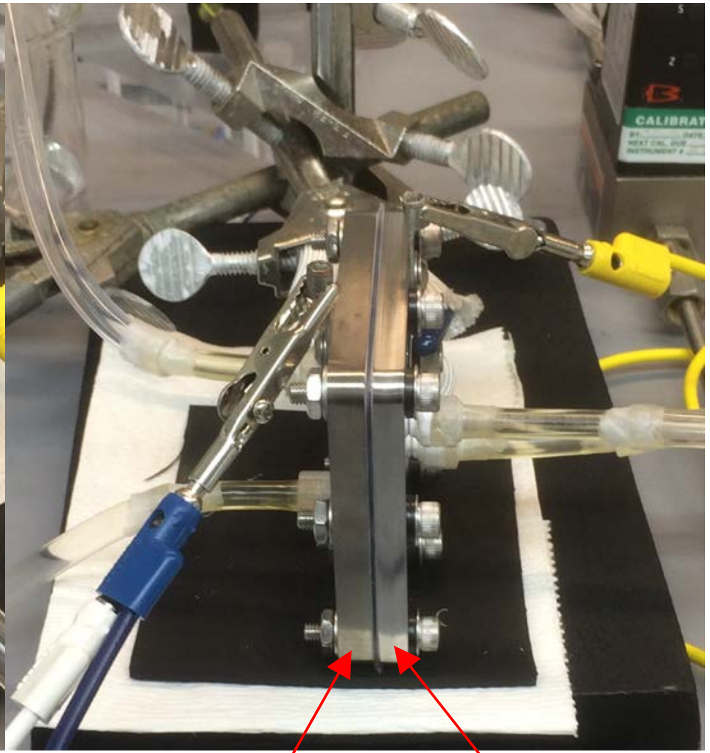
- CO_2 dissolved in 0.1M $KHCO_3$
- Mass transfer & current density limitations
- Not very scalable



Cathode Anode

- Gaseous CO_2 reacted at cathode
- Much higher mass transfer & current density
- Scalable (*e.g.* electrolyzer stacks)





Anode Cathode

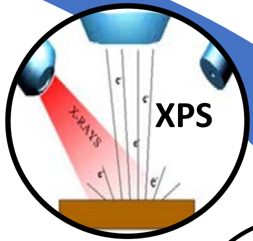
<u>Very</u> different reaction conditions; process parameters need optimized

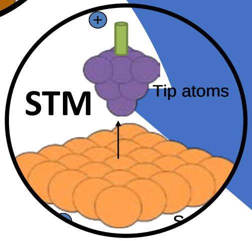
Combining Electrochemistry and Surface Science

"Bridging the pressure gap"

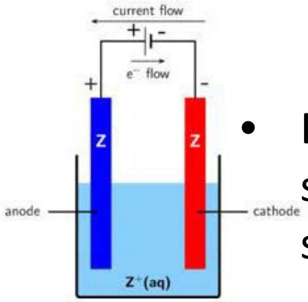
Surface Science

- Well-defined catalysts via precisely controlled growth: composition, size (lateral and vertical), shape
- Characterizations at atomic scale possible
- High electrical conductivity

