2006 DOE Hydrogen Program
Combinatorial Development of Water Splitting Catalysts Based on the Oxygen Evolving Complex of Photosystem II

Neal Woodbury, Arman Ghodousi, Trent Northen, Matt Greving, Pallav Kumar, Bharath Takulpalli, Nicolas Yakubchak, James Allen, JoAnn Williams, Trevor Thornton

Arizona State University and the Biodesign Institute

April 21, 2006

Overview

Timeline

- Start - July 1, 2005
- Finish - June 30, 2009
- 20% Complete

Budget

- Total Project Funding
  - DOE - $1,200,000
  - Contractor - $300,000
- Funding for FY06
  - $273,000 DOE
  - $230,470 Contractor

Barriers

- Barriers addressed
  - H. System Efficiency
  - J. Renewable Integration

Partners

- CombiMatrix Corp., Mukilteo, WA

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Objectives: Hydrogen Evolution Catalysts

- Develop a library-based solid-phase synthetic method for molecular evolution of a catalyst for electrolysis
- Evolve such a catalyst using metal binding peptide libraries based on photosynthetic complexes.
- Optimize the catalyst for minimum overpotential.

Approach: Optically Directed Evolution

- Using a photosynthetic model system for oxygen evolution, design a peptide library
- Synthesize the library using photolithographic or electrochemical solid phase synthesis methods directly on an array of electrodes
- Measure the voltage/current characteristics of each catalyst, model the best, and design a new library, etc.

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Technical Accomplishments

- Light Directed Peptide Synthesis
- Electrochemically Directed Peptide Synthesis
- Electrode and Electrode Array Fabrication
- Electrochemical Measurements
- Electrochemical Analysis

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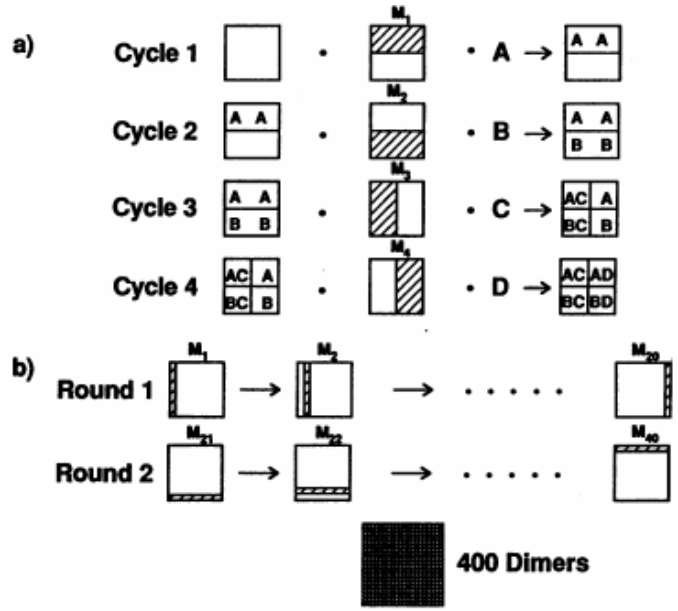
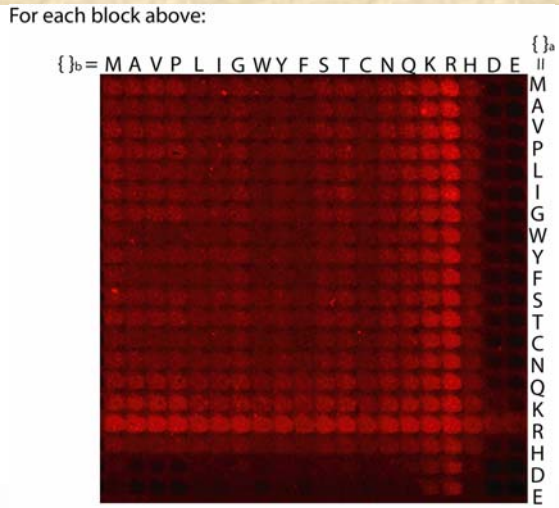
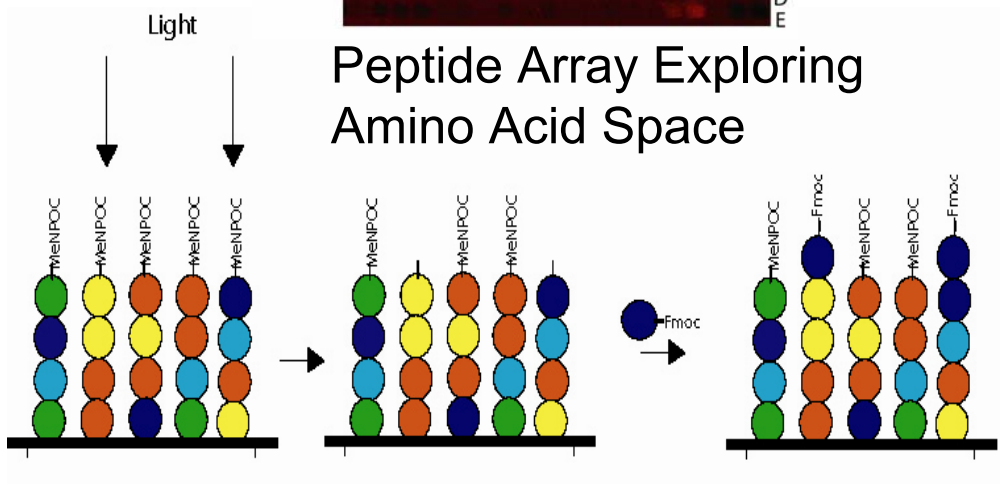
Light-Directed Peptide Synthesis

- Binary masking strategy used to synthesize all possible combinations of a subset of reactant monomers.





