NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

Catalytic Transformation of CO_2 to C1 Products

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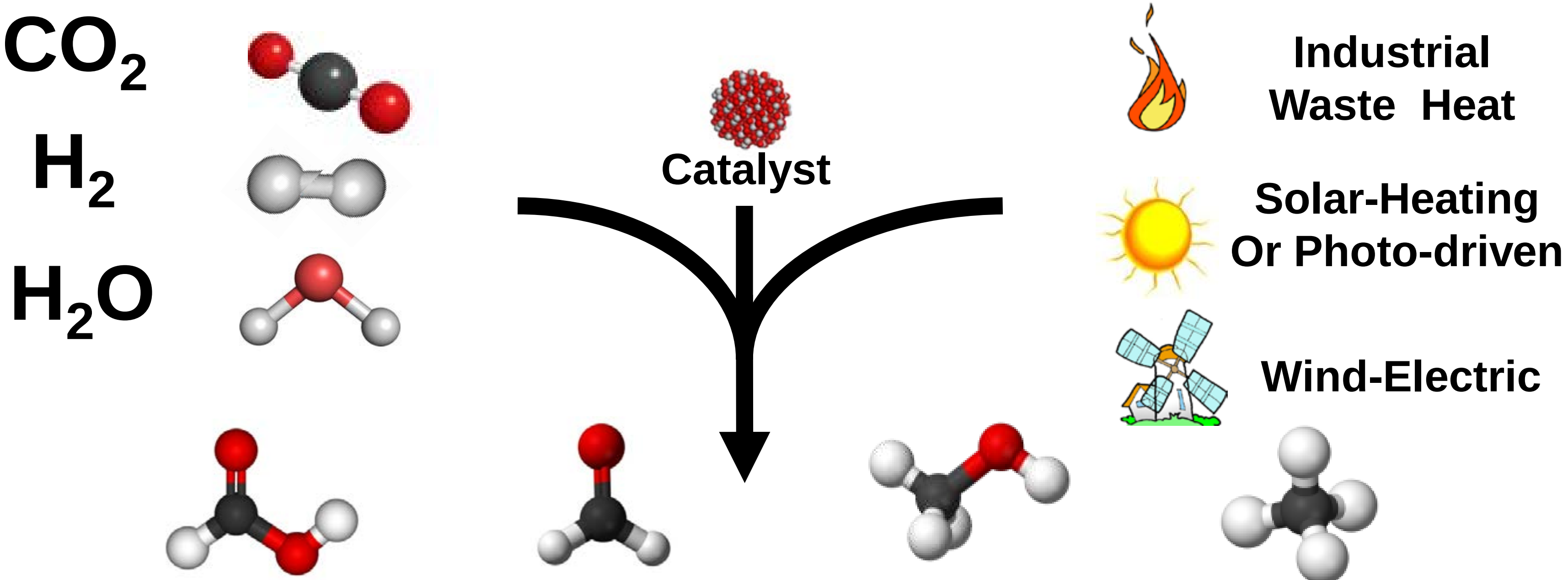
NETL-RUA: James Lewis (WVU), Ronchao Jin (CMU), Ken Jordan (PITT), Sittichai Natesakhawat (PITT)

DEPARTMENT OF ENERGY • UNITED STATES OF AMERICA

CO_2 Conversion to C1 Industrial Chemicals



CO_2

H_2

H_2O

Catalyst

Industrial Waste Heat

Solar-Heating Or Photo-driven

Wind-Electric

	Formic Acid	Formaldehyde	Methanol	Methane
Approx Yearly Market	25 K Ton[1] ($25 M)	3 M ton ($720 M)	3.6 M ton ($1440 M)	484 M ton ($210,000 M)
Uses	Leather, Pulp	Urea Resins Phenol Resins	Fuel/MTG Formaldehyde	Fuel Acetic Acid

[1] Global Formic Acid Market: 0.5 M Ton ($750 M)

Project Structure

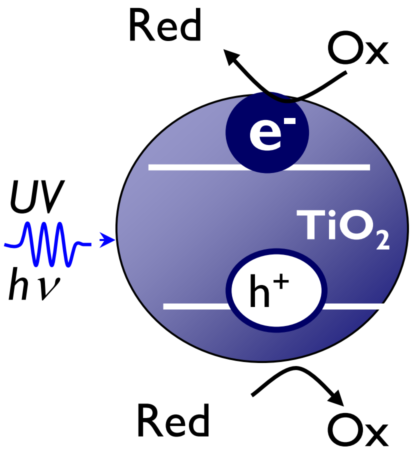
- **Photocatalytic Systems**
  - **Heterostructured Photocatalysts for CO_2 Reduction**
  - Symmetry Breaking and High Throughput Computational Screening of Delafossites for the Photocatalytic Reduction of CO_2
  - Scanning Tunneling Microscopy and Dispersion-corrected Density Functional Theory Studies of TiO_2 Surfaces

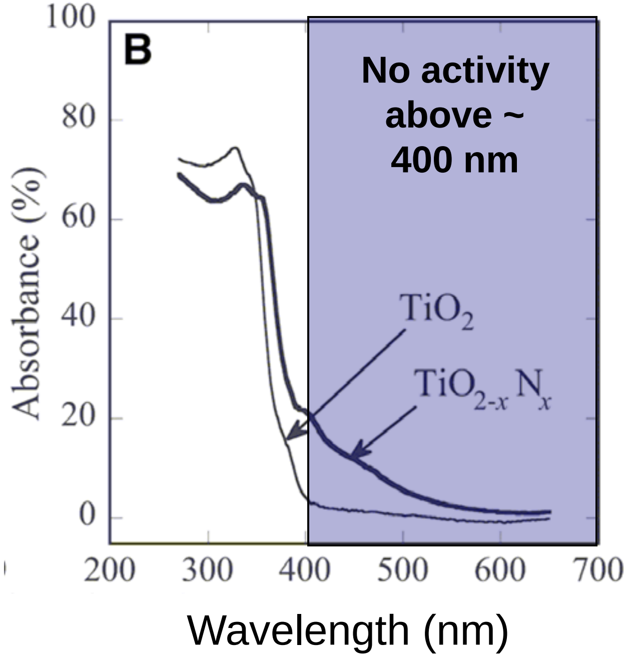
- **Electrocatalytic Systems**
  - **Electronic Structure and Catalytic Activity of Au_{25} Clusters**

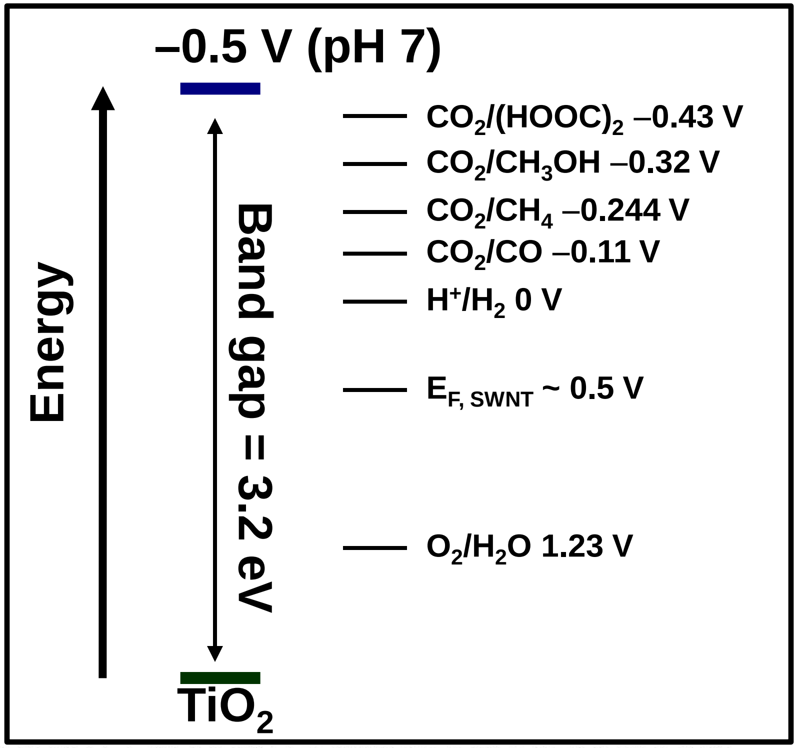
- Thermal Catalytic Systems
  - Atomic Structure and Catalytic Activity of Cu/ZnO-Based Materials

Technical Barriers for CO_2 Utilization Photocatalysts

- **Poor optical activity in visible & infrared**
- **Rapid recombination of e^- & h^+ pairs prevents useful redox photochemistry**
- **Slow CO_2 conversion kinetics**
- **Difficulty controlling product selectivity**






–0.5 V (pH 7)

Energy

Band gap = 3.2 eV

$CO_2/(HOOC)_2$ –0.43 V

CO_2/CH_3OH –0.32 V

CO_2/CH_4 –0.244 V

CO_2/CO –0.11 V

H^+/H_2 0 V

$E_{F,\ SWNT}$ ~ 0.5 V

O_2/H_2O 1.23 V

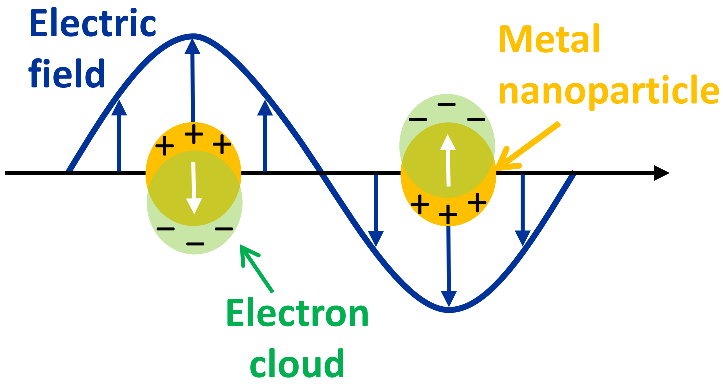
TiO_2

from R. Asashi et. al., Science, 293, 269 (2001)

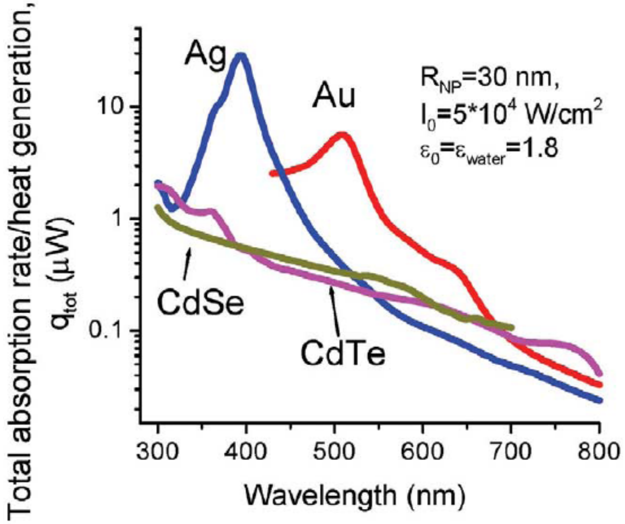
Plasmonic Heating in Heterostructures for Catalytic CO_2 Reduction

★ A “Hybrid” Photo- and Thermal-Catalytic Approach ★

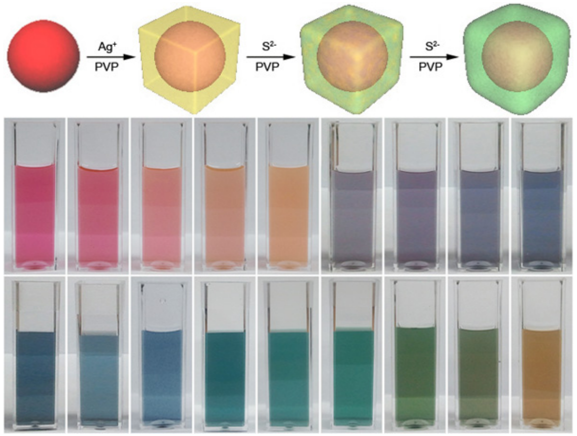
Light excites collective electron motions (Plasmons)



