DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Hybrid electro- and thermo-catalytic upgrading of CO_2 to fuels and C_{2+} chemicals

March 4-7, 2019

ChemCatBio and CO_2 Utilization

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ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL, NREL*)

Catalytic Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Electrocatalytic and Thermocatalytic CO_2 Utilization
(NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL, SNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

Catalyst Deactivation Mitigation for Biomass Conversion
(PNNL)

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

Goal Statement

- Goal: develop an electrocatalytic synthesis approach for the reduction of CO_2 to C_{2+} oxygenates and alcohols, as feedstocks for thermocatalytic upgrading to heavier hydrocarbons.
- Improve the state of the science for electrochemical synthesis of heavy molecules from CO_2.
- This project is relevant to the bioenergy industry because it provides a means to recycle CO_2 to molecules that were traditionally fossil-based, in a manner that is synergistic with biofuels and renewable electricity generation.

Quad Chart Overview

Timeline

- 10/1/2018
- 9/31/2020
- 5%

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	0	0	0	400,000
Project Cost Share*	0	0	0	0

- **Partners:** **If multiple DOE recipients are involved in the project, please list level of involvement, expressed as percentages of project funding from FY 17-18. [(i.e. NREL (70%); INL (30%)]**

Barriers addressed

Barrier: efficient catalytic upgrading of gaseous intermediates

Target: Selectively generating targets of desired chain lengths

Objective

To design electrochemical catalysts for the conversion of CO_2 to C_{2+} oxygenates for further thermocatalytic upgrading to desired products.

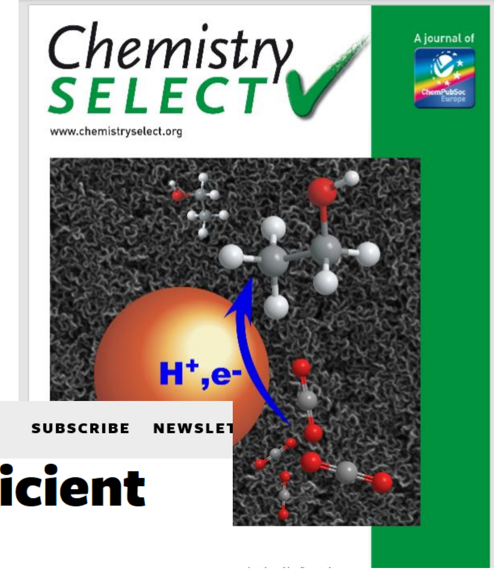
End of Project Goal

Develop a CO_2 electrocatalytic reduction pathway based on bimetallic M-Cu/CNS electrocatalysts with the target of achieving >58% Faradaic efficiency for C_{2+} products at -1.1V vs RHE (25% increase compared to current Cu/CNS -- 46% at -1.1V vs RHE).

1 - Project Overview

- Our team conducts research into nanoscale control of catalysis and electrochemistry
  - Heterogeneous Catalysis
  - Solid state batteries
  - Electrochemical Catalysis
- This project builds on a recently discovered mechanism for high yield conversion of CO_2 to ethanol
- Competitive advantage: nanoscale texture. We focus on using the principles of nanotechnology to control reaction mechanisms

Licensed in US, parts of Asia



POPULAR MECHANICS TECHNOLOGY CARS TOOLS GREAT GIFTS STAY WARM! SUBSCRIBE NEWSLET

Scientists Accidentally Discover Efficient Process to Turn CO2 Into Ethanol

The process is cheap, efficient, and scalable, meaning it could soon be used to remove large amounts of CO2 from the atmosphere.

SCIENCE ADVANCES | RESEARCH ARTICLE

ELECTROCHEMISTRY

A physical catalyst for the electrolysis of nitrogen to ammonia

Yang Song,[1] Daniel Johnson,[1] Rui Peng,[1] Dale K. Hensley,[1] Peter V. Bonnesen,[1] Liangbo Liang,[1] Jingsong Huang,[1,2] Fengchang Yang,[3] Fei Zhang,[3] Rui Qiao,[3] Arthur P. Baddorf,[1] Timothy J. Tschaplinski,[4] Nancy L. Engle,[4] Marta C. Hatzell,[5] Zili Wu,[1,6] David A. Cullen,[7] Harry M. Meyer III,[7] Bobby G. Sumpter,[1,2] Adam J. Rondinone[1]*

news & views

CARBON DIOXIDE REDUCTION

Geometry aids green carbon electrochemistry

Nanoscale texture of electrocatalysts, enabled by the tools of nanoscience, is emerging as an important lever for the control of electrochemical reaction pathways.

Adam J. Rondinone and Jingsong Huang

Nature Catalysis

OAK RIDGE National Laboratory

March 1 Press Release

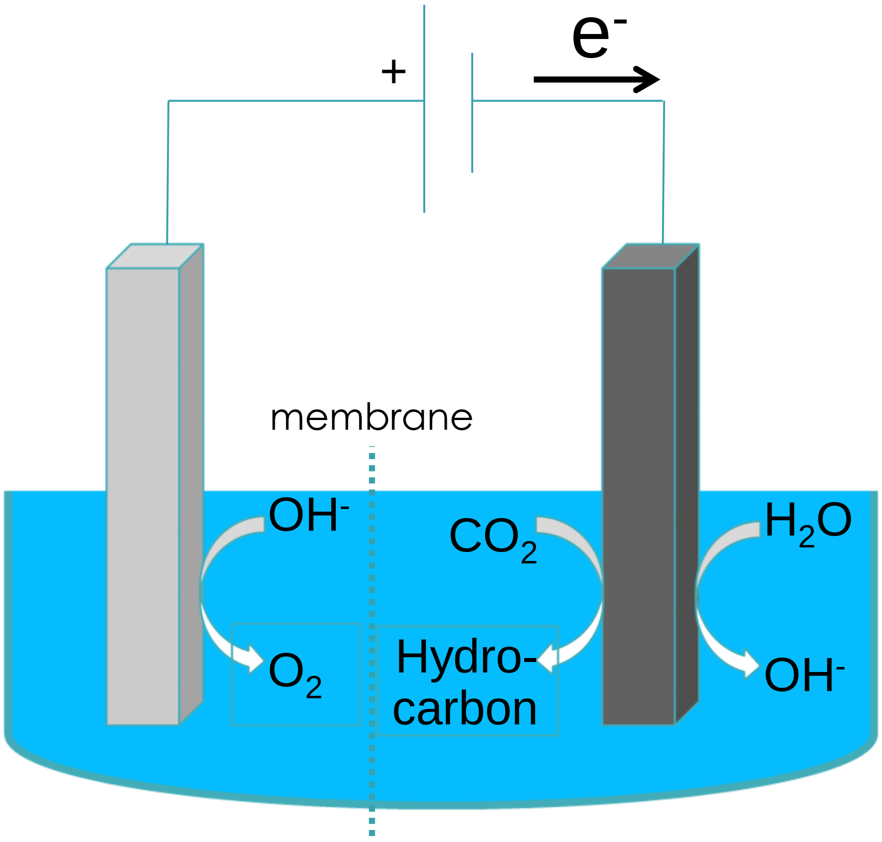
- Technology transfer activities funded through DOE Technology Commercialization Fund

March 1, 2019

OAK RIDGE, Tenn., March 1, 2019—ReactWell, LLC, has licensed a novel waste-to-fuel technology from the Department of Energy's Oak Ridge National Laboratory to improve energy conversion methods for cleaner, more efficient oil and gas, chemical and bioenergy production.

ReactWell will bring ORNL's electrochemical process, which converts carbon dioxide directly into ethanol, into the company's existing conversion solution known as the ReactWell process.

