

Development of Water Splitting Catalysts Using a Novel Molecular Evolution Approach

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The Biodesign Institute at Arizona State University

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Timeline

- **Start - July 1, 2005**
- **Finish - June 30, 2009**
- **70% Complete**

Budget

- **Total Project Funding**
 - DOE - \$1,200,000
 - Contractor - \$300,000
- **Funding for FY09**
 - \$300,000 DOE
 - \$75,000 Contractor

Barriers

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

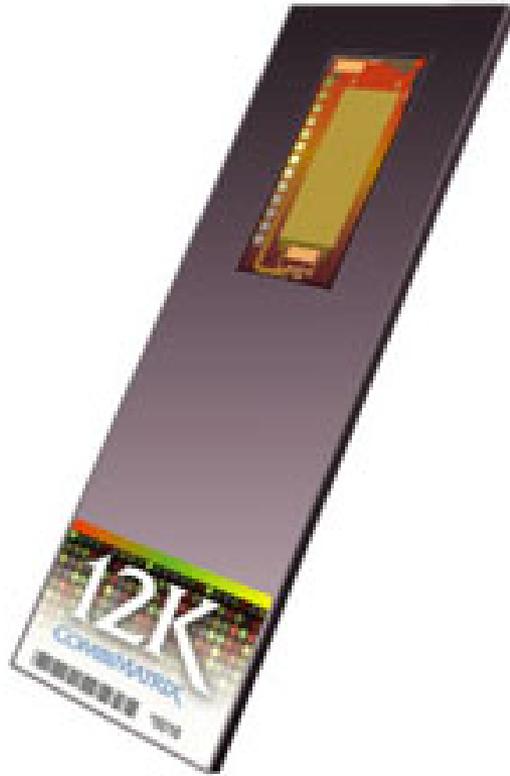
Partners

- **CombiMatrix Corp., Mukilteo, WA**
- **Prof. Bill Armstrong, Boston College**

- **Broad Objectives:**
 - **Develop a novel approach to creating molecular catalysts for redox reactions based on high throughput synthesis on electrodes**
 - **Mimick Nature's approach to water splitting**
 - **Reduce the overpotential by 30%**
- **Specific Objectives (FY09):**
 - **Optimize high throughput peptide synthesis on CombiMatrix Arrays**
 - **Optimize the multielectrode measurements of water splitting on the CombiMatrix Arrays**
 - **Demonstrate several rounds of optimization for catalytic activity**

- **The impact would be an energetically more efficient method for production of hydrogen from renewable electricity sources**
- **This addresses both System Efficiency and Renewable Integration**