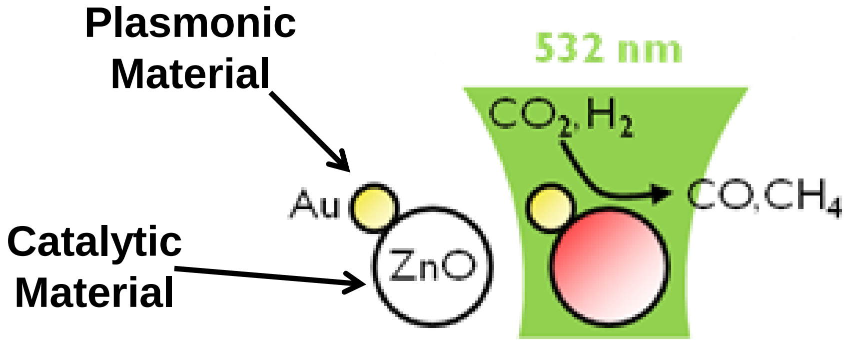
Light converted to Thermal energy (ohmic/joule heating)



Optical Activity Controlled by Size/Shape/Composition



Forming Heterostructures



S. Link, M. A. El-Sayed, *J. Phys. Chem. B* **103,** 4212 (1999); A. O. Govorov, H. H. Richardson, *Nano Today* **2**, 30 (2007), G. Park, D. Seo, H. Song, *Langmuir* **28**, 9003-9009 (2012)

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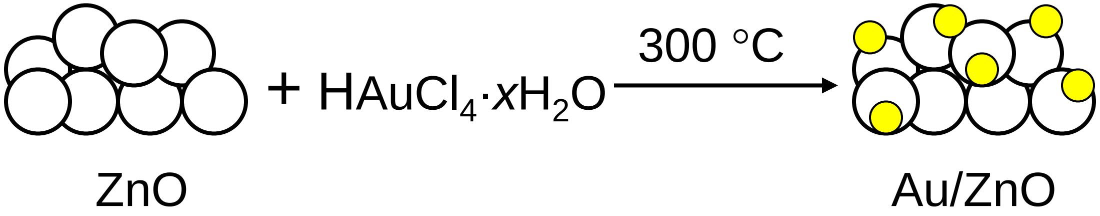
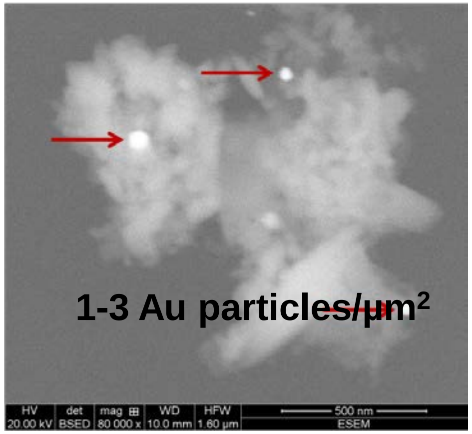
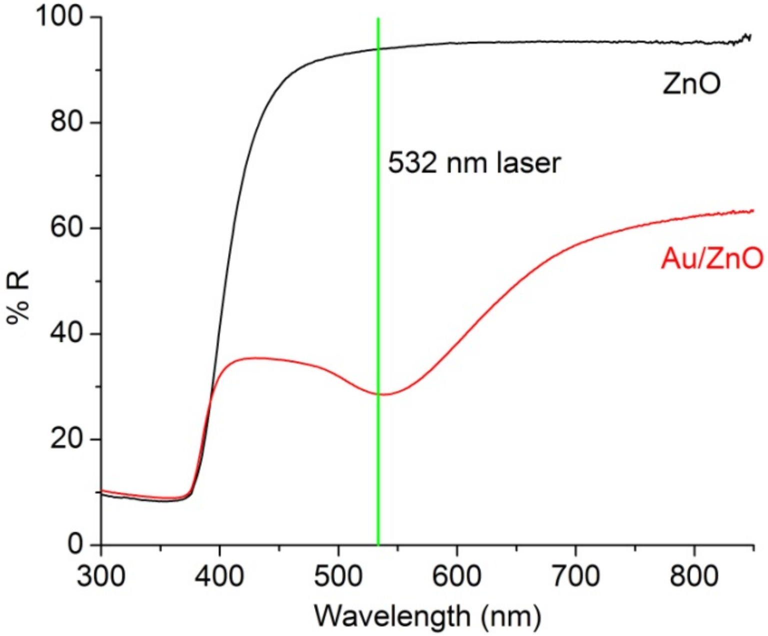
Synthesis and Characterization of Plasmonic Au/ZnO Heterostructured Catalysts



$\text{ZnO} + \text{HAuCl}_4\cdot x\text{H}_2\text{O} \xrightarrow{300\ ^\circ\text{C}} \text{Au/ZnO}$



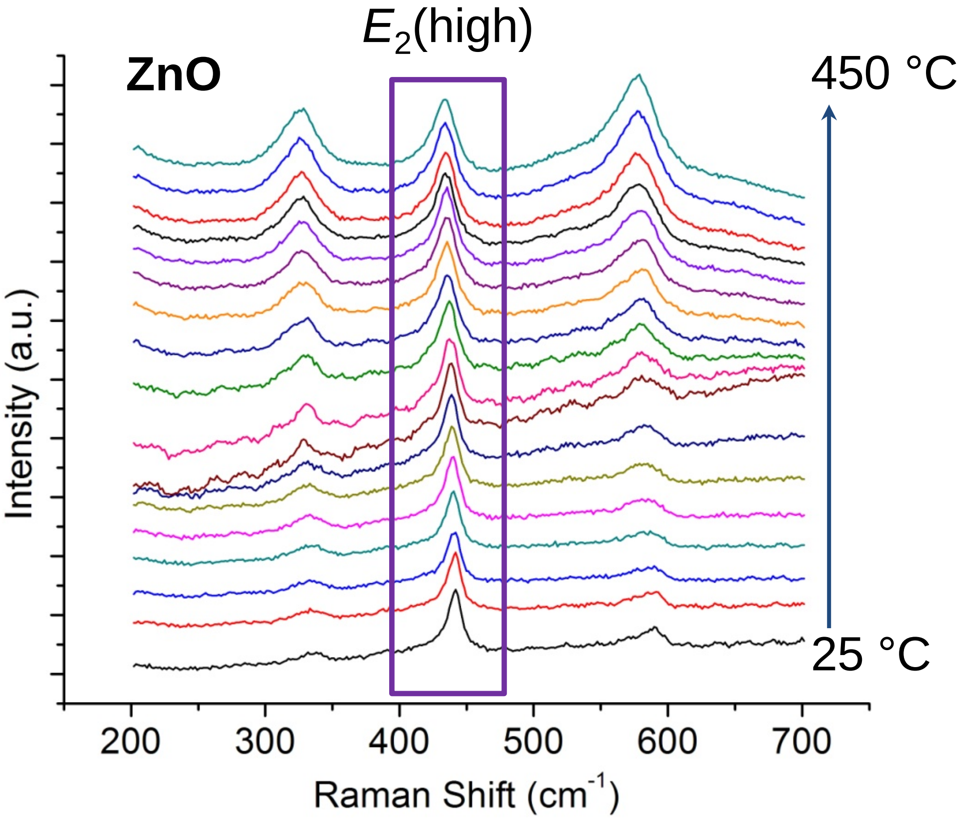
1-3 Au particles/μm^2

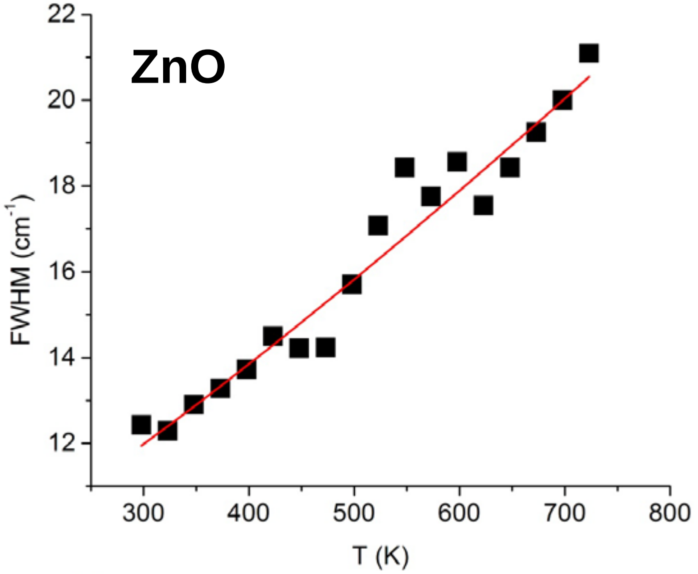


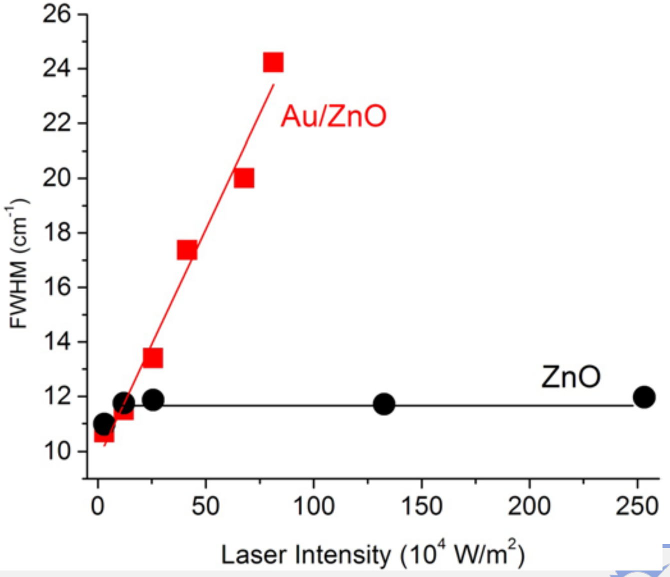
C. Wang, *et al.*, submitted (2013).

