Catalytic Transformation of CO$_2$ to C1 Products

Christopher Matranga, Molecular Science Division, NETL

Team Members & Collaborators:
NETL: Dominic Alfonso, Xingyi Deng, Doug Kauffman, Junseok Lee, Jonathan Lekse, Congjun Wang

NETL-RUA: James Lewis (WVU), Ronchao Jin (CMU), Ken Jordan (PITT), Sittichai Natesakhowat (PITT)
CO₂ Conversion to C1 Industrial Chemicals

\[
\begin{align*}
\text{CO}_2 & \quad \text{H}_2 \quad \text{H}_2\text{O} \\
\text{Formic Acid} & \quad \text{Formaldehyde} & \quad \text{Methanol} & \quad \text{Methane}
\end{align*}
\]

- Industrial Waste Heat
- Solar-Heating
- Or Photo-driven
- Wind-Electric

**Uses**
- Leather, Pulp
- Urea Resins
- Phenol Resins
- Fuel/MTG
- Formaldehyde
- Fuel
- Acetic Acid

**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)

\(^1\) 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 CO₂ Utilization Photocatalysts

- Poor optical activity in visible & infrared
- Rapid recombination of e⁻ & h⁺ pairs prevents useful redox photochemistry
- Slow CO₂ conversion kinetics
- Difficulty controlling product selectivity

from R. Asashi et. al., Science, 293, 269 (2001)
Plasmonic Heating in Heterostructures for Catalytic CO₂ Reduction

A “Hybrid” Photo- and Thermal-Catalytic Approach

Light excites collective electron motions (Plasmons)

![Electric field](image1)

Optical Activity Controlled by Size/Shape/Composition

![Optical Activity](image2)

Light converted to Thermal energy (ohmic/joule heating)

![Total absorption rate/heat generation](image3)

Forming Heterostructures

![Forming Heterostructures](image4)

Synthesis and Characterization of Plasmonic Au/ZnO Heterostructured Catalysts

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

Raman Spectroscopy to Estimate Localized Plasmonic Heating

Temp dependent ZnO phonon peaks used to monitor temperature

How Hot? How Localized?
20 nm Au on ZnO Support

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

\[ \Delta T = \frac{I_0 K_{\text{abs}} r_0}{4k_\infty} \]
Photocatalysis Experiments for Activity Evaluation

- IR source
- 300 Watt Xe arc lamp
- CO₂ + H₂O
- Cutoff filter
- Catalyst
- IR detector
- Laser

Gas sampling port for GC analysis
Visible Light CO₂ Reduction with Plasmonic Heating

CO₂ + H₂ ⇌ Products

(See next few slides for product distributions)

**Graphs**

**Left Graph**: CO₂ Conversion Rate (µmol/g/h) vs. Laser Intensity (10⁴ W/m²)
- **cw 532 nm laser**: Green Light
- **Au/ZnO**: Red squares
- **Au/SiO₂**: Blue pentagons
- **ZnO**: Black triangles

**Right Graph**: CO₂ Conversion Rate (µmol/g/h) vs. Peak Laser Intensity (10¹² W/m²)
- **Pulsed 532 nm laser**: Green Light
- **Au/ZnO**: Red squares
- **Au/SiO₂**: Blue pentagons
- **ZnO**: Black triangles
Determining Reaction Pathways

**Rxn Products**

- **CO**
- **CH₄**

**Pathways**

1. **Reaction scheme 1:**
   \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]  
   (Reverse water-gas shift (RWGS))

2. **Reaction scheme 2:**
   \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]  
   (RWGS)
   \[ \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  
   (Methanol synthesis)

3. **Reaction scheme 3:**
   \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]  
   (RWGS)
   \[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]  
   (CO-methanation)

4. **Reaction scheme 4:**
   \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]  
   (RWGS)
   \[ \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  
   (Methanol synthesis)
   \[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]  
   (CO-methanation)

**Selectivities**

- **CO selectivity**
- **CH₄ selectivity**
Temperature Programmed Reaction in Dark Confirm Rxn Mechanism

**Dark Reactions**

**CH₄**

- MS Signal CH₄ (a.u.)
- ZnO
- 5% Au/ZnO
- 5% Au/SiO₂

**Dark Reactions**

**CO**

- MS Signal CO (a.u.)
- ZnO
- 5% Au/ZnO
- 5% Au/SiO₂

**Light Reactions**

**CH₄**

- CH₄ Production Rate (μmol/g·h)
- Temperature (°C)

**Au/ZnO**

**Light Reactions**

**CO**

- CO Production Rate (μmol/g·h)
- Temperature (°C)

**Au/ZnO**

- Laser Intensity (10⁴ W/m²)

**Light Reactions**
Demonstrating Scalability
One Simple Plasmonic Reactor Run in Two Different Modes

**Fixed Bed Mode**
- Top Down View
- Gas Out
- Light
- Gas In
- Catalyst Coated On Wall

**Fluidized Bed Mode**
- Top Down View
- Gas Out
- Light
- Gas In
- Fluidize Bed w/Mechanical Vibration

### Cross Section View
- $\frac{1}{4}$ or $\frac{3}{8}$" Quartz Tube

### Longitudinal View
Project Structure

• Photocatalytic Systems
  – Heterostructured Photocatalysts for CO₂ Reduction
  – Symmetry Breaking and High Throughput Computational Screening of Delafossites for the Photocatalytic Reduction of CO₂
  – Scanning Tunneling Microscopy and Dispersion-corrected Density Functional Theory Studies of TiO₂ Surfaces