Electrochemical Synthesis ~ Charging a Battery

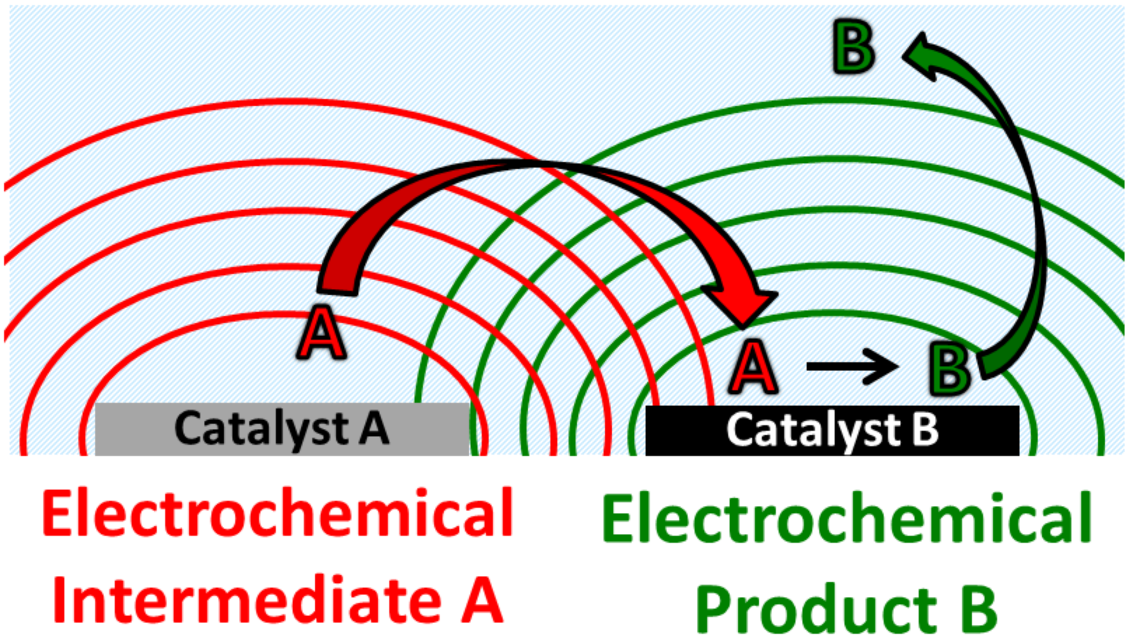


CABB Group GmbH

NaOH, KOH, Cl_2 manufactured electrochemically

Nanoscale Texture can Control Individual Steps

Sequential or tandem electrocatalysis

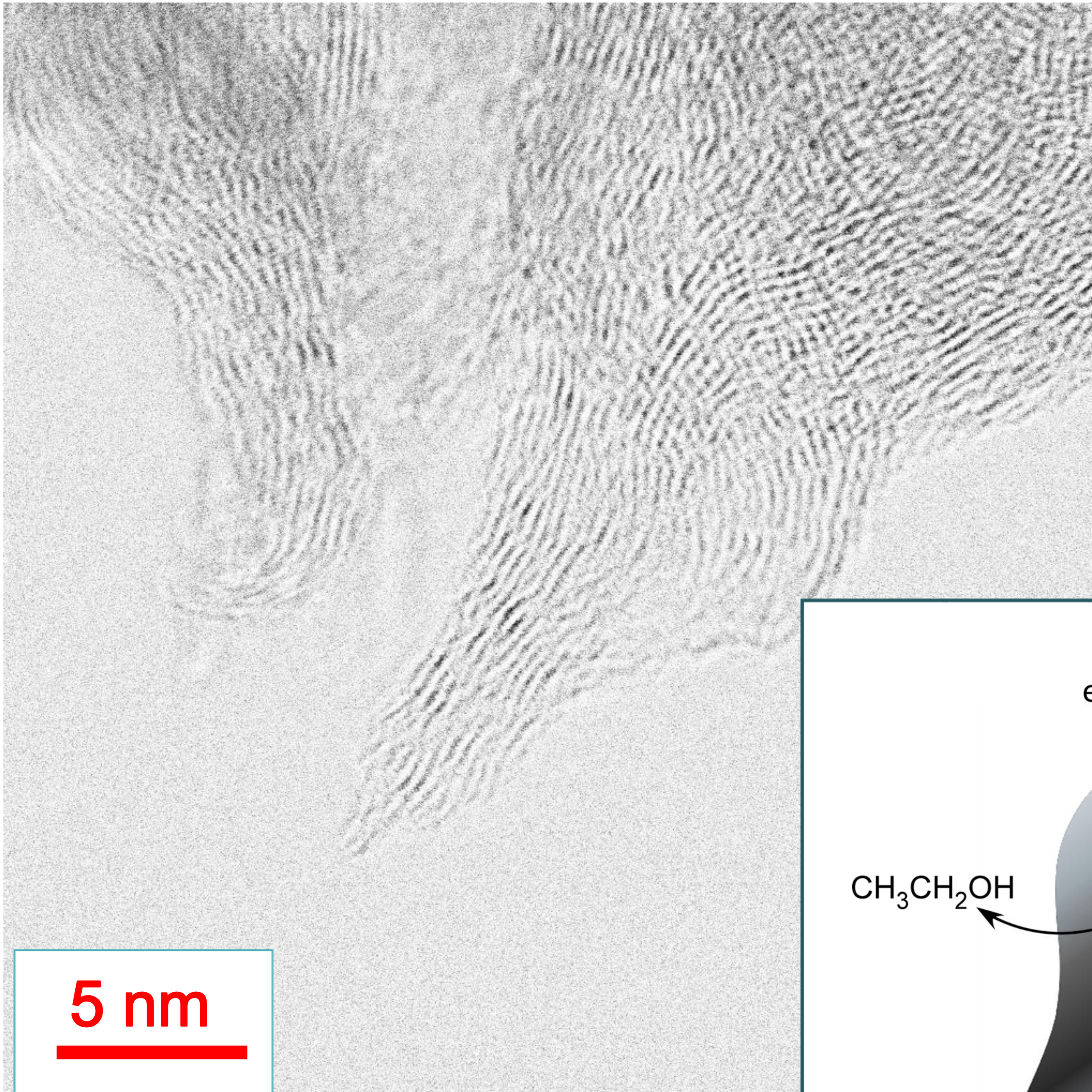


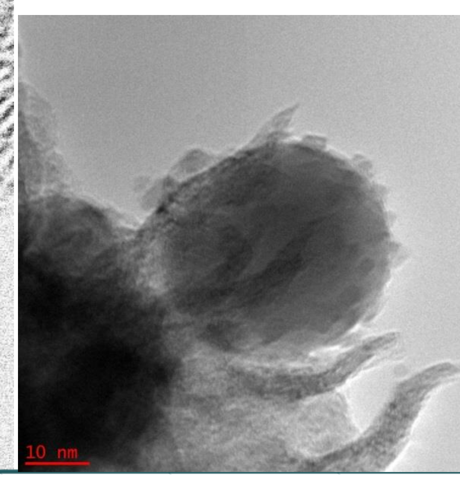
Can engineered, nanoscale electrocatalysts control the activity and/or selectivity?