Raman Spectroscopy to Estimate Localized Plasmonic Heating

Temp dependent ZnO phonon peaks used to monitor temperature



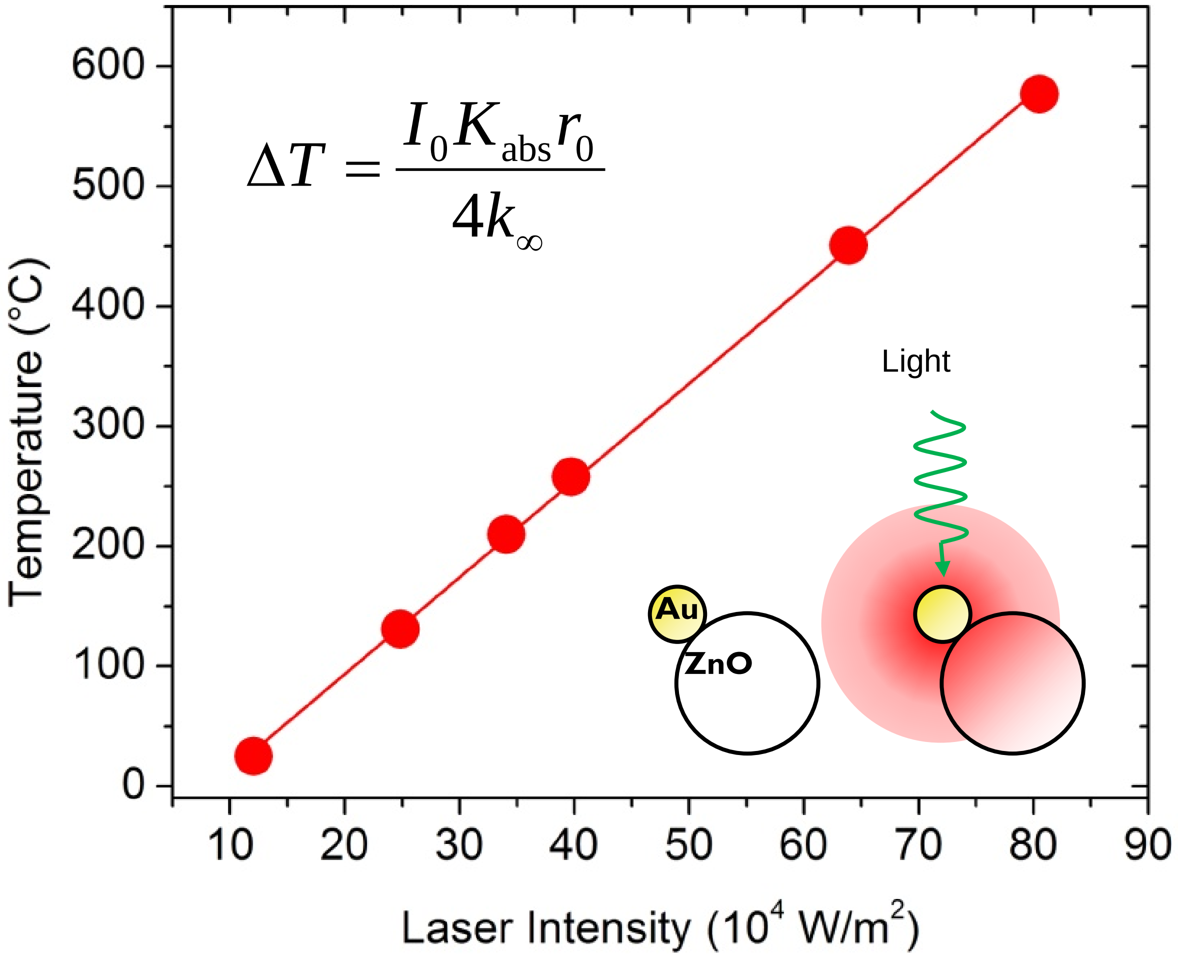




R. Cuscó, *et al.*, *Phys. Rev. B* **75**, 165202 (2007); H. K. Yadav, *et al.*, *Appl. Phys. Lett.* **100**, 051
et al., *Phys. Rev. B* **75**, 035208 (2007); J. Serrano, *et al.*, *Phys. Rev. Lett.* **90**, 055510 (2003); J.
Rev. B **29**, 2051 (1984).

How Hot? How Localized?

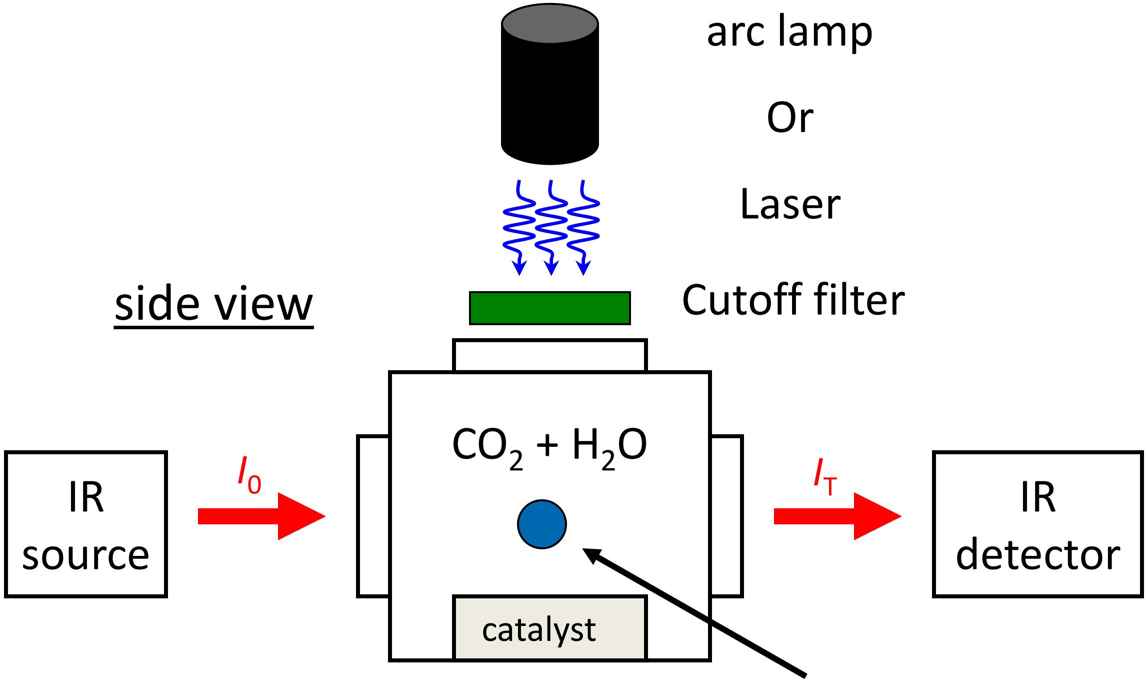
20 nm Au on ZnO Support



$$\Delta T = \frac{I_0 K_{\mathrm{abs}} r_0}{4k_\infty}$$

- **Surface of ZnO Support is Heated**
- **Sample Cell Still Cool to Touch**
- **Heating on/off in microseconds (or less)**

Photocatalysis Experiments for Activity Evaluation



side view

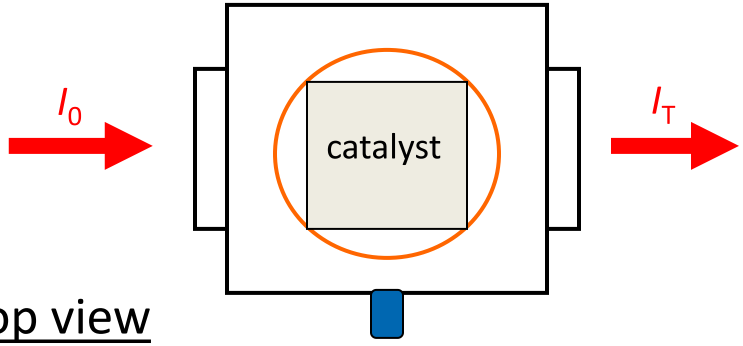
300 Watt Xe arc lamp

Or

Laser

Cutoff filter

Gas sampling port for GC analysis

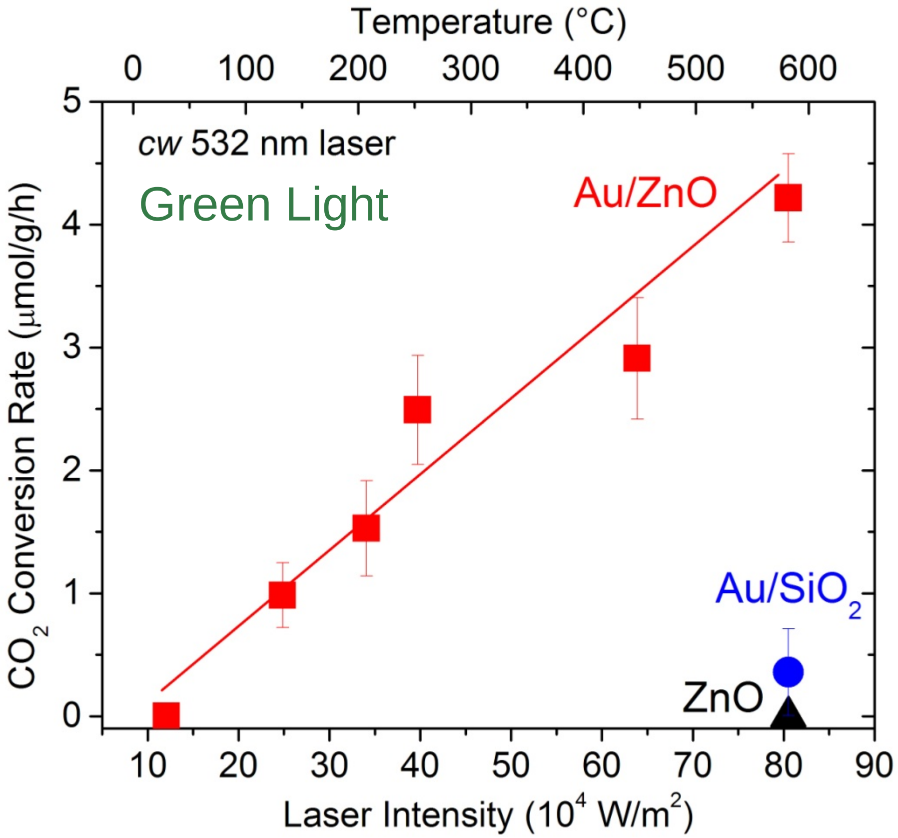


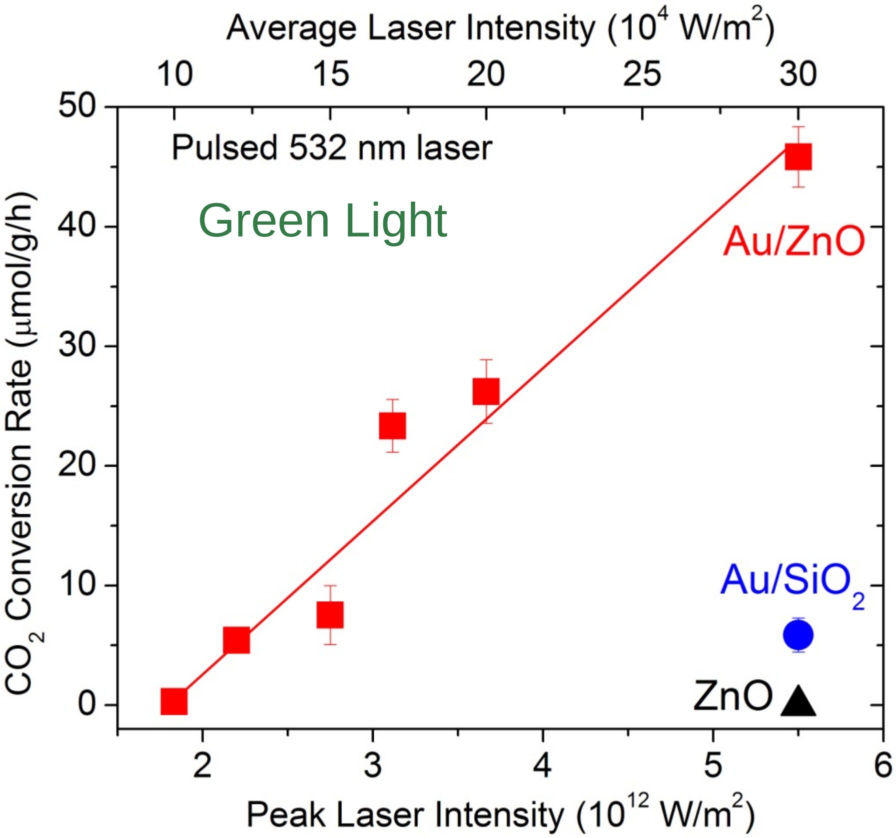
top view

Visible Light CO_2 Reduction with Plasmonic Heating

$$CO_2 + H_2 \leftrightarrows \text{Products}$$

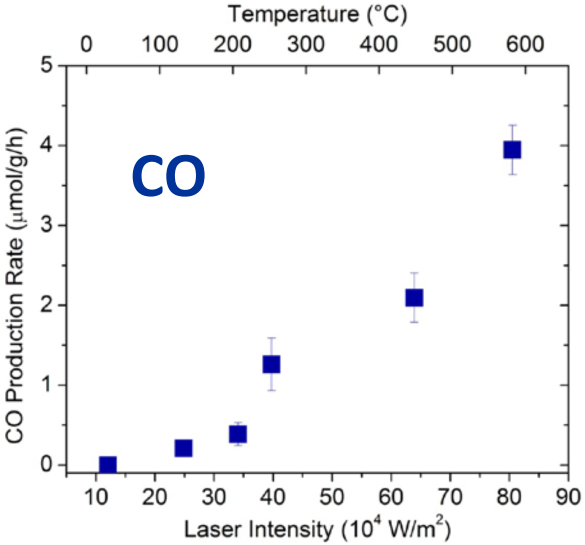
(See next few slides for product distributions)

