



# Center for Hybrid Approaches in Solar Energy to Liquid Fuels

## Optimizing Attachment Methods and Ligand Properties for Solar Fuels

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### Introduction

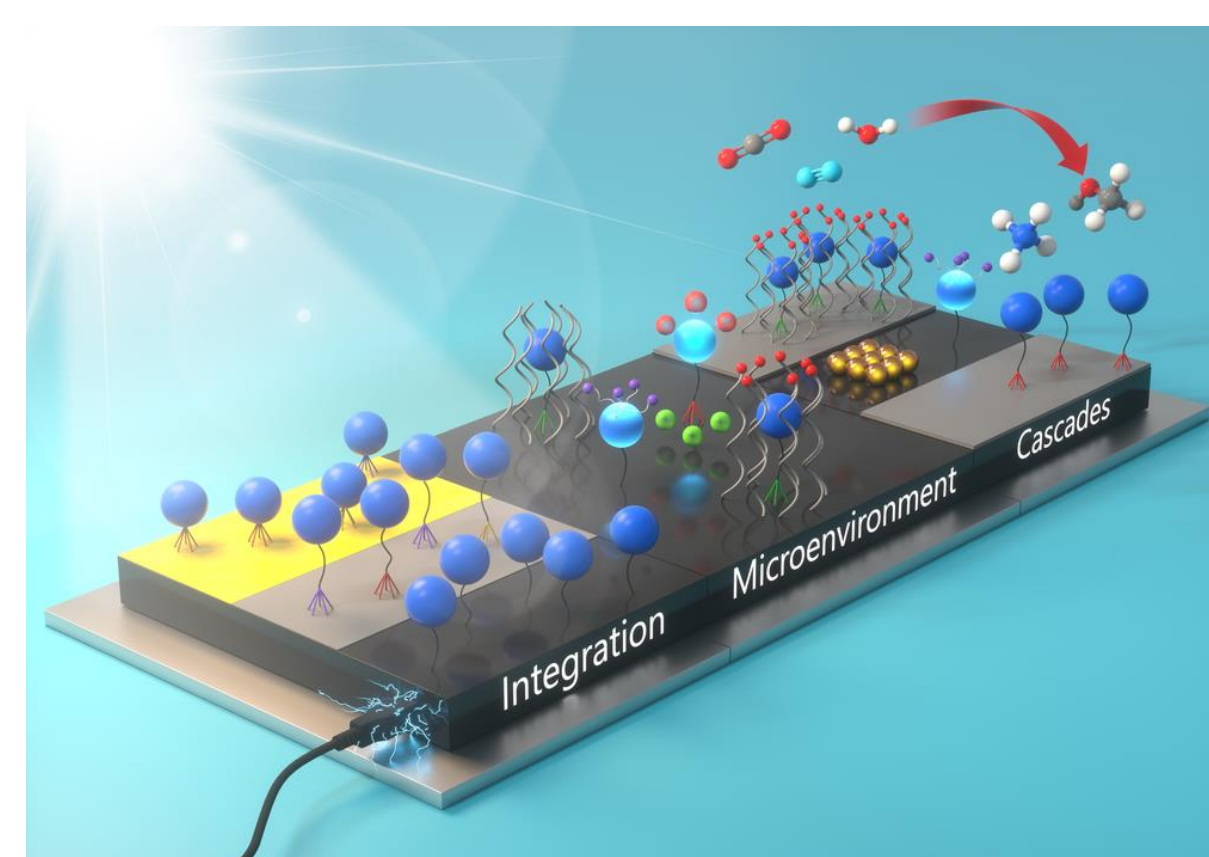
CENTER for HYBRID APPROACHES in SOLAR ENERGY to LIQUID FUELS

CHASE MISSION:

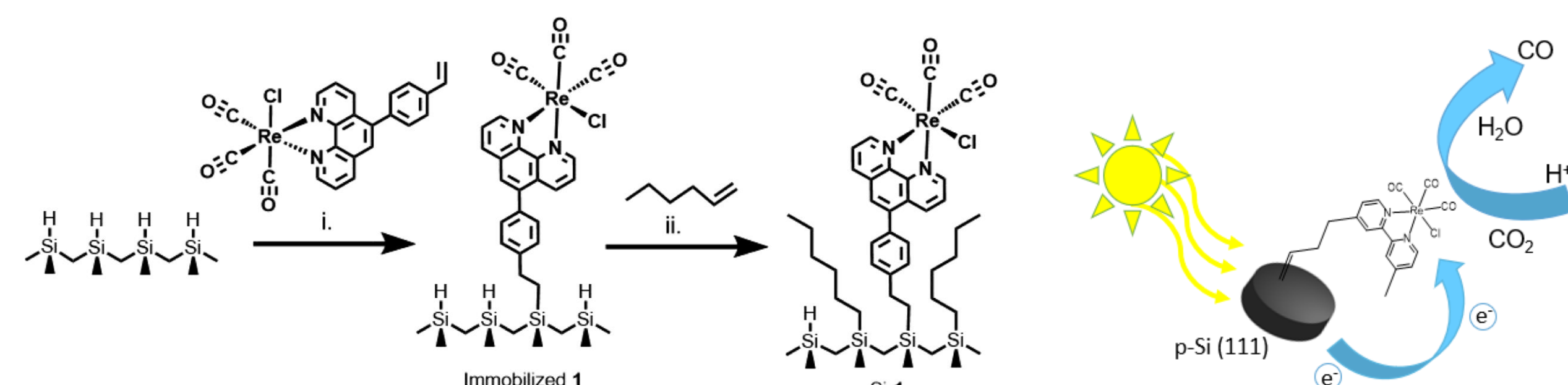
To develop molecule/material hybrid photoelectrodes for cooperative sunlight-driven generation of liquid fuels from carbon dioxide, nitrogen, and water

#### RESEARCH GOALS:

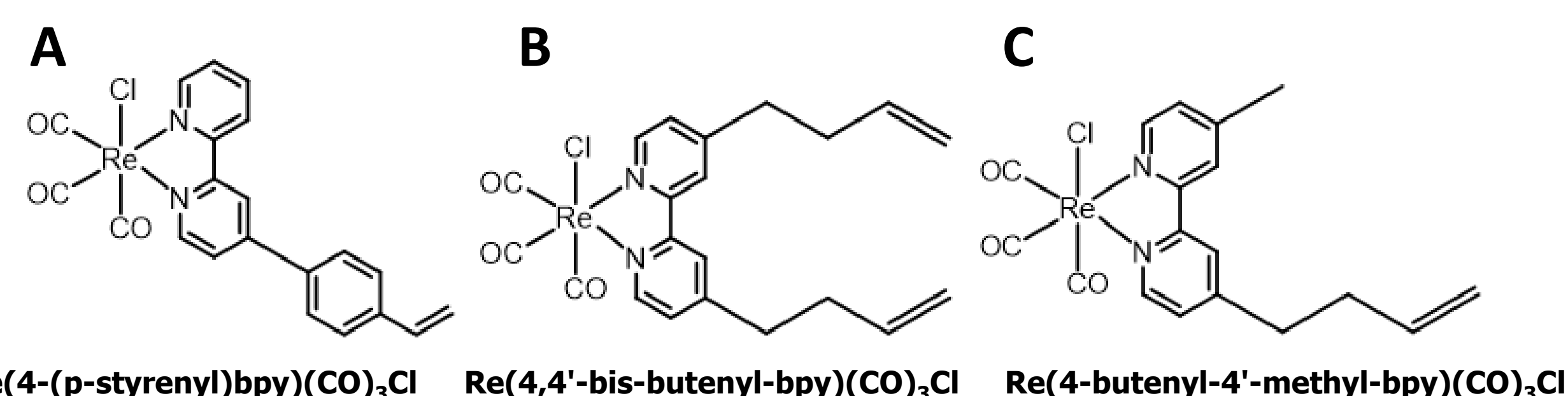
- Hybrid photoelectrodes couple a molecular electrocatalyst that is highly selective for carbon dioxide reduction with a visible light absorbing semiconductor.
- It is possible to alter the properties of these electrodes by choosing different catalysts, using different attachment reactions, or altering the reaction conditions of the attachment strategy.



- The Dempsey group advanced a catalyst immobilization technique based on sonochemical hydrosilylation, where silicon (111) wafers are submerged in a solution containing catalysts with alkene functionalities and reacted in an ultrasonic bath for 90 minutes.<sup>1</sup>
- 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.<sup>2</sup> Thus, there is a need to optimize this attachment method to various catalysts containing different functionalities.