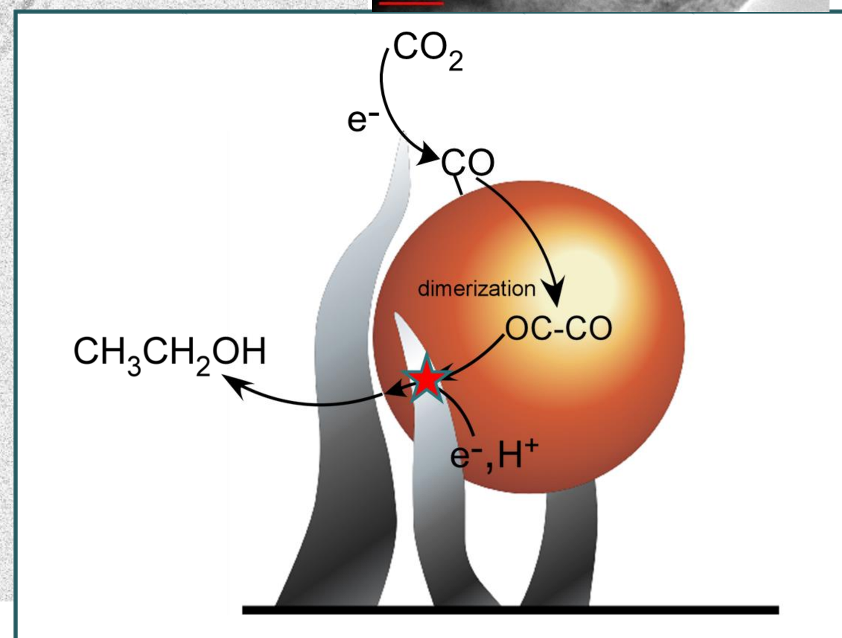
Needed a multi-electron test case: CO_2

Oak Ridge National Laboratory

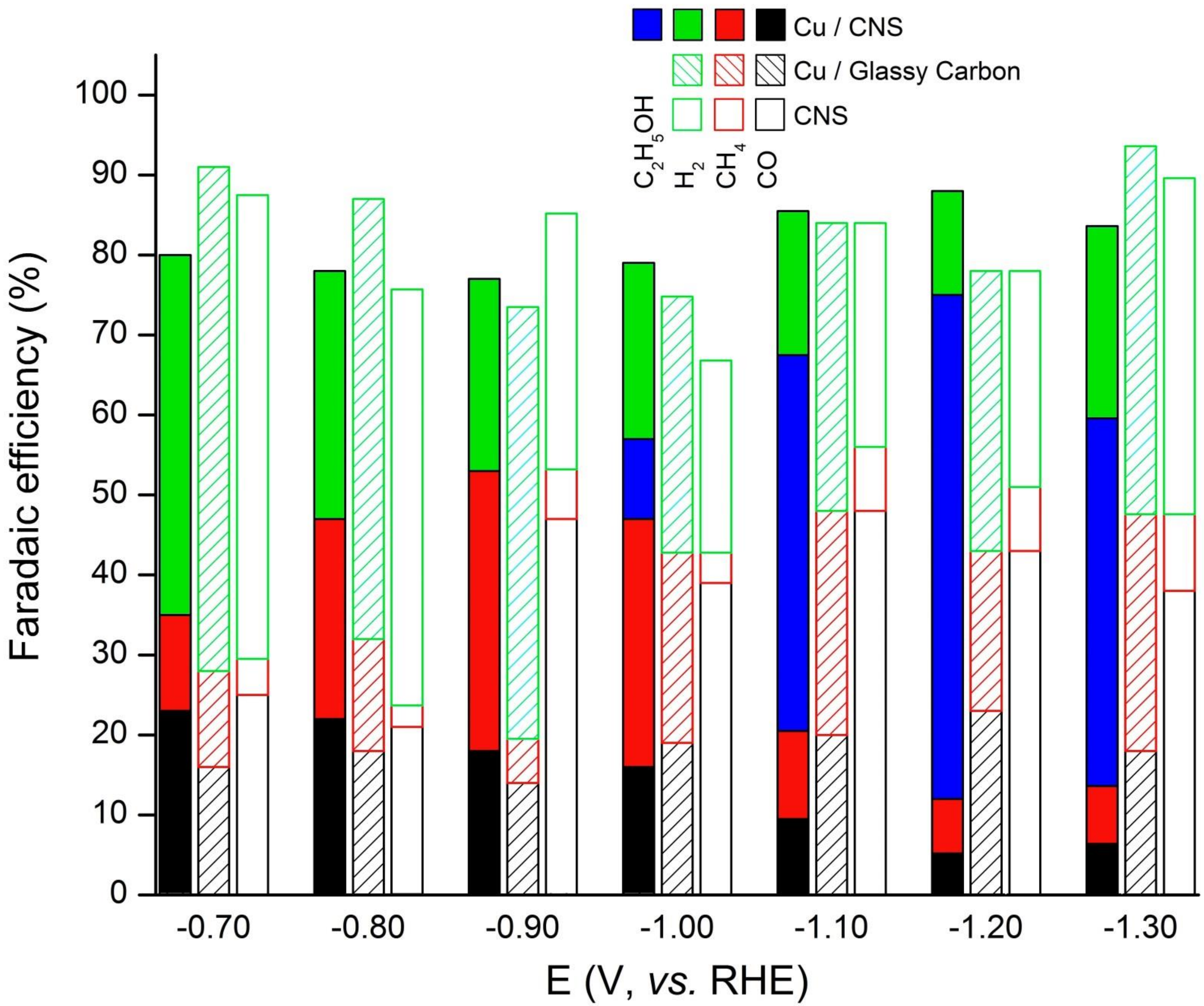
Carbon Nanospikes (CNS)







Original Product Mix



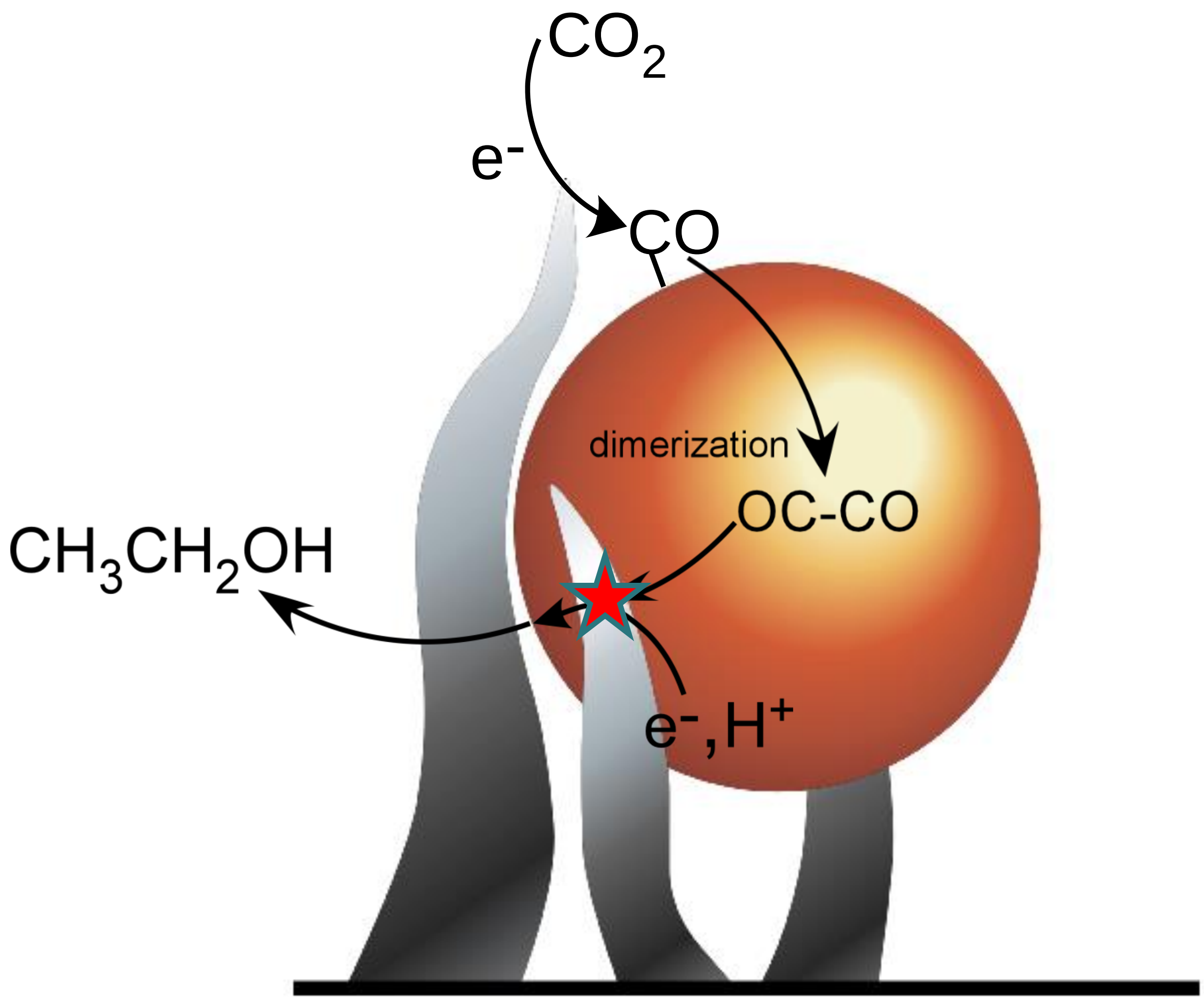
2 – Approach (Management)

- Small Seed-level project with 4 team members:
  - Adam Rondinone: PI, nanomaterials science and electrochemistry
  - PD: Electrochemistry and bi-metal synthesis
  - Zhenglong Li: Advises on thermal upgrading needs and approach
  - Michael Hu: Advises on nanoparticle synthesis strategies
- Periodic team meetings
- Weekly oversight of postdoctoral work

