Combining Experiment and Computation to Design CO_2 Conversion Nanocatalysts

NATIONAL ENERGY TECHNOLOGY LABORATORY

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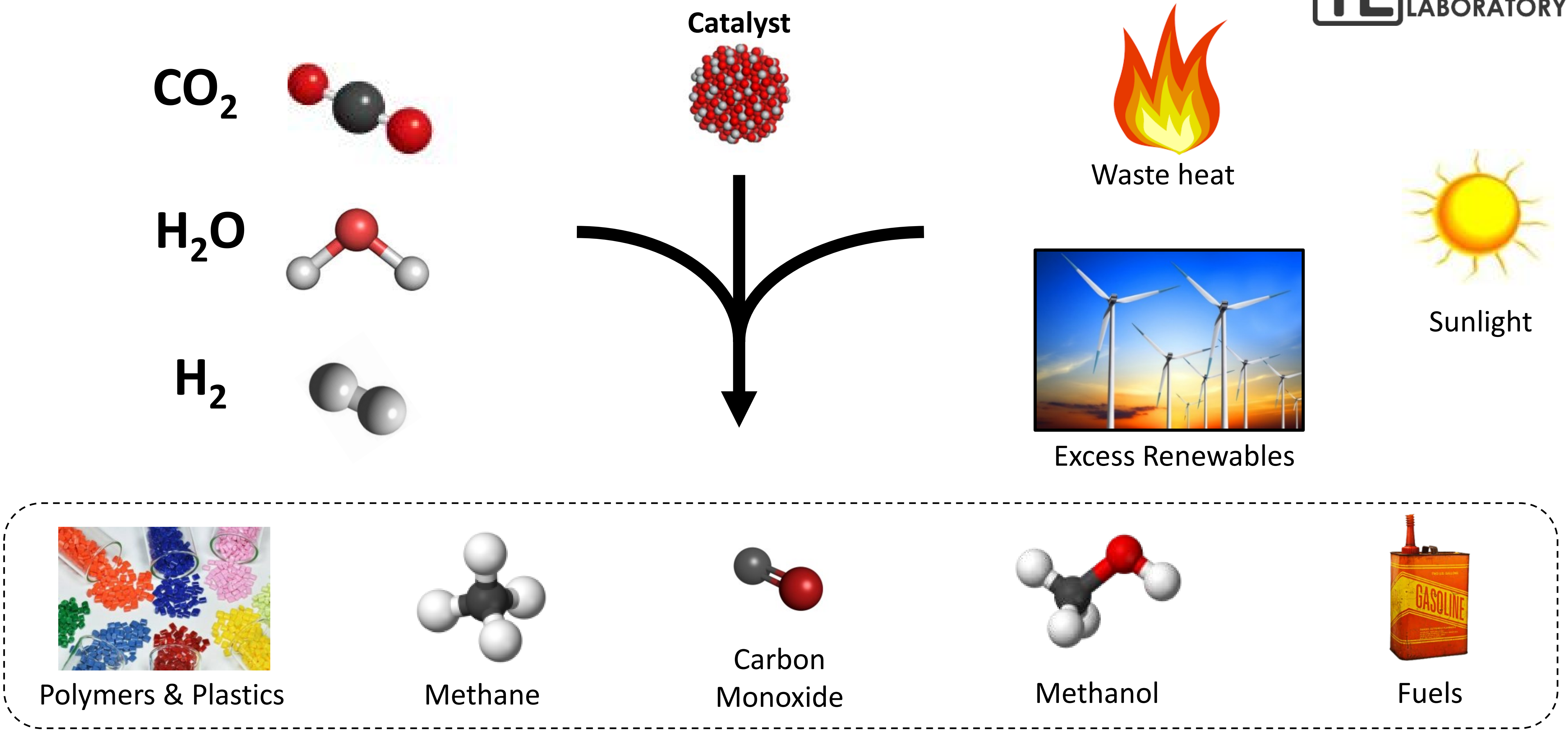
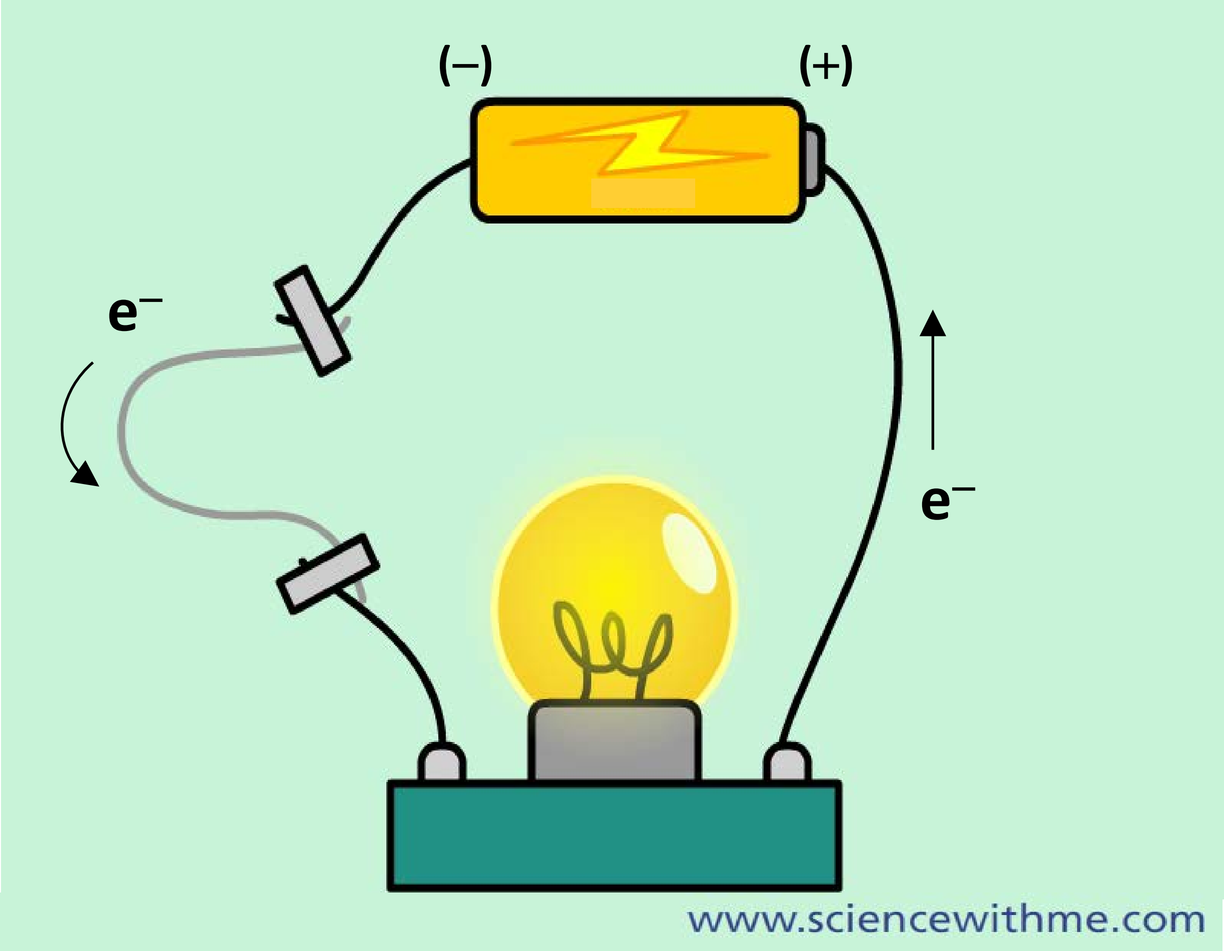
NETL Materials Research: Creating Value from Waste CO_2