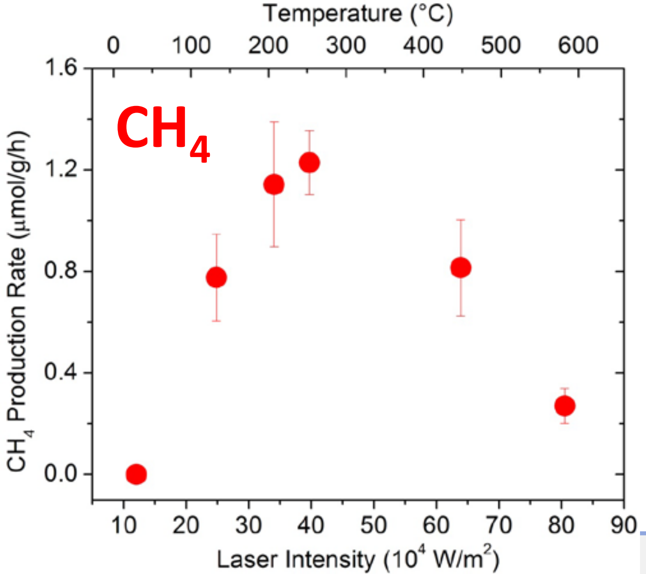




Determining Reaction Pathways

Rxn Products
$CO_2 + H_2 \leftrightarrows$ Products





Pathways

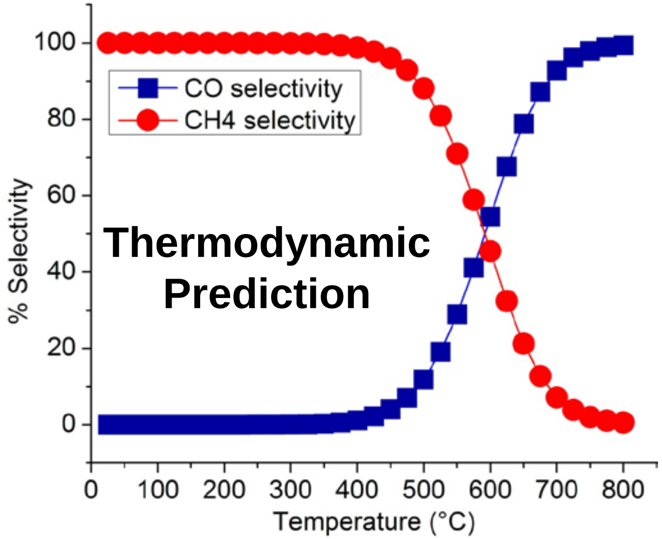
Reaction scheme 1:
$CO_2 + H_2 \leftrightarrows CO + H_2O$
(Reverse water-gas shift (RWGS))

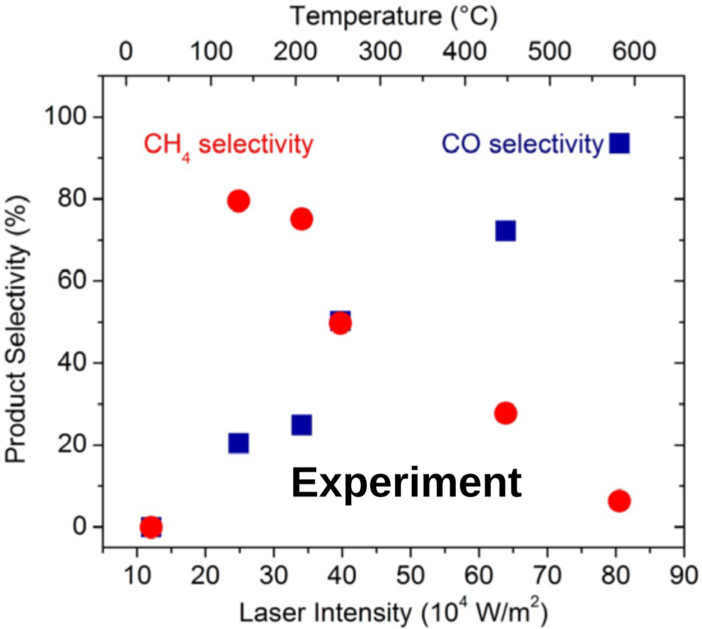
Reaction scheme 2:
$CO_2 + H_2 \leftrightarrows CO + H_2O$
(RWGS)
$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$
(Methanol synthesis)

Reaction scheme 3:
$CO_2 + H_2 \leftrightarrows CO + H_2O$
(RWGS)
$CO + 3H_2 \leftrightarrows CH_4 + H_2O$
(CO-methanation)

Reaction scheme 4:
$CO_2 + H_2 \leftrightarrows CO + H_2O$
(RWGS)
$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$
(Methanol synthesis)
$CO + 3H_2 \leftrightarrows CH_4 + H_2O$
(CO-methanation)