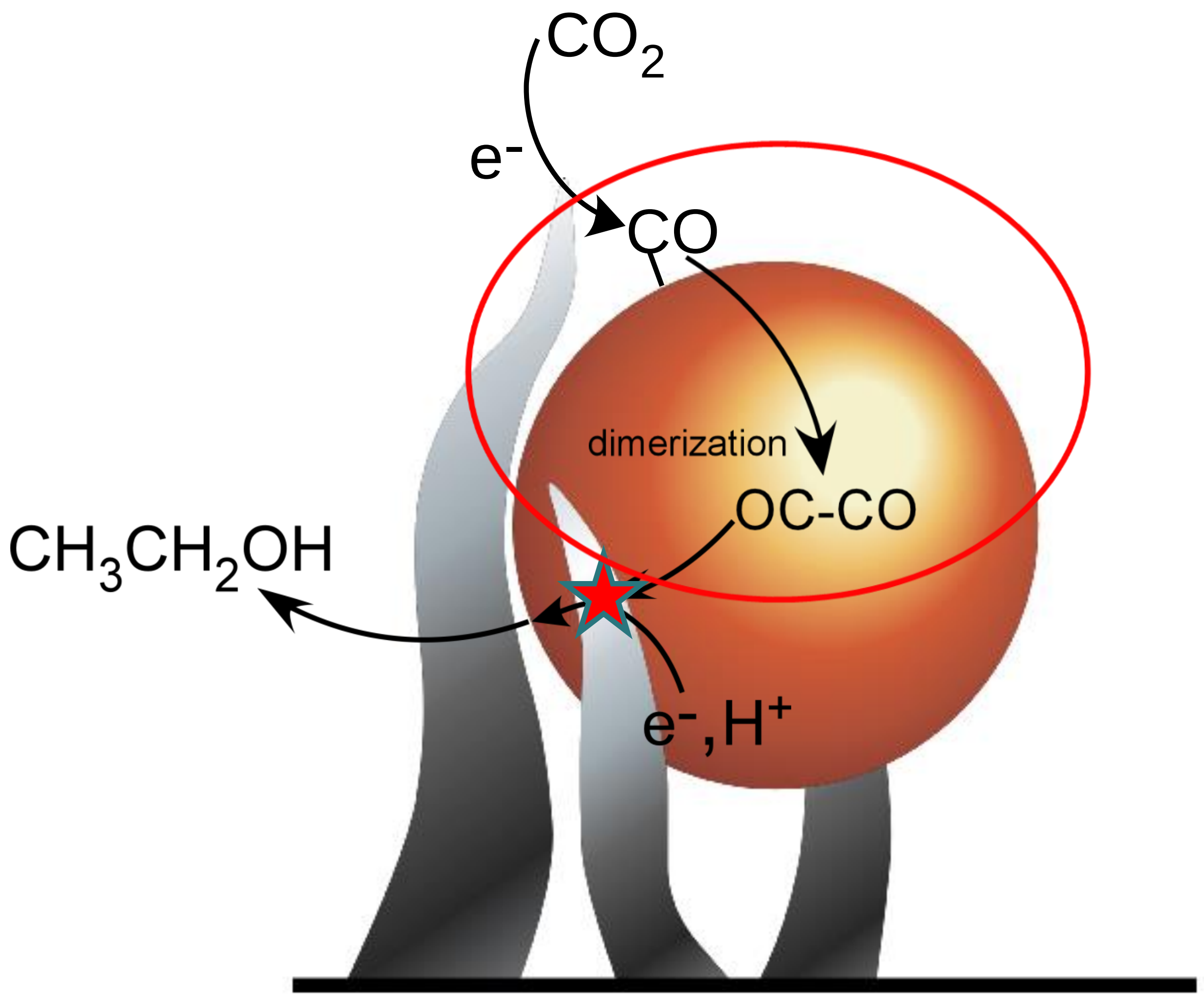
2 – Approach (Technical)

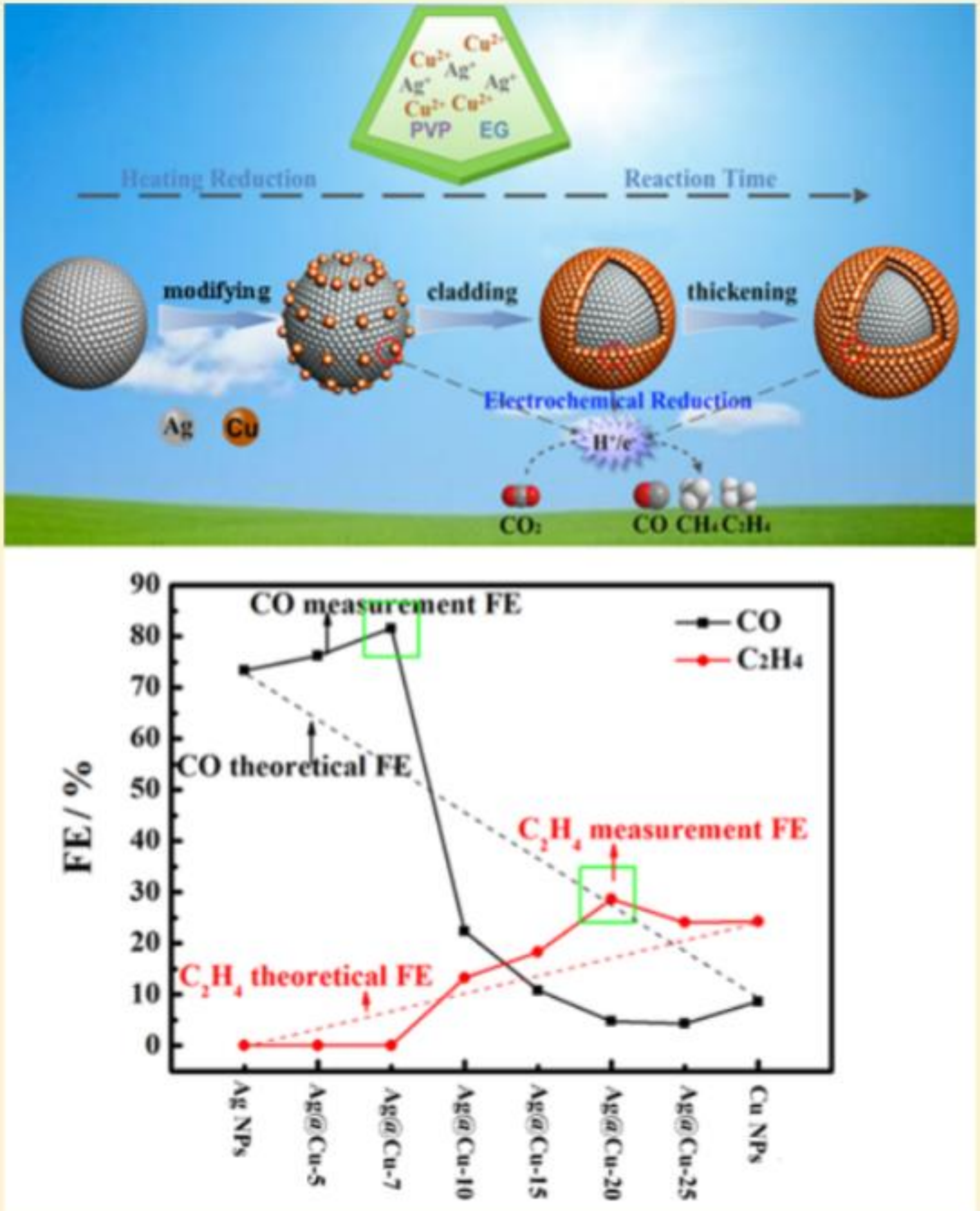
- Outline
  - Good understanding of the basic catalyst
  - Now want something heavier than EtOH
  - Bi-metal co-catalysts could be a pathway to heavier alcohols or other molecules
  - Test promising bi-metal catalysts with goal of heavier or alternative molecules with similar overall performance to original catalyst

Dimerization is Controlled by Metal Co-Catalyst



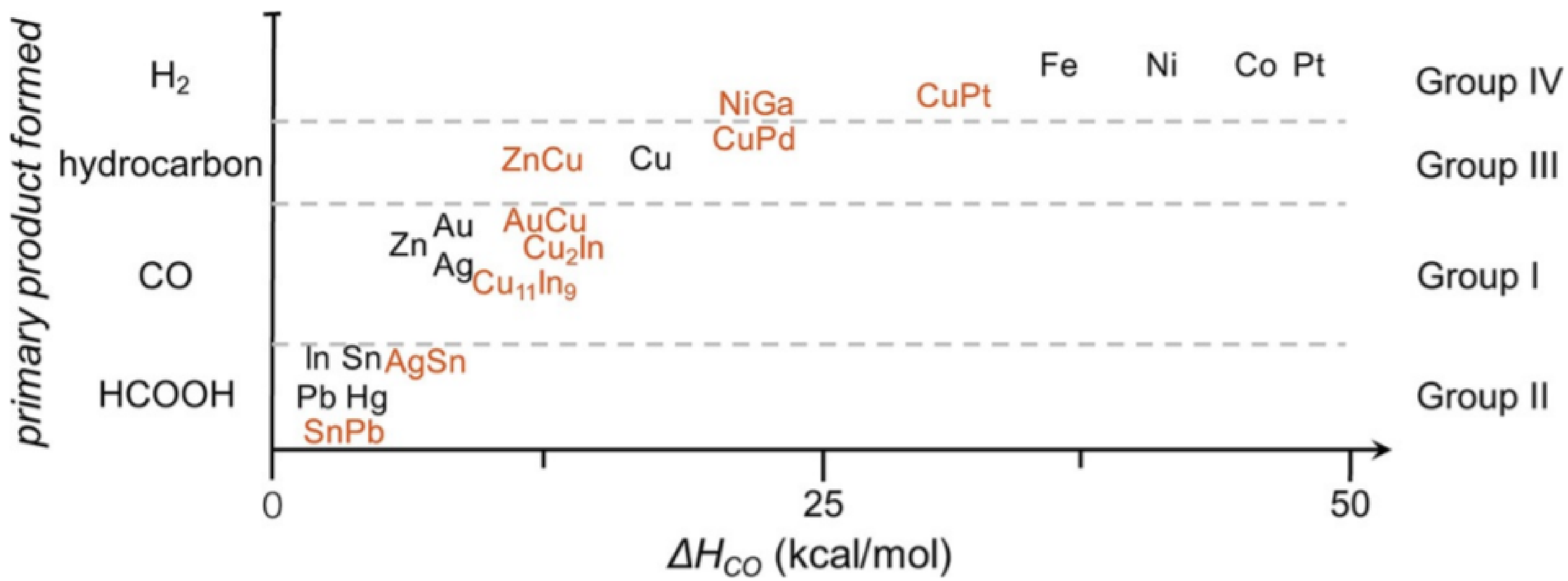
Dimerization is Controlled by Metal Co-Catalyst