General Approach: Electrochemical CO_2 Conversion

Electrochemistry moves electrons



General Approach: Electrochemical CO_2 Conversion

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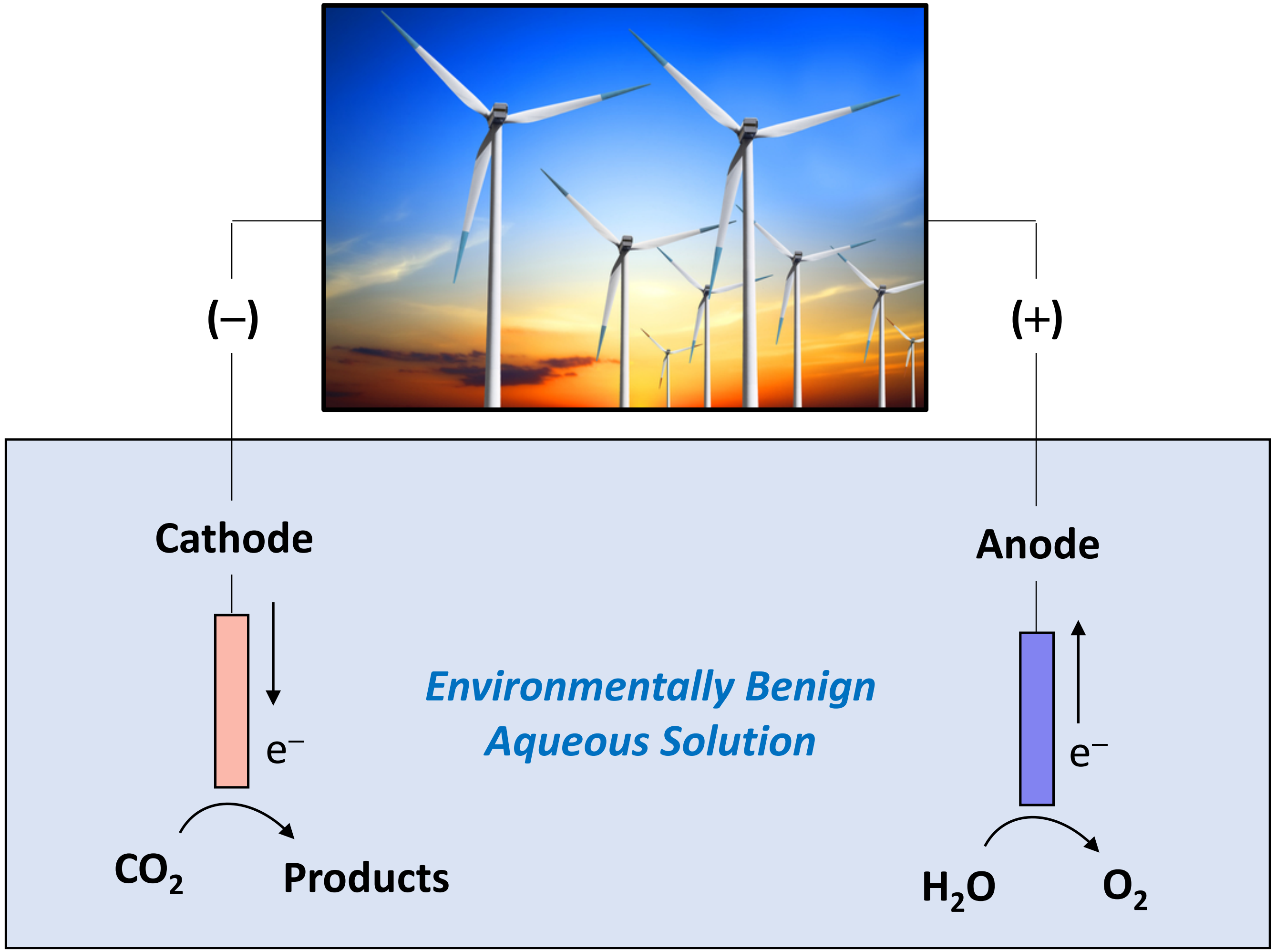
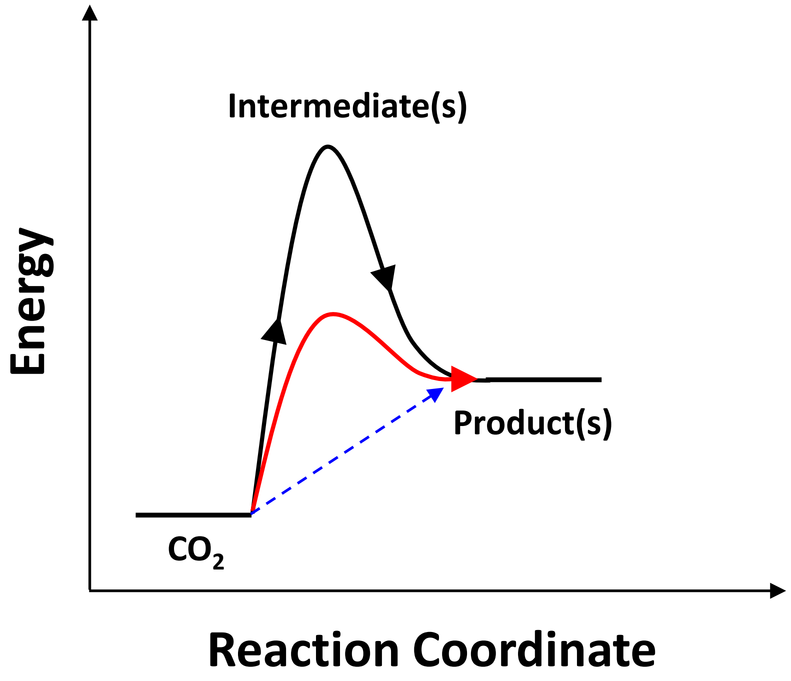
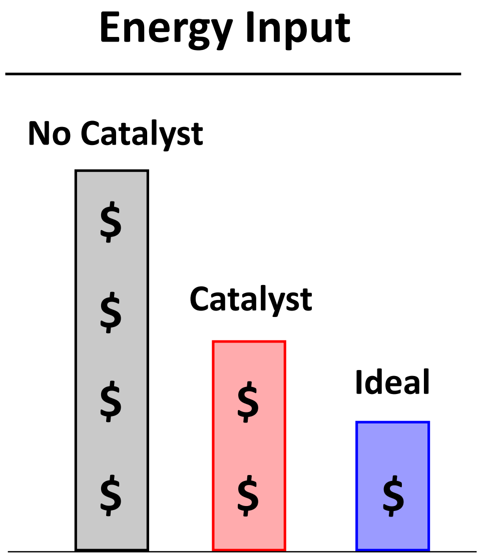
Use carbon-free electrons to convert CO_2 !