Peptide Array Exploring Amino Acid Space



Fodor, 1991 Science 251(4995):767

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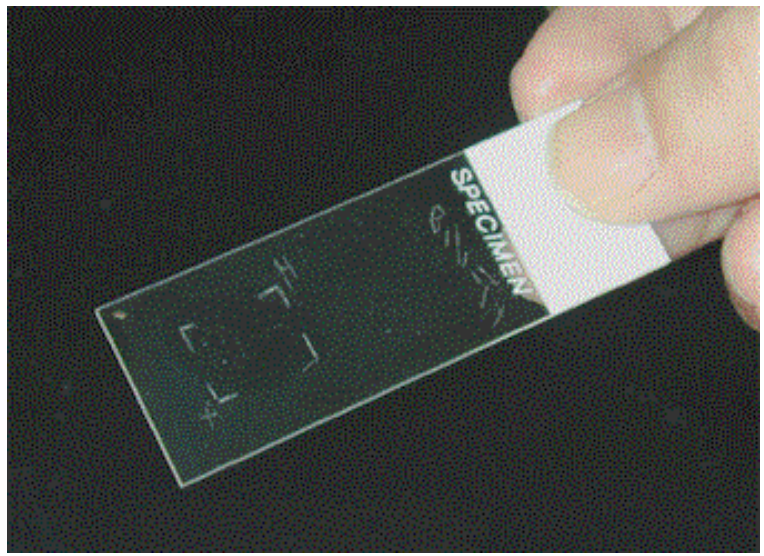
Challenge: Analyzing Light-Directed Synthesis products

- Very hard to analyze monolayers to verify synthesis
- Need surfaces that can be used for high density synthesis



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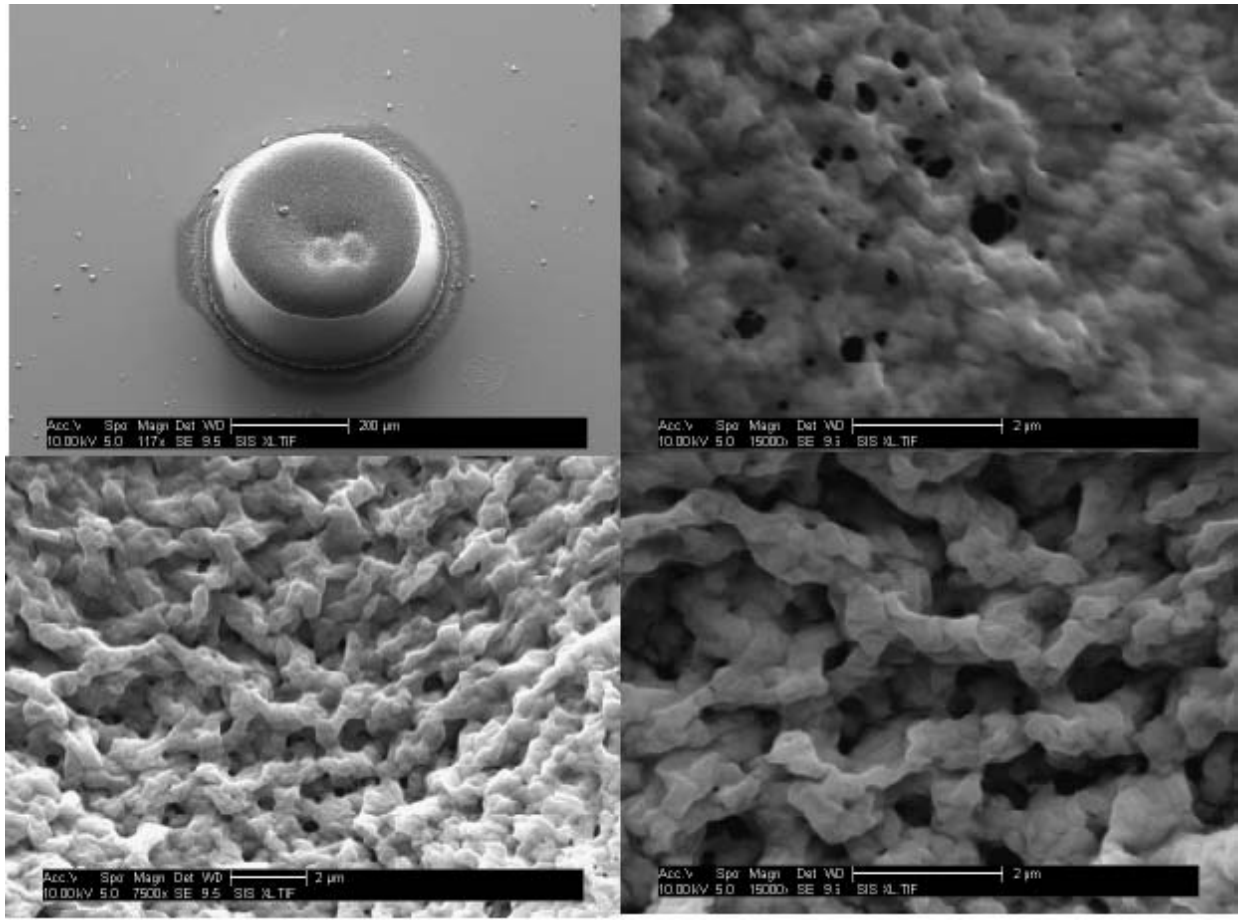
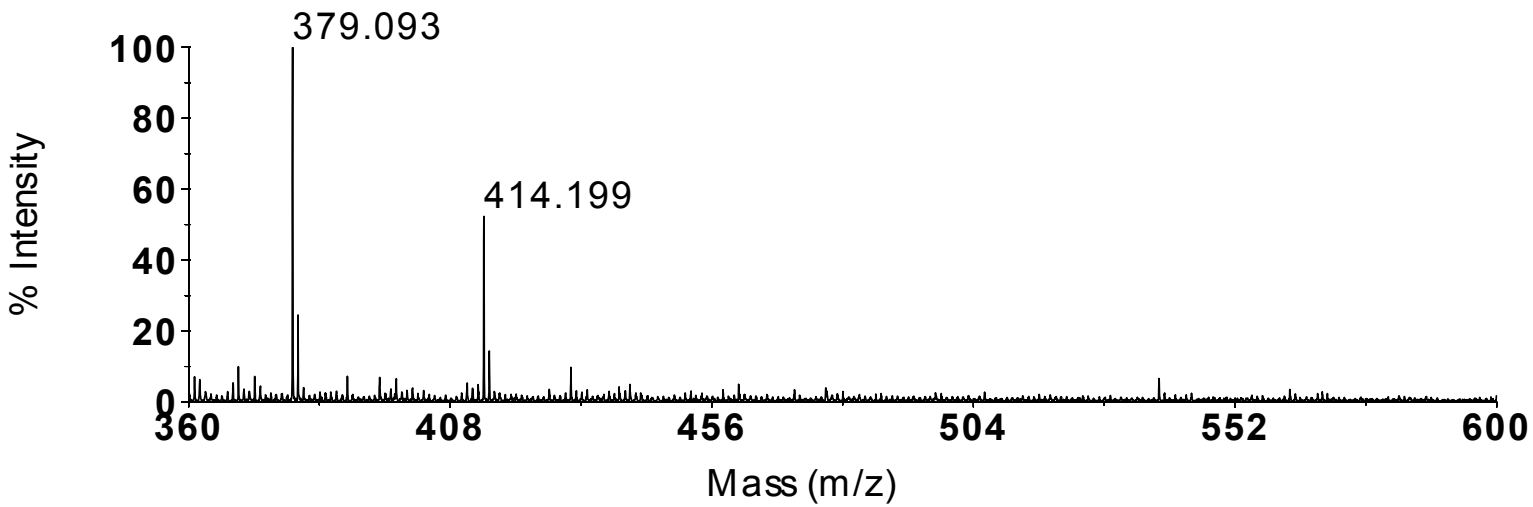
High Density Surface Synthesis