General Approach



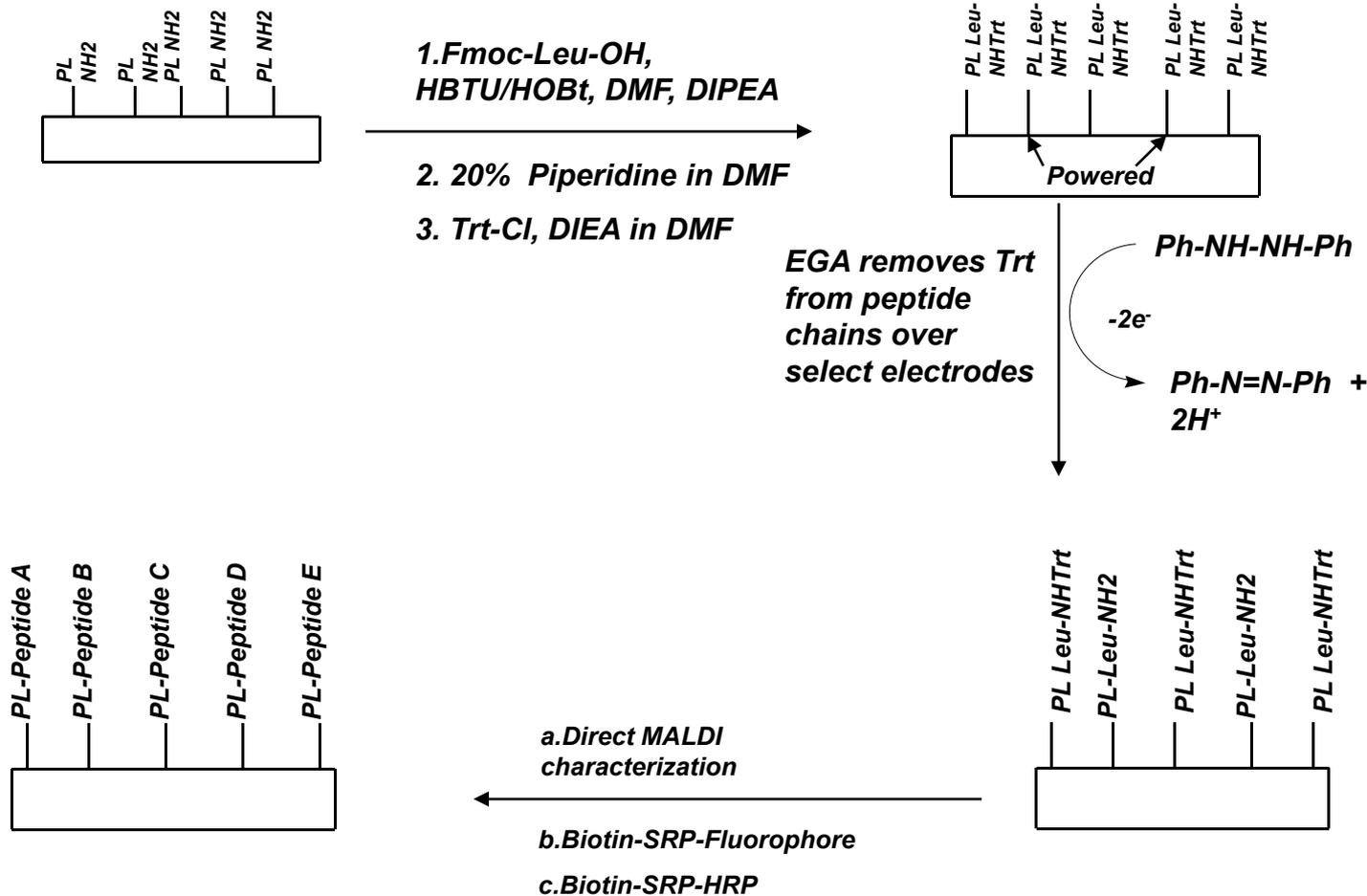
COMBIMATRIX

- **Synthesis of 12,000 different peptides directly on electrodes**
- **Binding of metal ions or metal complex catalysts to the peptides, mimicking PSII water splitting complex**
- **Direct electrochemical measurement of current due to electrolysis at each electrode**
- **Analysis of one library of molecules informs the production of the next library**
- **Iterative optimization should result in an efficient water splitting catalyst**