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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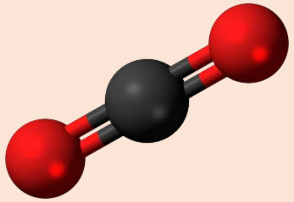
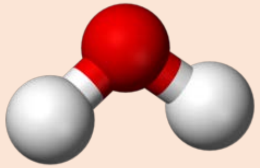
CO_2



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

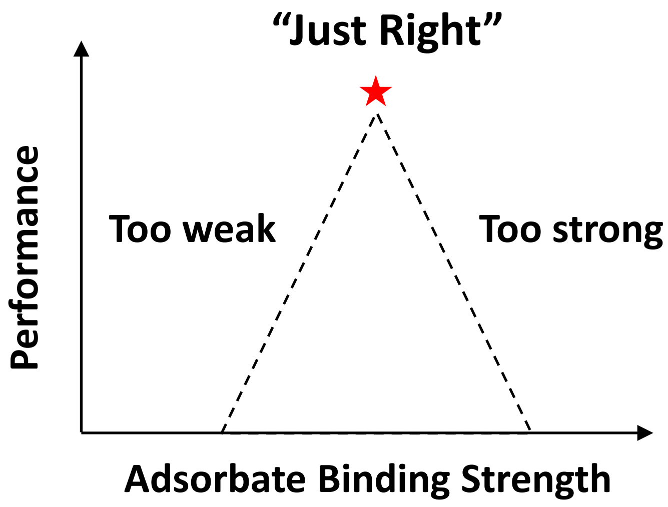
↑ Industrial Chemicals

Designing CO_2 Electrocatalysts

Can we reduce Au content or tune product selectivity?

★ **Molecular Binding Impacts: energy input, reaction rates, efficiency, selectivity and stability** ★

Sabatier Principle



Typical materials contain a mixture of shapes, sizes and "colors". Hard to identify which "piece" is doing what.

Designing CO_2 Electrocatalysts

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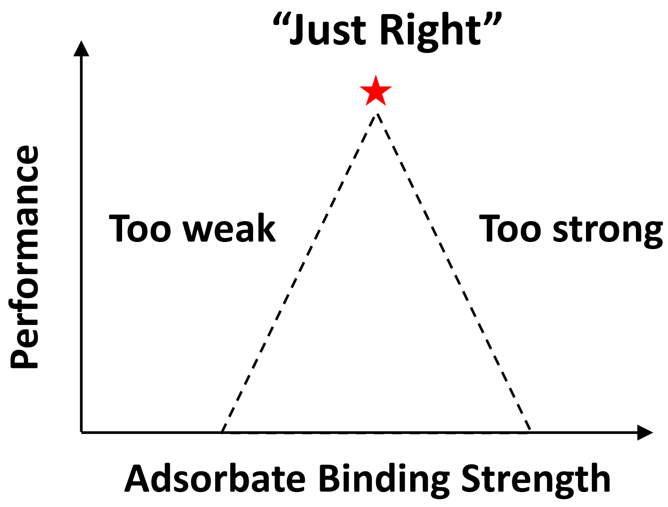
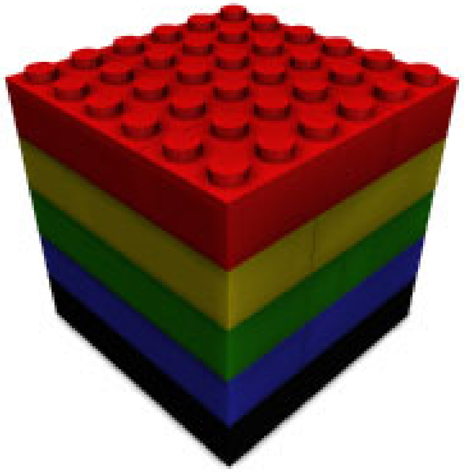
Sabatier Principle



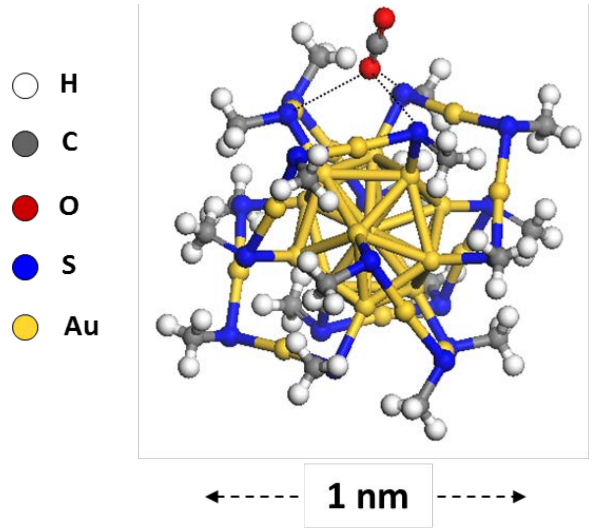
Design well-defined nanocatalysts to understand and eventually *control* chemistry



Previous Success with Ligand-Capped Nanocatalysts

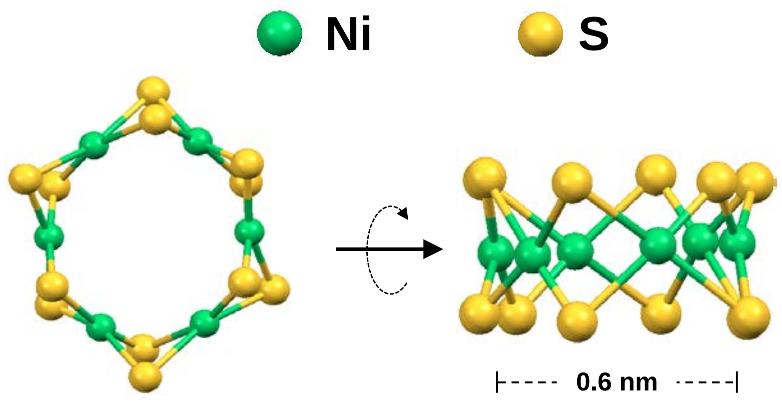
Ligands control catalyst structure and tune reactivity