• Electrocatalytic Systems
  – Electronic Structure and Catalytic Activity of Au₂₅ 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

 Disclaimer: This material is based upon work supported by the NSF. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

Possible Electrode Processes

Identification of a high efficiency catalyst with low overpotential and good product selectivity

Closely Spaced Products
- HCOOH
- CO
- H$_2$
- CH$_3$OH
- CH$_4$

Energy

Reaction Coordinate

J. Electroanal. Chem. 2006, 594, 1
Atomically Precise $\text{Au}_n$ clusters ($n < \sim 200$)

Spans sizes between molecules & “traditional” nanomaterials

Unique quantized electronic structure

High fraction of surface atoms for catalysis

**Au$_{25}$ (SR)$_{18}$ Crystal Structure**

Au$_{25}$ carries a ground state *negative* charge

TOA counterion balances charge in crystal structure

---

Reversible Optical Bleaching in Presence of CO$_2$

Experimental

Wavelength (nm)

Absorbance

Energy (eV)

Δ Abs

Normalized PL (10$^6$ a.u.)

Δ PL (10$^5$ a.u.)

Reversible bleaching due to charge redistribution


Electronic Structure

Energy level diagram reproduced from Schatz & Jin et. al. JACS 2008, 130 (18), pp 5883–5885
CO$_2$ Physisorption Reversibly Perturbs Electronic Structure

Optical Bleaching Results from Reversible Charge Redistribution

\[ \Delta e^- \]

\begin{tabular}{l}
CO$_2$ Adsorption Configuration \\
Three-fold O & One-fold O & One-fold C
\end{tabular}

\begin{tabular}{l}
Core Au Atoms & Shell Au Atoms & Shell S Atoms
\end{tabular}

Binding Energies
~ 80 – 140 meV

Unprecedented Catalytic Efficiency

No appreciable $E_a$, $\sim 100\%$ Selectivity

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.103 \text{ V (RHE)}$$

Graphs showing formation rates and Faradaic efficiency vs. electrode potential.

$\text{CO}_2$ Product $\rightarrow$ $\text{CO} + \text{H}_2$.

$\text{Au}_{25}$ Sonicate CB+ Nafion + $\text{Au}_{25}$ CB Support.

Working Electrode (cathodic voltage).

$E^0$ faradaic efficiency.

$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$

Comparison to other Au Materials

![Graph showing comparison of CO formation rate to other Au materials](image)

Thermodynamic Limit

Demonstrating Scalability

Continuous Flow Electrochemical Reactor

Proof-of-Concept in Small H-Cell

Scaled-Up Flowing H-Cell Reactor

Scale Up!

Au_{25}/CB on GC Electrode

Reference Electrode

Pt Counter Electrode

Lid with Headspace Sampling Port

Anode Compartment

Nafion Membrane

Working electrode

electrolyte out

CO_{2} saturated electrolyte

Lid with sampling port

Reference electrode

Working electrode

Au_{25} on carbon foam

CO

CO_{2}

Scale Up!
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 unprecedented catalytic efficiency towards CO$_2$ conversion
Charge Redistribution Impacts Electron Transfer to CO₂

Small but statistically significant anodic shift to + oxidizing potentials
Consistent with e⁻ depletion of HOMO donating levels

Δ = 21 ± 2 mV
> 99% CL

General Catalytic Approaches For CO₂ Conversion

- **Thermal Catalytic Conversion**
  - Thermally Initiated Reactions
  - Solar-Thermal Reactors
  - Traditional Catalysts
  - Lower Risk
  - Applications R&D

- **Electrochemical Catalytic Conversion**
  - Electrochemical Generation of electrons/holes
  - Geothermal, Wind, or Waste Electricity
  - Emerging Technology Utilizing Cu, Cu-oxide And Other Catalysts
  - Basic R&D

- **Photochemical Catalytic Conversion**
  - Photochemical Generation of electrons/holes or plasmonic heating
  - Sun Provides Energy Input
  - Emerging Technology Utilizing TiO₂ and Other photocatalysts
  - Higher Risk

Emerging Technology-utilizing Cu, Cu-oxide and other catalysts makes near term deployment more realistic.
Investigating “Quantum Alloys” with Computational & Experimental Screening

Computational

• DFT Screens ~176 alloy compositions

• \( \text{Au}_{22}\text{Ag}_3 \) predicted to be stable & confirmed experimentally

---

Experimental

Optical Properties

- Wavelength / nm
- Absorbance / a.u.
- PL Intensity / 10^5 arb. units

Electronic Structure

- Occupied orbital
- Unoccupied orbital

Potential / V (vs. SHE)

- Current / µA

---

\( \text{Au} \quad \text{S} \quad \text{Ag} \)