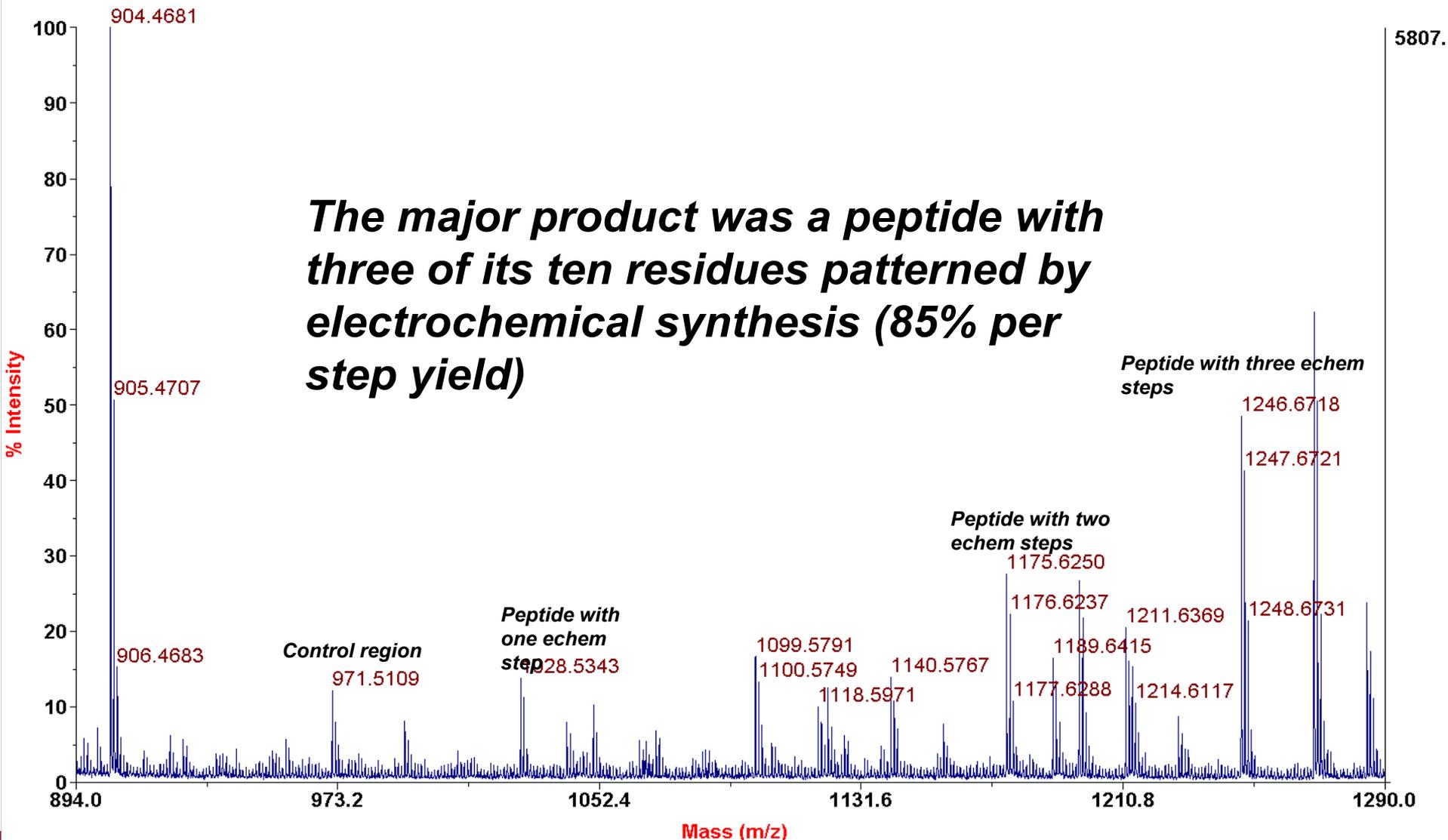
- 1. Multi-step patterned synthesis of peptides in an array**
- 2. Verification of synthesis via direct MALDI spectroscopy on the surface**
- 3. Automation of array synthesis**
- 4. Background current measurements on the arrays**
- 5. Comparing currents from peptides with and without Mn on the arrays**
- 6. Iterate synthesis and measurement to result in a sequence optimization**

Go/No Go to continue pursuing this approach depends on 1) ability to measure catalytic signal above noise and 2) ability to reproducibly synthesize arrays with multiple variable residues

- 1. Tested two platforms, light directed on home-built arrays and electrochemically directed via CombiMatrix arrays: elected CombiMatrix arrays**
- 2. Design, synthesis and characterization of initial Mn binding peptides**
- 3. Partnership formed with Mn-complex chemist**
- 4. Developed MALDI method for measuring products of in situ synthesis directly on the surface**
- 5. Partnered with CombiMatrix to modify sensing equipment to measure currents at 12,500 electrodes**
- 6. Demonstrated ability to perform standard solid phase synthesis on the arrays (by nonpatterned methods)**
- 7. Demonstrated ability to remove blocking groups using patterned electrochemically generated acids and create peptide bonds**