- High density reactive sites in a thin, transparent layer
- Can be photopatterned
- Enough material to do mass spec.
- Visual chemical testing also possible



Can Now use MALDI to Characterize Peptides Synthesized



In Situ MALDI-MS on MMA fabricated microstructures confirms the Fmoc synthesis of GGFL-amide.

- Sodium adduct 414.199 Da vs predicted 414.211 Da).
- The matrix dimer of α-CN at 379.093 Da was used for calibration

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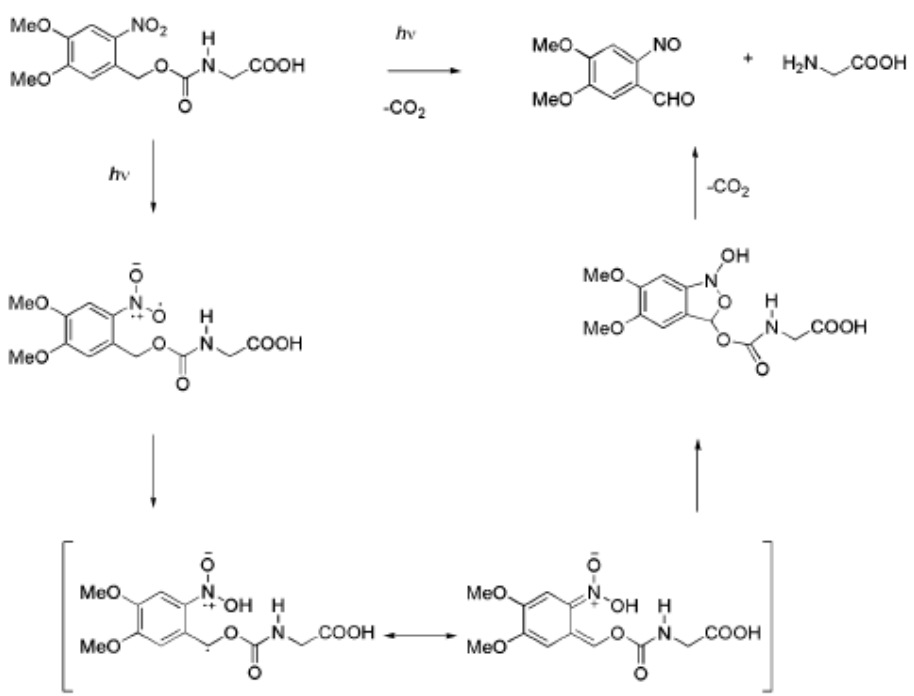
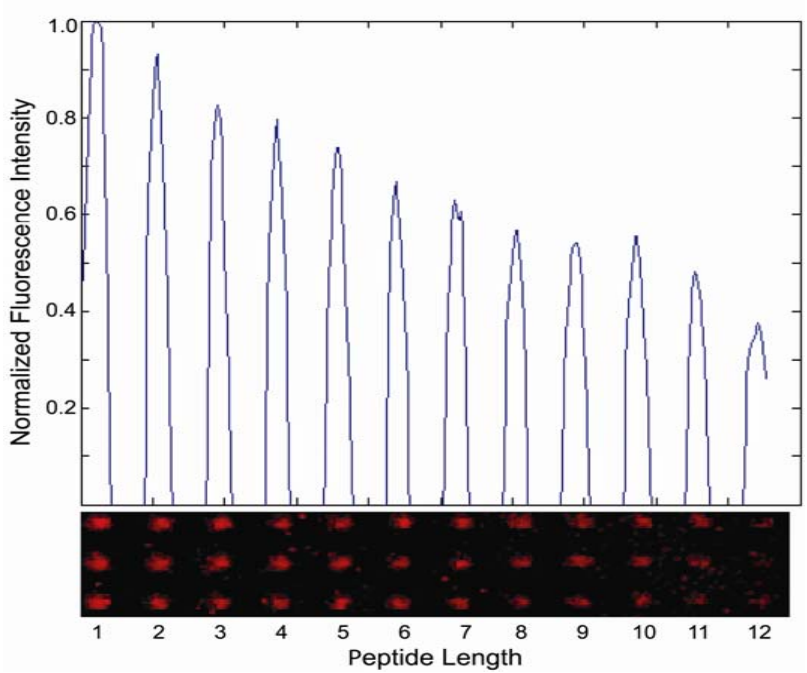
Challenge: Improving the Yield of Photodeprotection