J. Phys. Chem. C 2017, 121, 11368−11379

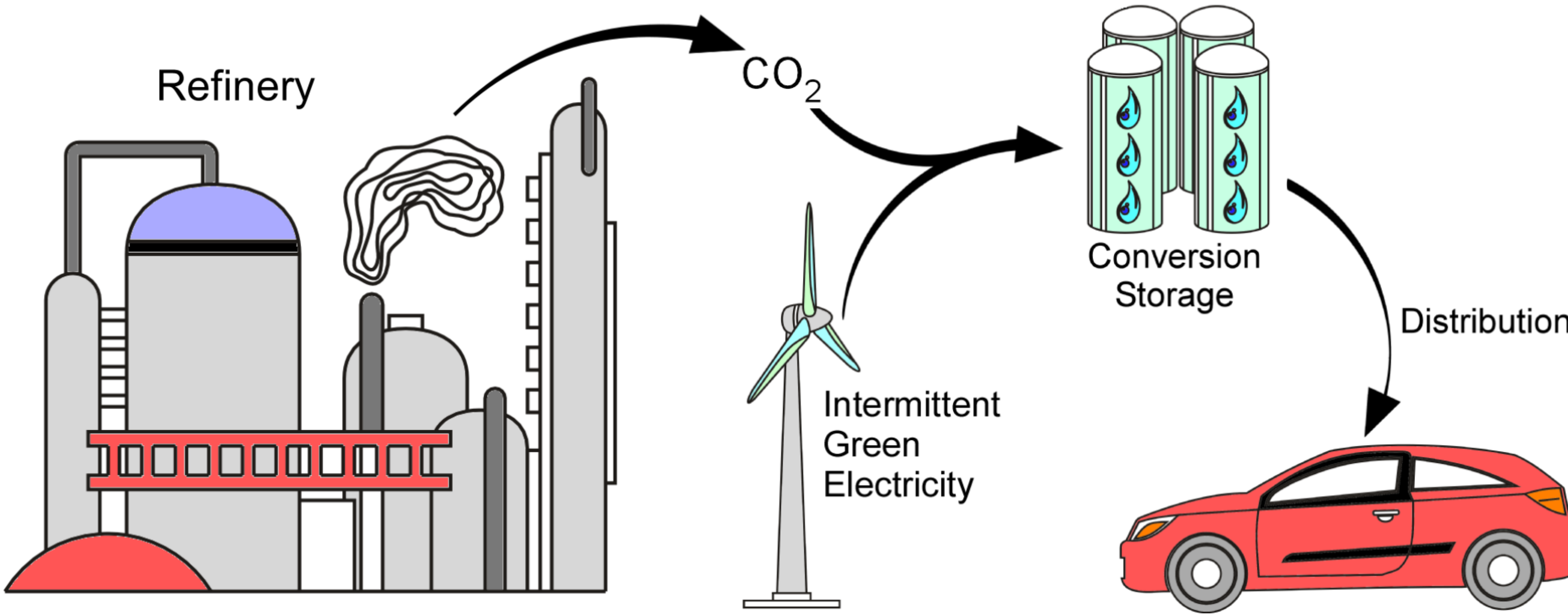
Oligomerization Rate may be Accessed Through CO Binding Energy



ChemSusChem **2018**, *11*, 48 – 57

4 – Relevance

Develop Electrochemical Catalyst for Recycling CO_2 into Useful Molecules



- Fermentation releases 1/3 of C atoms as CO_2
- Electrochemical systems are tolerant of intermittency and appropriate for renewable energy
- Make a green process greener

The Economics Can Work

Consider 1g electrochemical ethanol:

$$\left(\frac{1g}{46g/mol}\right) \times 6.02e^{23} \times \frac{12\mathrm{e}^{-}}{molecule} \div \frac{6.24e^{18}\ \mathrm{e}^{-}}{Coulomb} \times 2.99\mathrm{V} = 75.3\mathrm{kJ\ energy\ in}$$

$$\mathrm{Ethanol\ energy\ density} = 26.4\ \mathrm{kJ/g}$$

$$\mathrm{Energy\ Efficiency} = \frac{26.4\mathrm{kJ}}{75.3\mathrm{kJ}} = 35.1\%$$

$$35.1\% \times 63\%\ \mathrm{Faradaic\ Efficiency} = 22\%\ \mathrm{Total\ Energy\ Efficiency}$$

H_2, CH_4 considered throw-away

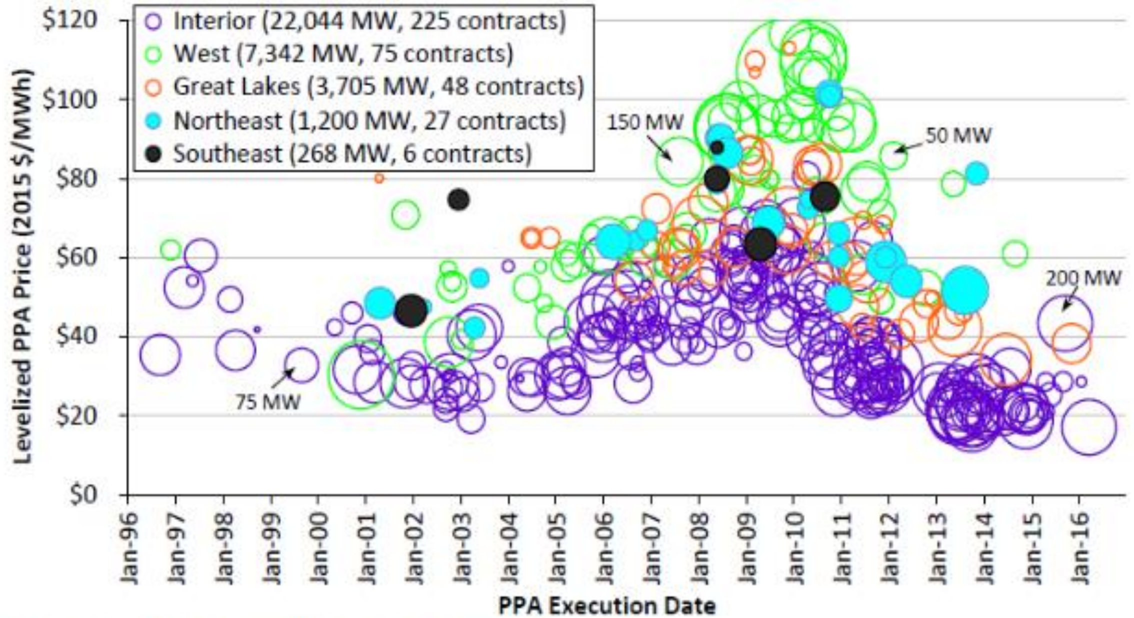
Consider 1 gallon ethanol:

$$78.8\ MJ/gallon = 21.9\ kW \cdot h/gallon$$

$$21.9\ kW \cdot h/gallon \div 22\% = 99.2\ kW \cdot h$$

$99.2\ kW \cdot h\ \times \$0.02/kW \cdot h = \$1.98$ per gallon ethanol for electricity based on laboratory-scale experiments

- Commercial overpotential will be lower due to non-Pt counter electrode
- We have observed single-sample efficiencies closer to 25%