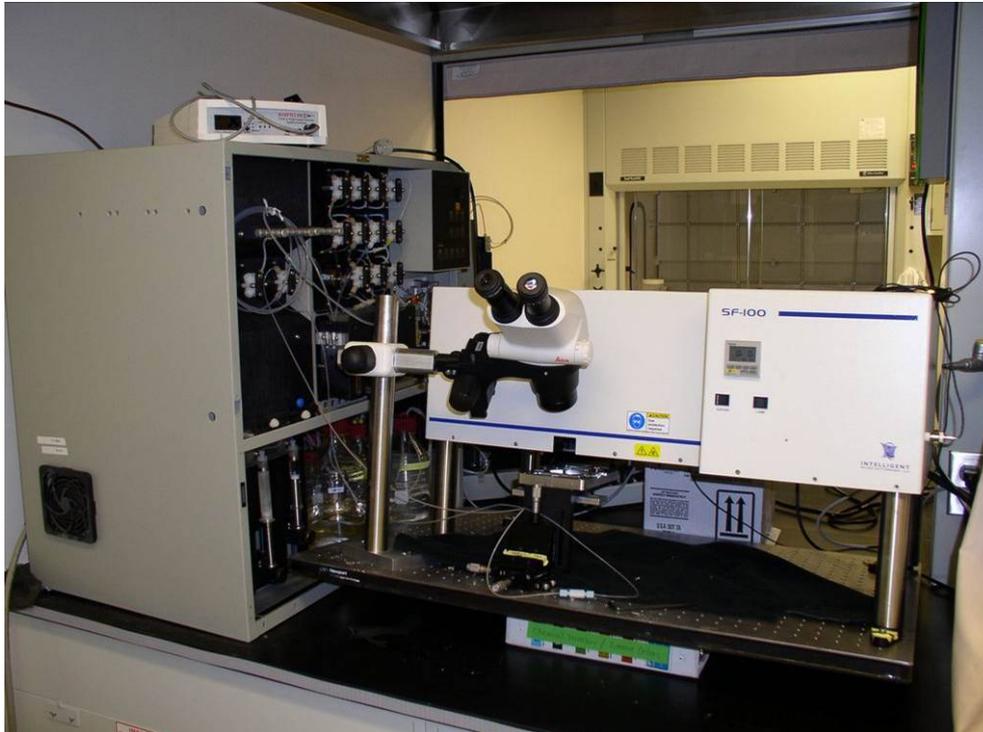


Voyager Spec #1=>MC[BP = 295.2, 19833]

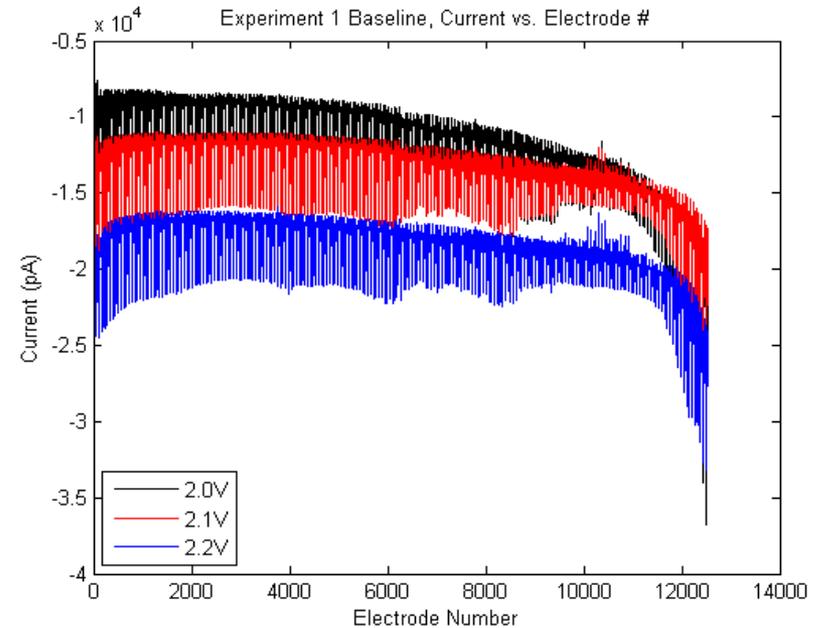
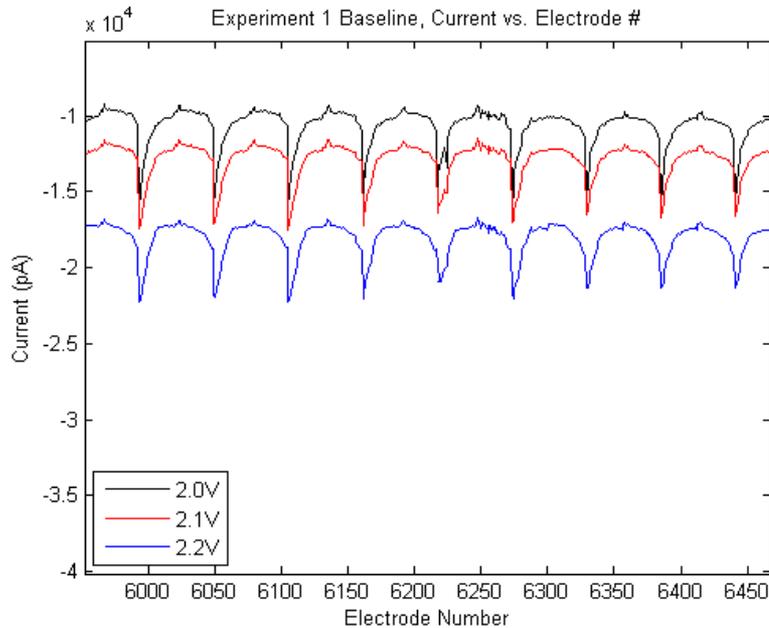