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



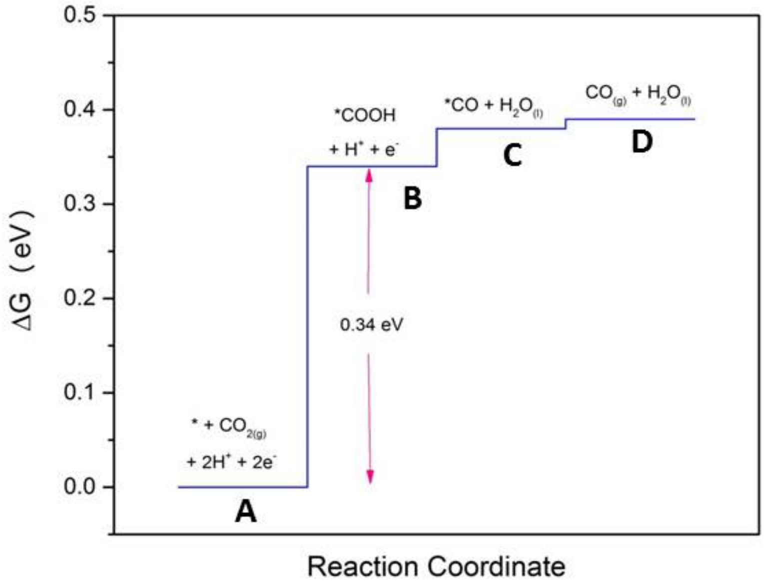
Extremely active CO_2 reduction catalyst

$Ni_6(SR)_{12}$ Nanocatalyst



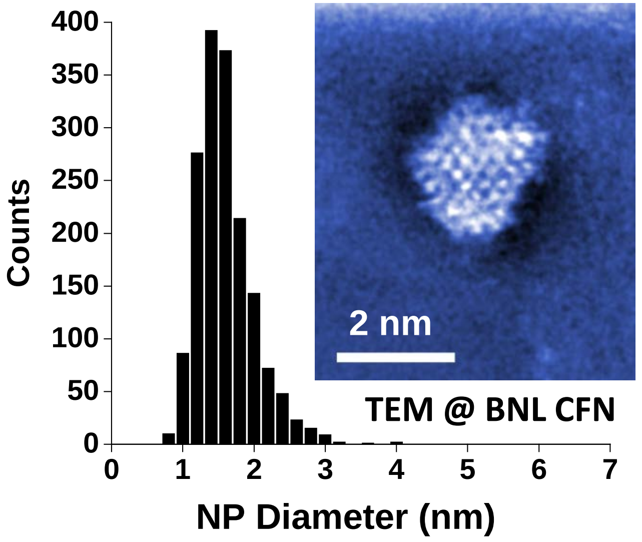
Extremely active water oxidation catalyst

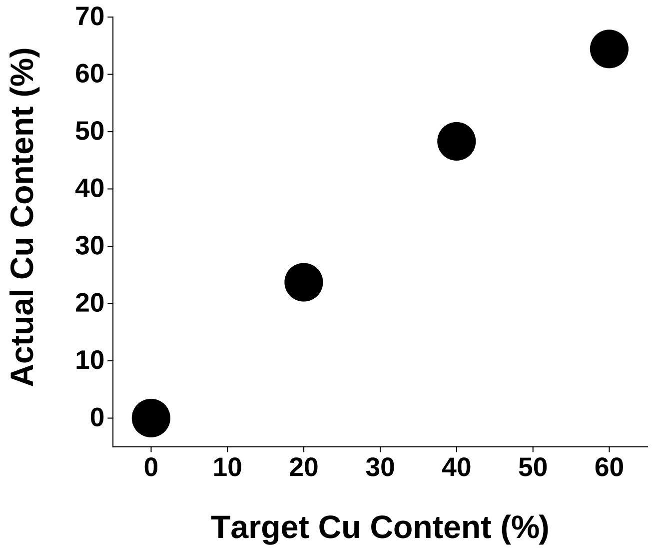
Atomic Level Computational Electrochemistry (DFT)

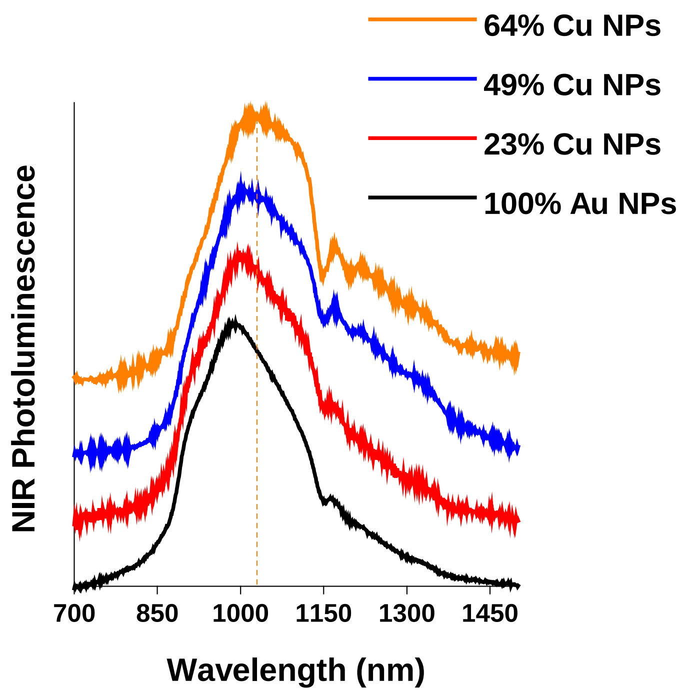


J. Am. Chem. Soc. 2012; J. Phys. Chem. Lett. 2013; Chemical Science 2014; ACS Applied Materials and Interfaces 2015; J. Chem. Phys. 2016; ACS Catalysis 2016; MRS Commun. 2017, US Patent 9,139,920.