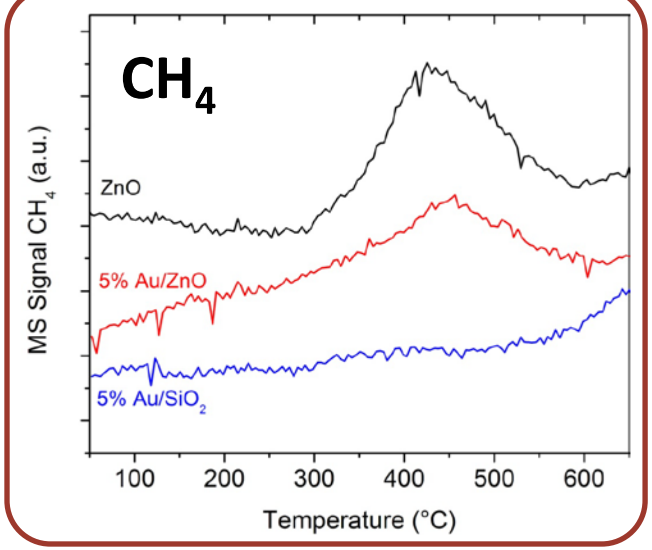
Selectivities

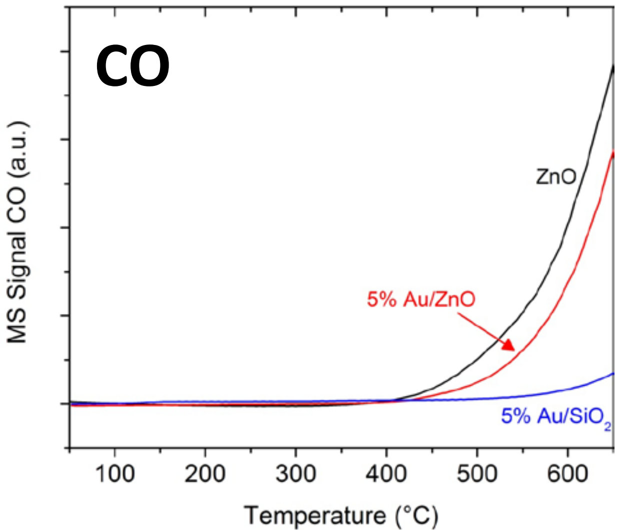




Temperature Programmed Reaction in Dark Confirm Rxn Mechanism

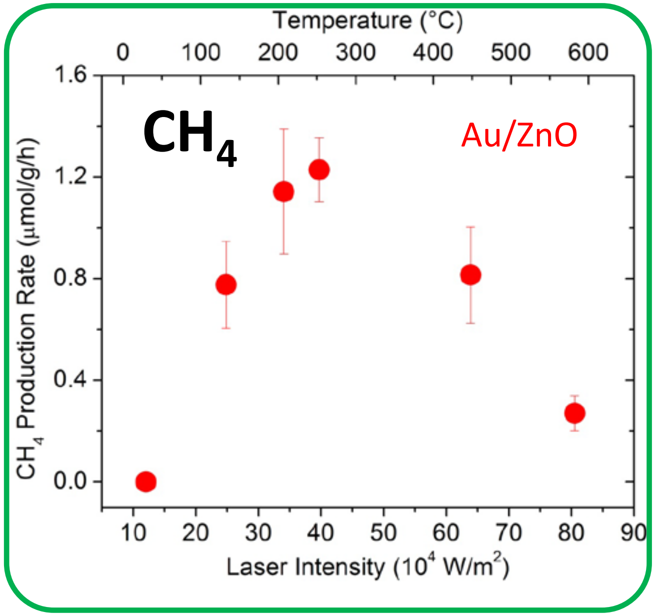
Dark Reactions

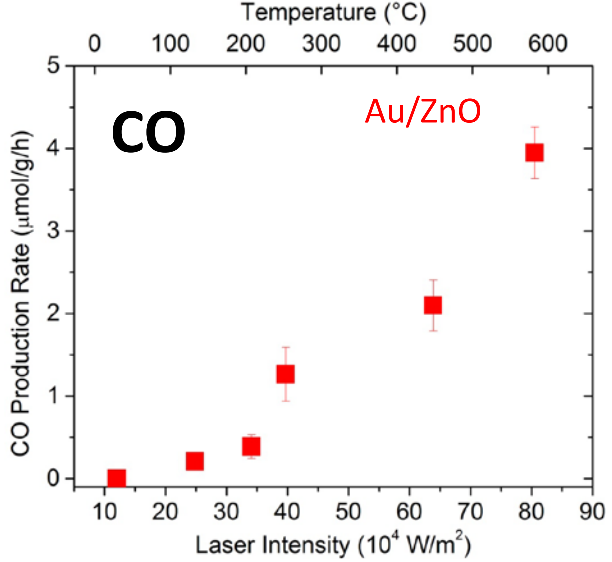




Dark Reactions

Light Reactions

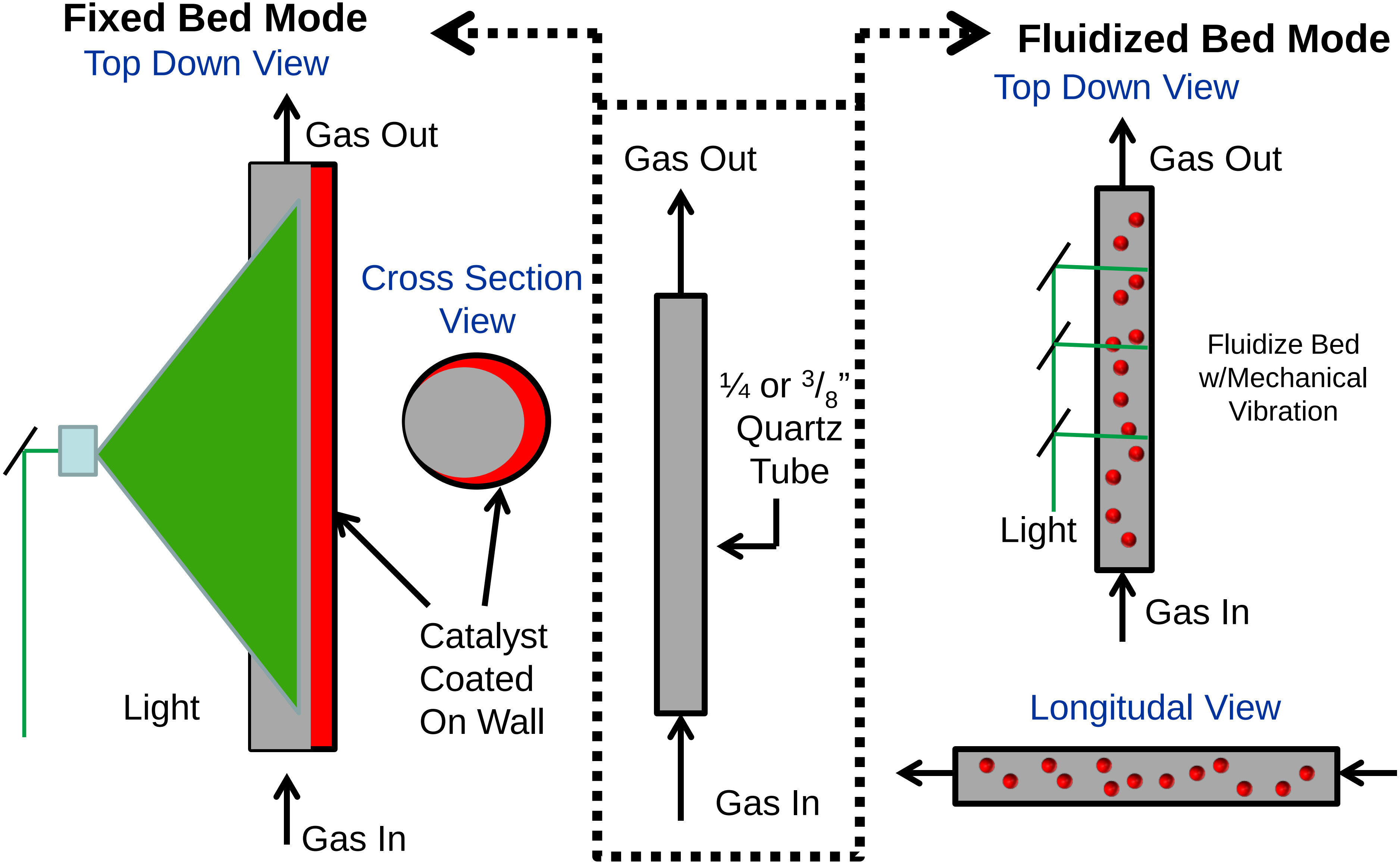




Light Reactions

Demonstrating Scalability

One Simple Plasmonic Reactor Run in Two Different Modes



Fixed Bed Mode

Top Down View

Gas Out

Light

Gas In

Cross Section View

Catalyst Coated On Wall

Gas Out

¼ or $^3/_8$” Quartz Tube

Gas In

Fluidized Bed Mode

Top Down View

Gas Out

Fluidize Bed w/Mechanical Vibration

Light

Gas In

Longitudal View

Project Structure

- Photocatalytic Systems
  - Heterostructured Photocatalysts for CO_2 Reduction
  - Symmetry Breaking and High Throughput Computational Screening of Delafossites for the Photocatalytic Reduction of CO_2
  - Scanning Tunneling Microscopy and Dispersion-corrected Density Functional Theory Studies of TiO_2 Surfaces

- **Electrocatalytic Systems**
  - **Electronic Structure and Catalytic Activity of Au_{25} Clusters**

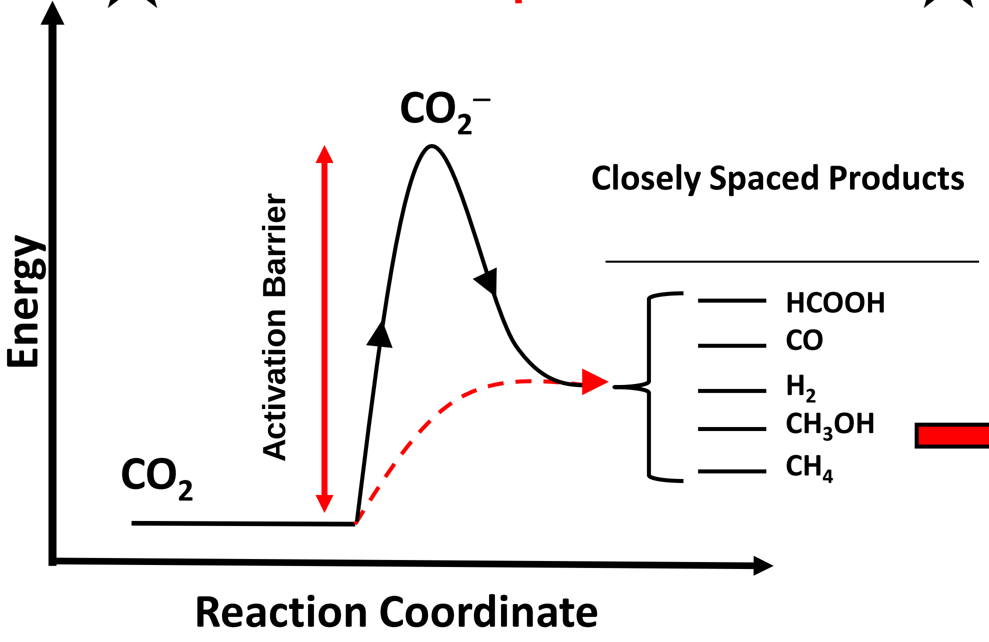
- Thermal Catalytic Systems
  - Atomic Structure and Catalytic Activity of Cu/ZnO-Based Materials

Technical Barriers for CO_2 Electrocatalysis

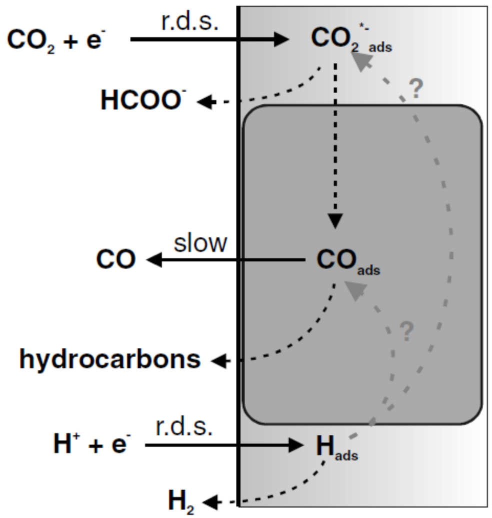
Technical Issues

- Large overpotentials required
- Low Efficiency
- Poor product selectivity
- Parasitic H_2 evolution

★ **Barrier = Overpotential = Cost!** ★



Possible Electrode Processes



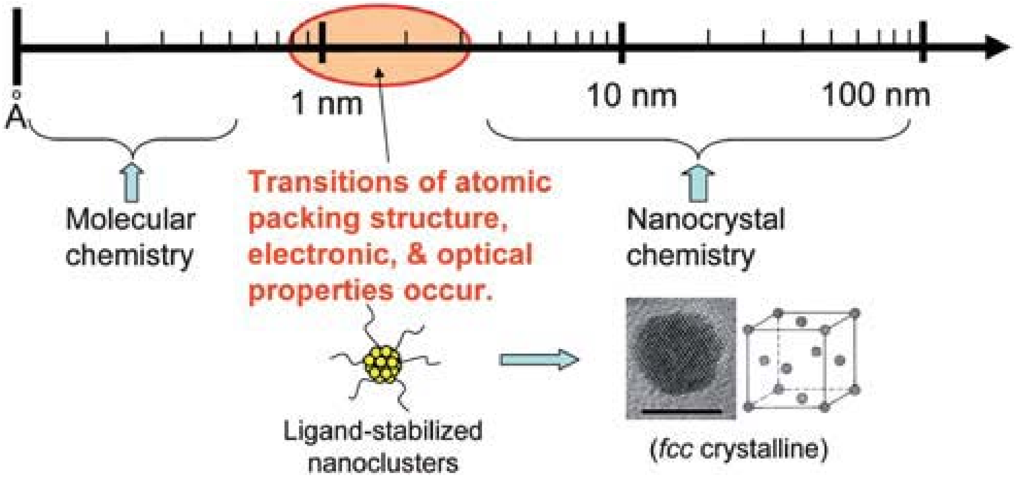
J. Electroanal. Chem. 2006, *594*, 1

Challenge

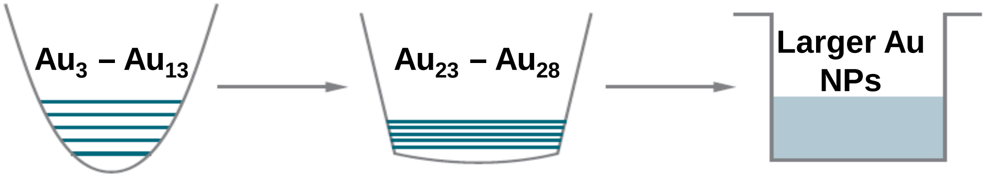
Identify a high efficiency catalyst with low overpotential and good product selectivity

Atomically Precise Au_n clusters (n < ~200)

Spans sizes between molecules & "traditional" nanomaterials



Unique quantized electronic structure



No plasmons

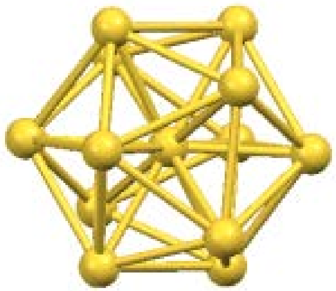
Molecular like orbitals

High fraction of surface atoms for catalysis

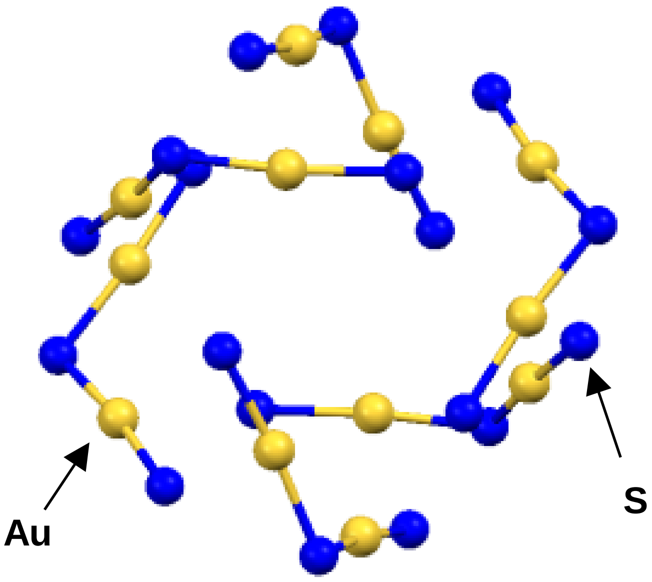
* From R. Jin, *Nanoscale, 2010, 2, 343–362*

Au_{25} $(SR)_{18}$ Crystal Structure

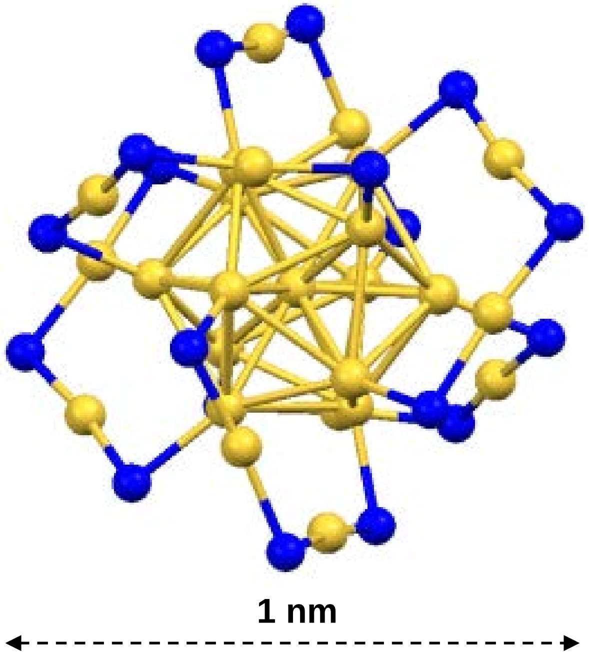
Au_{13} “core”