Note: Area of "bubble" is proportional to contract nameplate capacity

Source: Berkeley Lab

Figure 47. Levelized wind PPA prices by PPA execution date and region

American Wind Energy Association, 2016

U. Iowa business school techno-economic analysis: best case is wind farm operator owning electrolysis systems

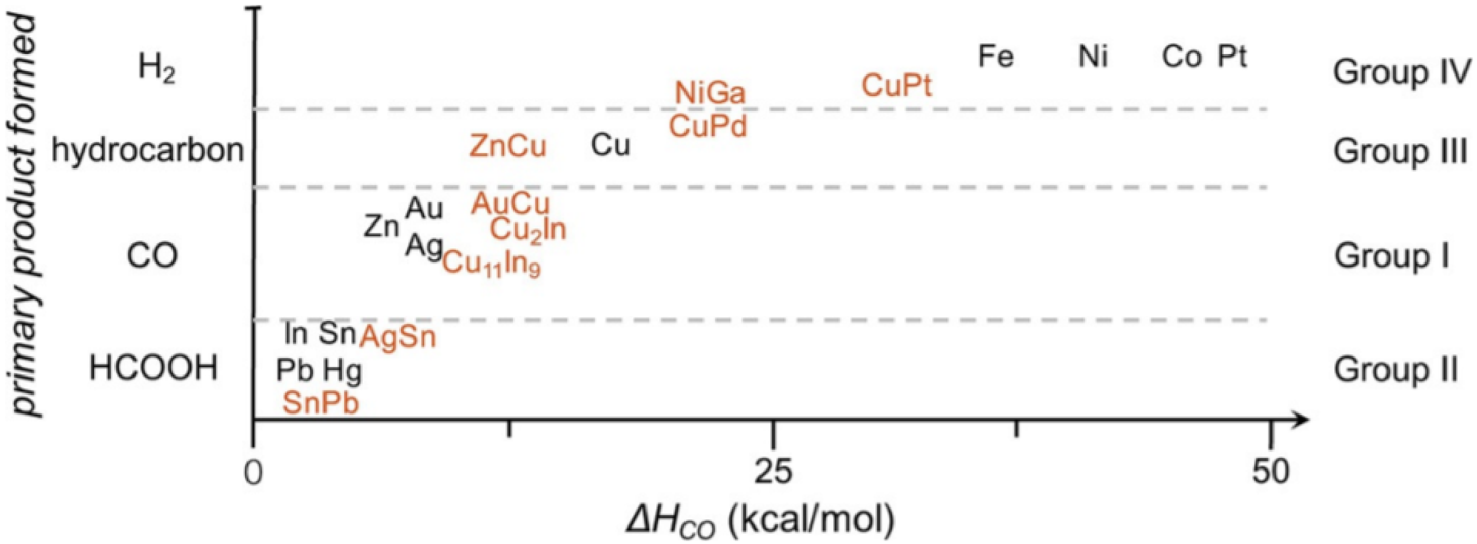
5 – Current and Future BETO Tasks

- 2-year project that started in October 2018
- Task 1: Synthesize bimetallic nanoparticle to use as co-catalysts with carbon nanospikes
- Task 2: Test CNS/bimetal nanoparticles for improved oligomerization rate OR ability to synthesize alternatives to ethanol
  - Use results to optimize Task 1

If successful, this process will feed into future thermocatalytic upgrading for fuels and durable molecules

Task 1

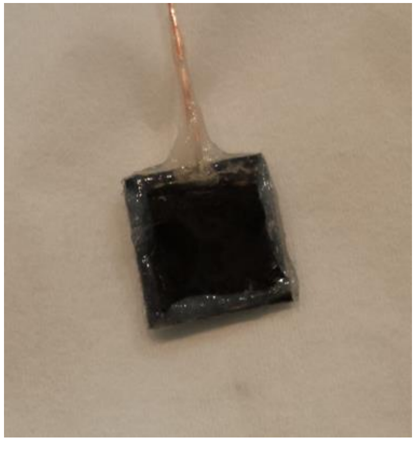
- Synthesize bimetallic M-Cu/CNS electrocatalysts with metal (M) candidates, such as Ag, Zn, Pt or Pd, using electrochemical synthesis techniques.



- Characterizations to understand the catalyst structure and correlate with catalyst performance. Interact with ChemCatBio enabling project -- Advanced Catalyst Synthesis and Characterizations.

Task 2

- Perform electrocatalytic testing of the bimetallic M-Cu/CNS catalyst for CO_2 conversion to C_{2+} products.
  - Analytical electrochemistry: cyclic voltammetry, linear scan voltammetry
  - Longer term (6-hour) experiments under stable conditions (chronoamperometry) for product distributions, stability
- Optimize the catalyst structure and performance with the help of advanced characterizations and computational modeling.
  - Operando X-ray absorption, X-ray photoelectron spectroscopy



Milestones

Quarterly	Synthesize at least one bimetallic electrocatalyst on CNS using electrochemical deposition, which will be characterized with electron microscopy to understand the catalyst morphology and composition.	12/31/2018
Quarterly	Develop at least 3 carbon nanospike supported bimetallic electrocatalysts with different formulations.	3/31/2019
Quarterly	Perform electrocatalytic testing on the prepared bimetallic catalysts on CNS with more than one analytical electrochemistry techniques. This will help to prescreen these bimetallic catalysts by measuring the reduction potentials, activity, and types of reactions that occur.	6/30/2019
Annual SMART	Demonstrate one bimetallic catalyst on CNS that is stable for C_{2+} production. This catalyst will be well characterized with at least 3 different techniques (e.g., EXAFS, HRTEM and XPS).	9/31/2019
End of Project	Develop a CO_2 electrocatalytic reduction pathway at lab scale based on bimetallic M-Cu/CNS electrocatalysts with the target of achieving >58% Faradaic efficiency for C_{2+} products at -1.1V vs RHE (25% increase compared to current Cu/CNS -- 46% at -1.1V vs RHE).	9/31/2020