Ligand Capped Au/Cu Nanoparticles



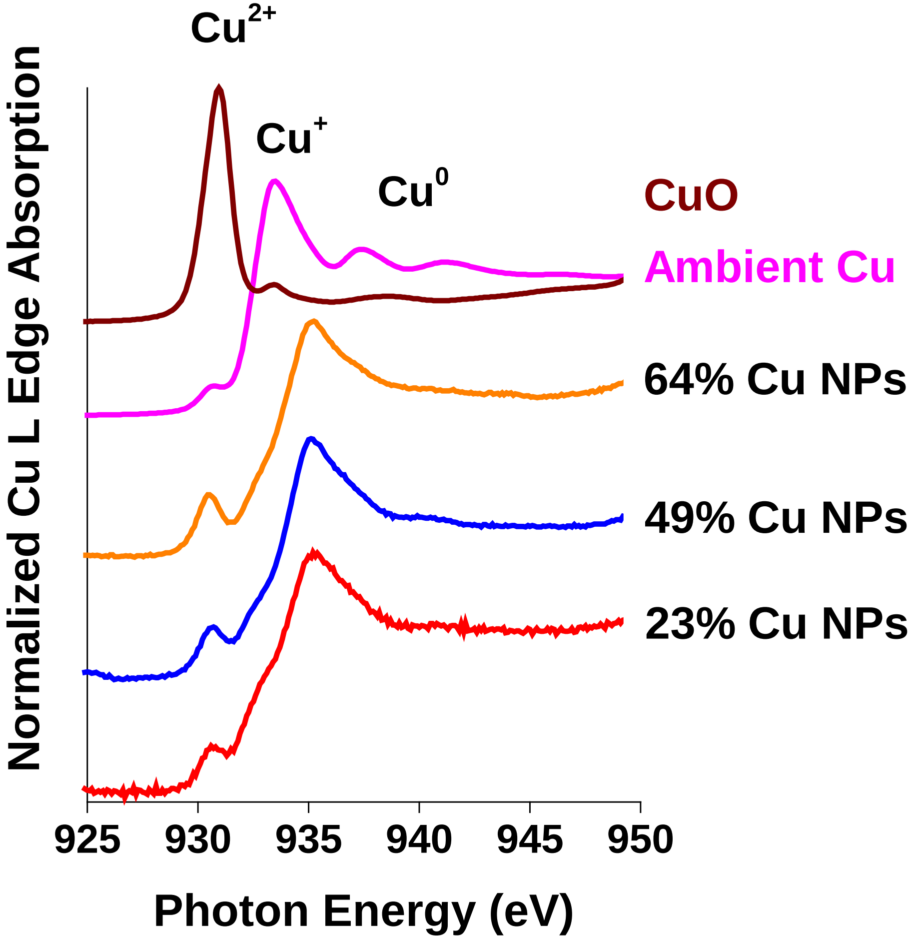




Strongly bound thiol ligands, narrow size distribution, controlled composition near infrared photoluminescence: Cu incorporation into NP

Kauffman *et al.* **2017**, *submitted for publication*

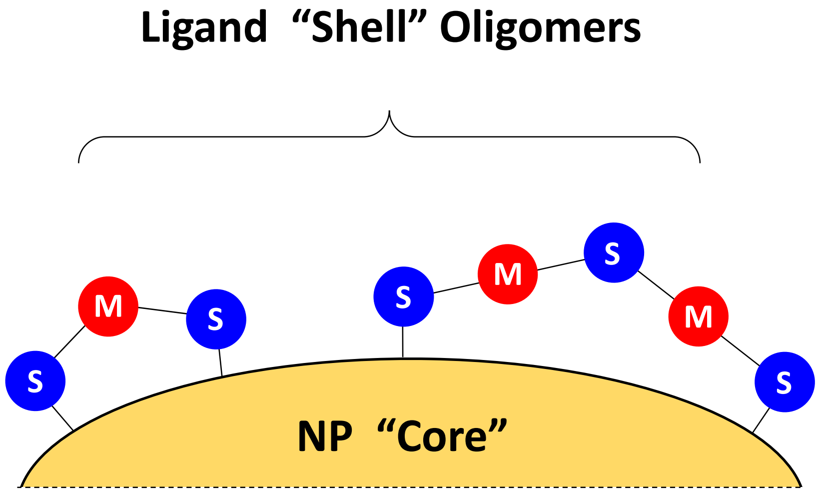
Cu L-edge X-ray Absorption Spectroscopy

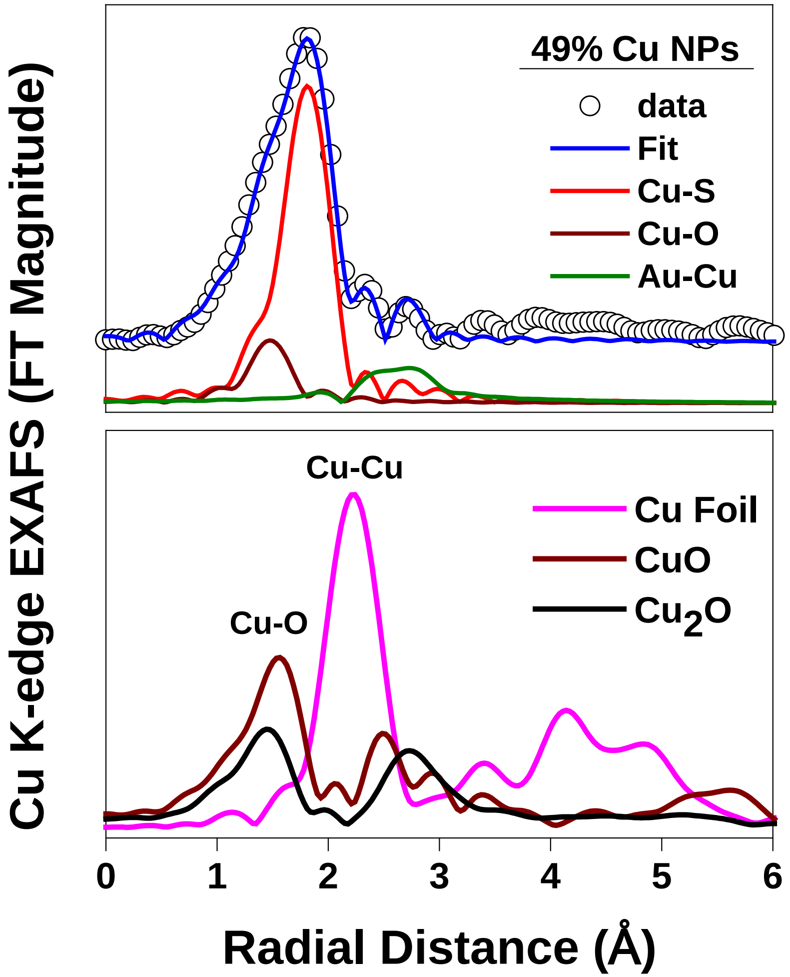


- **NPs contain mostly Cu^{+} with minor Cu^{2+}**
  - consistent with lab-based XPS and Auger
- **Upshifted from bulk Cu-oxide**
  - Copper-sulfur interactions
  - Confirmed with sulfur L-edge XAS
- **Thiol ligands preserve unique Cu^{+} species**
  - Ligand-free Au/Cu NPs contain mostly Cu^{2+}

