Key Intermediates of Carbon Dioxide Reduction on Silver from Vibrational Nanospectroscopy

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Collective Phenomena in Energy & Matter Transport

**Designer Light/e- Interactions**
- *JPC Lett*, 2013
- *Angew Chem*, 2013
- *Israel J Chem*, 2013
- *JPC Lett, (Persp)* 2014
- *JPCC*, 2014
- *JPC Lett*, 2014
- *Nano Lett*, 2015
- *JPCC*, 2015
- *JPCC*, 2016
- *JPCC*, 2016

**Reaction Dynamics**
- *Nature Comm*, 2013
- *Nano Lett*, 2013
- *Angew Chem*, 2014
- *Nano Lett*, 2015
- *Angew Chem*, 2015
- *JACS*, 2016
- *Angew Chem*, 2016
- *PCCP*, 2016
- *Nature Comm*, 2017
- *JMCA*, 2017

**Multi-Electron Photocatalysis**
- *Nano Today*, 2014
- *ACS Cat*, 2017
- *Nature Chem*, submitted

**Microscopy Spectroscopy Nanochemistry Theory**
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A New Regime for Physical Chemists: Complex Reactive and Catalytic Solids


Commercial LiFePO$_4$ cathodes
Image credit: http://www.azom.com


Nanoscale granularity
But Bulk Measurements Often Resolve Neither

- Heterogeneity information lost
- No reaction trajectory/dynamics

% Conversion and Rate →
ensemble-averaged activity, e.g.
diffraction studies of Li batteries
We Use Optical Spectroscopy to Probe Chemical Reactions In Situ One Nano-Domain At a Time

SM materials science labs: Peng Chen, Stephan Link, Kallie Willets, Christy Landes, Bjorn Reinhard
See early work on single NC spectroscopy: Van Duyne, Brus, Bawendi, Nesbitt groups
Bridging the Materials and Pressure Gap With In Situ Single-Nanocrystal Studies

Ion Exchange in Semiconductors
Photoluminescence Emission

Galvanic Processes
Plasmonic Scattering

CO₂ Reduction on Noble Metals
(SE) Raman Scattering

Redox Catalysis in Proteins
(SE) Phonon Scattering

Courtesy: Grassian group, U. Iowa
Studying Artificial Photosynthesis

- Three major steps in artificial photosynthesis:
  a) Solar harvesting
  b) Charge separation and transport
  c) Redox reactions

- Carbon in CO$_2$ is in highest oxidation state, it can be reduced to form products with various oxidation states of carbon

\[ \text{CO}_2(g) \rightarrow \text{CO}^-_2 \rightarrow \text{HCOO}^- \]

\[ \text{HCOOH, CO} \]
State-of-the-art Single Nanoparticle Catalysis

Challenges of Catalytic CO$_2$ Reduction

$E^o$ (V) vs. NHE

1 atm, 25 °C

-0.5

CO$_2$ + 2H$^+$ + 2e$^-$ $\Leftrightarrow$ HCOOH (-0.250 V)

CO$_2$ + 2H$^+$ + 2e$^-$ $\Leftrightarrow$ CO + H$_2$O (-0.106 V)

2H$^+$ + 2e$^-$ $\Leftrightarrow$ H$_2$ (0.0 V)

CO$_2$ + 6H$^+$ + 6e$^-$ $\Leftrightarrow$ CH$_3$OH + H$_2$O (0.016 V)

2CO$_2$ + 12H$^+$ + 12e$^-$ $\Leftrightarrow$ C$_2$H$_4$ + 4H$_2$O (0.064 V)

2CO$_2$ + 12H$^+$ + 12e$^-$ $\Leftrightarrow$ C$_2$H$_5$OH + 3H$_2$O (0.084 V)

CO$_2$ + 8H$^+$ + 8e$^-$ $\Leftrightarrow$ CH$_4$ + 2H$_2$O (0.169 V)

0.0

0.5

1.0

2H$_2$O $\Leftrightarrow$ O$_2$ + 4H$^+$ + 4e$^-$ (1.23 V)

- Complex: Multiple electron and proton coupling steps
- Large overpotentials $\rightarrow$ Kinetic challenges, slow reaction rate
- Competing reaction: H$_2$O reduction (favorable)
- Little known about photocatalysis

Research issues
- How to increase the reaction rate (QE)
- How to control selectivity
- Stability of catalyst
- Kinetic and mechanistic insights

CO$_2$ + e$^-$ $\rightarrow$ CO$_2^-$ $E^o = -1.9$ V

Intermediates Reveal Reaction Mechanisms Governing Product Selectivity

Surface-enhanced Raman scattering probing of adsorption and catalysis on bimetallic nanostructures

See work of Van Duyne, Moskovits, and Willets groups

40 or 60 nm Ag NPs
Addressing individual (emissive) sites of the supported Ag nanocatalyst

![Image of emitter sites with corresponding emission spectra](image_url)
In-situ SERS spectra of single emitter under CO$_2$ flow
Catalytic Heterogeneity Across Nanoparticles

Smith and Jain*, JPCC, 2017
Dynamic Catalytic Activity Under Light

![Graph showing dynamic catalytic activity under light.](image)

- CO$_2$ activity in air and CO$_2$.
- Formic acid activity in air and CO$_2$.

**Notes:**
- 40 a.u. represents CO$_2$ intensity.
- 70 a.u. represents formic acid intensity.

**Graph Details:**
- Time / s: 0, 40, 80, 120, 160, 200
- Raman shift / cm$^{-1}$: 500, 1000, 1500, 2000, 2500, 3000
- Activity in air and CO$_2$.
- HCOOH activity.
Physisorbed CO$_2$

$\nu_1 = 1334$

$\nu_2 = 649$

$\nu_3 = 2349$

Fermi resonance

1280 cm$^{-1}$

1388 cm$^{-1}$

Raman spectrum of solid CO$_2$

Fermi resonance modes
Key Species Discovered in In-Situ Spectra