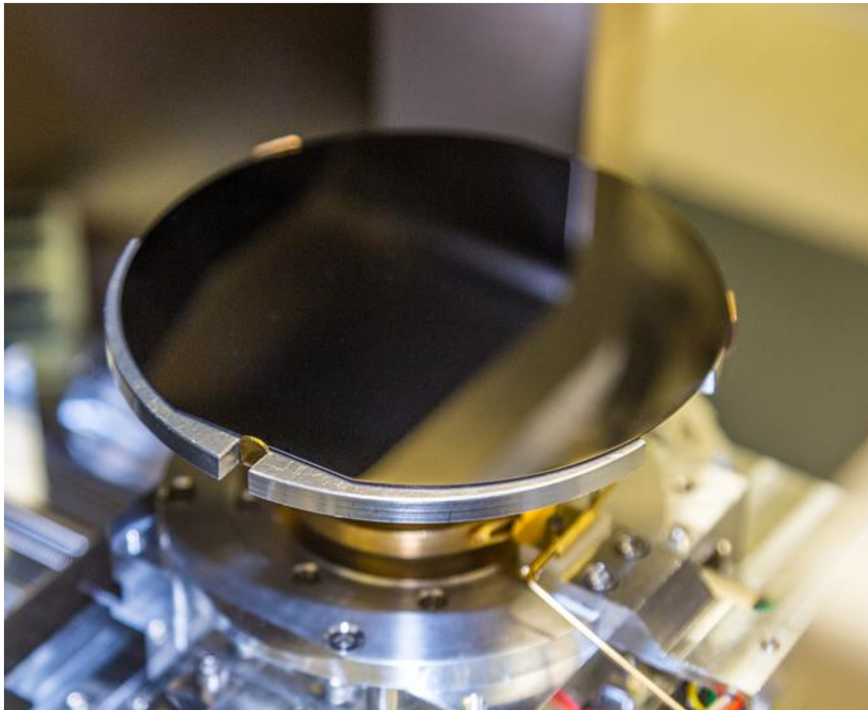
Decision Point

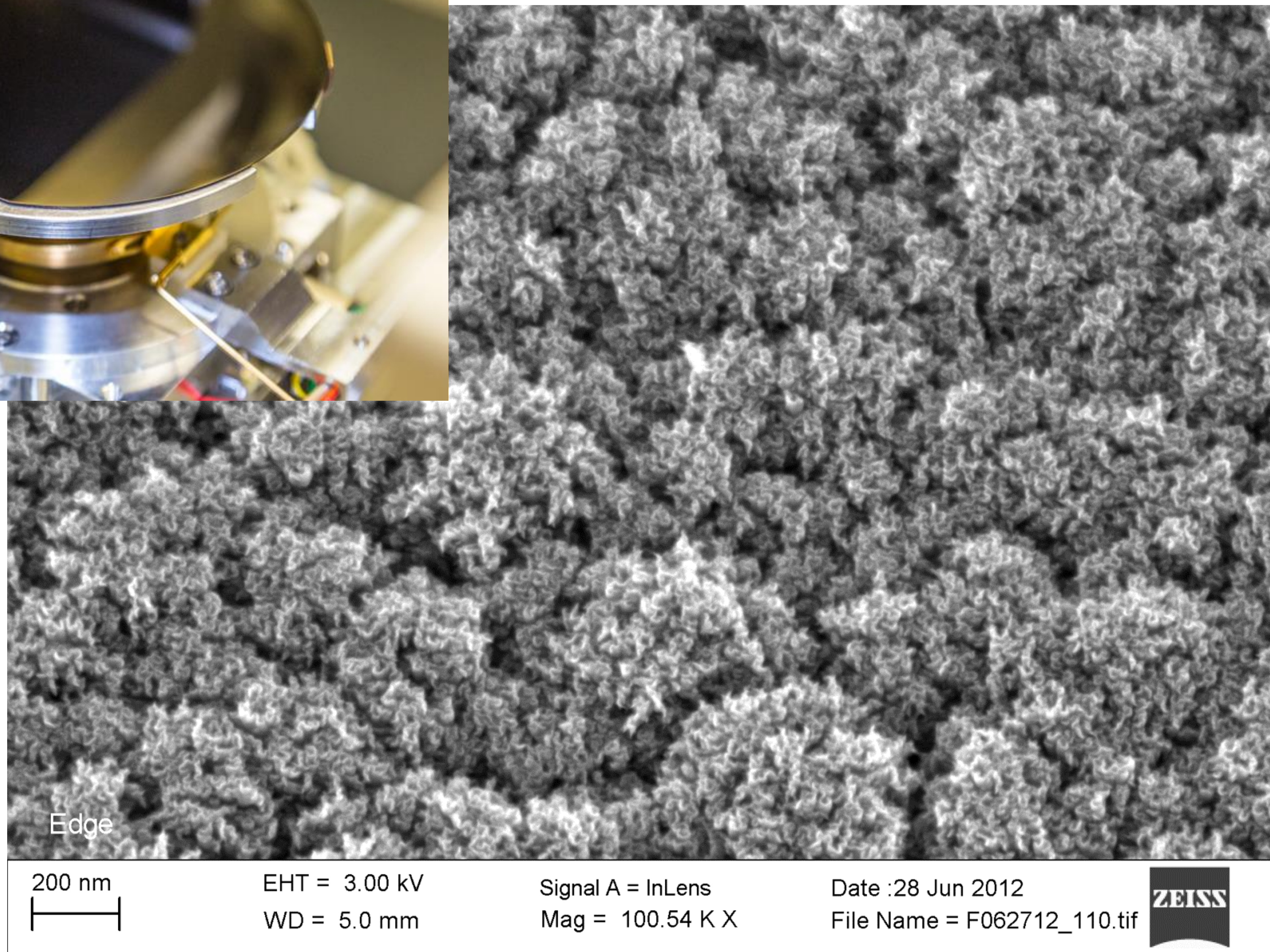
Decision	Criteria	Date
Evaluate Bimetallic M-Cu/CNS Electrocatalysts to Meet Faradaic Efficiency Target	Demonstrate at least one bimetallic M-Cu/CNS electrocatalyst which can exceed 46% Faradaic efficiency for C2+ products at -1.1V vs RHE, better than current Cu/CNS.	3/31/2020

Summary

- This project will develop a nanotextured carbon supported bimetallic catalyst with improved selectivity for heavy alcohols and/or alternative molecules
- Focusing on bimetallic nanoparticle synthesis and electrochemical analysis
- Electrochemical synthesis is complimentary to biofuels production
- Nanotexture is a means to improve reaction control

Additional Slides

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Date :28 Jun 2012
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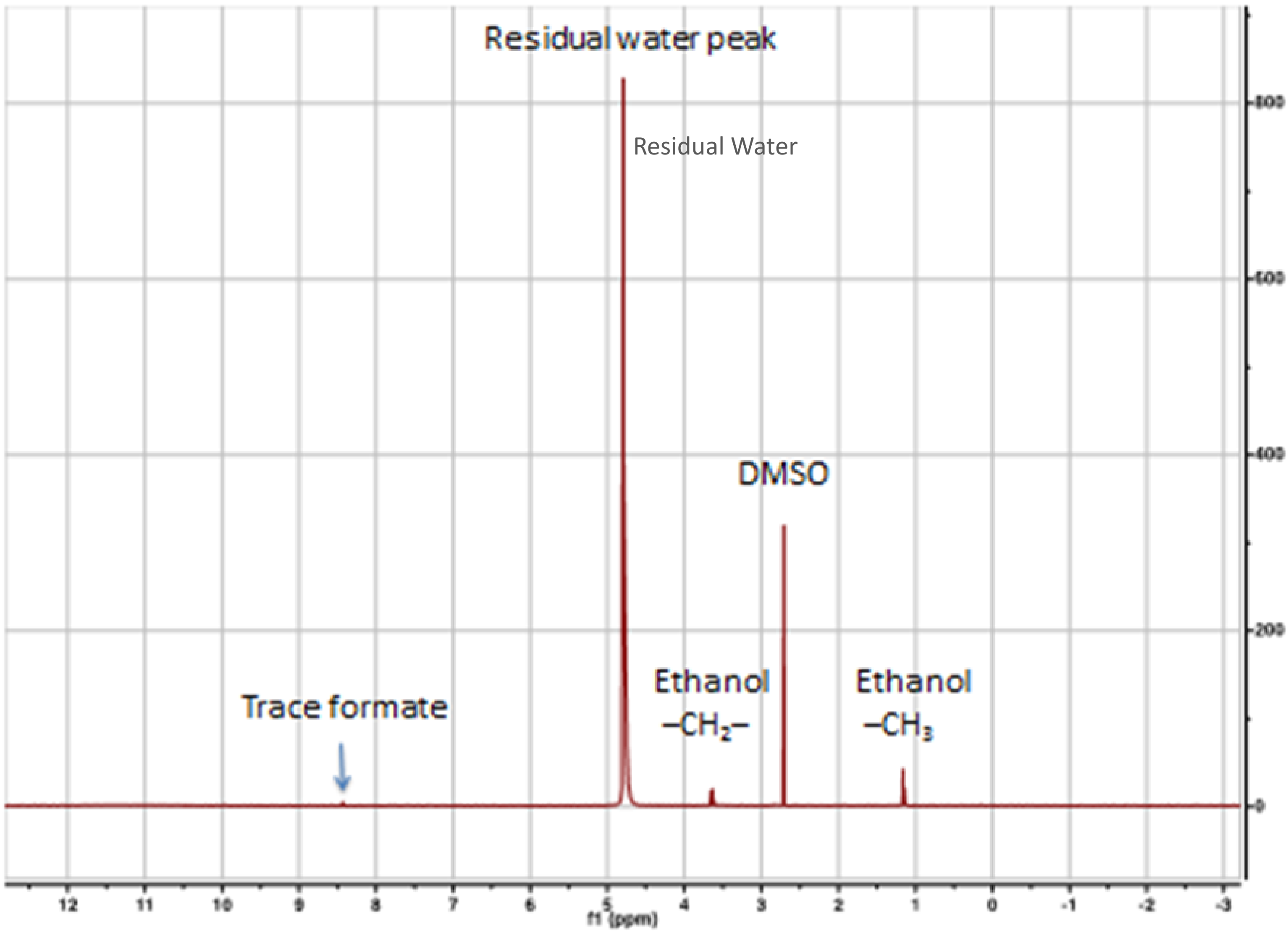
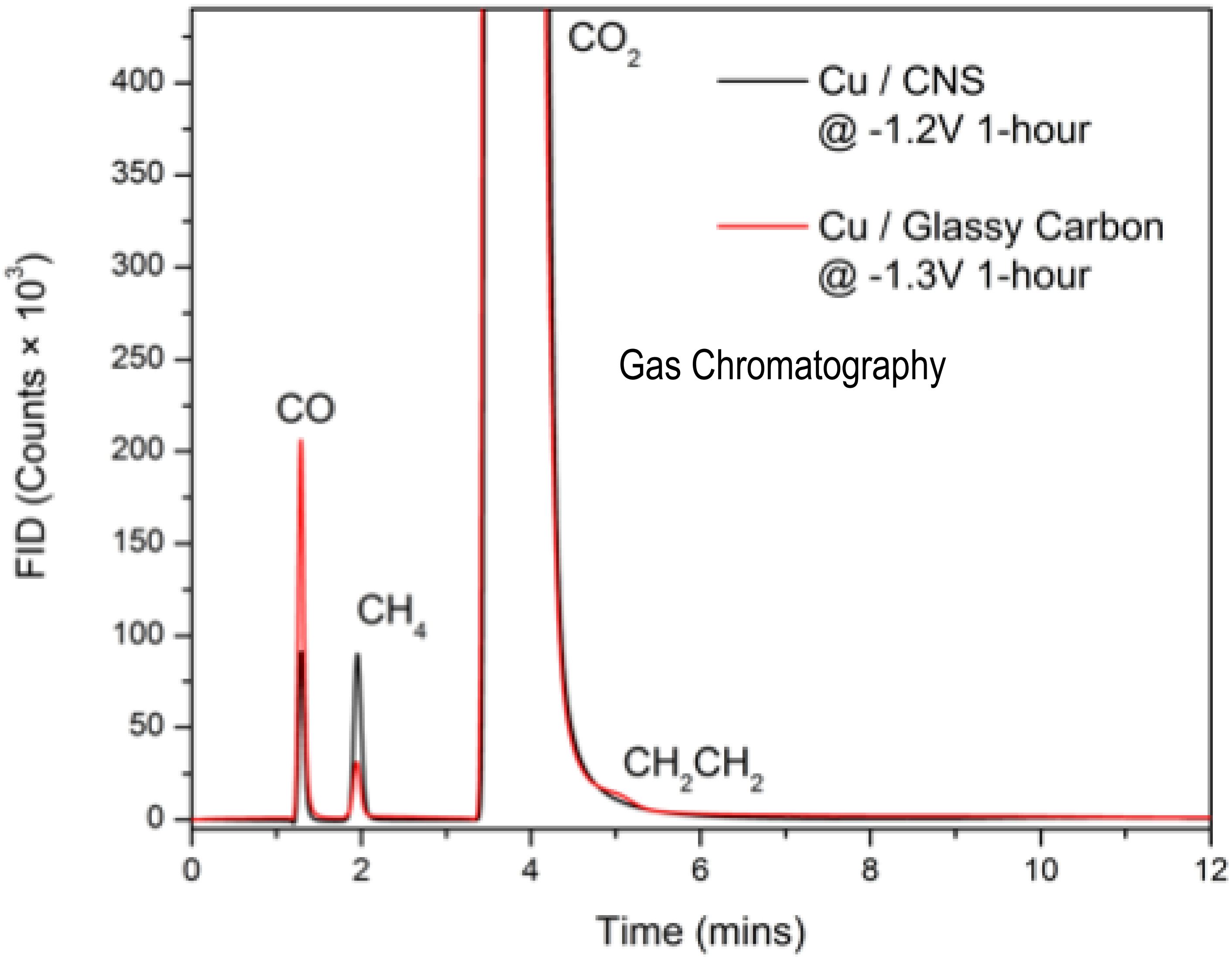
ZEISS