$(–S–Au–S–Au–S–)_6$ “shell”



Au_{25} cluster



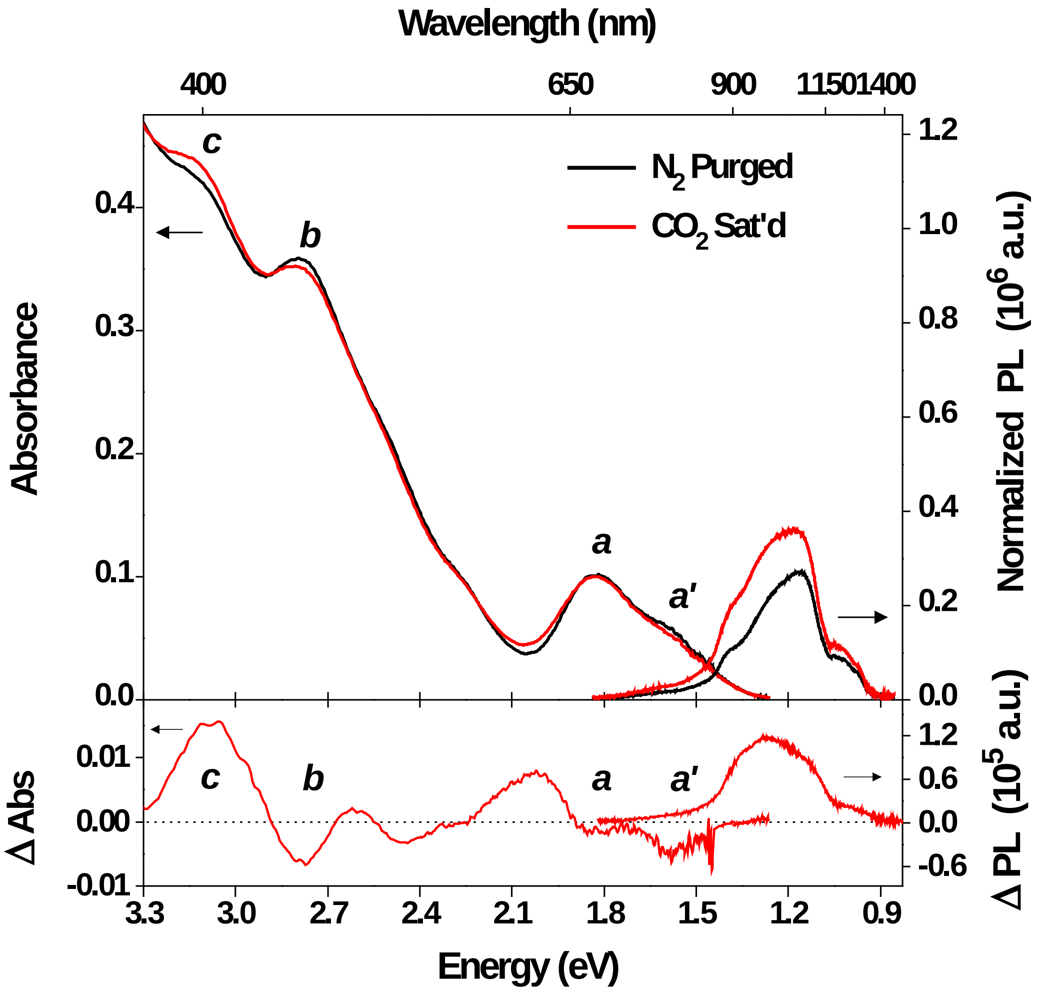
Au_{25} carries a ground state *negative* charge

TOA counterion balances charge in crystal structure

Zhu et, al. J. Am. Chem. Soc. 2008, *130*, 5883-5885.

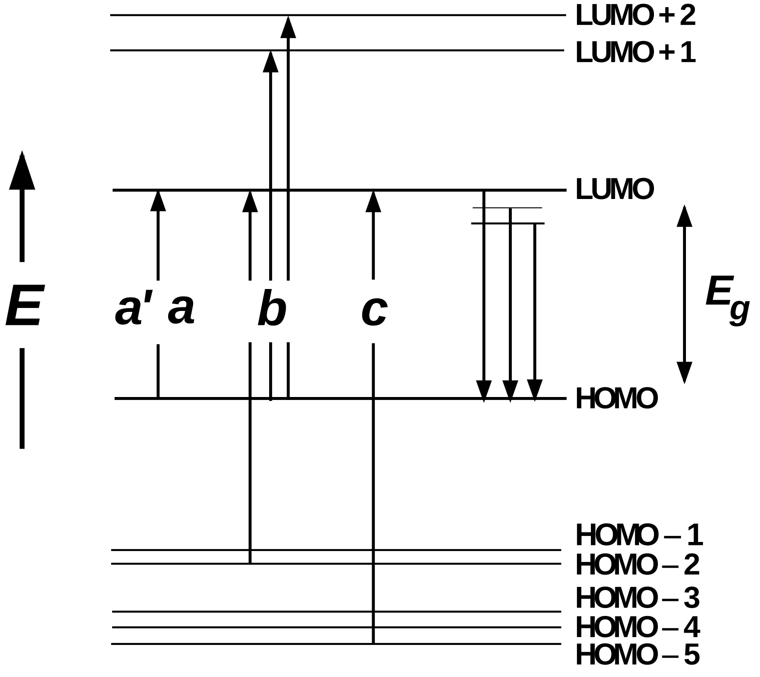
Reversible Optical Bleaching in Presence of CO_2

Experimental



***Reversible* bleaching due to charge redistribution**

Electronic Structure

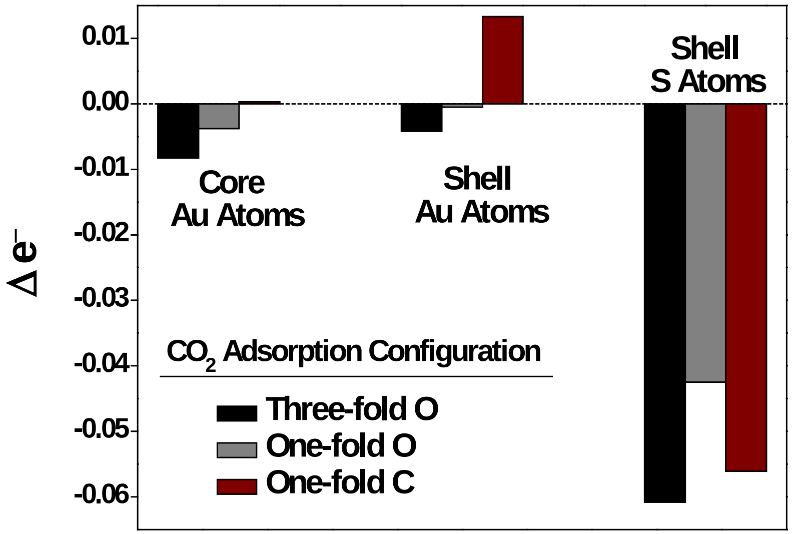


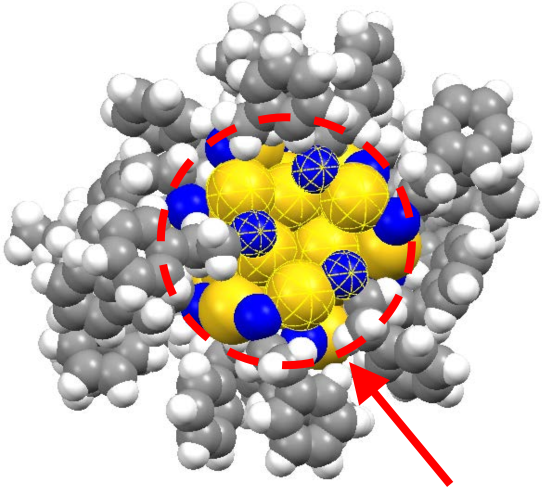
Energy level diagram reproduced from Schatz & Jin et. al. JACS 2008, 130 (18), pp 5883–5885

Kauffman, et, al. J. Am. Chem. Soc. **2012, *134*, 10237−10243.**

CO_2 Physisorption Reversibly Perturbs Electronic Structure

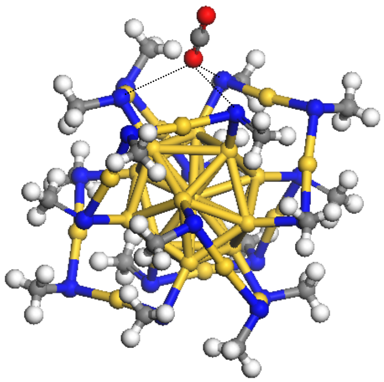
Optical Bleaching Results from Reversible Charge Redistribution



