DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

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

March 11, 2021

CO_2 Utilization

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Oak Ridge National Laboratory

Goal Statement

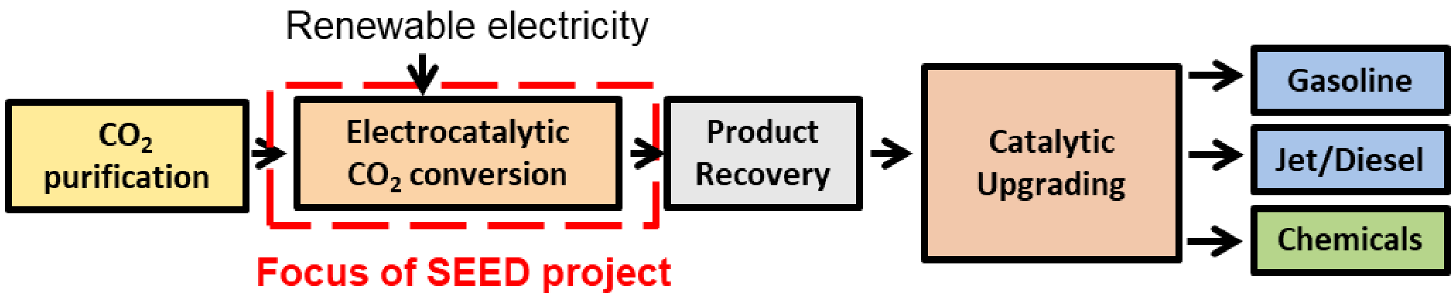
- **Goal**: develop an **electrocatalytic synthesis** approach for the **reduction of CO_2 to C_{2+} products** to achieve the target of >58% faradaic efficiency for C2+ products at -1.1V vs RHE (25% increase compared to Cu/carbon nanospike -- 46% at -1.1V vs RHE)
- **Outcome**: **advance the state of technology** for electrochemical synthesis of C_{2+} molecules from CO_2 over new carbon nanospike-based electrocatalysts
- **Relevance:** this project is relevant to the bioenergy industry because it provides a means to **recycle CO_2 from the biorefinery to molecules** that were traditionally fossil-based, in a manner that is synergistic with biofuels and renewable electricity generation

Project Overview

Importance of CO_2 utilization:

- Mitigate the CO_2 emission challenges
- CO_2 as a carbon-based feedstock for producing chemicals and fuels
- CO_2 reduction as a useful means to store renewable electricity in chemical energy

Hybrid electro- and thermo-catalytic CO_2 utilization approach for making hydrocarbon fuels and valuable chemicals



This SEED project seeks to electrocatalytically synthesize C_{2+} products that can be tailored for further thermal catalytic upgrading to transportation fuels, chemicals and polymers.

Quad Chart Overview

Timeline

- 10/1/2018
- 09/30/2020

	FY19	FY20	Total Planned Funding
DOE Funding	$200,000	$200,000	$400,000

Barriers addressed

Efficient catalytic upgrading of gaseous intermediates

Project Goal

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

End of Project Milestone

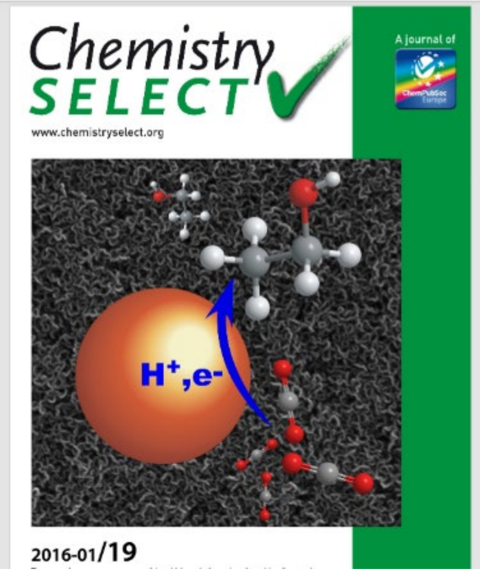
Develop a CO_2 electrocatalytic reduction pathway based on bimetallic M-Cu/CNS electrocatalysts with the target of achieving >58% Faradaic efficiency for C_{2+} products at -1.1V vs RHE (25% increase compared to current Cu/CNS - 46% at -1.1V vs RHE).

Project Overview

This project builds on a technology for selective conversion of CO_2 to ethanol over carbon nanospikes (CNS).

R&D 100 AWARDS

2019 R&D100 Award



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

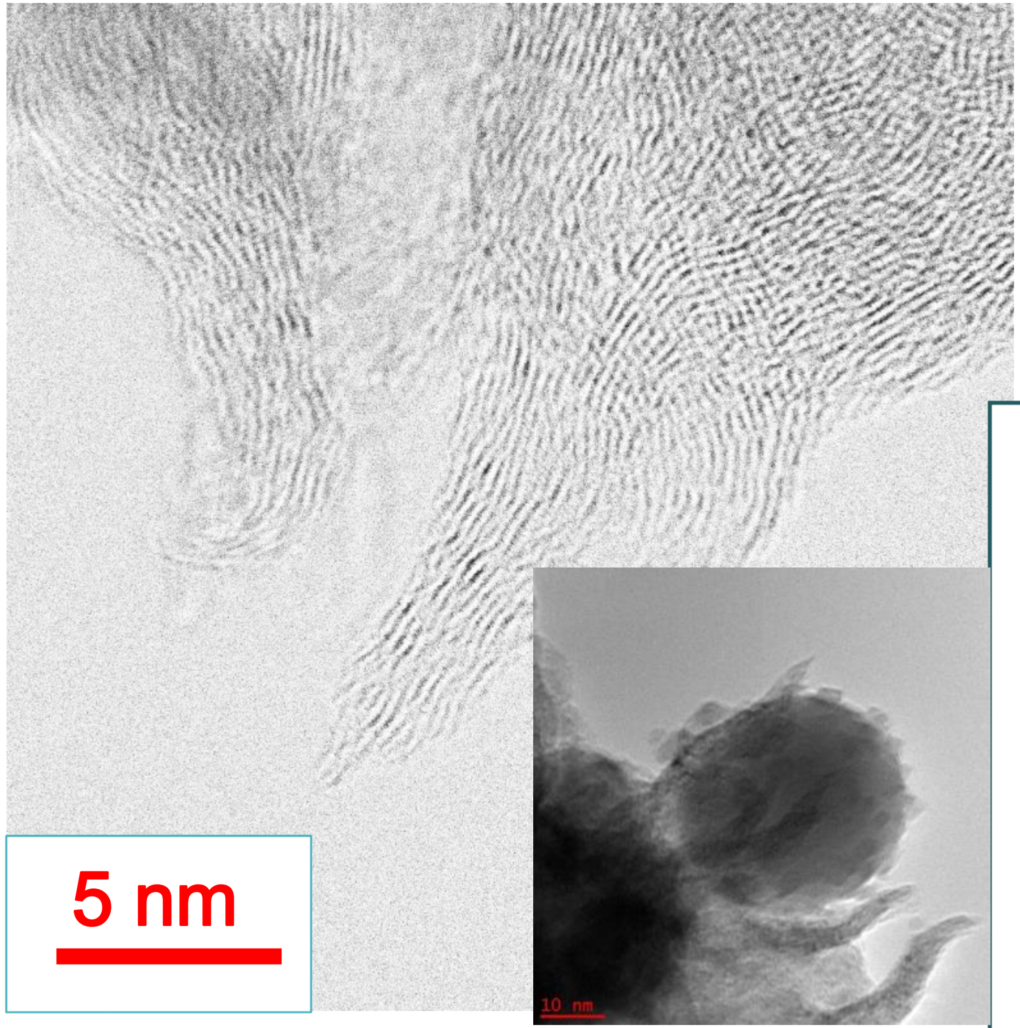
Nanoscale texture of electrocatalysts, enabled by the tools of nanoscience, is emerging as an important lever for the control of electrochemical reaction pathways.