Structural Analysis using Hard X-ray Spectroscopy

Small, thiol-capped NPs contain unique surface structures

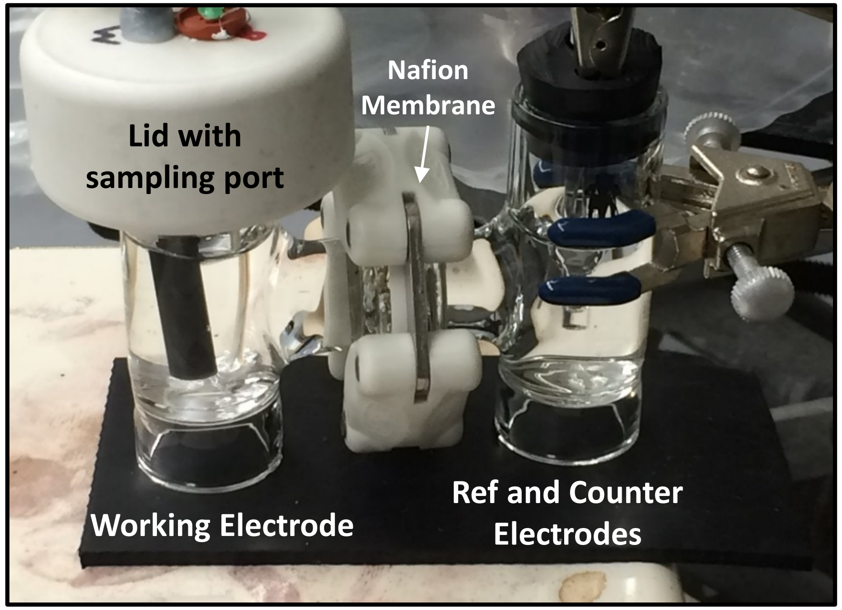




CO_2 Conversion Product Distributions

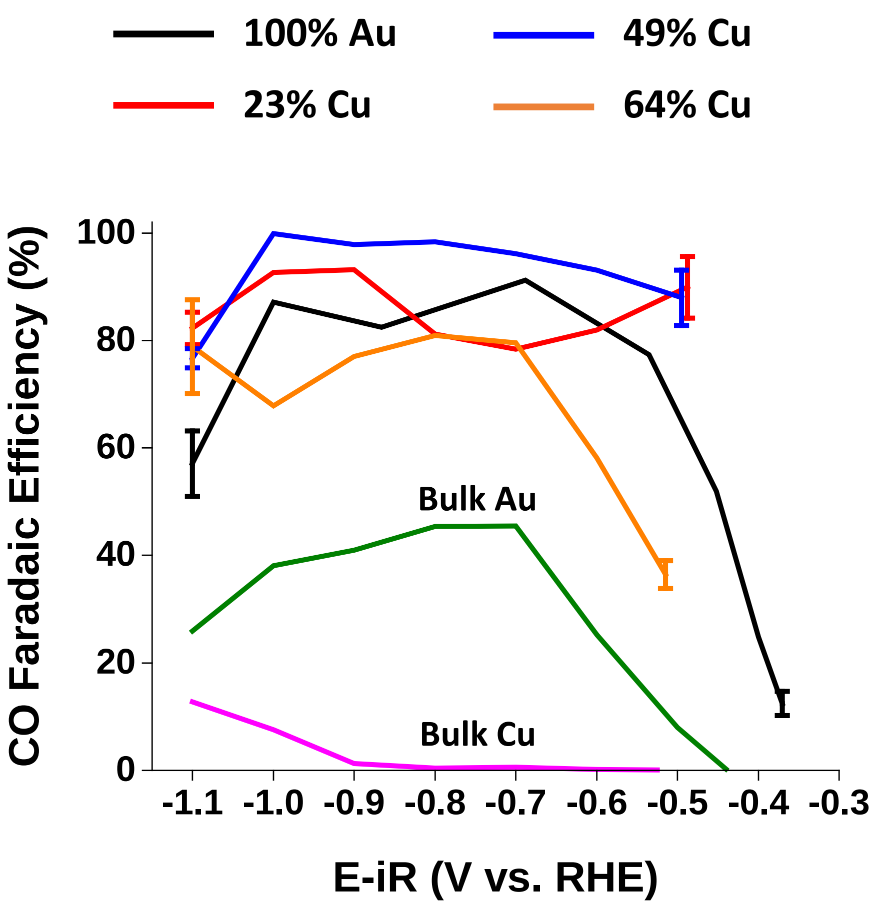
Timed injections

CO_2 in (20 sccm) → Effluent gas → Gas Chromatograph



Quantify electrolysis charge *vs.* product formation

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO + H_2$$

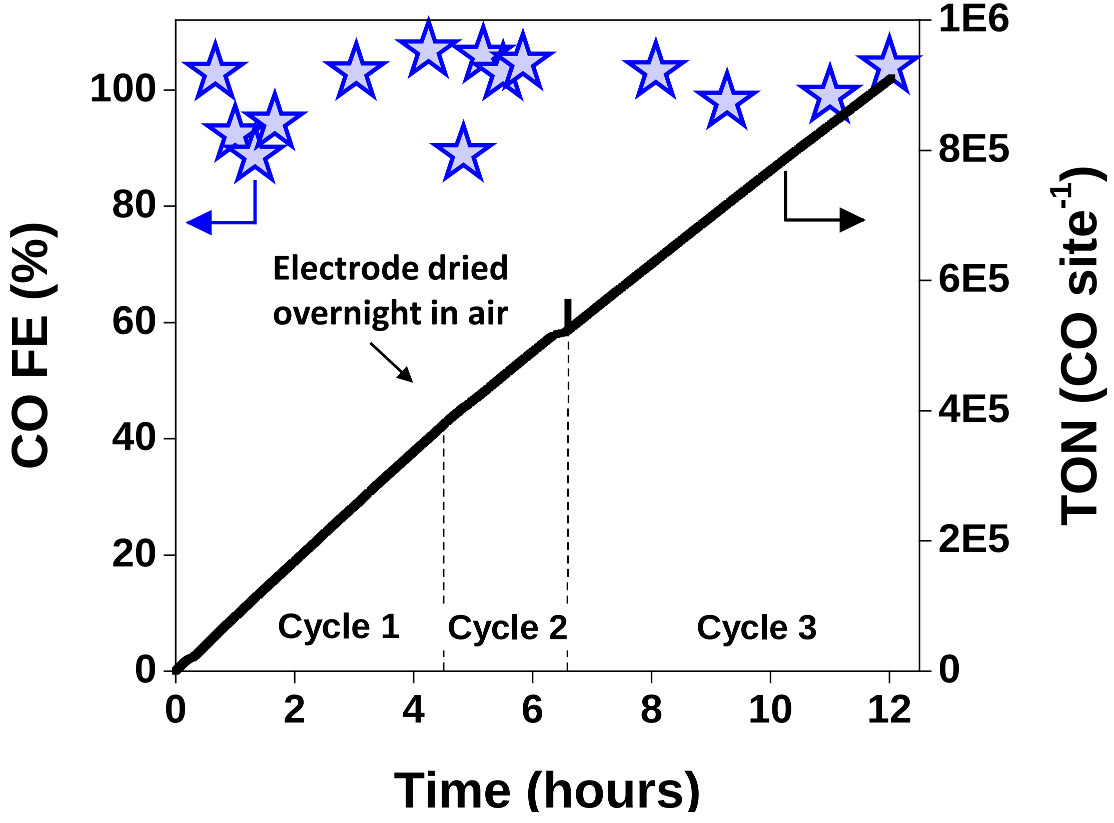


Post-reaction analysis confirmed NP stability