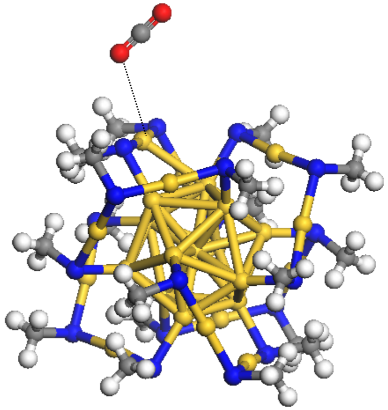


Adsorption Pocket

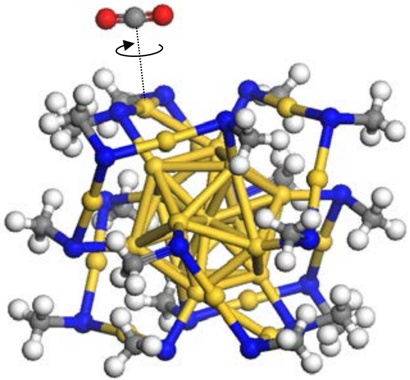
Three-fold O Coordination



One-fold O Coordination



One-fold C Coordination



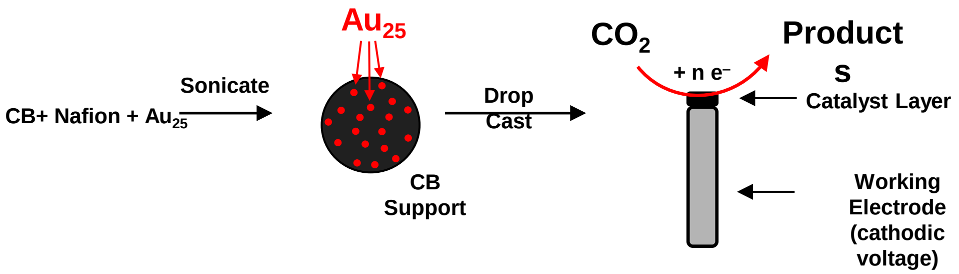
Binding Energies

~ 80 – 140 meV

Kauffman, etl, al. J. Am. Chem. Soc. **2008, *130*, 5883-5885.**

Unprecented Catalytic Efficiency

No appreciable E_a , ~ 100 % Selectivity



Au_{25}

CB+ Nafion + Au_{25}

Sonicate

CB Support

Drop Cast

CO_2

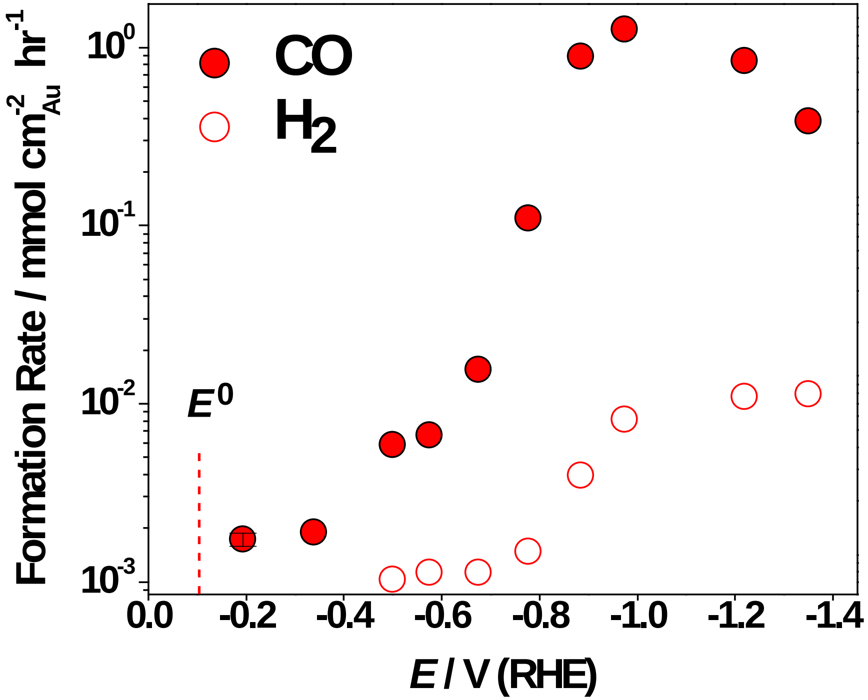
+ n e⁻

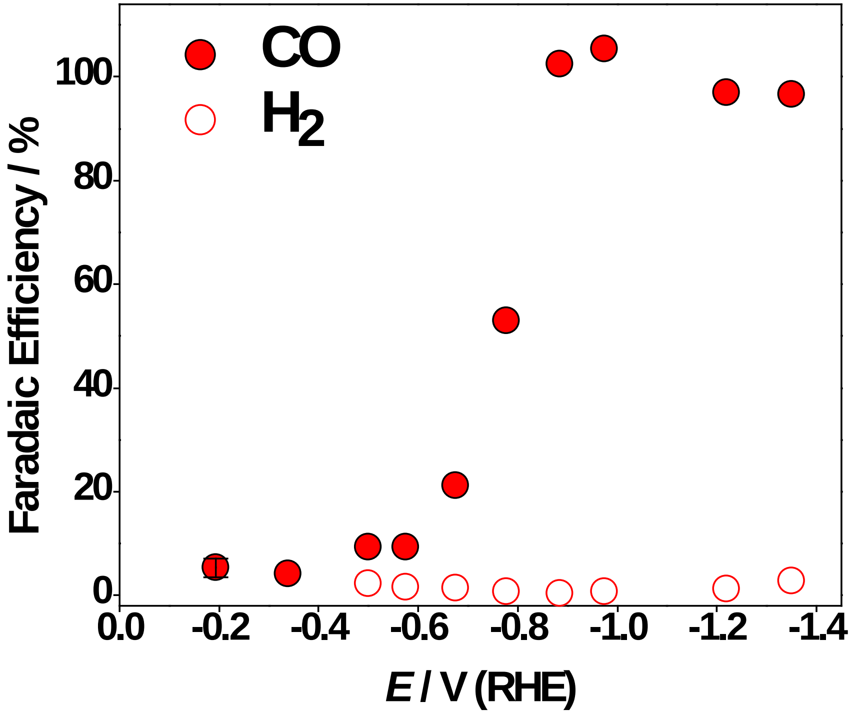
Products

Catalyst Layer

Working Electrode (cathodic voltage)

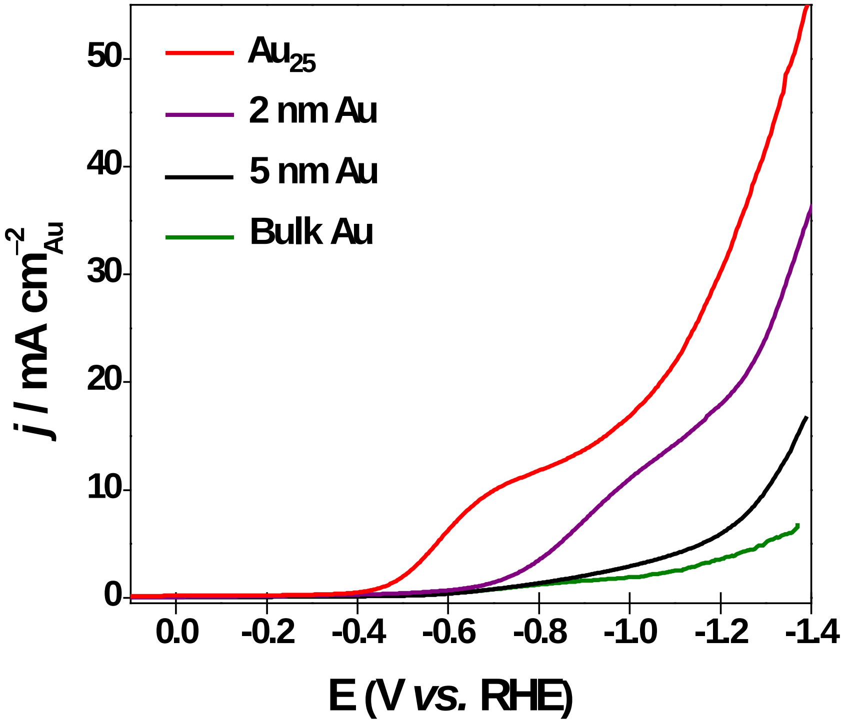
$CO_2 + 2H^+ 2e^- \rightarrow CO + H_2O$ $E^0 = -0.103$ V (RHE)

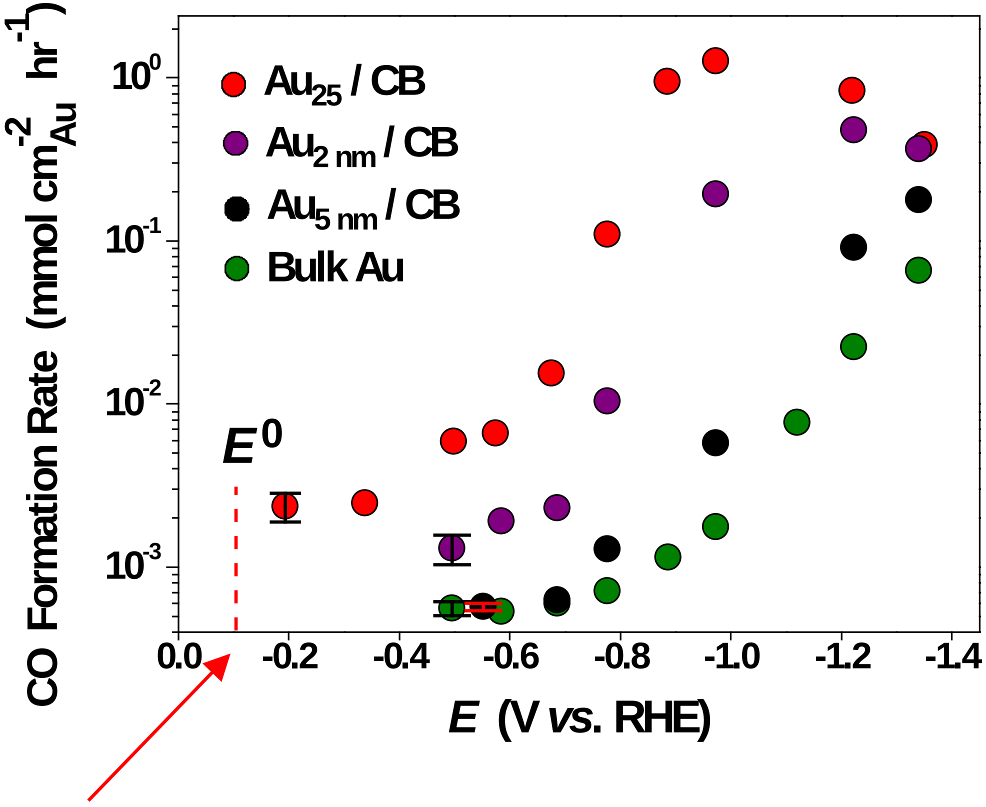




Kauffman, etl, al. J. Am. Chem. Soc. 2008, *130*, 5883-5885.

Comparison to other Au Materials





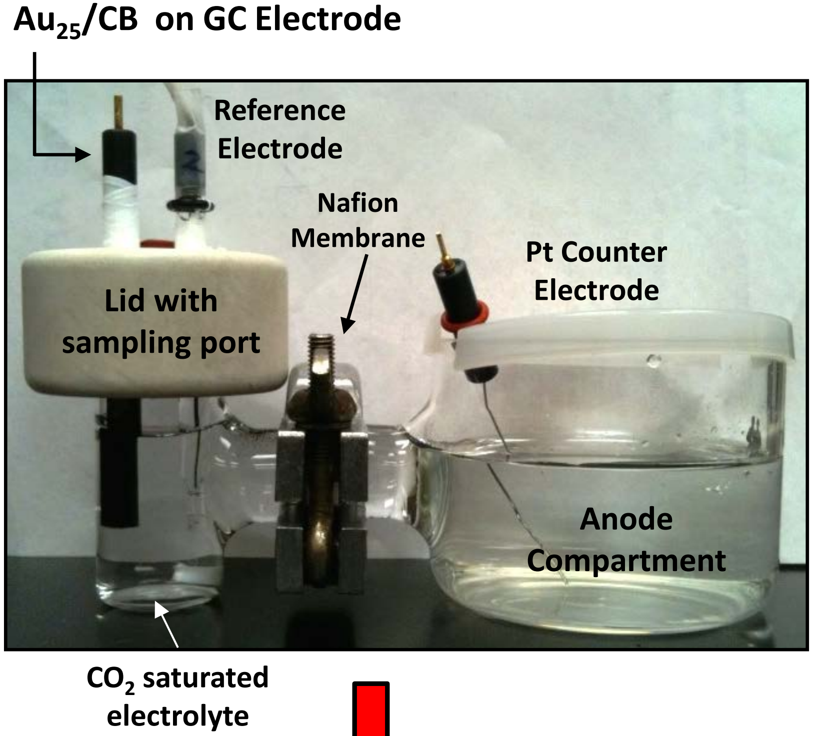
Thermodynamic Limit

Kauffman, etl, al. J. Am. Chem. Soc. 2008, *130*, 5883-5885.