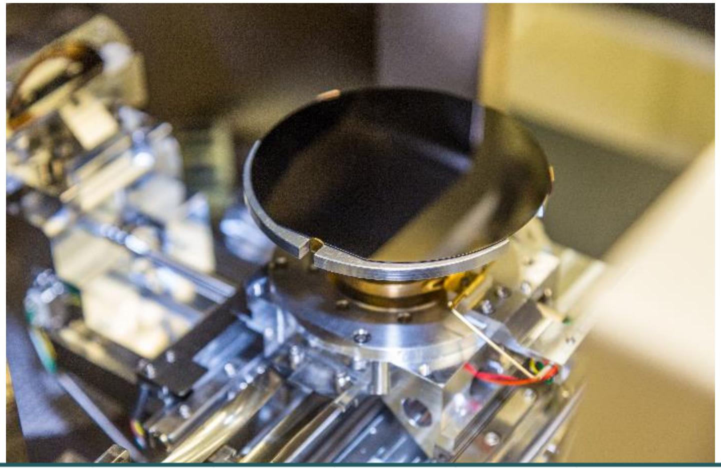
Adam J. Rondinone and Jingsong Huang

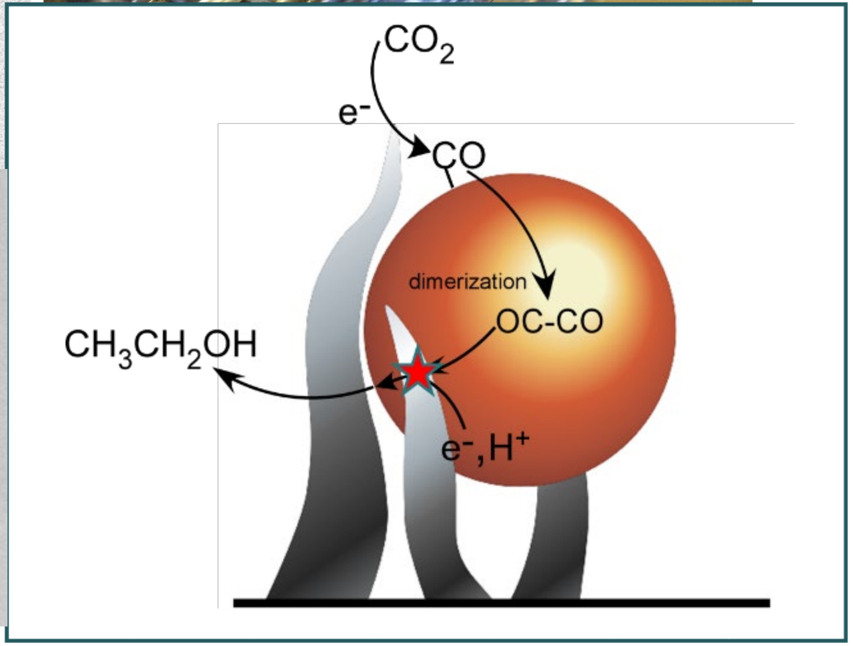
Nature Catalysis

Project Overview

Cu on carbon nanospikes can catalyze cascade reaction of CO_2 conversion to ethanol