- To test the generalizability of this method and optimize functionalization reaction conditions, various time trials and subsequent characterization experiments were conducted using **A**, **B**, and **C**.



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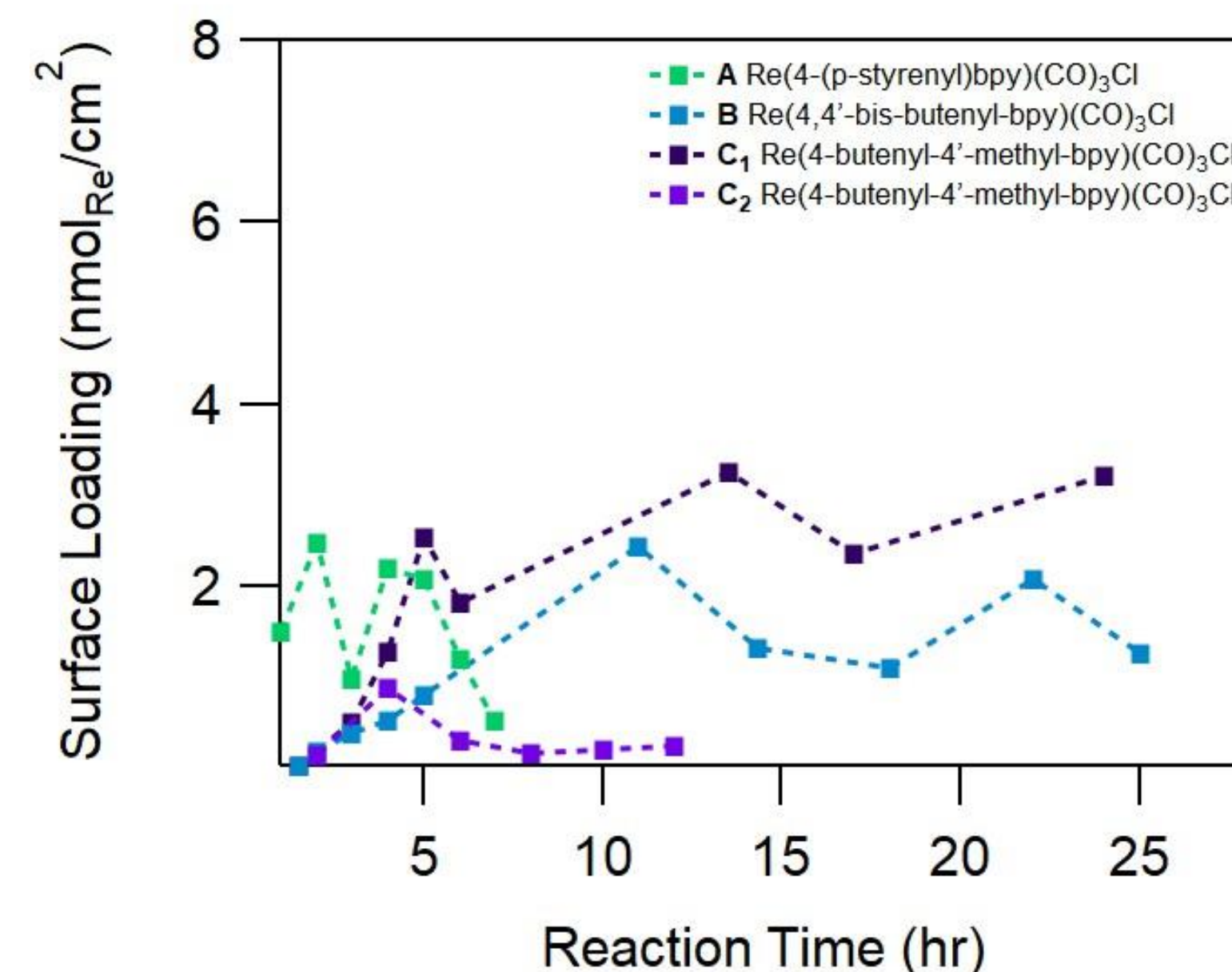
### Conclusions & Future Research Plans

- Preliminary results suggest the presence of a physisorbed layer on top of a covalently bound multilayer, which is stripped upon further sonication in clean solvent for samples from early time points.
- An increase in current density of cycled CVs of C-Si samples that sonicated for 20+ hours indicates a possible charging ability in these samples that has not been demonstrated in samples sonicated for less time.
- Future work seeks to determine the nature and integrity of the multilayer during and after photoelectrochemical experimentation.