NMR Analysis For Soluble Products



Product Quantification

Gas chromatography headspace analysis for volatile products



Cost to Drive

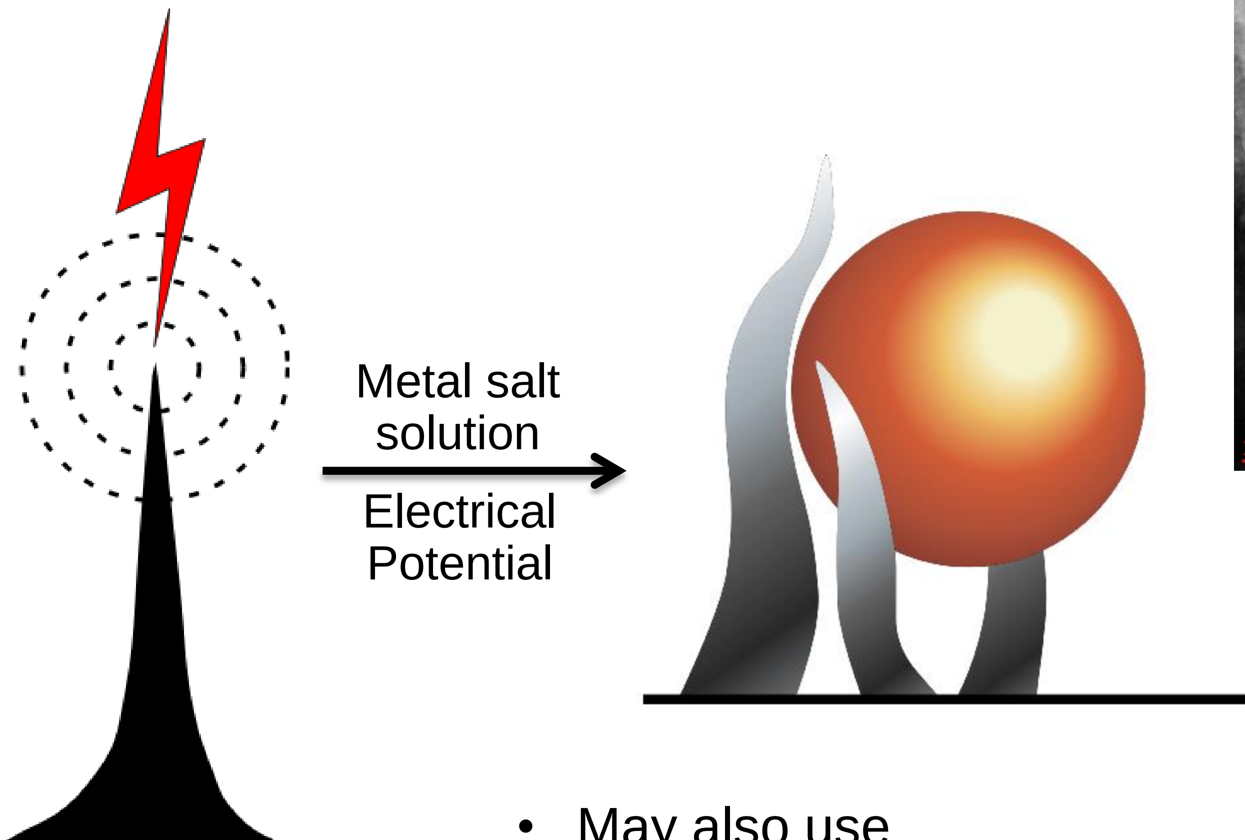
	Leaf		Sentra		Sentra EtOH		Sentra EtOH	
Base Cost Car	$30,680.00		$16,990.00		$16,990.00		$16,990.00	
Energy Efficiency Car	2.94	mile/kwh	33	mpg	33	mpg	33	mpg
Lifetime Miles	150000		150000		150000		150000	
Fuel During Lifetime	51020	kwh	4545	gal	4545		4545	gal
Cost Per Unit Energy	$0.09	/kwh residential	$2.00	gal	$3.00	gal	$4.00	gal
Total Cost Fuel	$4,744.90		$9,090.91		$13,636.36	gal	$18,181.82	
Total Cost Lifetime	$35,424.90		$26,080.91		$30,626.36		$35,171.82	
	Does not include charger installation or tax credits							
	Does not include oil, filters, IC maintenance							

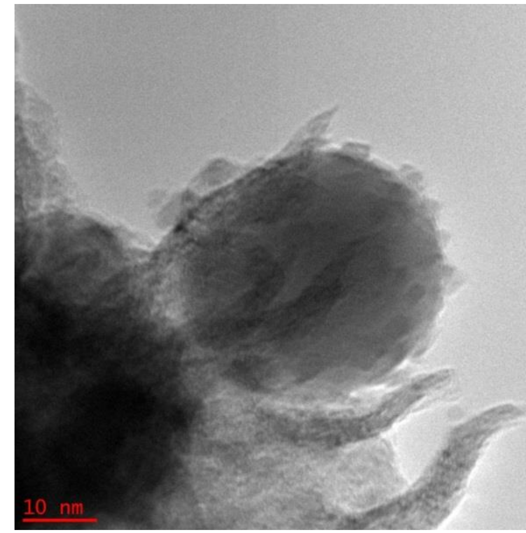
Leaf

Sentra

Metal Co-Catalyst is Nucleated in situ

- Approximately 1×10^{14} spikes per m^2 CNS





- May also use
  - In situ particle synthesis with chemical doping
  - ex situ nanoparticle synthesis