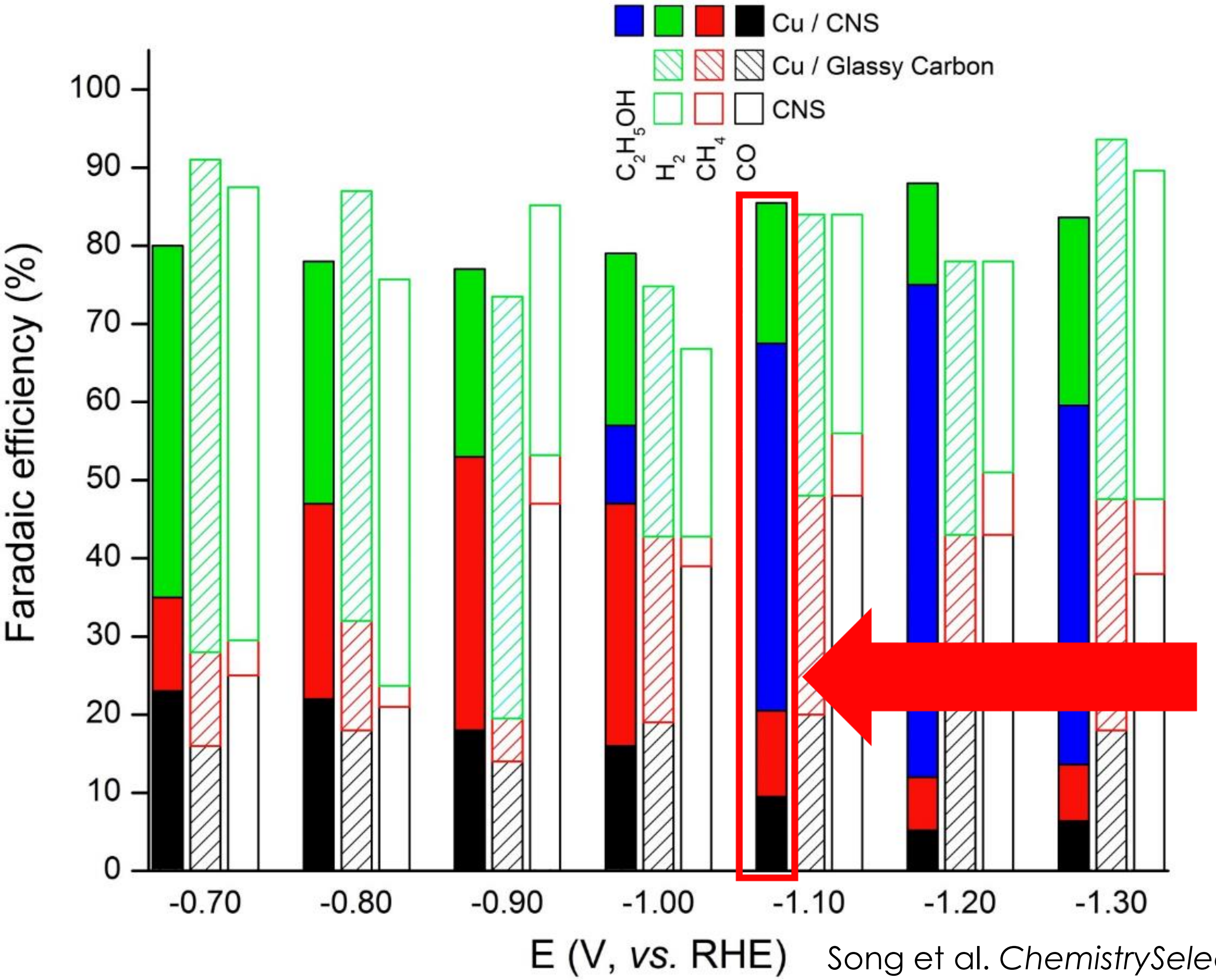






1 – Technical Approach

Original Product Mix over Cu/CNS



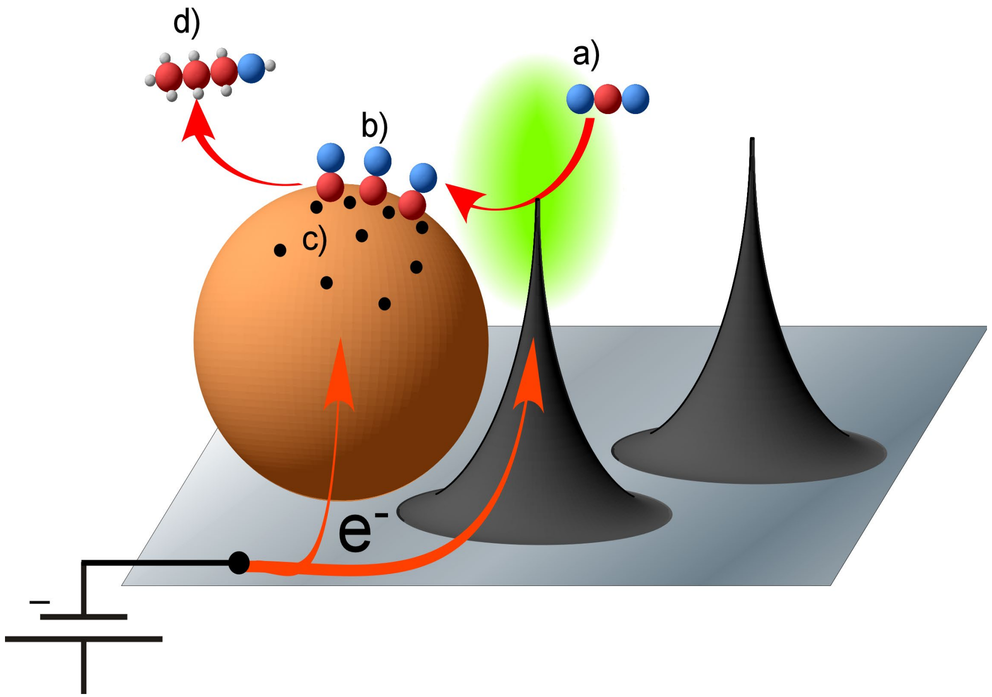
Song et al. *ChemistrySelect*. **2016**, 1, 6055.

Cu/CNS serves as the baseline for further development

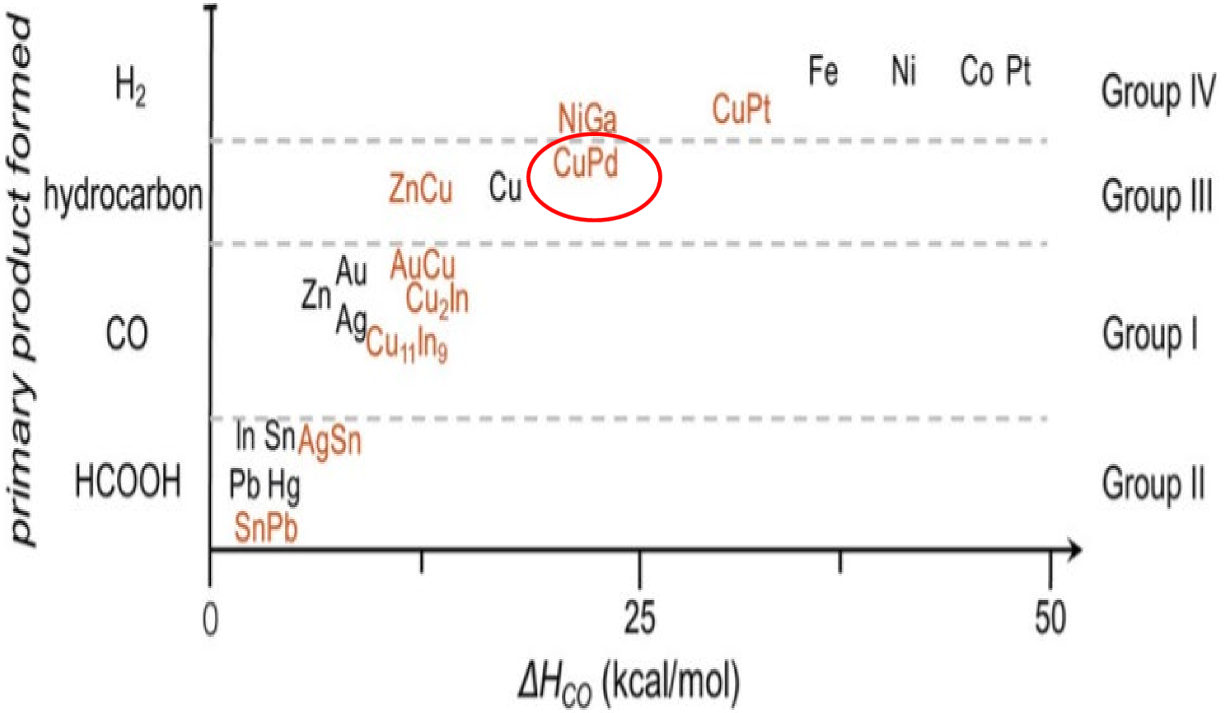
Cu/CNS performance @-1.1V vs RHE is the benchmark

1 – Technical Approach

Oligomerization is controlled by metal co-catalyst



Develop bimetallic co-catalyst to enhance the oligomerization rate by tuning CO binding energy



ChemSusChem **2018**, *11*, 48 – 57

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2 – Management Approach

- **Small seed-level project with 4 team members**:
  - Zhenglong Li: PI, catalyst design
  - Adam Rondinone: (prior PI*), nanomaterials science and electrochemistry
  - Dale Hensley: synthesize carbon nanospike material
  - Seonah Jin: electrochemistry, bimetallic catalyst synthesis
- **Monthly team meetings**
- **Project structure**:
  - Task 1: Bimetallic electrocatalysts synthesis and characterizations
  - Task 2: Electrocatalytic testing and electrocatalyst optimization
- **Interaction with ChemCatBio (CO_2 upgrading)**