Bochet, 2002 *J. Chem. Soc.* 1:125

Current Stepwise Photochemistry Yield = 92%

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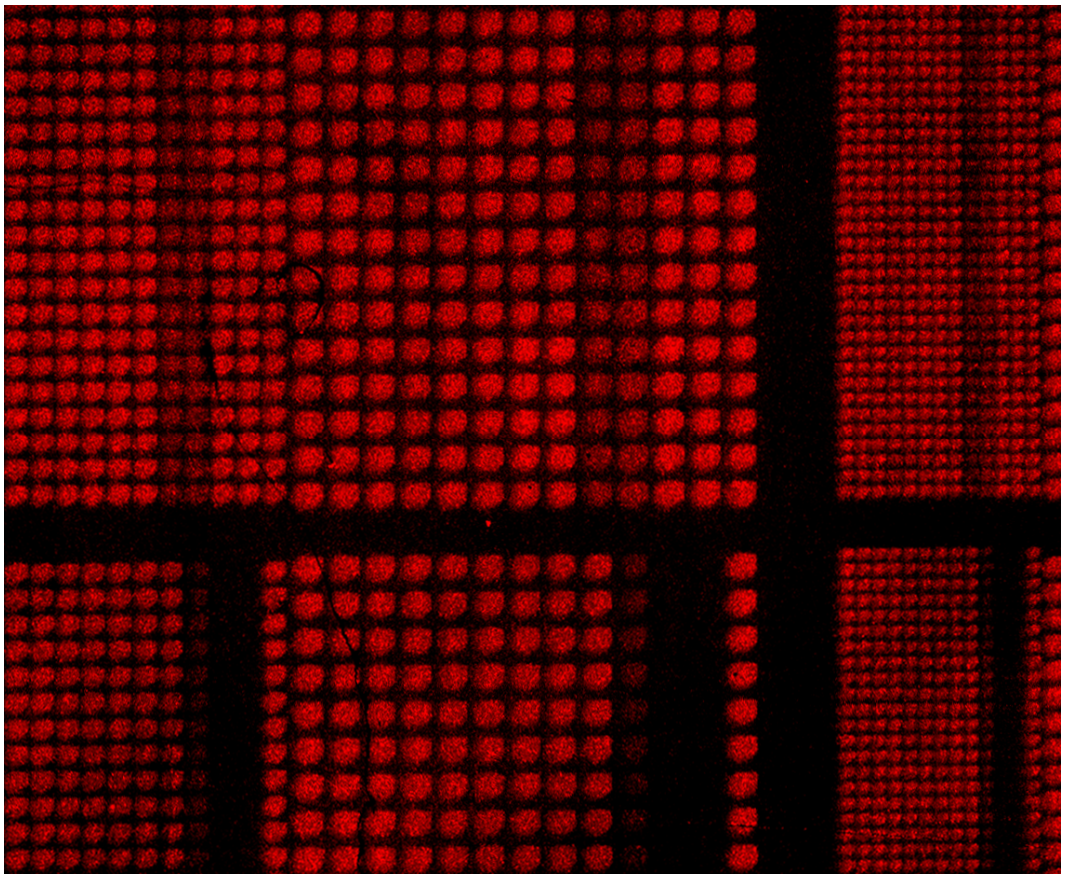
Current Peptide Array Technology:



Combining photochemical steps to substitute at specific amino acids and standard (high yield) FMOC synthesis chemistry, we can now easily produce 10,000 unique peptide “mutants” of up to 20 amino acids each.

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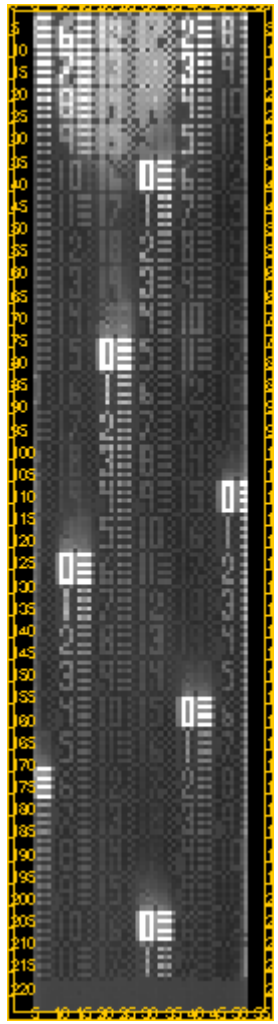
Synthesizing Catalysts Electrochemically on Electrode Arrays, 12,500 at a time.

COMBIMATRIX*

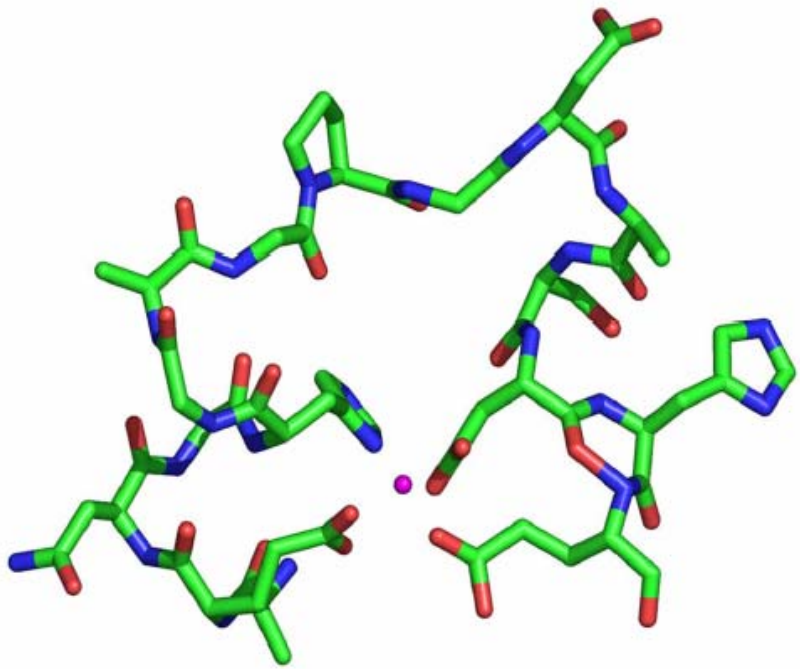


CombiMatrix has developed an electrochemical array technology for making nucleic acids. Their machines have been set up in our lab and we are converting them for peptide chemistry. Electrochemical measurements can be performed on each element in the array.