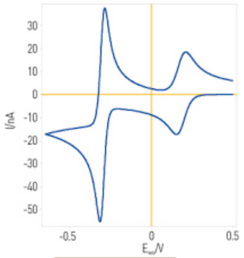




Combination provides exquisite structure-property details

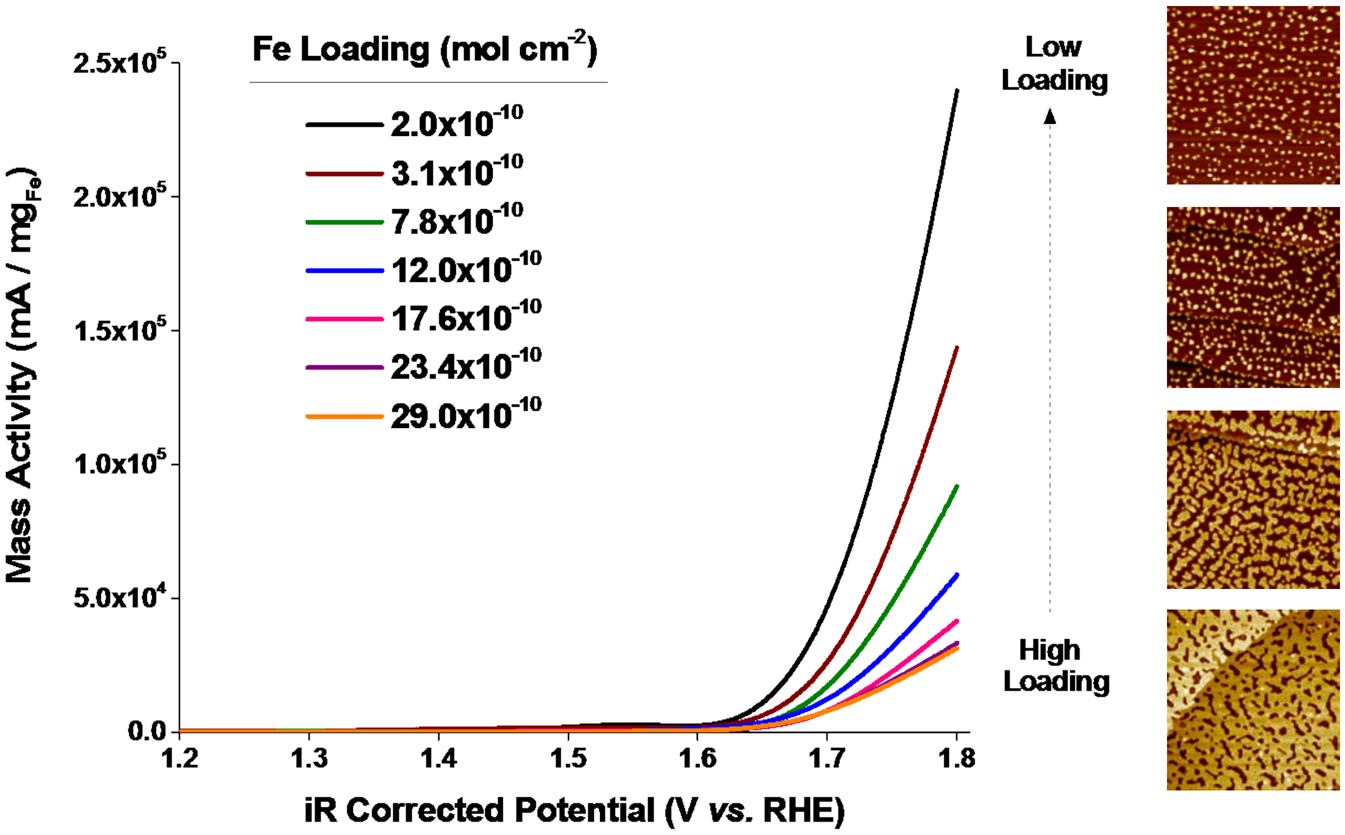


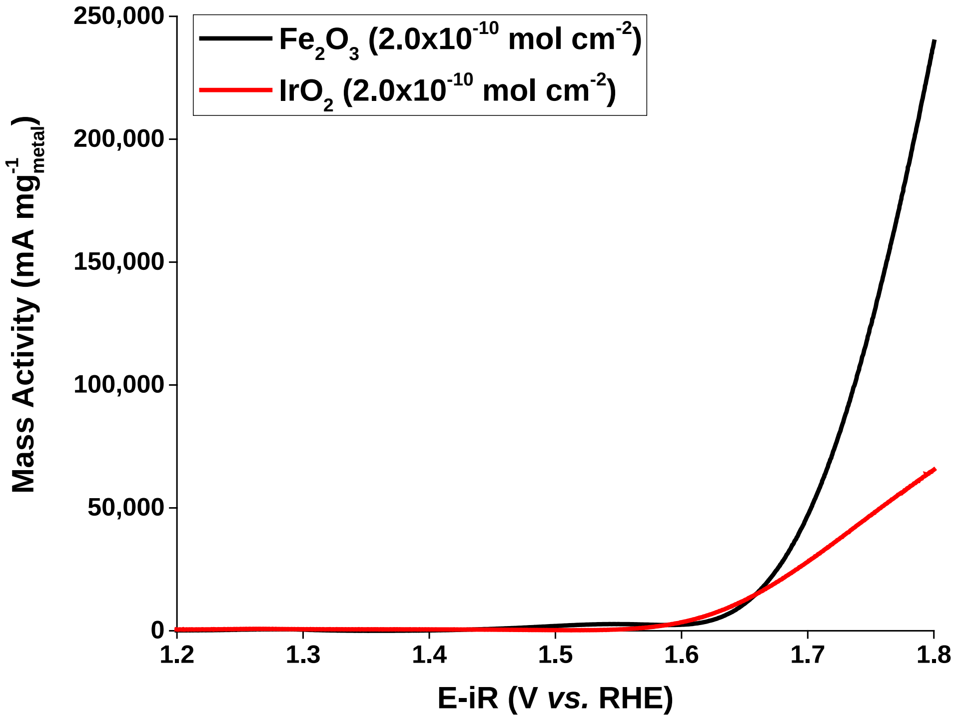
- Extremely sensitive to surface composition and structure