*Currently at Los Alamos National Laboratory

2 – Management Approach: Risk and Mitigation

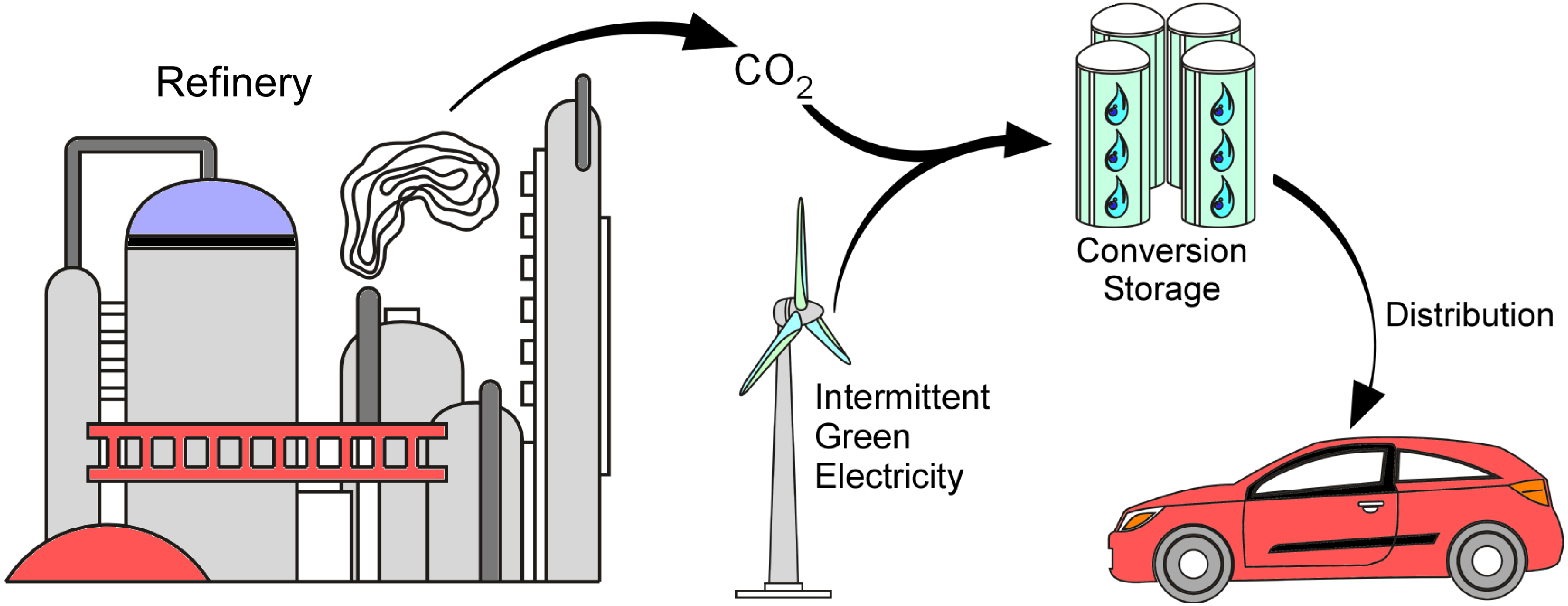
Risks	Mitigation
Bimetallic electrocatalysts **could not promote the formation of C_{2+} products to reach the targeted faradaic efficiency**	**Advanced catalyst characterizations and electrocatalyst testing** will provide useful information about the catalyst structure and performance. Alternative bimetallic co-catalysts will be studied based on evidence of this information.
Cu and the 2nd metal **do not form alloys** but distribute separately on the CNS using electrochemical deposition synthesis method.	**Wet chemical synthesis** method will be employed to prepare the bimetallic nanoparticles first, and then load onto CNS.
Some of the advanced characterizations, such as XAS, may not be available at the time needed.	Make plans earlier and schedule the beam time beforehand via better coordination with Advanced Catalyst Synthesis and Characterizations within ChemCatBio Consortium.

Milestones Associated with Risk Mitigations

- ***FY19 Q2:*** Develop at least 3 carbon nanospike supported bimetallic electrocatalysts with different formulations for electrocatalytic testing
- ***FY20 Q4 (delayed):*** 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)

3 – Impact: Relevance to Bioenergy Industry

Develop electrochemical catalyst for recycling CO_2 from biorefinery into useful molecules



- Generate valuable products from fermentation derived CO_2
- Electrochemical systems are tolerant of intermittency and appropriate for renewable energy storage
- Make a green process greener

3 – Impact : Relevance to Bioenergy Industry

- **Transitioning R&D discovery of CO_2 utilization to bioenergy industry**

  ReactWell licensed ORNL technology on electrocatalytic CO_2 conversion to ethanol

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.

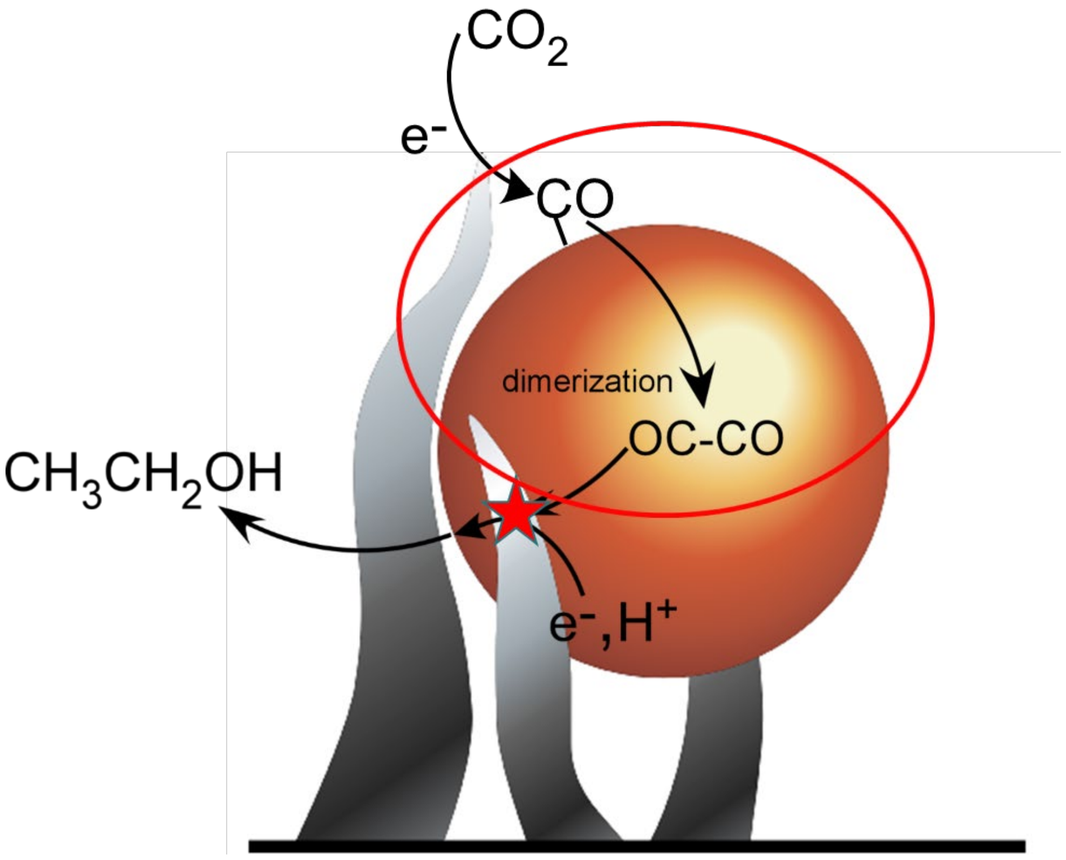
ReactWell will bring ORNL's electrochemical process, which converts carbon dioxide directly into ethanol, into the company's existing conversion solution known as the ReactWell process.

- **Additional research license was added to expand further collaboration with industry**

4 – Progress and Outcomes

Two major objectives of this project:

- Understand CO_2 activation over CNS electrocatalyst
- Demonstrate the **proof-of-concept** results for enhancing C_{2+} product formation from CO_2 with bimetallic co-catalyst to achieve the **target of >58% faradaic efficiency for C_{2+} products** at -1.1 V vs RHE (25% increase compared to benchmark)