Ligand Free Au/Cu NPs show drastically different products

Long Term Performance

49% Cu NPs produced 4-8 times higher performance than 100% Au NPs



Stable performance at -0.8V *vs.* RHE

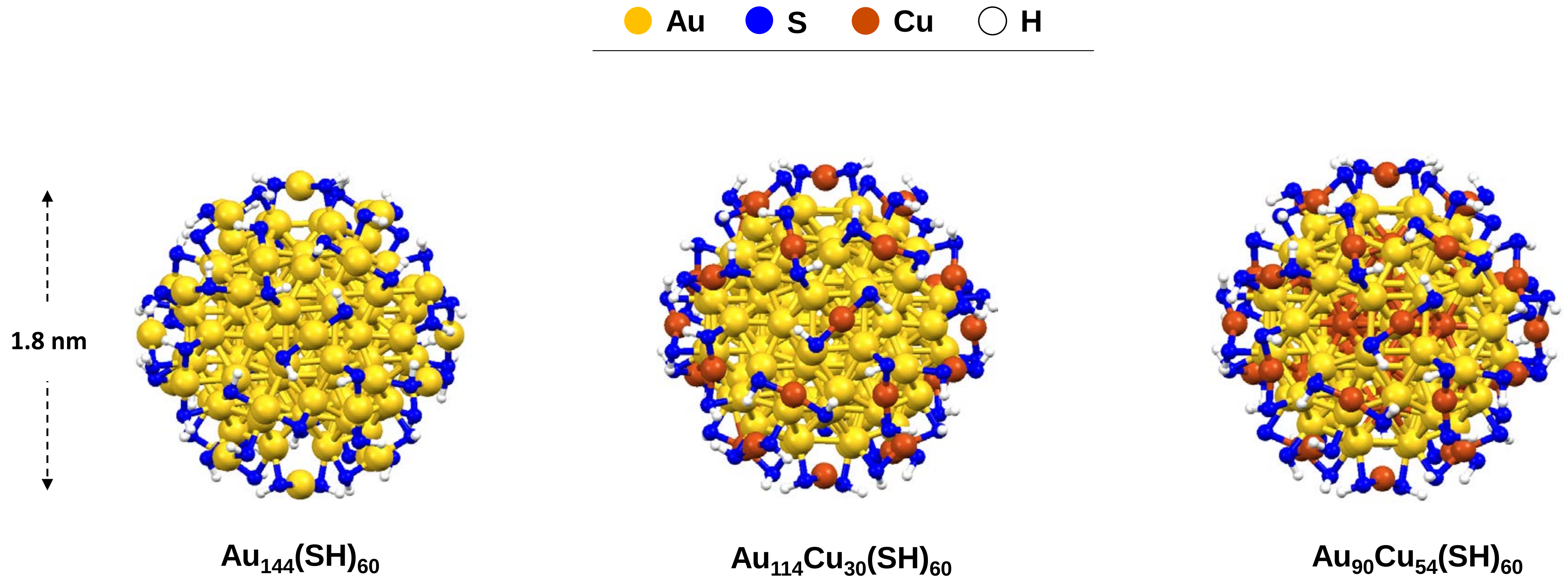
- 100% CO selectivity…no H_2
- 100 ± 6% CO FE
- 911,000 CO $site^{-1}$
- 22 ± 3 CO $site^{-1}$ s^{-1}
- 9 ± 1 mA cm^{-2}_{metal}

★ Mass transfer limitations

★ Reactor design

Computational Electrochemistry

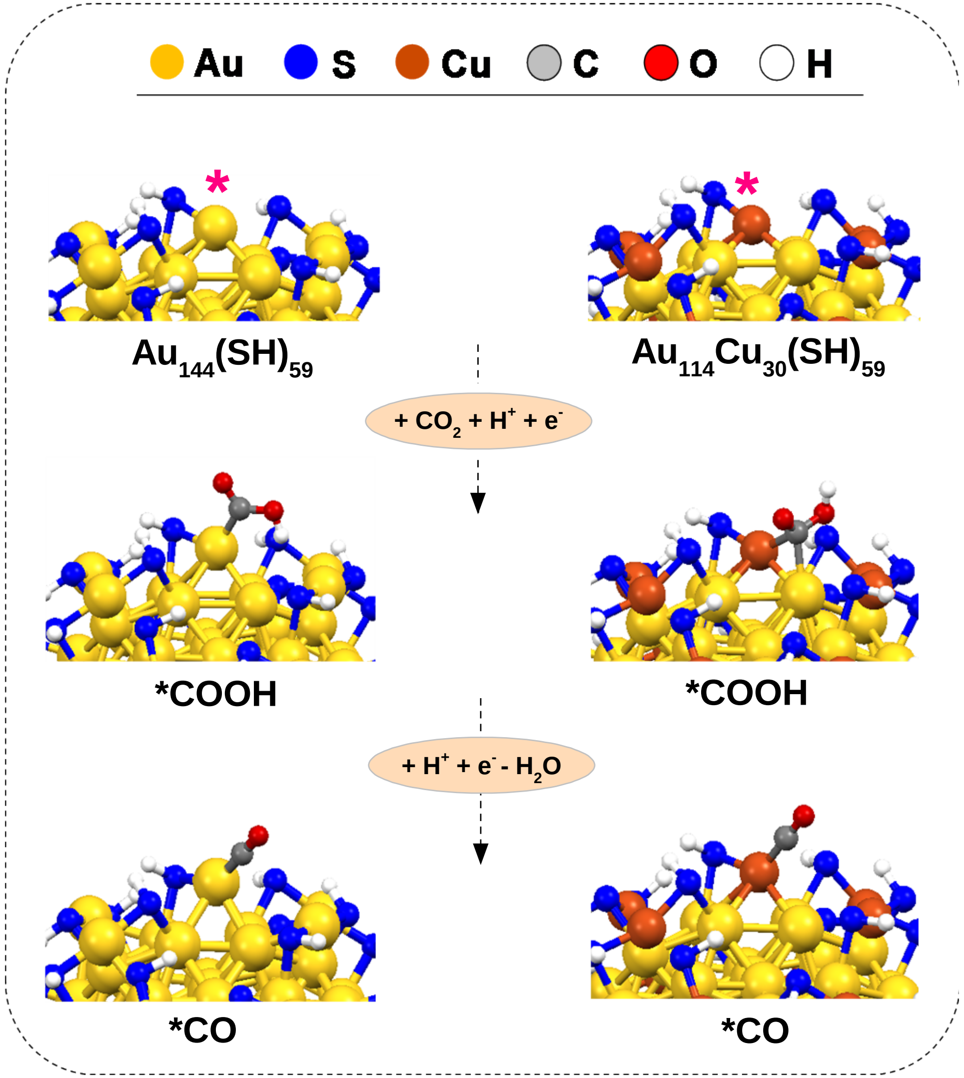
Why does copper improve performance?