Electrochemistry

Combining Electrochemistry and Surface Science





Tafel slope = 75 ± 9 mV dec^{-1}

Iron is 1000s times cheaper than Iridium
(precious metal … ~ $40k per kg)

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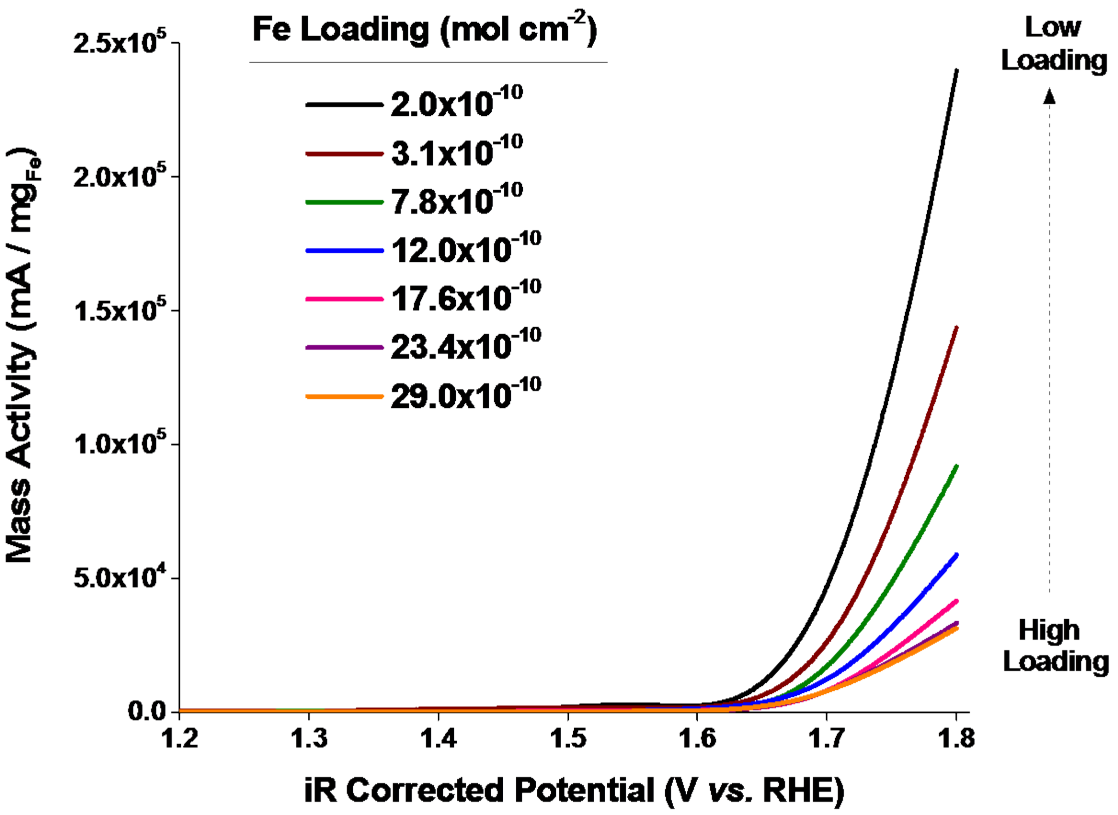
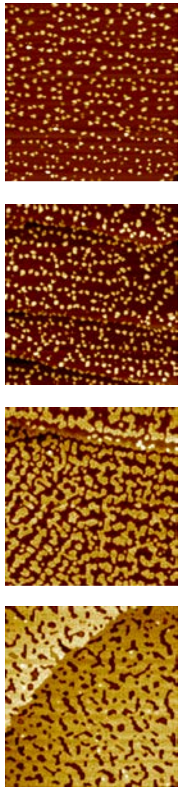
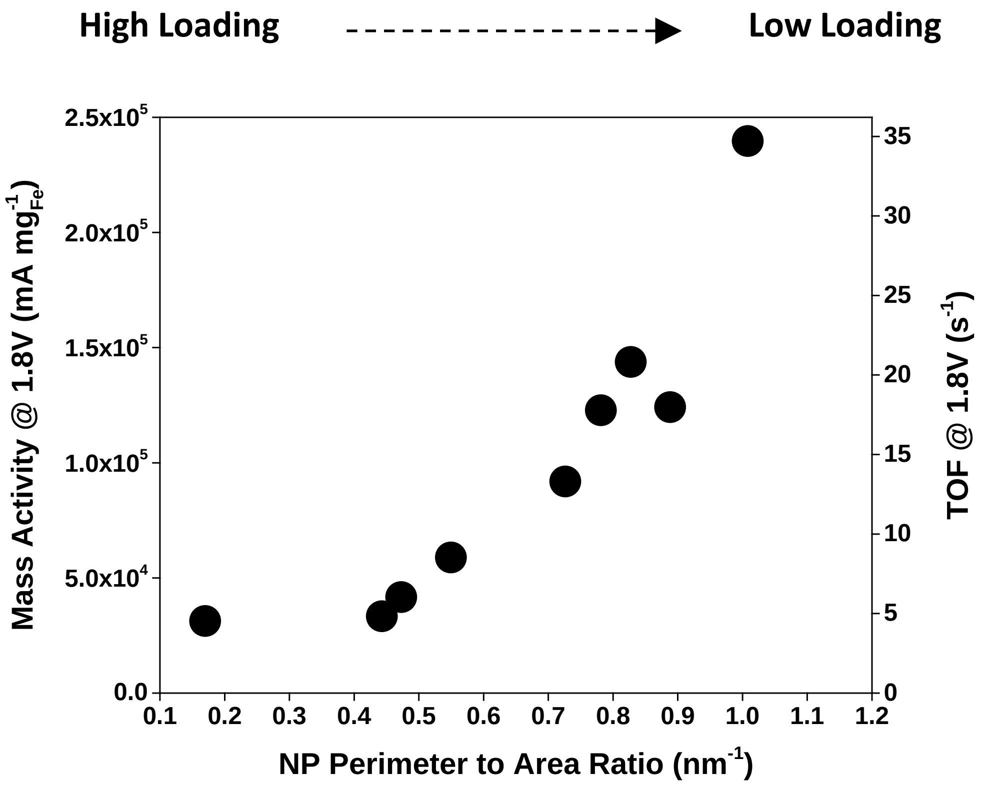
Kauffman , Deng, Sorescu; Manuscript in preparation