The major product was a peptide with three of its ten residues patterned by electrochemical synthesis (85% per step yield)

1. **Fluidic connection between Pioneer synthesizer and Combimatrix synthesis chamber**
2. **Software control interface developed between synthesizer and synthesis system**

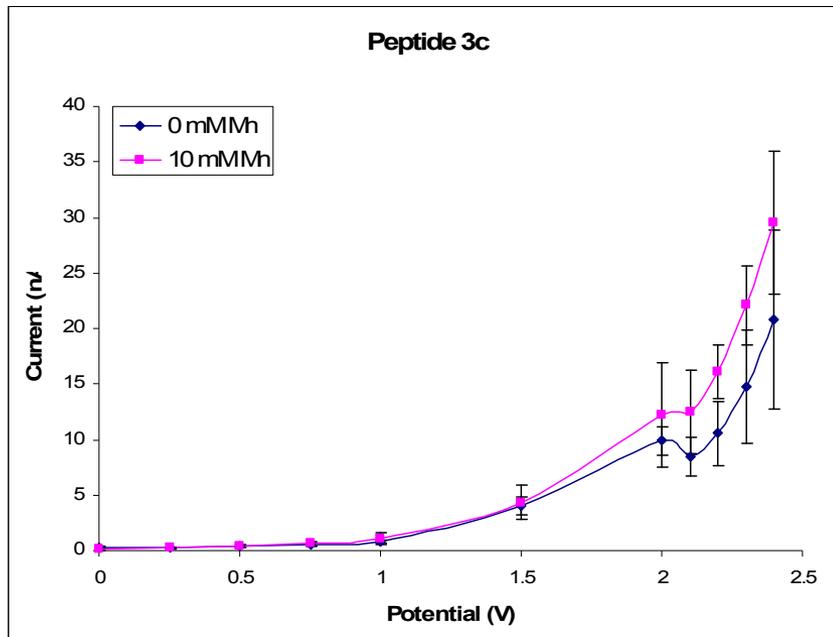


Large, but systematic current variations across electrodes

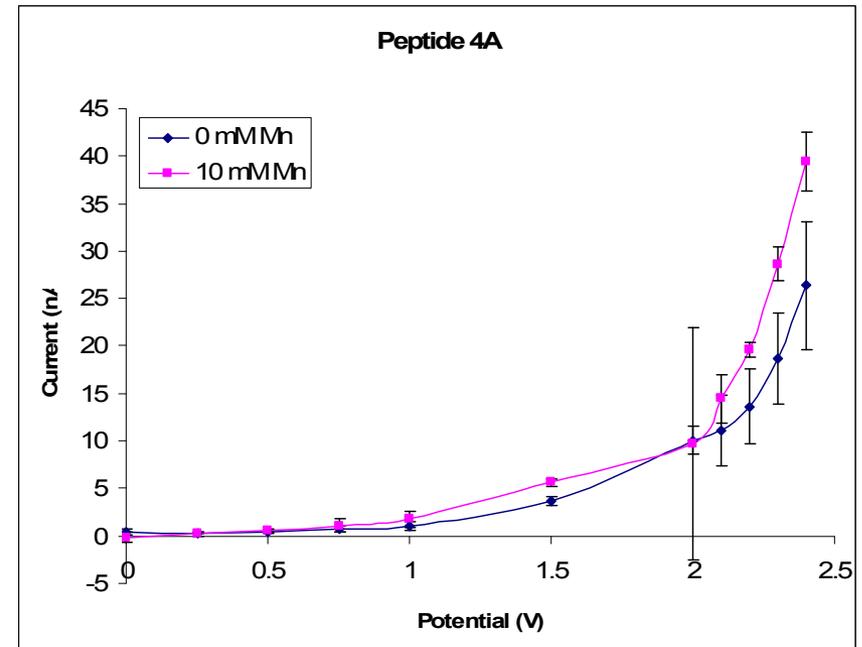


No significant difference between Mn binding peptide and control

Mn binding Peptide