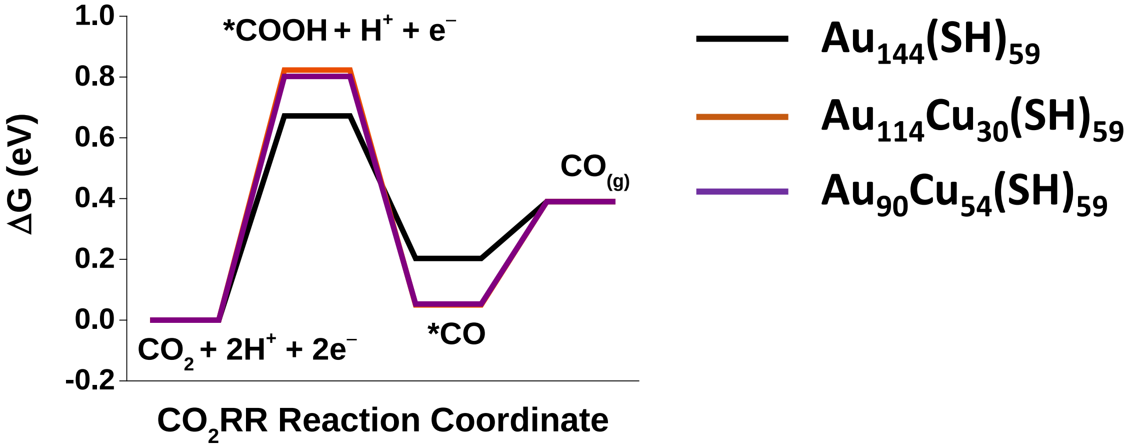


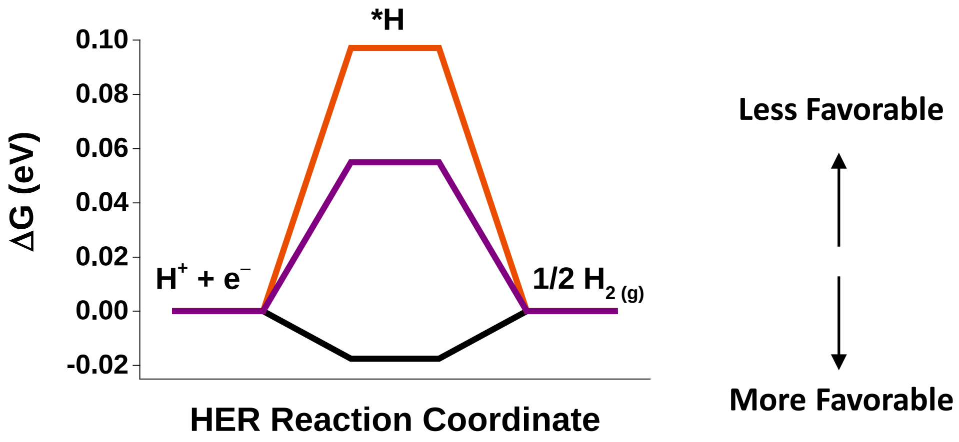
Kauffman *et al.* **2017**, *submitted for publication*

Model from Hakkinen, *J. Phys. Chem. Lett.* 2015, *6*, 515−520

Computational Electrochemistry



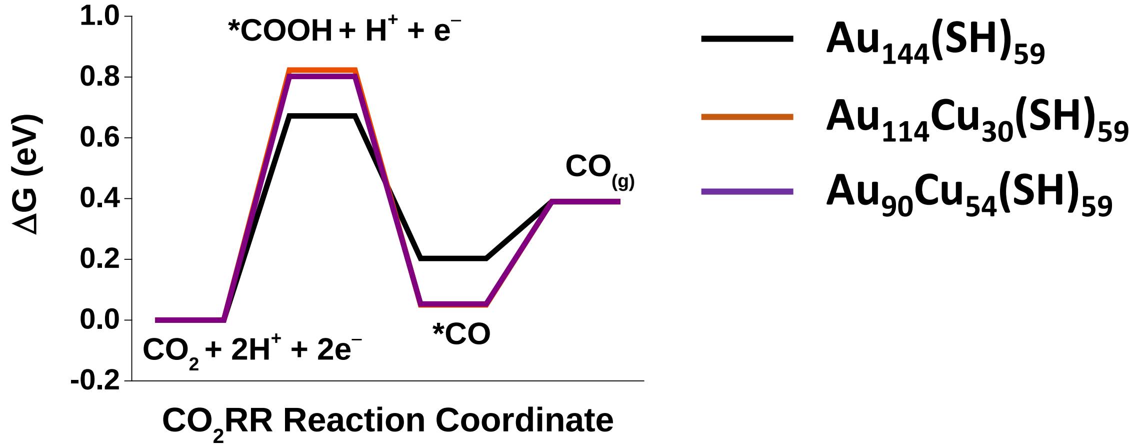




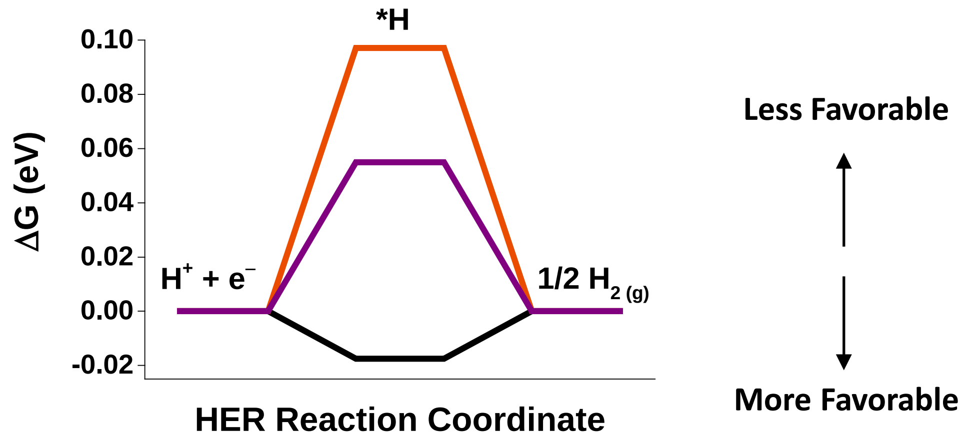
Kauffman *et al.* **2017**, *submitted for publication*

Computational Electrochemistry

- **Cu sites enhance CO_2 reduction**
  - Better stabilize *CO intermediate
  - Inhibit *H formation
  - Possible H_2 increase at very high Cu content
  - *experimentally confirmed



- **Ligand Free Au/Cu NPs show stronger intermediate binding**
  - Likely H_2 and hydrocarbon production
  - *experimentally confirmed



Conclusions and Moving Forward

1. Combining experiment and computation reveal atomic-level design considerations

2. Ligands allow us to "atomically engineering" the nanocatalyst surface structure

3. Copper-thiol groups improve reaction rates and product selectivity compared with ligand-protected gold nanoparticles

4. Intentional ligand removal allowed particle growth, less efficient CO_2 reduction, and wider product distribution due to stronger *CO and *H binding

5. Need to incorporation into realistic reactor architectures

We welcome any suggestions and/or collaborations!

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The End!

Questions or Comments?