Combining Electrochemistry and Surface Science

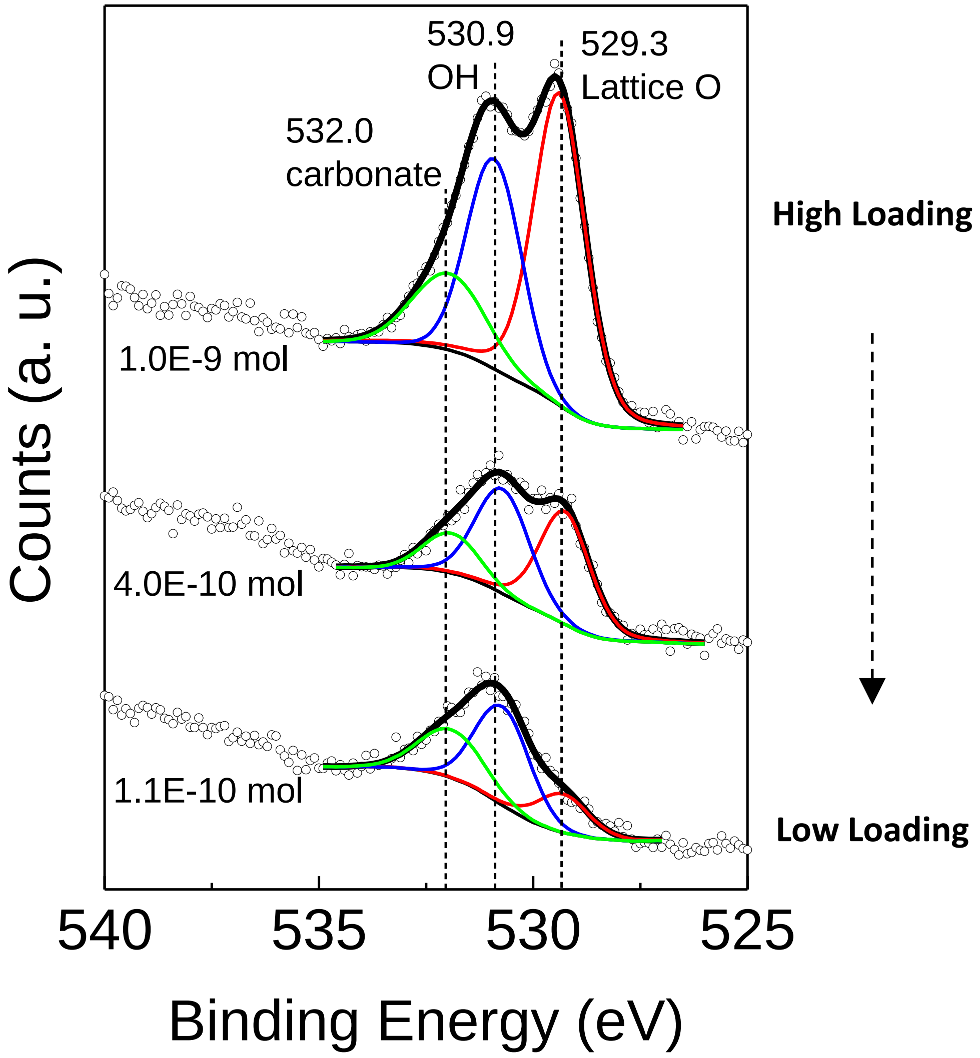


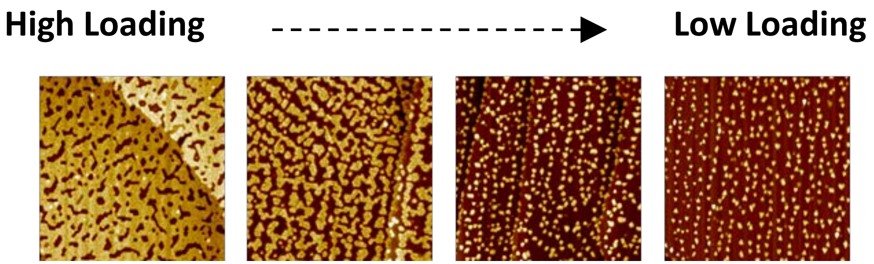


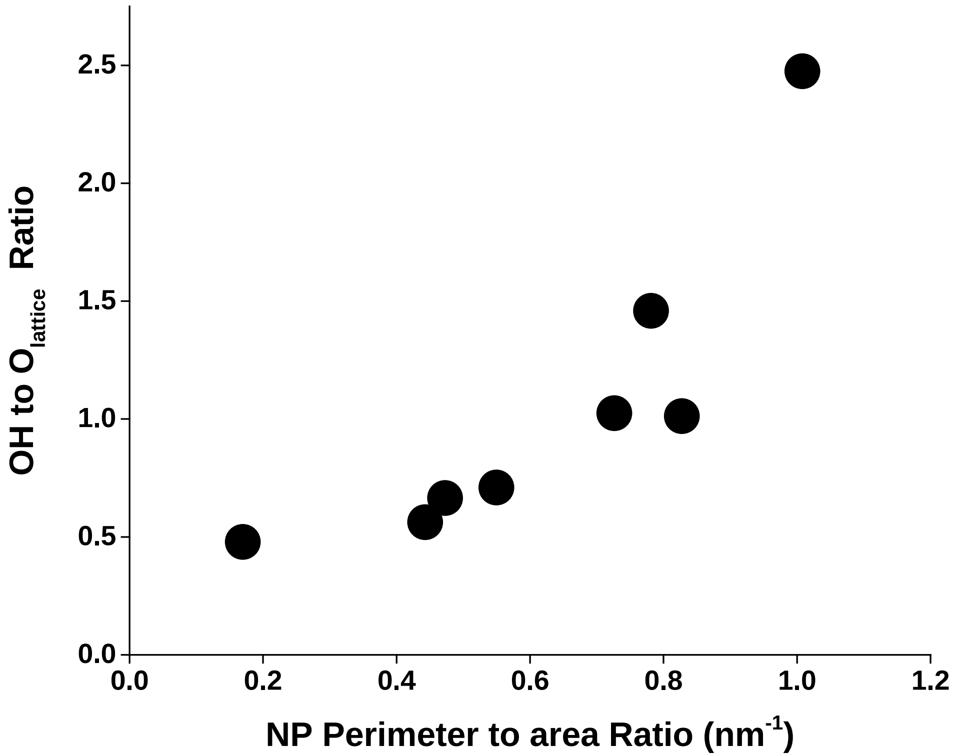


Kauffman , Deng, Sorescu; Manuscript in preparation

OH to $O_{lattice}$ ratio scales w/ perimeter site density



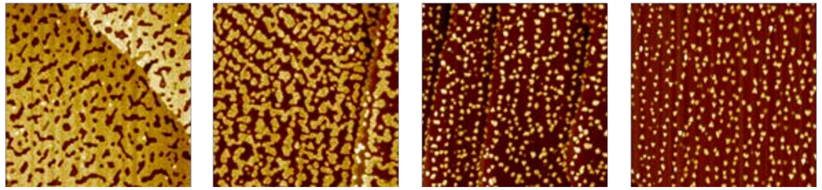


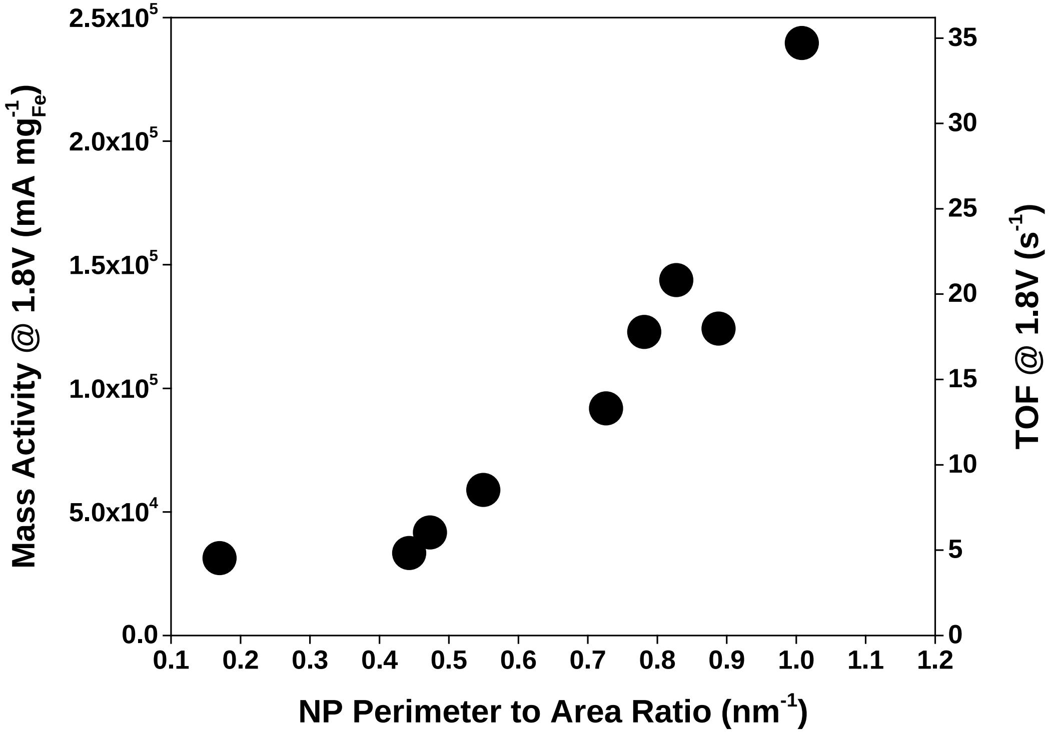


Spectroscopic Signature of OER Active Sites: Perimeter Fe sites