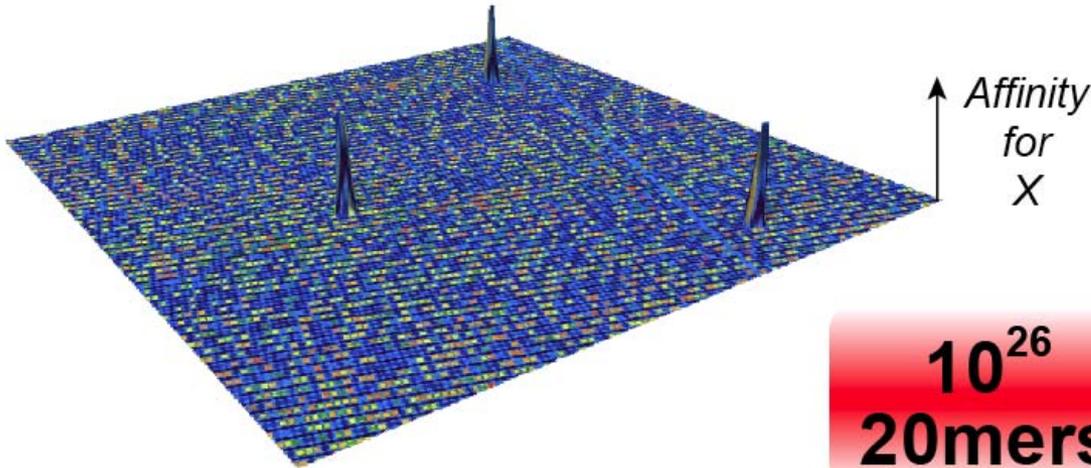


Control Peptide



- 1. Multi-step patterned synthesis of peptides in an array** ✓
- 2. Verification of synthesis via direct MALDI spectroscopy on the surface** ✓
- 3. Automation of array synthesis** ✓
- 4. Background current measurements on the arrays** ✓
- 5. Comparing currents from peptides with and without Mn on the arrays** ✓
- 6. Iterate synthesis and measurement to result in a sequence optimization**

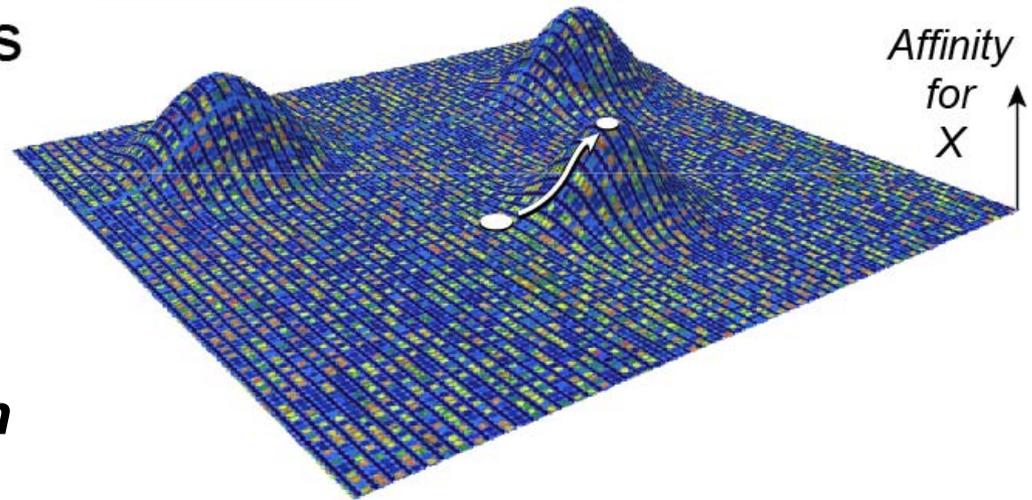
Key Additional Finding (Not DOE funded)