### Acknowledgments

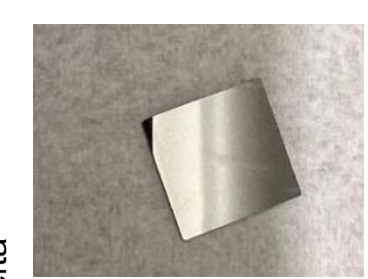
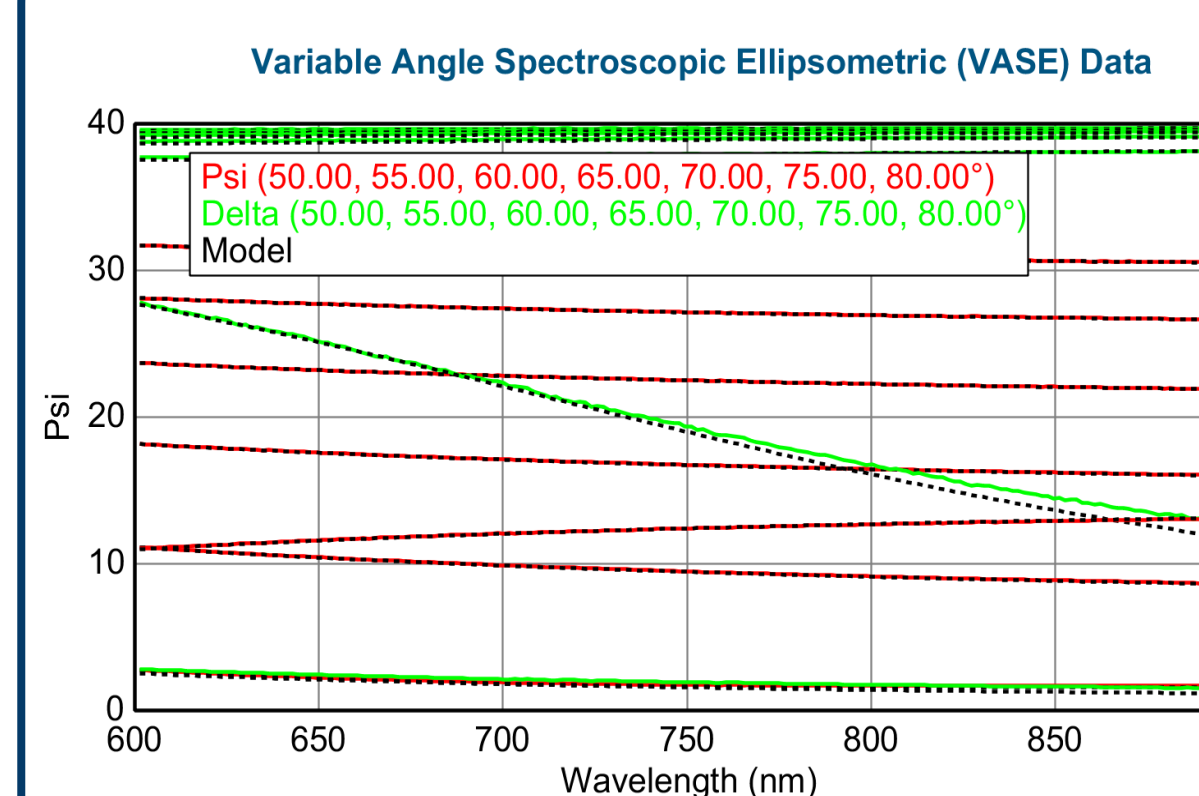
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### Inductively Coupled Plasma Mass Spectrometry of Modified Wafers