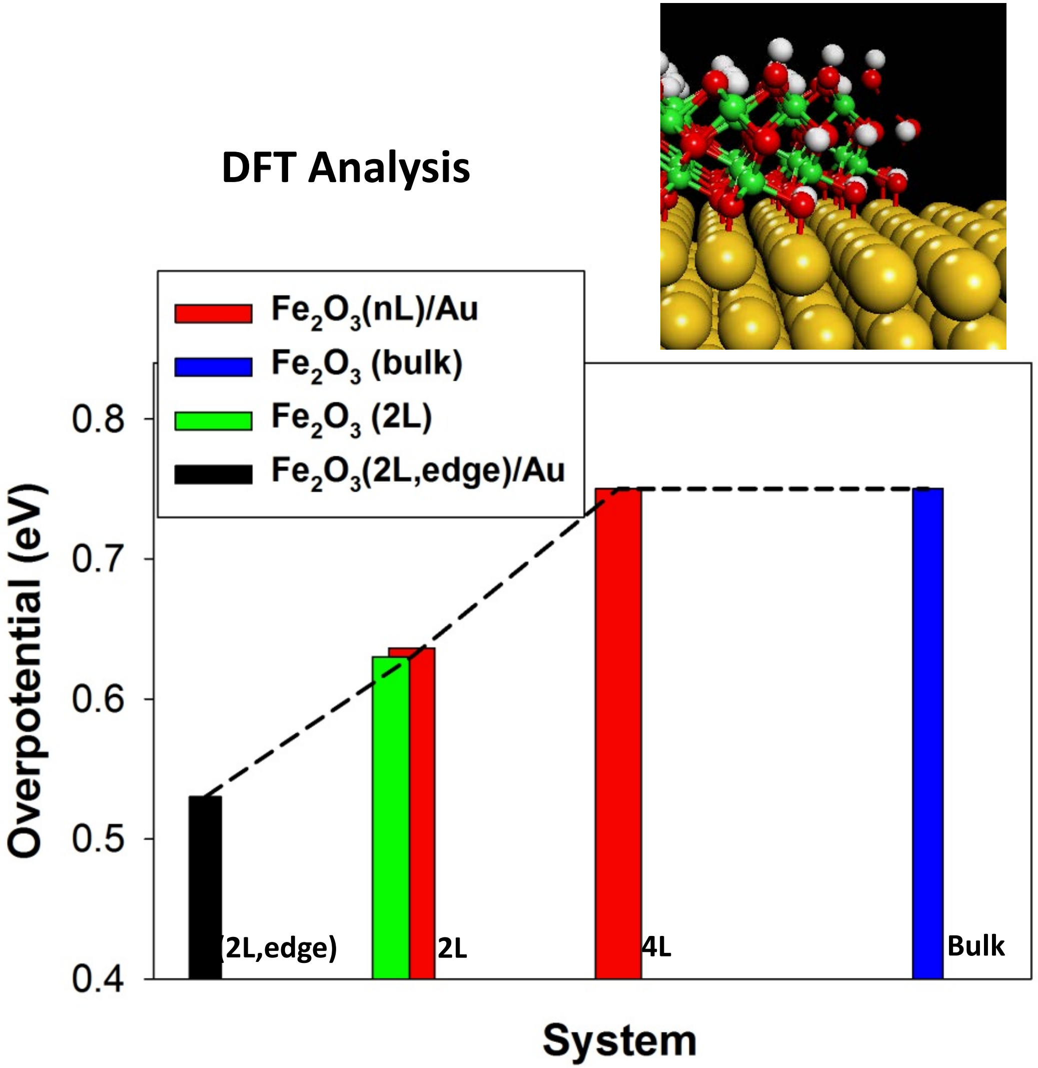
Combining Electrochemistry and Surface Science

High Loading → Low Loading





DFT Analysis



Perimeter Fe Sites are O_2 Evolution Reaction Centers

Conclusions and future efforts

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1. **Developing a variety of approaches for catalyst design**
   - Precise identification of structure-property relationships
   - Couple with DFT modeling

2. **In situ X-ray characterization (XANES, EXAFS, XRD, XPS)**
   - Provide information on structure and chemical properties during reaction
   - Refine DFT models

3. **Incorporate into realistic reactor architectures**

4. **New concepts (next year's presentation) … microwave-assisted thermal catalysis**

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