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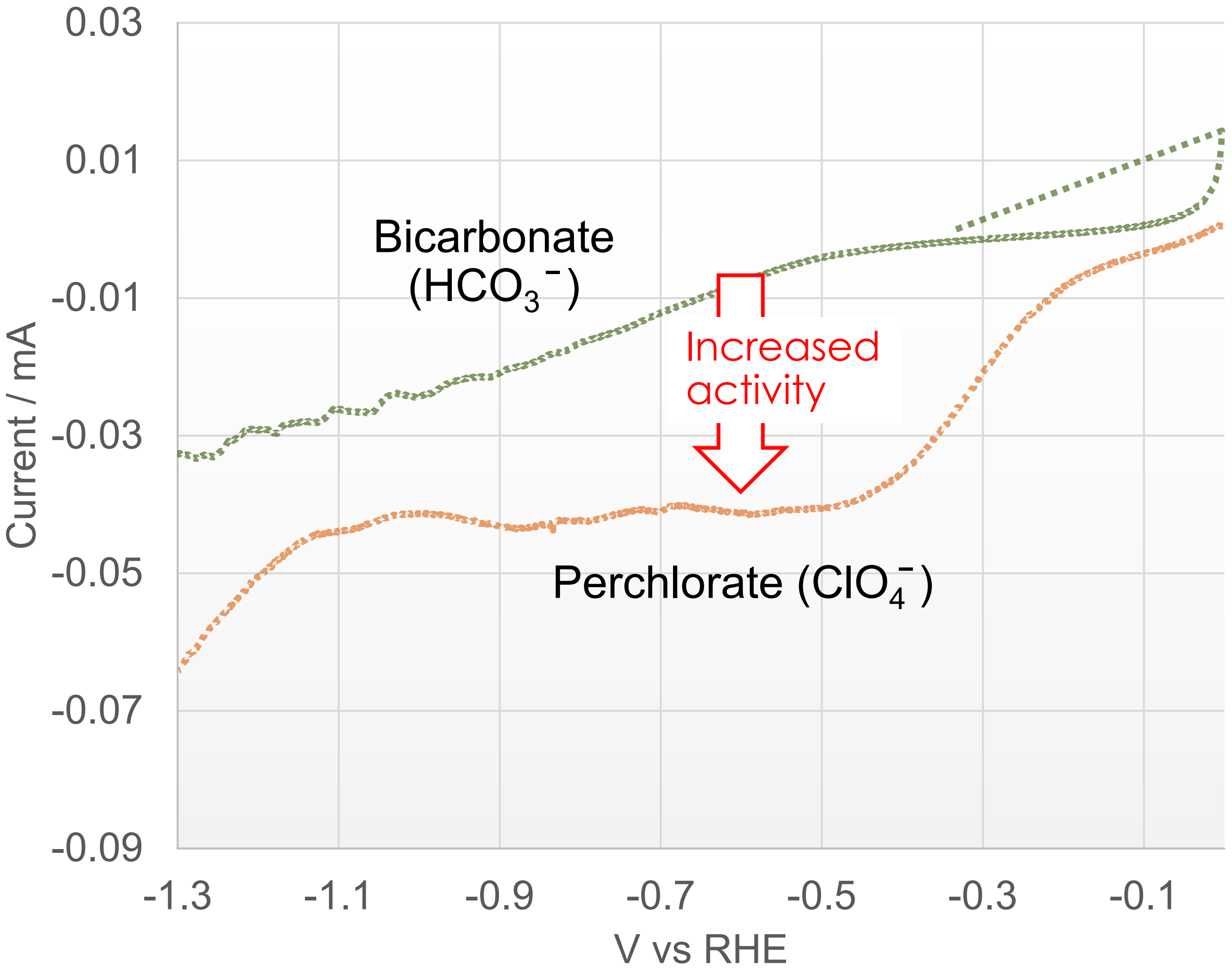
4 – Progress and Outcomes

Understand the role of bicarbonate in CO_2 activation over CNS



Literature study:

- *CO_2 molecules are mediated to the Cu surface via their equilibrium with bicarbonate anions instead of direct adsorption from the solution**

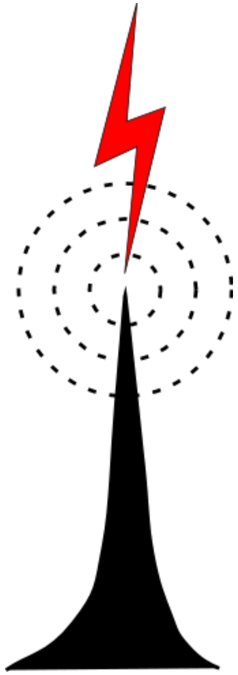
This study suggests:

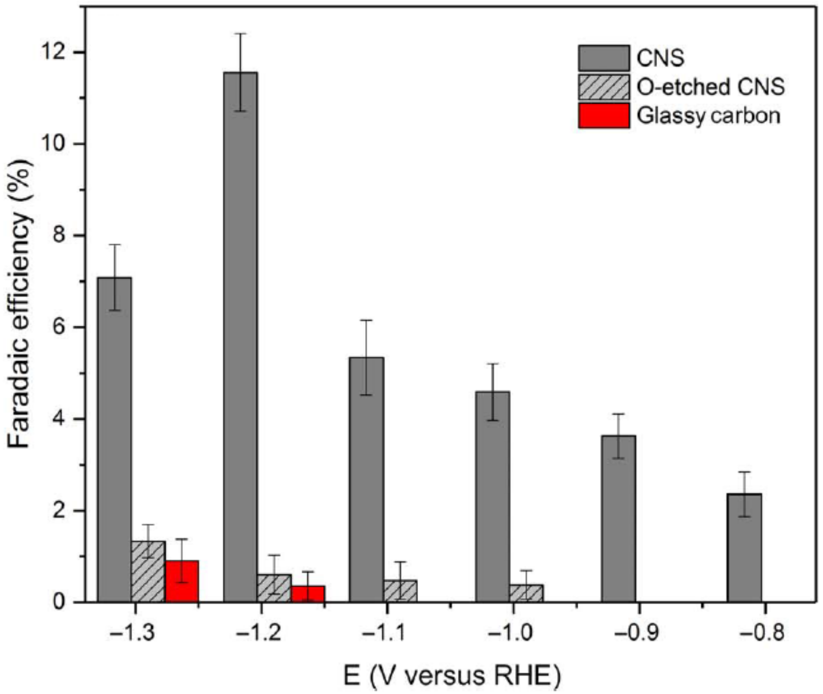
- *CO_2 reduction with bicarbonate as electrolyte is less active than with perchlorate over CNS*
- ***Dissolved CO_2 is more likely to react**, consistent with hypothesis of **CNS mediated e^- injection***

*J. Am. Chem. Soc. 2017, 139, 3774–3783
*J. Am. Chem. Soc. 2017, 139, 15664-15667

4 – Progress and Outcomes: role of CNS in activating CO_2

Sharp tips of CNS lead to enhanced electric field, enables N_2 activation via direct e^- injection (BES efforts)

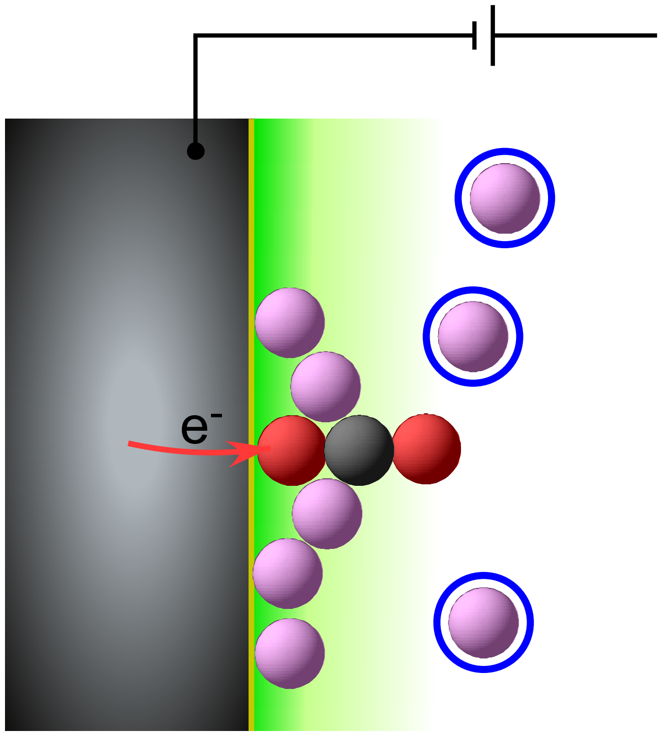




Faradaic efficiencies for NH_3 synthesis

- CO_2 polarization over CNS has higher dipole moment than N_2

Induced Dipole Stabilizes CO_2 in Stern Layer



- **Enhanced CO_2 surface coverage** facilitates direct activation of CO_2 over CNS via e^- injection.
- **Neighbor C-C coupling sites** are needed to further promote the formation of C_{2+} products.

