Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Optimizing Attachment Methods and Ligand Properties for Solar Fuels

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Introduction

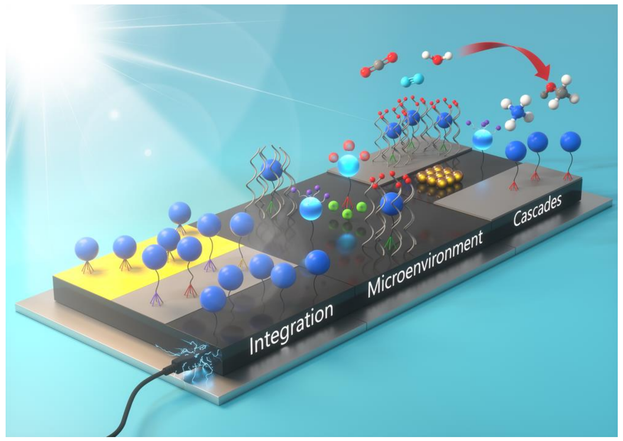
CENTER for HYBRID APPROACHES in SOLAR ENERGY to LIQUID FUELS

CHASE MISSION:

To develop molecule/material hybrid photoelectrodes for cooperative sunlight-driven generation of liquid fuels from carbon dioxide, nitrogen, and water

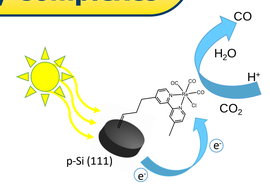
CHASE RESEARCH GOALS:

1. Understand fundamental principles and design strategies that enable integration of durable semiconductor light absorbers with molecular catalysts to drive liquid fuel production (**INTEGRATION THRUST**)
2. Tailor local environment around catalyst on a molecular scale to direct reactivity along desired pathways (**MICROENVIRONMENTS THRUST**)
3. Develop design principles that enable cooperative integrated photosynthesis of liquid fuels through multi-catalyst cascades (**CASCADES THRUST**)

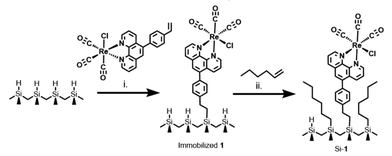


Optimization of Sonochemical Hydrosilylation for Re-bpy Complexes

- Hybrid photoelectrodes couple a molecular electrocatalyst that is highly selective for carbon dioxide reduction with a visible light absorbing semiconductor. These molecular-material catalysts can achieve artificial photosynthesis.

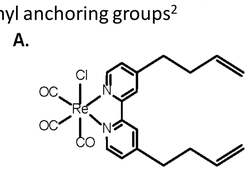


- It is possible to alter the properties of these electrodes by choosing different catalysts, using different attachment reactions, or altering the reaction conditions of the attachment strategy.



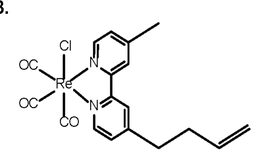
- The Dempsey group developed a catalyst immobilization technique through sonochemical hydrosilylation, where silicon (111) wafers are submerged in a catalyst solution and reacted in an ultrasonic bath for 90 minutes[1]
- This method was demonstrated for a rhenium tricarbonyl phenanthroline complex containing a styrene attachment group, but not yet for newly synthesized catalysts with butenyl anchoring groups[2]

A.



bis-butenylbpyRe(CO)$_3$Cl

B.



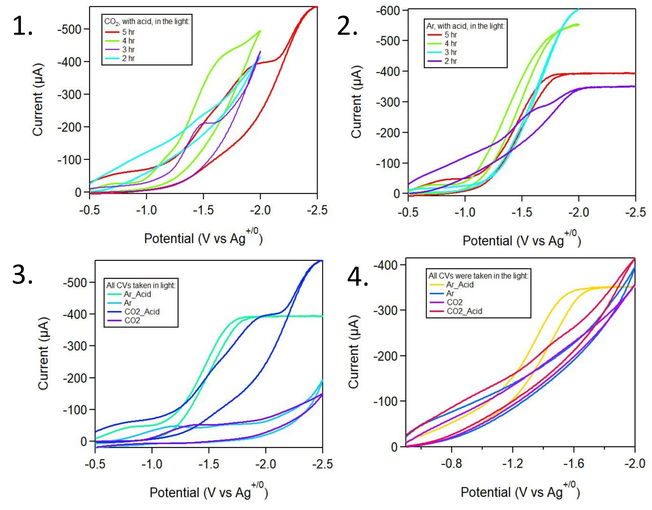
mono-butenylbpyRe(CO)$_3$Cl

- To test the generalizability of this method and optimize the conditions, a reaction time trial was conducted using **A** and p-type Si (111) wafers