**Currently have partnership agreement with CombiMatrix*

Peptide Design

- Initial guesses for Mn^{2+} binding peptides modeled after natural sites



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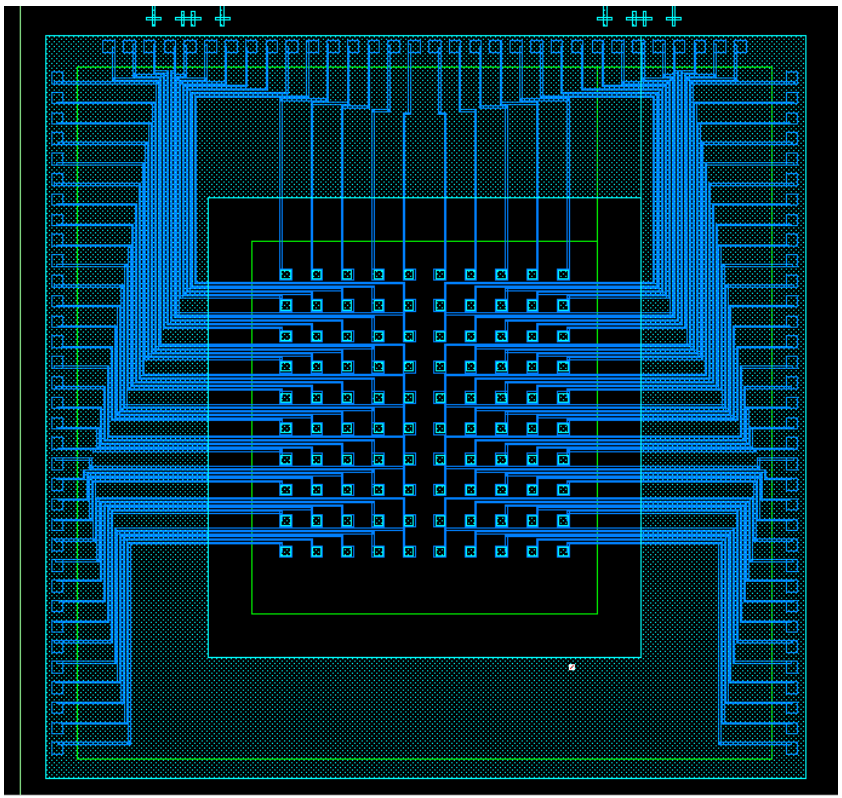
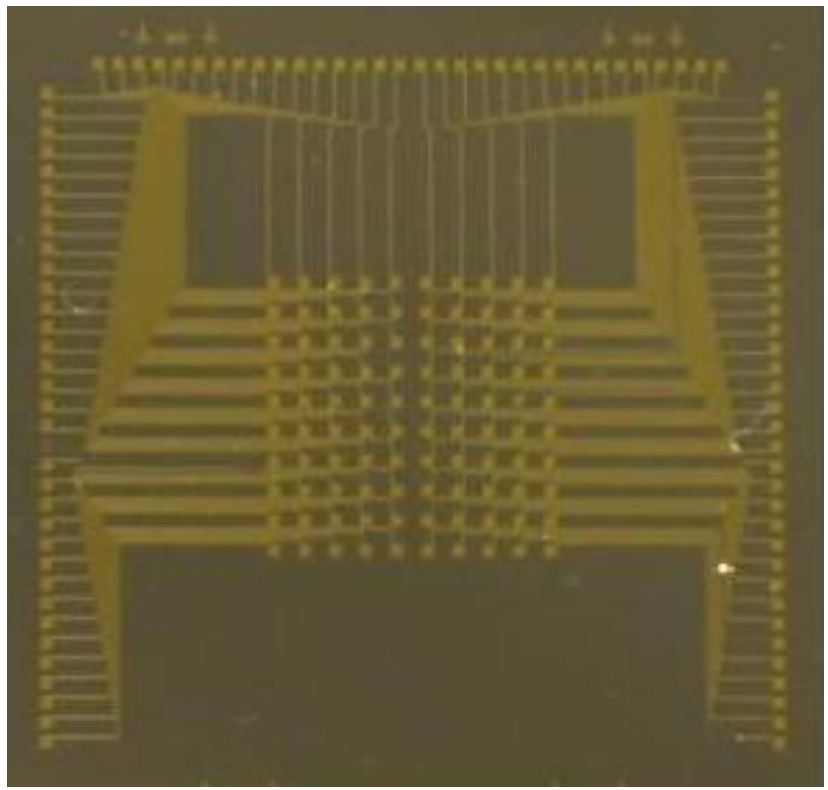
Fabricating Electrode Arrays:

10 x 10 Arrays have been generated

CAD Design of Final Array



Micrograph of Gold Electrode array



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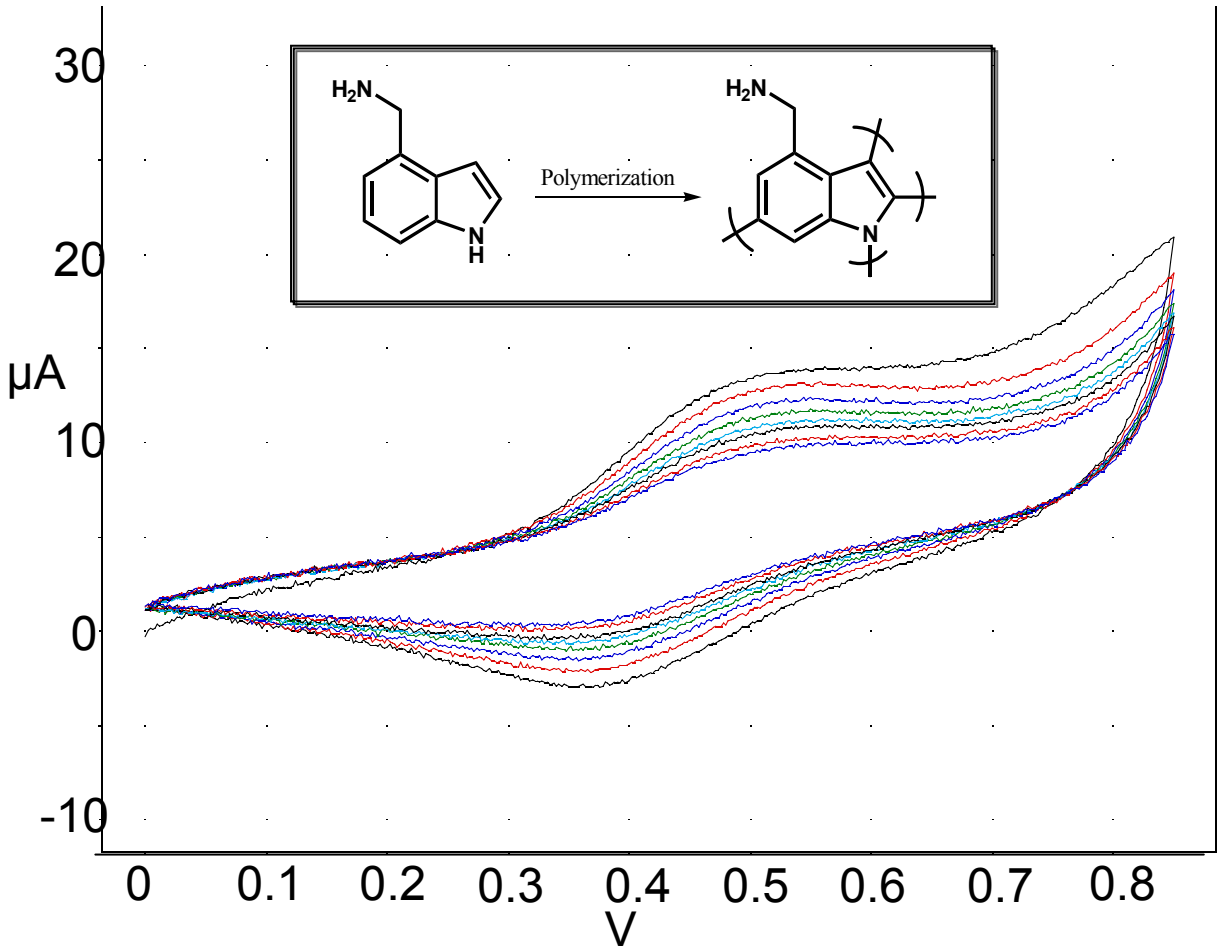
Electrochemical Formation of the Indole Film on Electrodes using Cyclic Voltammetry



Modified indole film is deposited on the electrode. This will be the substrate for peptide synthesis.

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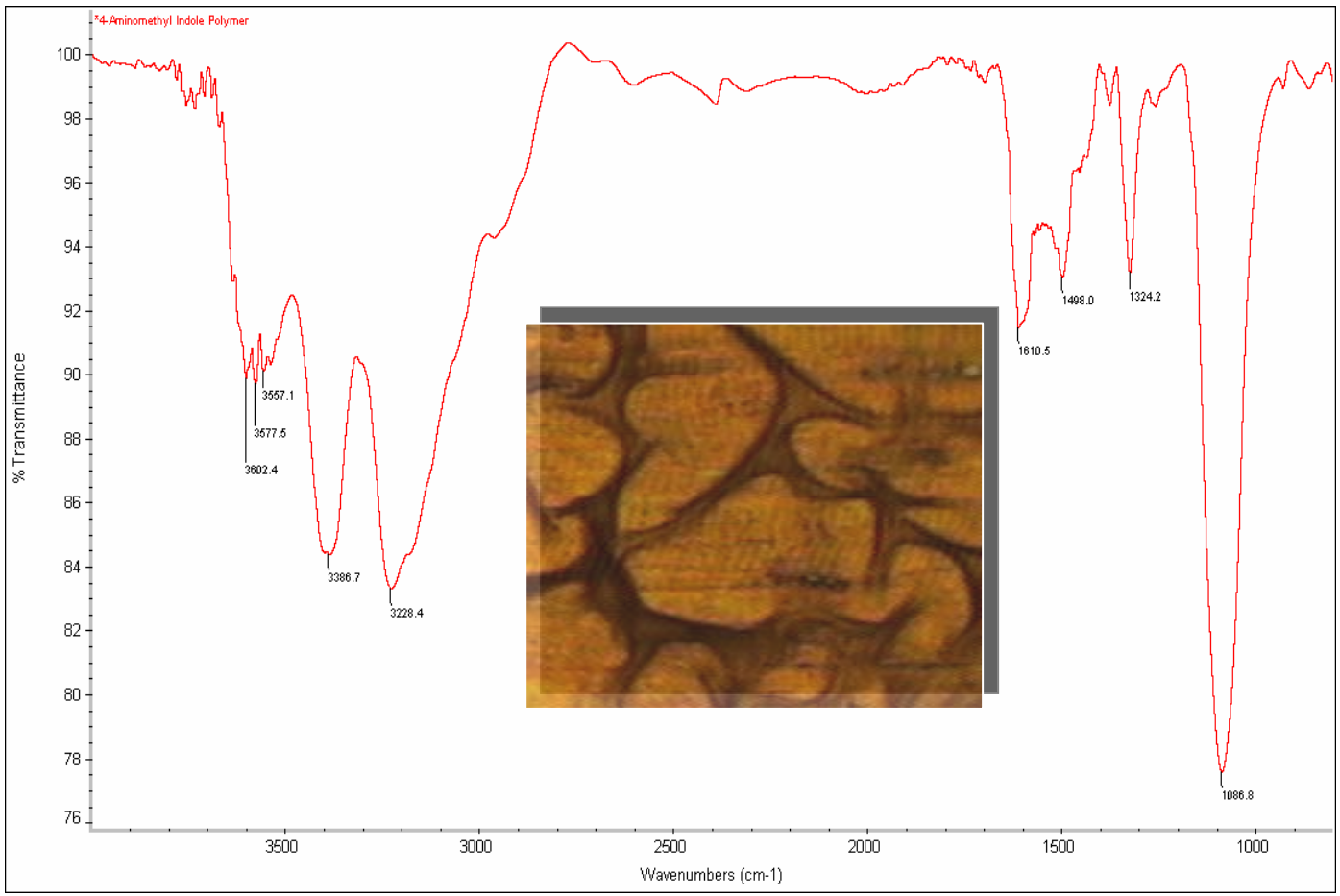
IR Signature of the Indole Film



The film on the electrode surface is roughly 5 microns thick.