Demonstrating Scalability

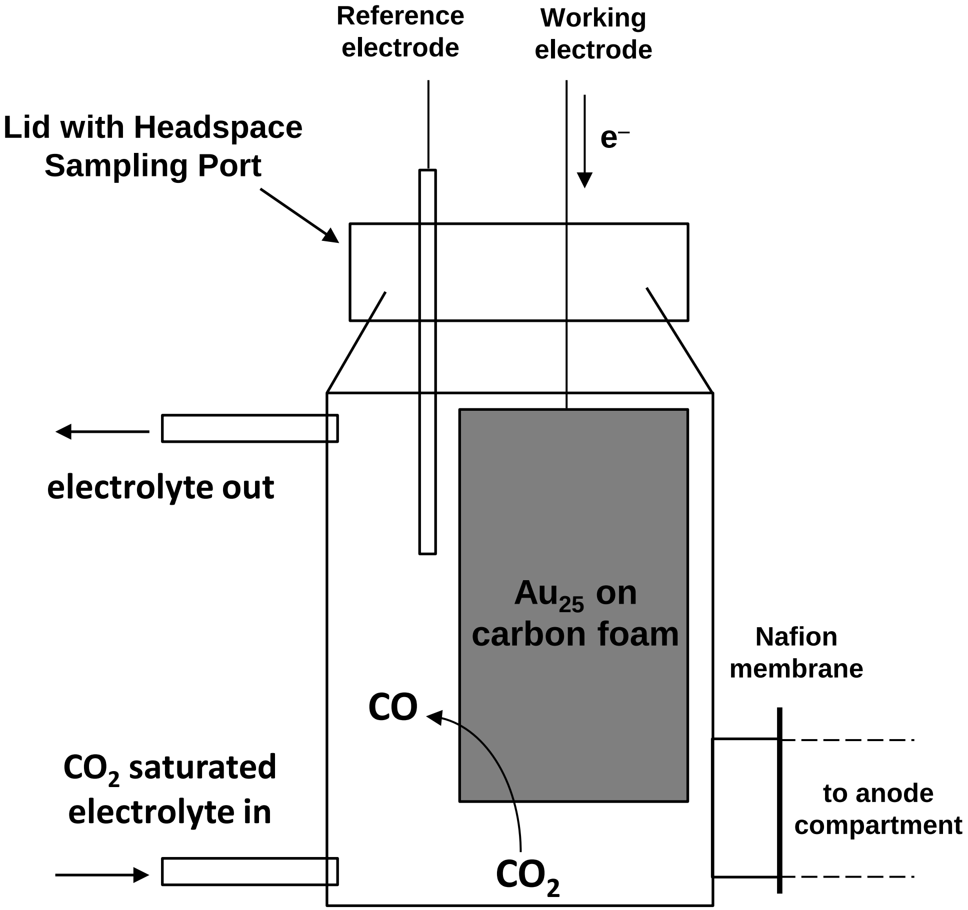
Continuous Flow Electrochemical Reactor

Proof-of-Concept in Small H-Cell



Scale Up!

Scaled-Up Flowing H-Cell Reactor



Summary

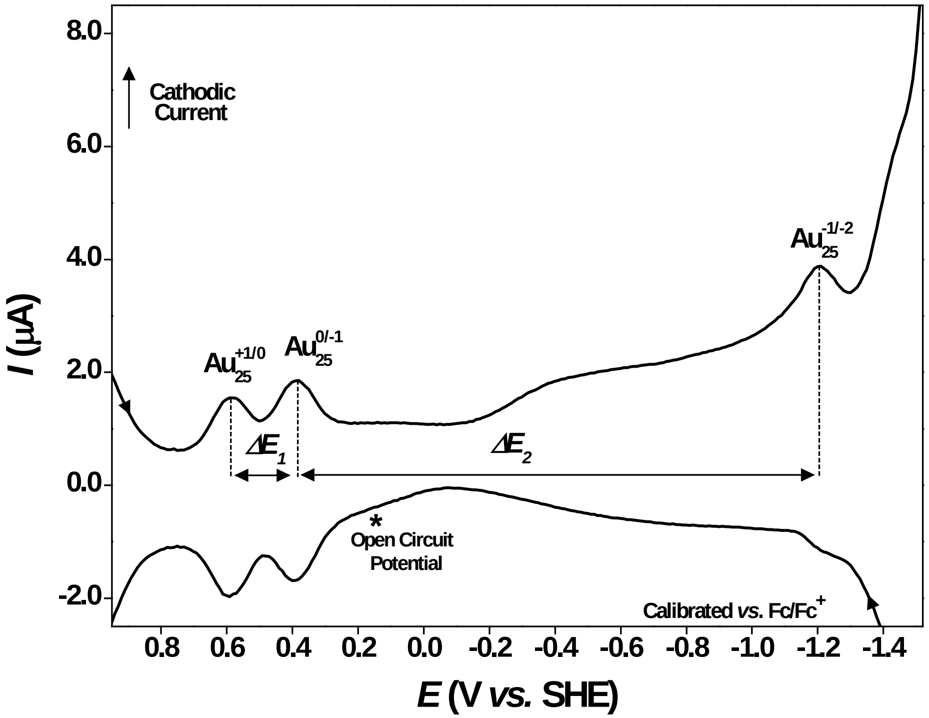
- **Visible light plasmonic heating can be used to convert CO_2 into CH_4, CO, and other products**

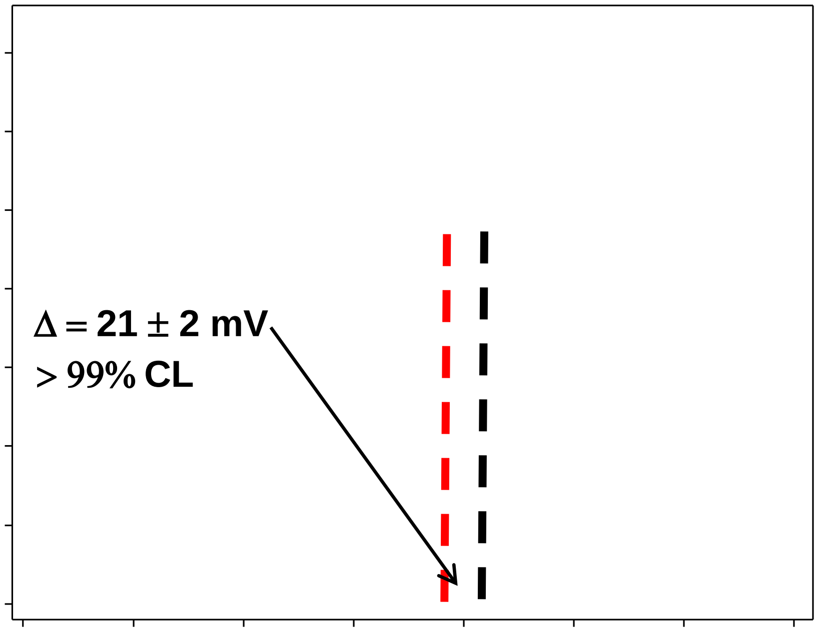
- **Catalytic mechanism is “photothermal”**

- **Au_{25} exhibits spontaneous electronic coupling to CO_2**

- **Au_{25} shows unprecendented catalytic efficiency towards CO_2 conversion**

Charge Redistribution Impacts Electron Transfer to CO_2





$\Delta = 21 \pm 2$ mV

$> 99\%$ CL

Small but *statistically significant* anoidic shift to + oxidizing potentials

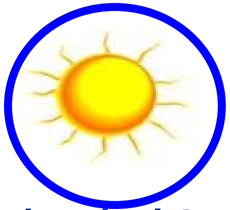
Consistent with e^- depletion of HOMO donating levels

***Kauffman, etl, al. J. Am. Chem. Soc.* 2008, *130*, 5883-5885.**

General Catalytic Approaches For CO_2 Conversion

Thermal Catalytic Conversion

Electrochemical Catalytic Conversion



Photochemical Catalytic Conversion

Lower Risk

Higher Risk

Applications R&D

Basic R&D

Thermally Initiated Reactions

Solar-Thermal Reactors Waste/Plasmon Heat For Energy Input

Traditional Catalysts Make Near Term Deployment More Realistic

Electrochemical Generation of electrons/holes

Geothermal, Wind, or Waste Electricity Provides Energy Input

Emerging Technology Utilizing Cu, Cu-oxide And Other Catalysts

Photochemical Generation of electrons/holes or plasmonic heating

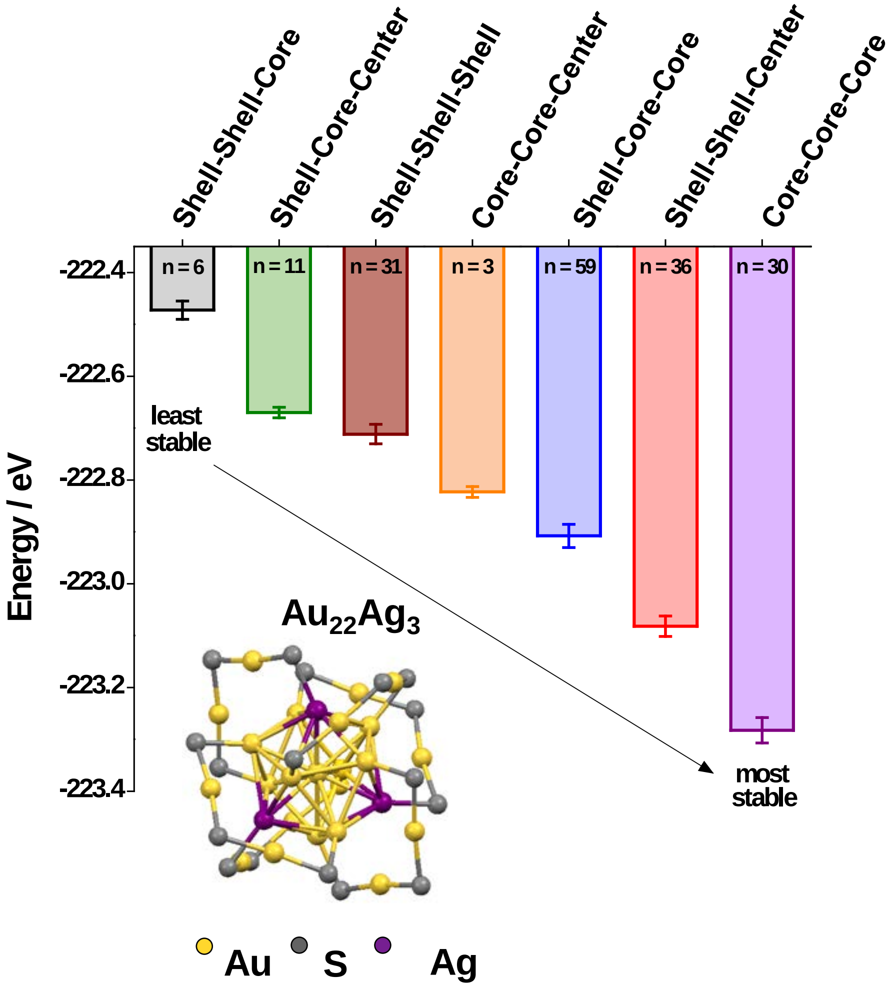
Sun Provides Energy Input

Emerging Technology Utilizing TiO_2 and Other Photocatalysts

Investigating “Quantum Alloys” with Computational & Experimental Screening

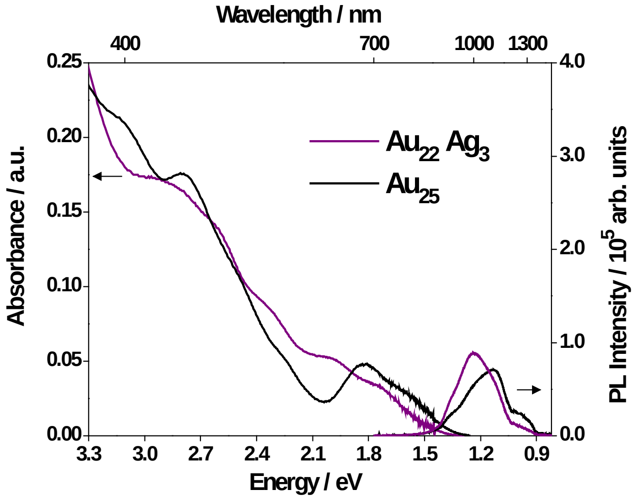
Computational

- DFT Screens ~176 alloy compositions
- $Au_{22}Ag_3$ predicted to be stable & *confirmed experimentally*



Experimental

Optical Properties



Electronic Structure