(1) ACS Appl. Mater. Interfaces 2023, 15, 1, 984–996; (2) *Inorg. Chem.* 2023, 62, 5, 2359–2375

Cyclic Voltammetry on Wafers

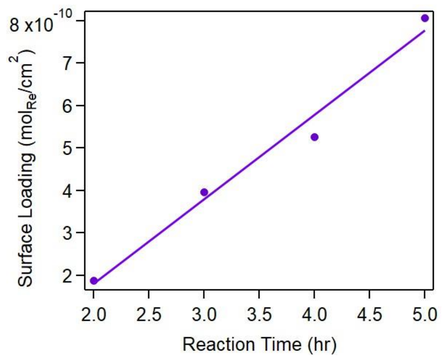
- Hybrid **A**-Si (111) wafers were prepared as working photoelectrodes for photoelectrochemical cyclic voltammetry experiments.



1. Comparison of wafers from each time stamp under CO_2 with a proton source
2. Comparison of wafers from each time stamp under Ar with a proton source
3. CVs on the 5-hr wafer under each condition
4. CVs on the 2-hr wafer under each condition

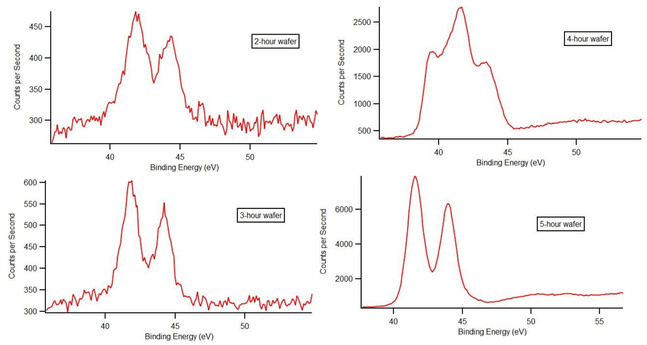
Experimental details: 250 mM [nBu_4][PF_6] supporting electrolyte solution in deoxygenated acetonitrile, Ohmic contact made to p-type **A**-Si (111) working photoelectrodes by applying In-Ga eutectic and copper tape, Pt mesh counter electrode, and Ag pseudoreference electrodes, all scans taken at 0.1 V/s

Inductively Coupled Plasma Mass Spectroscopy of Modified Wafers



- Hybrid **A**-Si (111) wafers were digested in a 20% Nitric Acid solution and diluted to a 2% solution
- The linear trendline (R^2=0.9808) supports an increase in catalyst surface loading with an increase in reaction time

X-Ray Photoelectron Characterization



- XPS scan of the Re 4f region for modified Si wafers from each timed trial
- A distinct Re 4f doublet at 41 eV is displayed in the 2, 3, and 5-hour samples
- This supports the covalent attachment by sonochemical hydrosilylation

Conclusions & Future Research Plans

- Sonochemical hydrosilylation is a viable attachment method for various functional groups, if the reaction time is increased. It may also be the preferred method, given that it does not require the harsh reaction conditions and long reaction times that comparable attachment methods require.
- As sonication time increases, the observed photovoltage and the magnitude of current passed under CO_2 also increase. There is also an observed decrease in the magnitude of current passed under Ar. This, along with characterization data from ICP-MS and XPS, indicates that the surface catalyst loading increases over reaction time.
- More samples will be prepared to determine at which point the surface loading has gone beyond a monolayer
- Data will be gathered about the integrity of the bound molecules using infrared spectroscopy
- A similar sonochemical hydrosilylation time trial will be conducted using **B**
- Thermal hydrosilylation time trials will be conducted, separately, with both **A** and **B**

Acknowledgments

This research is supported as part of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0021173.