10^{26}
20mers

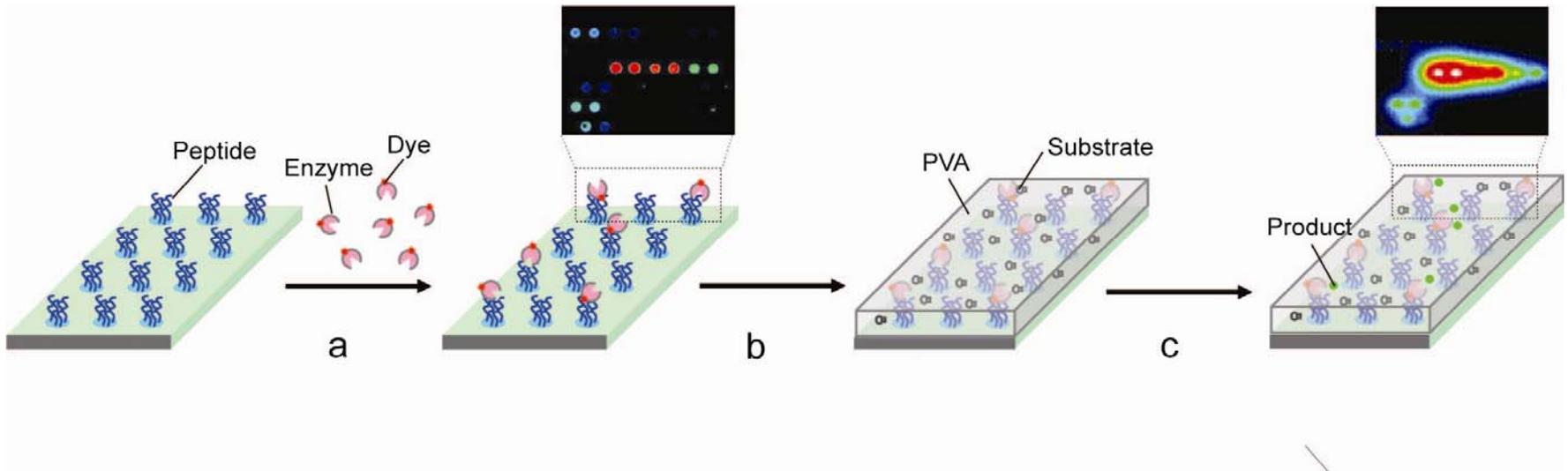
Requires Large Libraries

*Peptide space is smooth
and can be searched
through iterative mutation*



Sparse Sampling Effective

Key Additional Finding (Not DOE funded)



Peptides can be used to stabilize or modify activity of existing catalysts

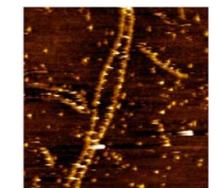
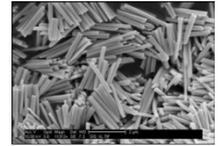
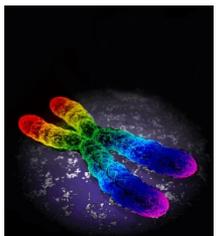
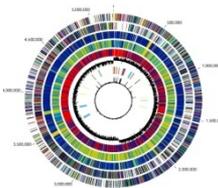
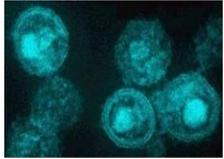
- **CombiMatrix**
 - Industry partner
 - Funded through equipment purchase
 - Provides software/hardware development assistance
 - Outside DOE hydrogen program
- **Professor William Armstrong**
 - Boston University
 - Currently unfunded
 - Will provide Mn-complex catalysts
 - Outside DOE hydrogen program

- **FY09 is final year of DOE funding (official end June 09, but no cost extension to December granted)**
- **Perform an Iterative optimization:**
 1. **Start with one of our peptides known to bind Mn**
 2. **Select 3-4 residues thought to be key to catalysis**
 3. **Synthesize array with all possible variants**
 4. **Measure currents vs. voltage**
 5. **Pick best**
 6. **Repeat for 3 additional residues**
 7. **Etc.**

- **After choosing the electrochemical patterning platform, synthesis was optimized to about 85% yield**
- **Still limited by issues with side chain reactivity**
- **Using a modified CombiMatrix sensing instrument, have made electrochemical measurements at 12,500 electrodes**
- **Current Mn binding peptides do not show high enough catalysis to measure on the electrode arrays**
- **Goal is not to create an array and attempt and optimization in remaining 8 months**

The Biodesign Institute at ASU

- Eradicating Cancer
- Rapid Vaccine Discovery System
- Defending Against HIV
- Diabetes Detection and Management
- Preventing Pneumonia in Newborns
- Treating Childhood Mitochondrial Diseases
- Using Nature to Clean Water
- Energy from Waste



500x500nm