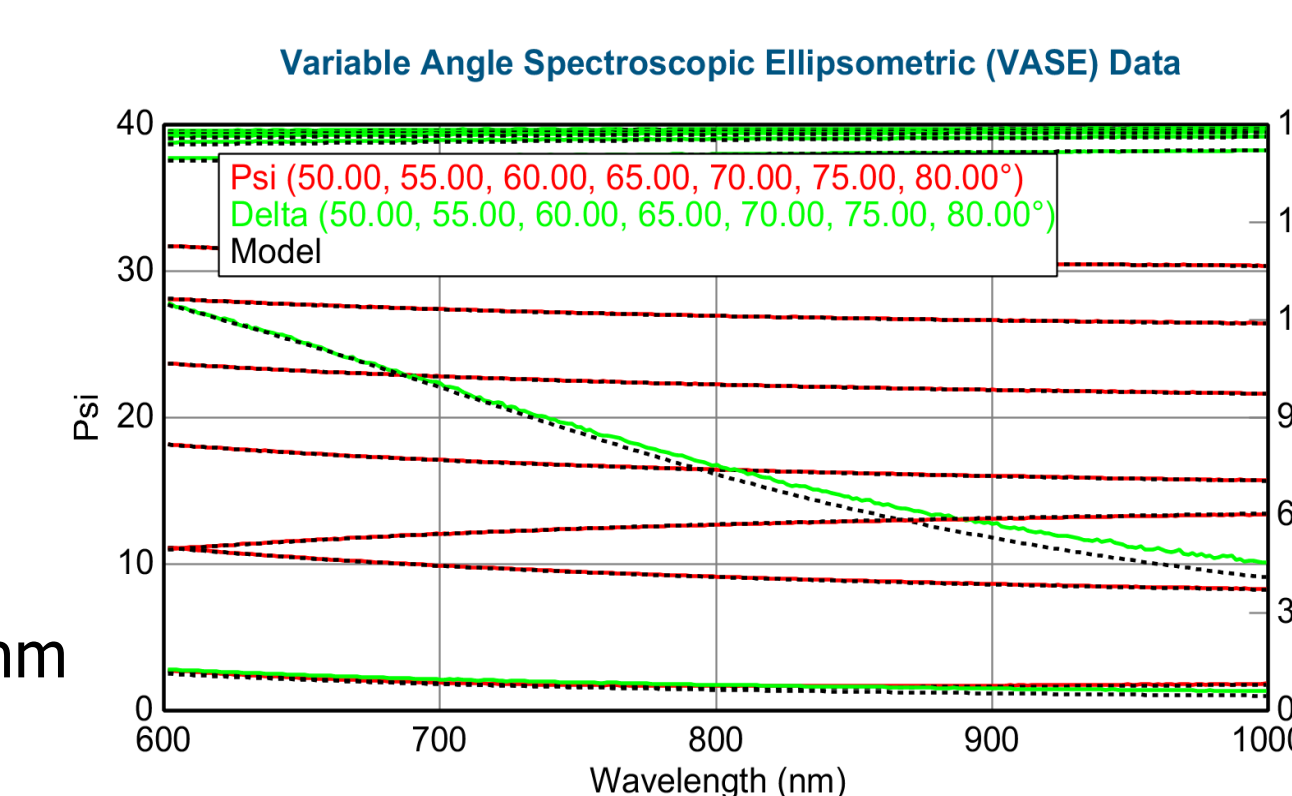


- Hybrid p-Si (111) wafers were submerged in a 20% Nitric Acid solution for 24 hours, during which time the concentrated Nitric Acid stripped the metal ions from the catalyst centers.
- This 20% stock solution of Re ions was then diluted to 2% Nitric Acid for experimentation via ICP-MS.
- The concentration of Re ions in solution, in ppb, was measured and converted to moles using the volume of solution. The number of moles was then divided by the surface area of the sample.
- C<sub>1</sub>** and **C<sub>2</sub>** represent samples functionalized with **C**. **C<sub>2</sub>** was sonicated in DCM after functionalization for an additional 5 minutes to probe the integrity of the catalytic multilayer.
- Surface loading for **A**, **B**, and **C<sub>1</sub>** plateaus at coverages of ~1 nmol<sub>Re</sub>/cm<sup>2</sup>, while that for **C<sub>2</sub>** does so at coverages of ~0.3 nmol<sub>Re</sub>/cm<sup>2</sup>.