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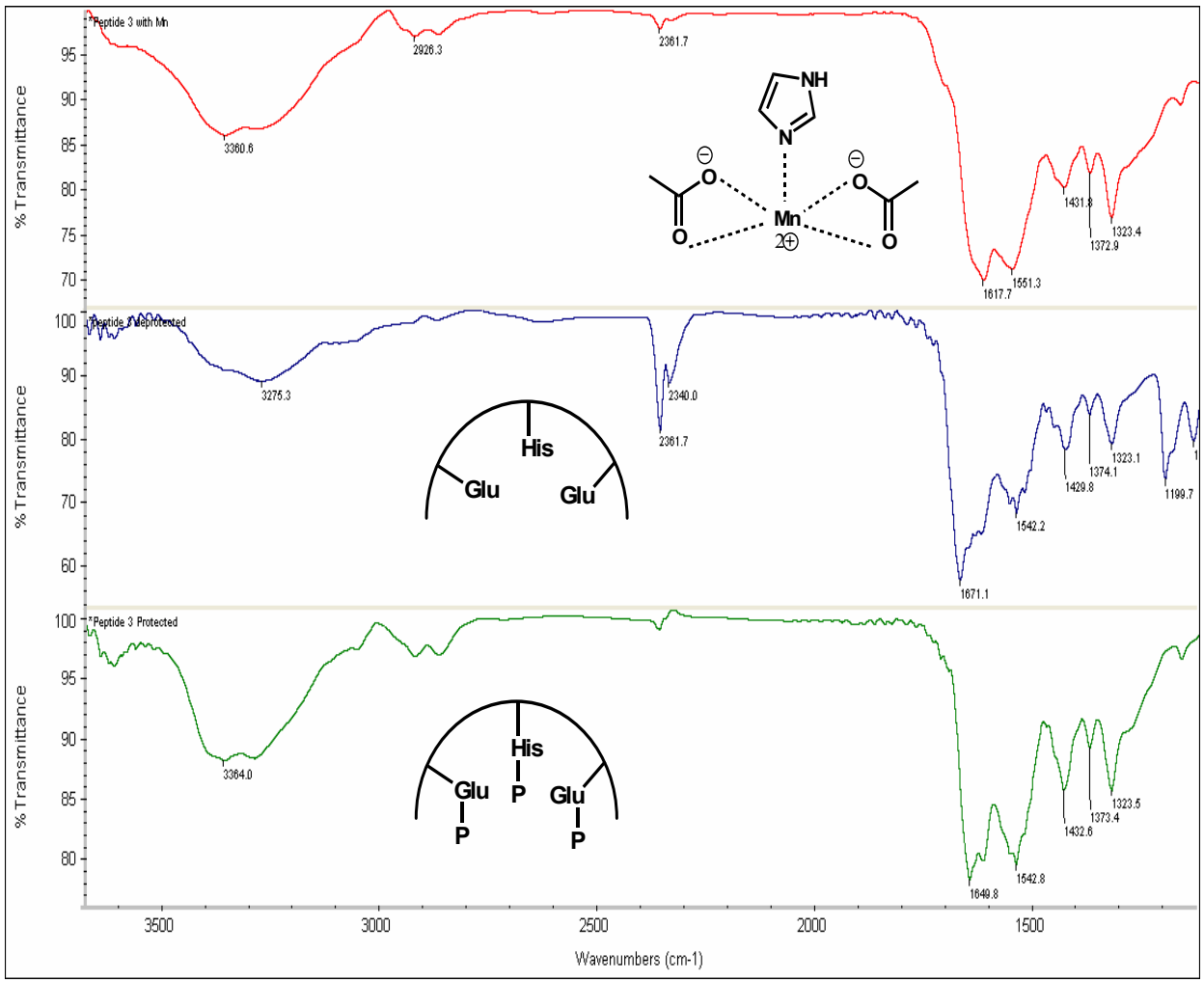
IR Spectra of the Bound Peptides



The spectral signatures of the peptide attached to the electrode change depending on whether it is protected (bottom), deprotected (middle) or has Mn bound (top).

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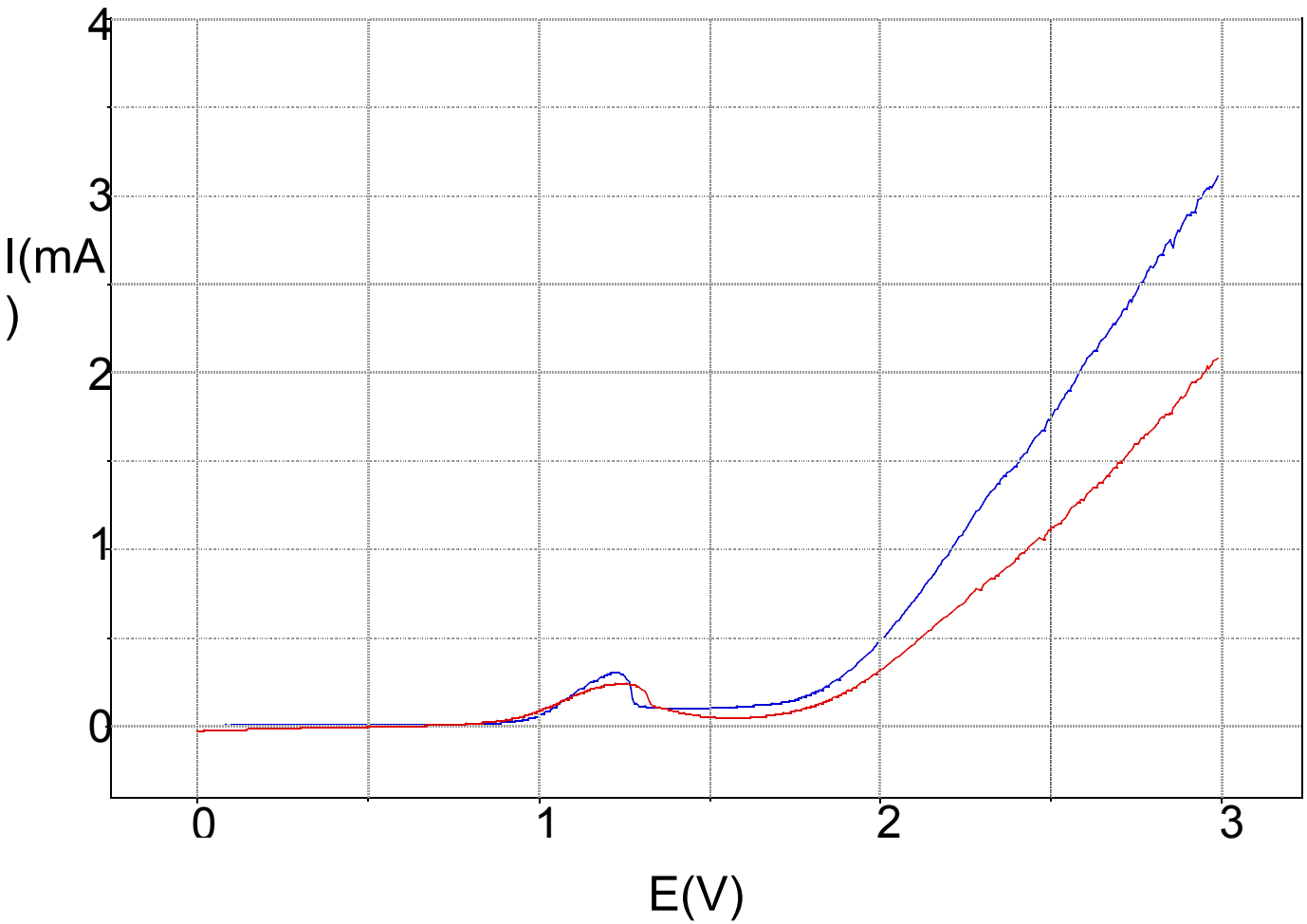
Current/Voltage Curve for Peptide Before (red) and After Mn^{2+} Titration