Song et al., **Sci. Adv.** 2018, 4: e1700336

4 – Progress and Outcomes

Demonstrate electrochemical synthesis of bimetallic PdCu/CNS electrocatalysts

Challenge:

- How to locate metal co-catalyst close to CNS

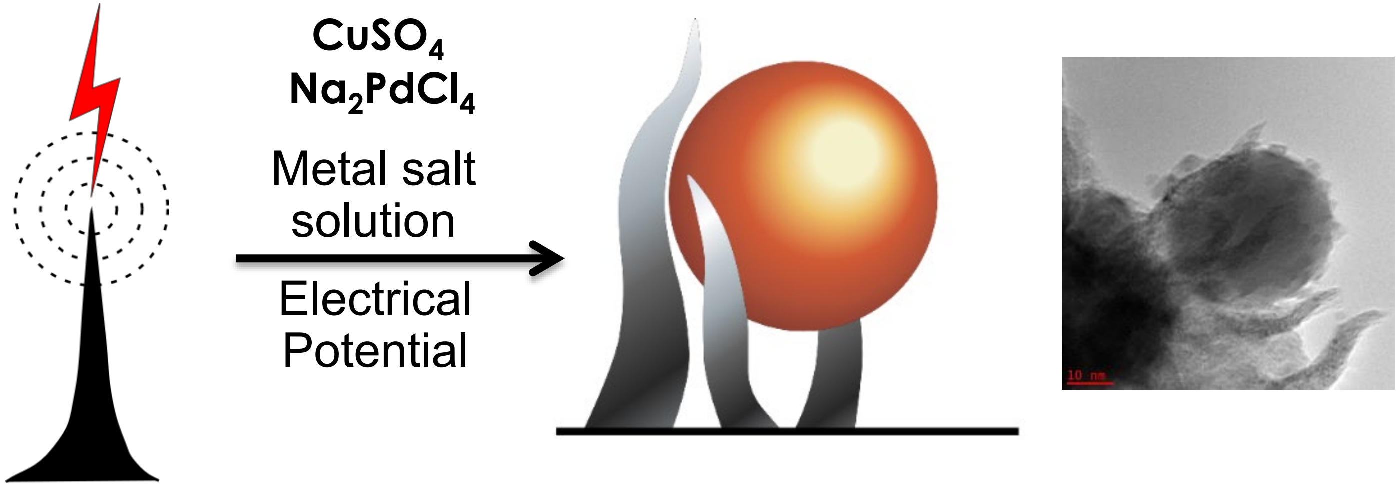
In situ electrochemical deposition synthesis:

- **Simple** synthesis methodology
- **Direct formation** of metal nanoparticles at catalytically relevant locations
- **Avoid using surfactants** in metal nanoparticle synthesis

Further advantage over CNS:

- CNS unique configuration facilitates the ***in situ* nucleation** of metal nanoparticles
- Form **nanoparticles close to carbon nanospikes**, CO generated from nanospikes can directly react over nanoparticle surface

In situ electrochemical synthesis of bimetallic PdCu nanoparticles over CNS

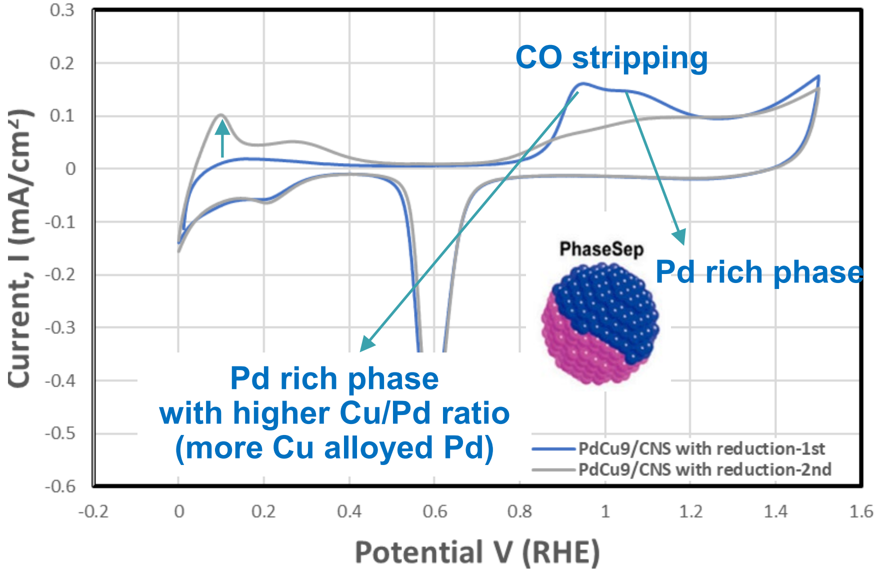


4 – Progress and Outcomes

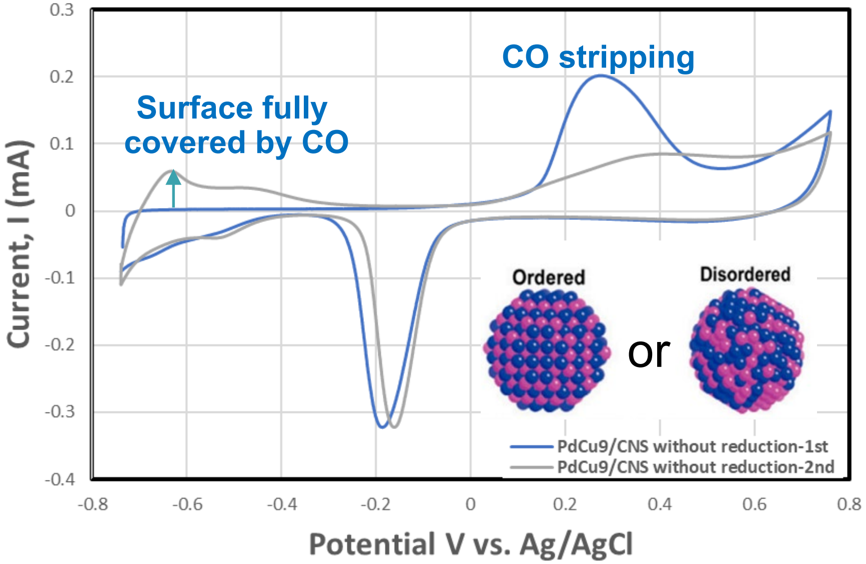
CO stripping experiments were leveraged to understand metal particle composition