### Spectroscopic Ellipsometry of Modified Wafers



Thickness: 4.23 ± 0.623 nm



Thickness: 4.11 ± 0.669 nm

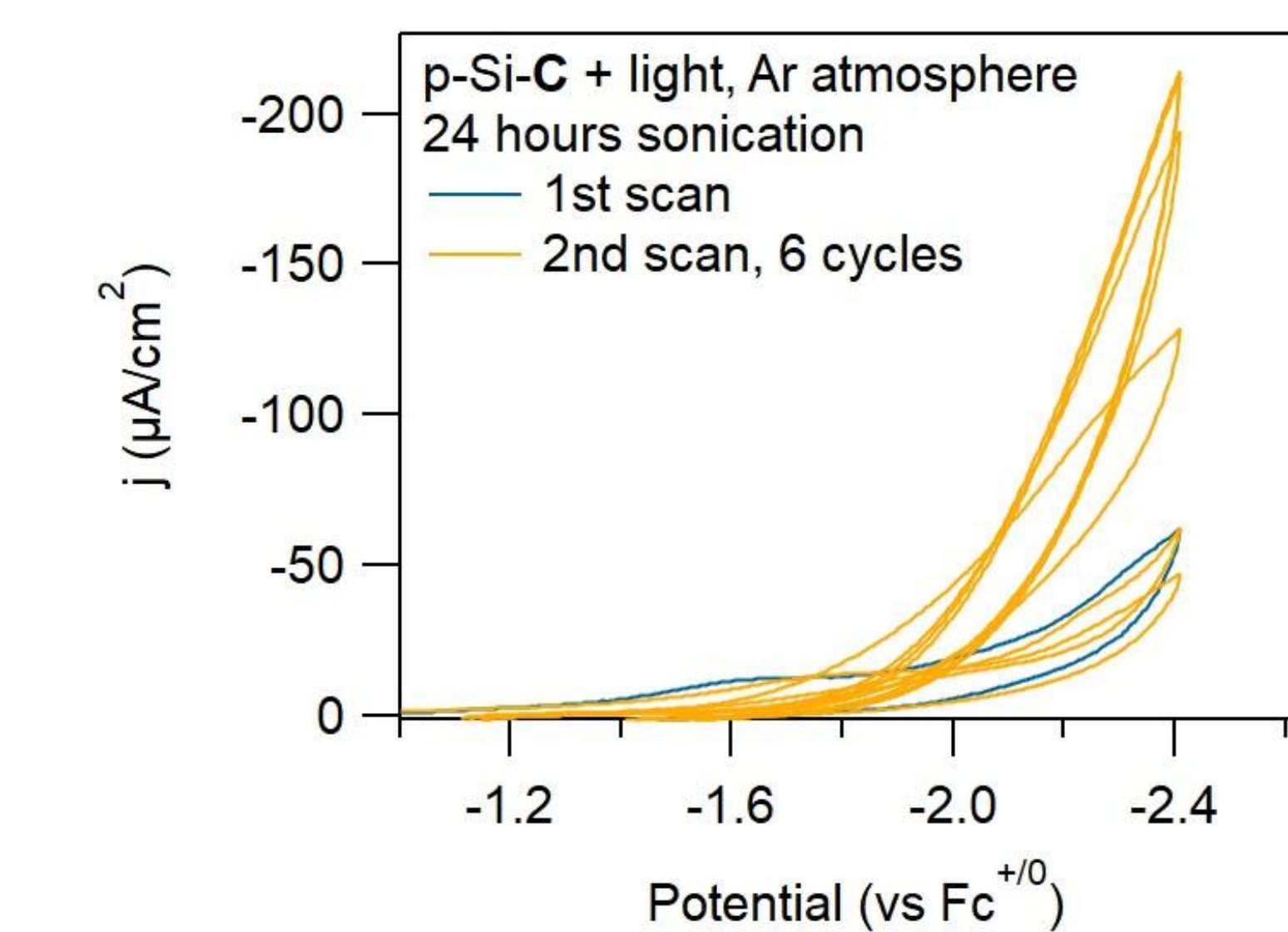
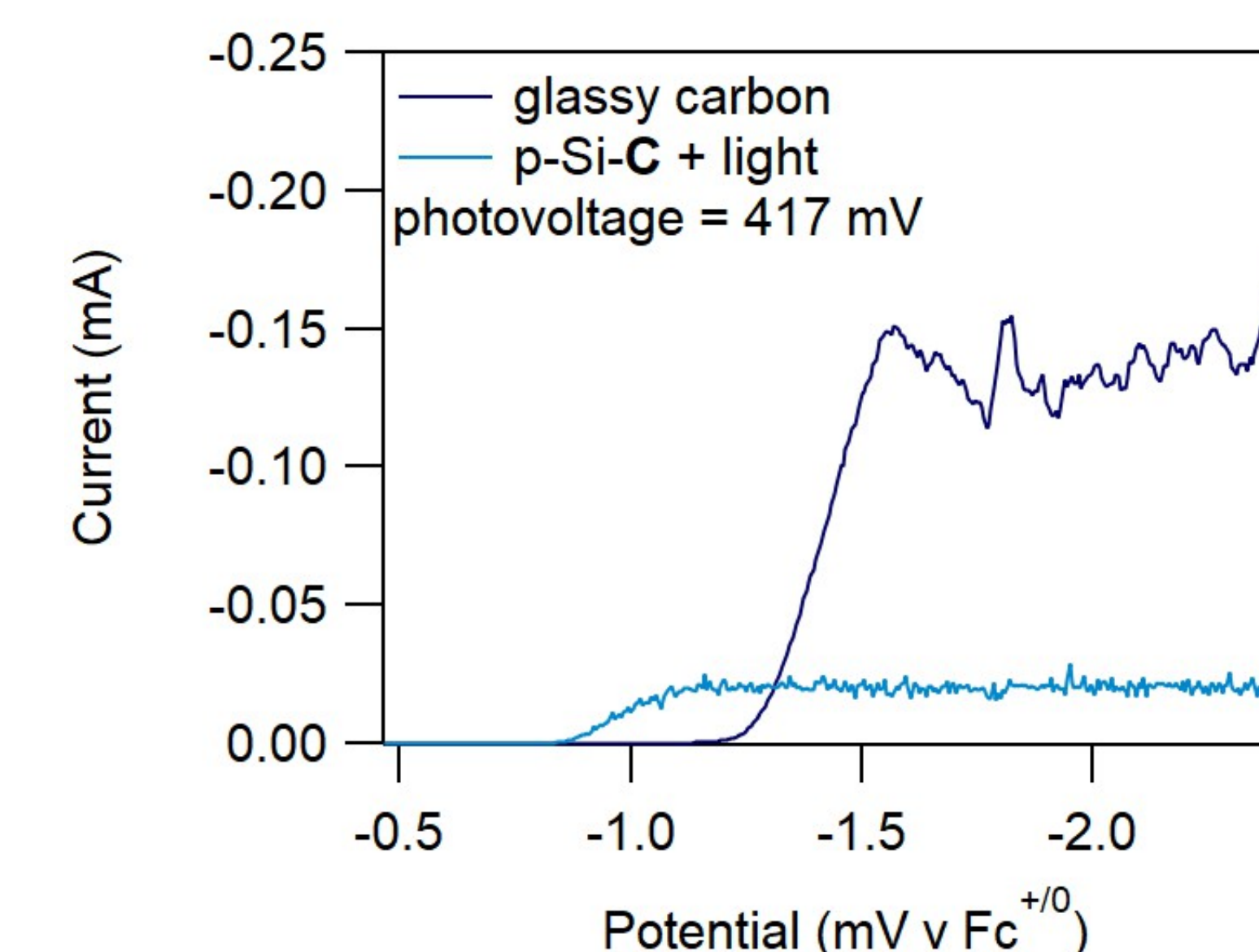
Ellipsometry measurements were performed to determine the thickness of the catalytic multilayer on the surface of representative C-Si samples. Samples were sonicated for 24 hours and demonstrated multilayer thicknesses of ~4 nm. Thickness of catalytic multilayers was determined by exposing samples to polarized light, with wavelengths ranging 600 to 900 nm, and analyzing the reflected light by fitting it to a model. Model was decided using experimentally determined values for the reduction potential and wavelength of maximum absorbance of **C**.