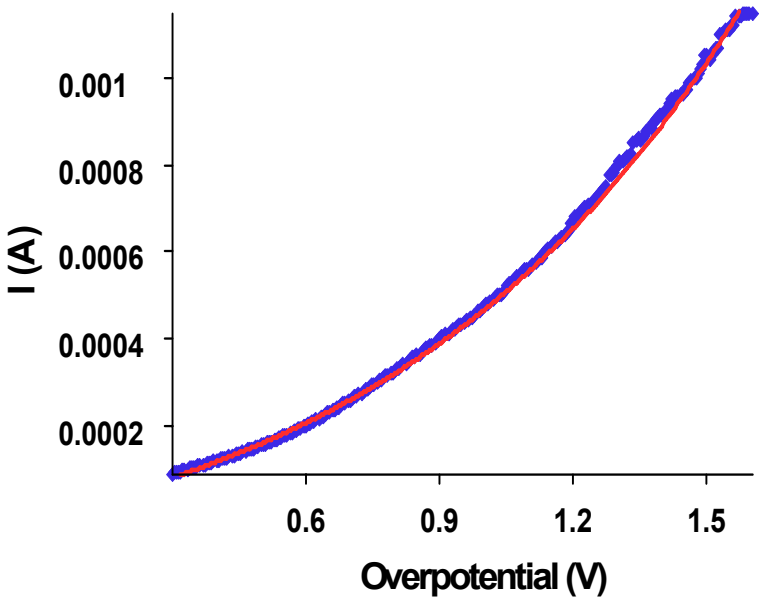


Mn^{2+} binding can be detected electrochemically in our initial metal-binding catalysts and affects the rate of catalysis

Fitting to the Butler-Volmer Equation

$$i = i_0\left[\exp\left(\frac{\alpha_A nF}{RT}\eta\right) - \exp\left(\frac{-\alpha_C nF}{RT}\eta\right)\right]$$

$H_2O \longrightarrow H_2 + 1/2\ O_2$



I_0 is the current at zero overpotential

I_0 increases by 10% between the peptide alone and the peptide with Mn^{2+} bound, corresponding to a small, but significant, catalysis

The fractional increase in i_0 upon addition of metal ion will be used as the gauge of catalytic activity.

Future Work

- Light Directed Synthesis: Improve Yields, Implement on Electrodes
- Electrochemical Synthesis: Optimize Synthesis Conditions
- Electrochemical Measurements: Move to Multielectrode Systems
- Catalyst Optimization Through Variation and Screening.

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Summary

- Light Directed Peptide Synthesis is Functional at >10,000 Peptides/Slide
- Electrochemically Directed Synthesis is Initiated in Collaboration with CombiMatrix
- Electrode Arrays for Testing have been Fabricated (up to 10x10)
- Electrode Surfaces have been Modified with Polyindole + Peptide
- Initial Peptide Guesses have been used to Determine Baseline Catalytic Currents at Zero Overpotential.

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Publications

- T. Northen, D. Brune and N. Woodbury. (2006) Synthesis and Characterization of Peptide Grafted Porous Polymer Microstructures. *Biomacromolecules 7*, 750-754.
- T. Northen and N. Woodbury. (2005) Light-Directed Movement of Polymer Microstructures. *Langmuir 21*, 4949 - 4953.

Critical Assumptions and Issues

- Variability between electrodes can make it difficult to measure catalytic improvement
- Light directed peptide synthesis on the electrode surfaces may not work the same as on our methacrylate surfaces
- Multiple peptides may be needed to form the optimum catalyst

Electrode Variability

- By measuring each electrode without peptide, with peptide and with peptide + metal ion bound, one always looks at the catalytic activity relative to no catalyst, providing a internal reference on each electrode.

Light Directed Synthesis on Electrode Surfaces

- Yields of light directed synthesis on the polyindole covered electrodes have not yet been measured
- The reactive groups are the same and the polymer provides a relatively high density of free amines
- Other modified polyindole groups can be tried if necessary (e.g., longer linkers on the amine)

Using Multiple Peptides

- Lysine can be used as a branch-point to connect multiple peptides to one chain
- Alternatively, a base structure, such as a porphyrin can be used
- This may allow the development of more complex, multi-metal centers that mimic the natural systems more closely