CO-stripping results for $PdCu_9$/CNS

With reduction process before CO adsorption



Without reduction process before CO adsorption

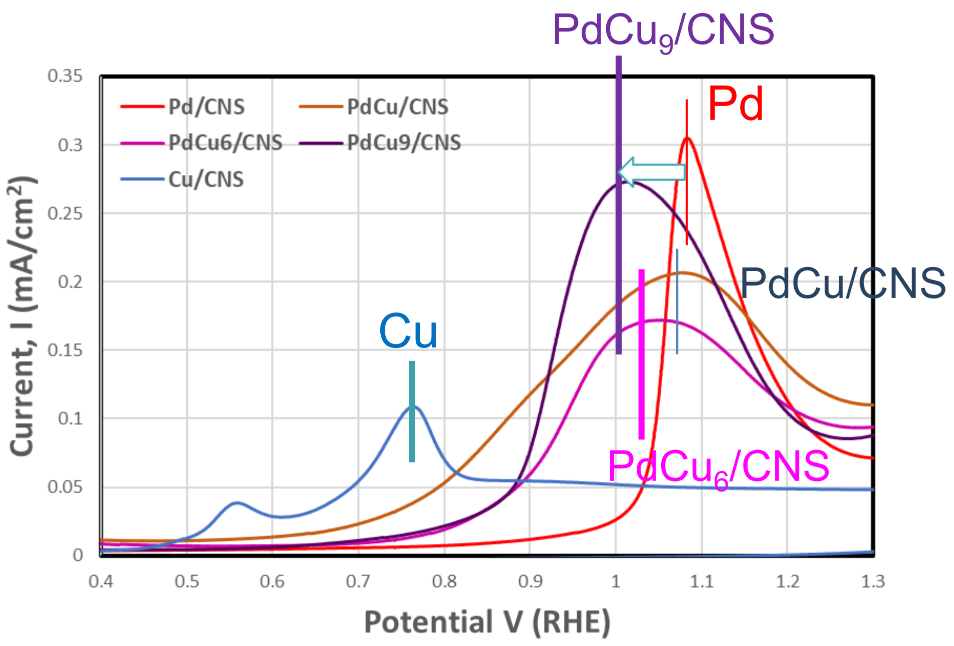


Bimetallic PdCu/CNS can be electrochemically made either in separated phases or well mixed form

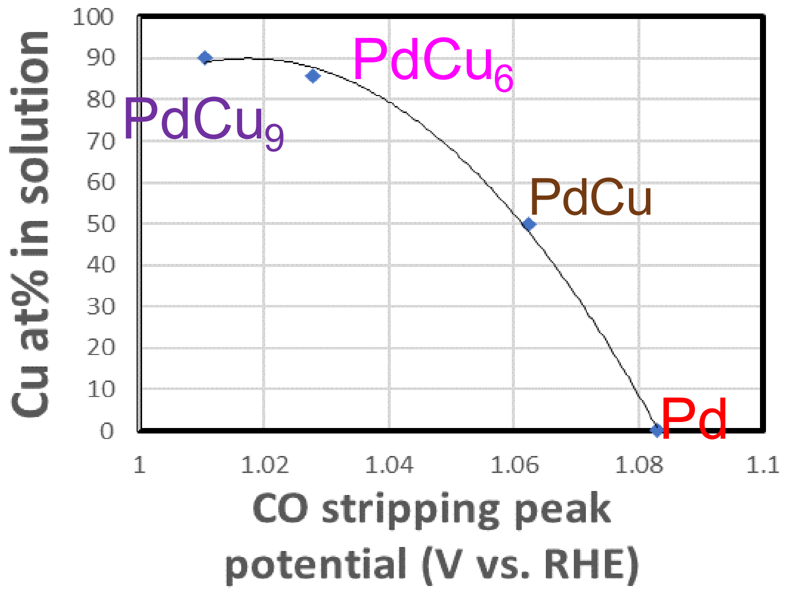
Catalyst images from: Ma et al. J. Am. Chem. Soc. 2017, 139, 1, 47-50 https://pubs.acs.org/doi/10.1021/jacs.6b10740

4 – Progress and Outcomes

Synthesize bimetallic PdCu with varied surface composition to control CO binding energy



CO stripping experiment



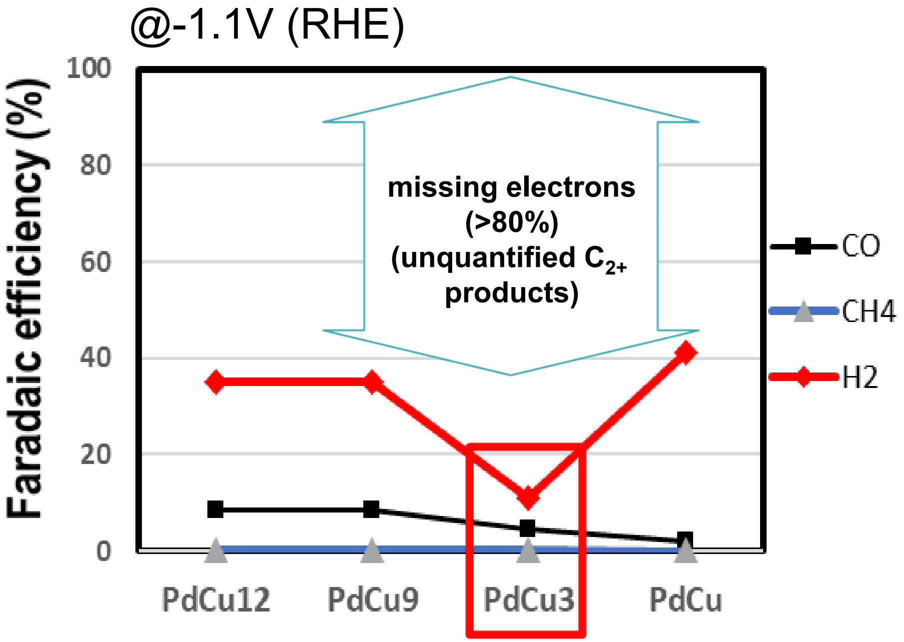
- (Pd:Cu=initial conc. ratio in solution)
- Deposition condition: -0.8V 1 sec for Cu, -0.2V 0.5 sec for Pd-Cu alloy and Pd

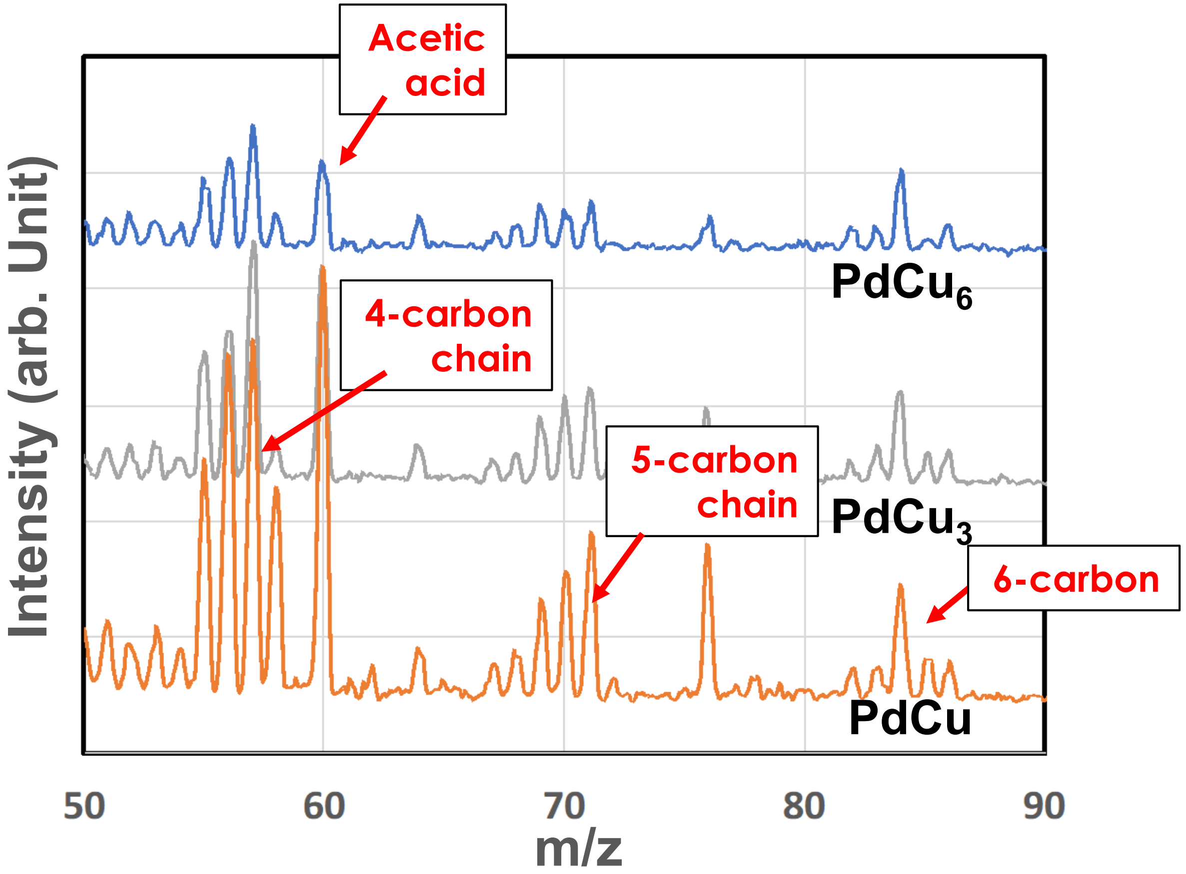
Outcomes:

- **Indicate formation of Pd-rich bimetallic PdCu nanoparticles for $PdCu_9$, $PdCu_6$, PdCu**
- **The difference of surface Cu/Pd ratio can help to tailor the CO binding energy**

4 – Progress and Outcomes

Demonstrate the feasibility of producing C_{2+} products from CO_2 over bimetallic $PdCu_3$/CNS





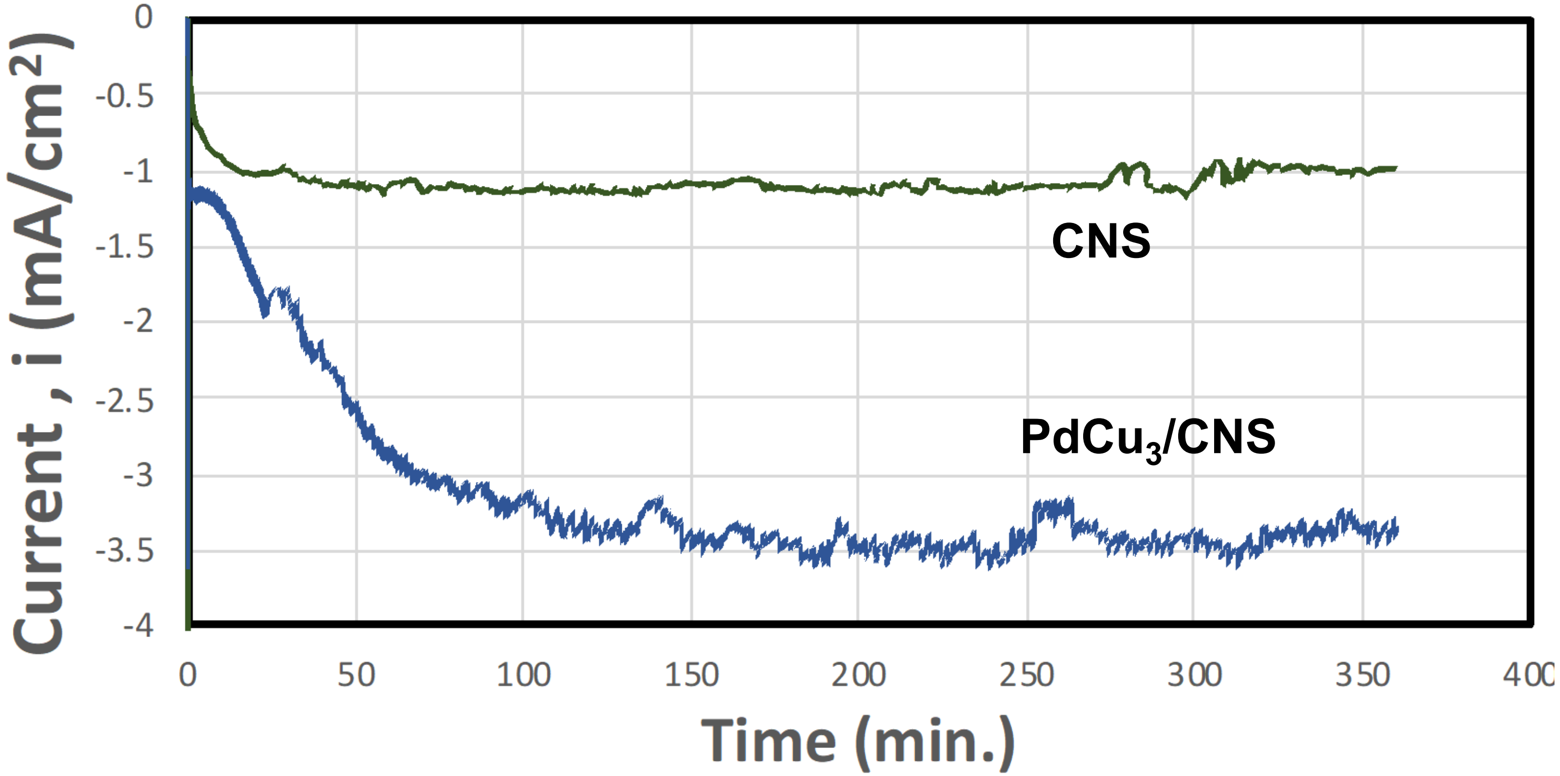
Future work:

- **Identify and quantify the products in the liquid phase (delayed due to the impact of COVID)**

- **Qualitative mass spectrometry measurements indicate the presence of heavier products**

4 – Progress and Outcomes

Bimetallic $PdCu_3$/CNS shows relatively stable performance after initial induction period



Future work:

- **Improve the current density via designing gas diffusion electrode**

Summary

This project builds on the success of the CO_2 to ethanol technology developed at ORNL

- CO_2 to ethanol technology was licensed to Reactwell
- Received 2019 R&D100 Award

Outcome

- Advance **electrocatalytic synthesis** approach for **reduction of CO_2 to C_{2+} oxygenates**, as feedstocks for thermocatalytic upgrading to hydrocarbon fuels

Approach

- Developing bimetallic co-electrocatalyst to tune the CO binding energy to enhance the C_{2+} product formation

Progress and Outcomes

- Carbon nanospike electrocatalyst can directly activate CO_2 to form CO, and metal co-catalyst is needed to further oligomerize CO
- **Bimetallic PdCu/CNS** can be electrochemically **synthesized *in situ***
- Bimetallic PdCu/CNS electrocatalyst could **synthesize C_{2+} product from CO_2**
- Further product identification and quantification are needed

Acknowledgement

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Junyan Zhang
Dr. Michael Hu
Dr. Aimee Church
Dr. Art Baddorf

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Oak Ridge National Laboratory | Center for Nanophase Materials Sciences

U.S. Department of Energy
Bioenergy Technologies Office

- **Bioenergy Technologies Office:**
  - Ian Rowe

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

- Rondinone, Adam. "Carbon nanospikes as a physical catalyst for the electrolysis of carbon dioxide." ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY. Vol. 257. 1155 16TH ST, NW, WASHINGTON, DC 20036 USA: AMER CHEMICAL SOC, 2019.
- "ALLOY BASED CATALYST FOR THE ELECTROCHEMICAL SYNTHESIS OF HYDROCARBONS FROM CARBON DIOXIDE" US Provisional Application Serial No. 63/085,340, filed on September 30, 2020. (This work has led to a research license.)