### Quantitative Analysis of Surface Loading v. Reaction Time

Complex:	Monolayer Estimate (nmol <sub>Re</sub> /cm <sup>2</sup> ):	Reaction Time (hr)																			
		1	1.5	2	3	4	5	6	7	8	10	11	12	13.5	14.3	17	18	22	24	25	26.5
<b>Experimentally Measured Values (nmol<sub>Re</sub>/cm<sup>2</sup>)</b>																					
<b>B</b>	9.03 × 10 <sup>-2</sup>		8.70 × 10 <sup>-3</sup>	0.188	0.395	0.526	0.806							2.45		1.33		1.11	2.08		1.26
<b>C<sub>1</sub></b>	8.15 × 10 <sup>-2</sup>		3.28 × 10 <sup>-2</sup>		0.520	1.28	2.53	1.82							3.27		2.37			3.22	11.1
<b>C<sub>2</sub></b>	8.15 × 10 <sup>-2</sup>			0.159		0.889		0.317		0.172	0.204	0.257									
<b>A</b>	9.03 × 10 <sup>-2</sup>	1.51		2.48	0.981	2.21	2.08	1.21	0.531												

- Using a protocol laid out by CHASE for estimating a monolayer of catalyst coverage on the surface of planar p-Si (111), the moles of Re required for a monolayer, per unit surface area, was estimated for each **A**, **B**, and **C**.
- This protocol likely overestimates a monolayer, given that it assumes a singular orientation for all molecules, but it indicates that a multilayer is achievable after ~2 hours sonication. The values collected for **C<sub>2</sub>** also indicate that an appreciable percentage of the multilayer persists despite additional sonication.

### Characterization by Cyclic and Linear Sweep Voltammetry



Experimental details: Cyclic Voltammograms and Linear Sweep Voltammograms taken in 250 mM [nBu<sub>4</sub>][PF<sub>6</sub>] supporting electrolyte solution in deoxygenated acetonitrile, Ohmic contact made to functionalized C-Si (111) working photoelectrodes by applying In-Ga eutectic and copper tape. Pt mesh counter electrode and Ag pseudoreference electrodes were used for all experiments. Reported biases externally referenced to Fc<sup>+/0</sup>. All scans taken at 0.1 V/s. Linear Sweep Voltammograms were stirred vigorously and taken at glassy carbon and hybrid C-Si, respectively, in a solution of 50 mM [CoCp<sub>2</sub>][PF<sub>6</sub>]. A positive shift in the reduction onset potential of 417 mV was used to determine C-Si's photovoltage.

$$\text{Area of the hexagon is: } A_H = \frac{3\sqrt{3}}{2} D^2$$

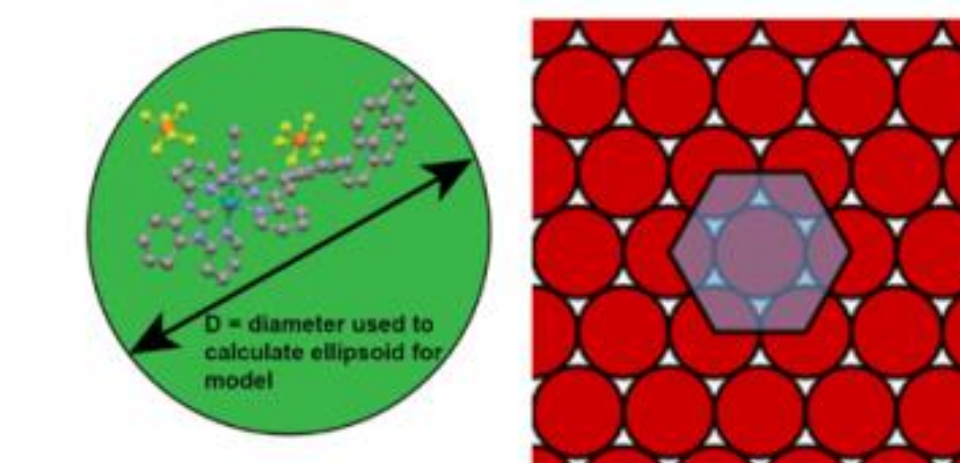
where the side length of the hexagon is equal to the diameter of the catalyst footprint, D.

The area within the hexagon covered by circles is equal to the area of 3 circles so we can write the following

$$\frac{\text{Catalysts}}{\text{Area}} = \frac{3}{\frac{3\sqrt{3}D^2}{2}}$$

Which reduces to

$$\frac{\text{Catalysts}}{\text{Area}} = \frac{2}{\sqrt{3}D^2}$$



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