

Development and Optimization of Cost Effective Material Systems For Photoelectrochemical Hydrogen Production

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Project ID # PD-38

Overview

Timeline

- Start date September 1, 2004
- End date May 31, 2009
- 75% Complete

Budget

- Total project funding
 - DOE share \$ 894k
 - Contractor share \$ 223k
- No Funding Received in 2006, then Restarted 2007 \$200 k
- Funding for FY08 \$221k

Barriers

Technical Barriers Addressed

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device
- (AB) Bulk Material Synthesis

Technical Targets

2013 DOE PEC

- Solar-to-Hydrogen Conversion Efficiency $>8\%$
 - Bandgap $\sim 1.7\text{-}2.2$ eV
- Lifetime > 1000 hours

Technical Targets

UCSB

- Scalable to produce hydrogen at a cost less than PV-electrolysis

Objectives

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material system for photoelectrochemical production of bulk hydrogen using solar light energy as the primary energy input making use of novel syntheses and high throughput experimentation methods.

- ***Task #1. Identify improved materials for solar photon absorption using high throughput methods and exploratory design and synthesis of new mixed metal-oxides.***
- ***Task #2. High-throughput screening of selected properties, and photoelectrochemical characterization of new host materials.***
- ***Task #3. Optimize the morphology of the PEC material system for maximum efficiency; i) minimize charge carrier path lengths, ii) maximize surface area.***
- ***Task #4. Explore processing and synthesis parameters to optimize the conductivity and minimize charge trapping and surface recombination of selected materials.***
- ***Task #5. Identify and minimize electrokinetic limits by synthesis of appropriate electrocatalysts compatible with the host, electrolyte, and reactant/product properties.***
- ***Task #6. Develop a complete, “photoelectrochemical unit”, combining material absorption, charge transport, stability, and electrokinetic design features.***
- ***Tasks #7, #8, and #9: Evaluate conceptual model reactor systems, theoretical and practical economic potential of alternative redox reactions, estimate hydrogen production costs.***

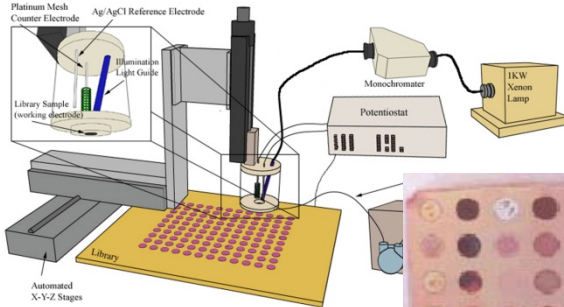
Approach/Selection Criteria

New Candidate Material
Discovery: High Throughput
Synthesis and Screening

No

Absorption Edge
< 2.2 eV ?

Yes



Synthesis of
Optimal Compositions
and Structures

No

Solar Photon-electron Current
Conversion Efficiency
> 10%

Yes

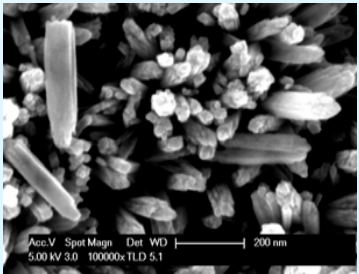
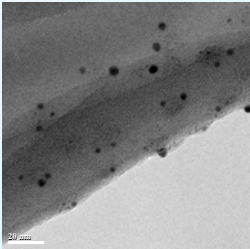


Processing, Surface, Electrolyte,
and
Electrokinetic Optimization

No

Solar/Hydrogen
Efficiency
> 8% @ 10000 hours

Yes

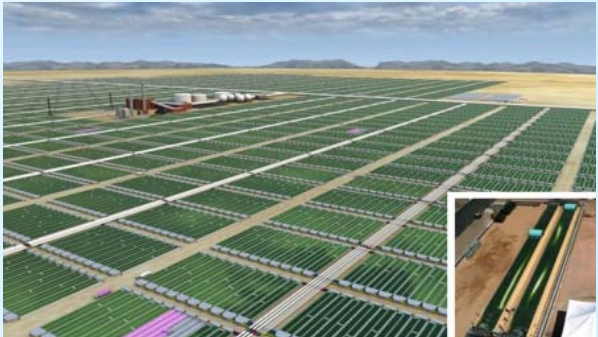


Optimized Large Scale Reactor
System Techno-economics

No

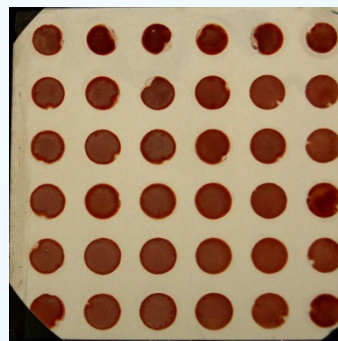
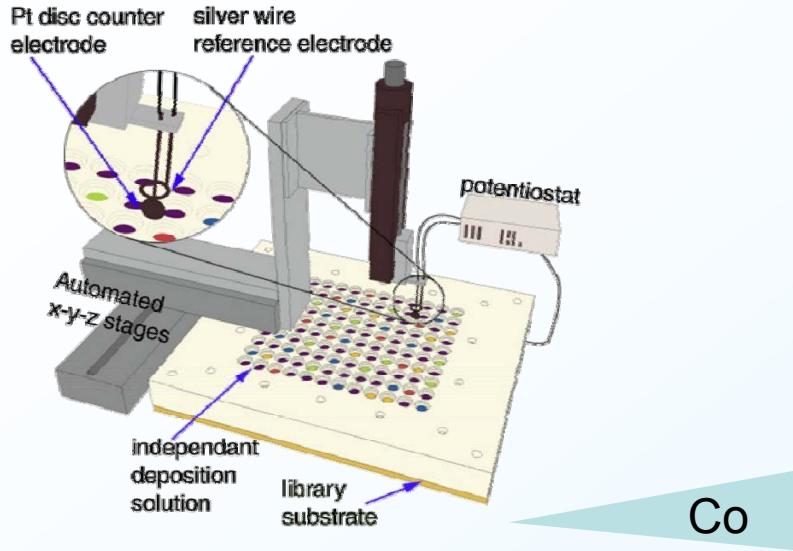
Hydrogen
Cost Estimate
< \$5/Kg

Yes
Success!



Technical Accomplishments/Progress/Results:

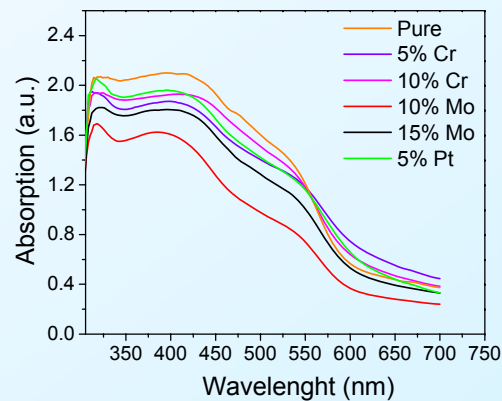
Task #1. Identify improved materials for solar photon absorption using high throughput methods and exploratory design and synthesis of new mixed metal-oxides.



High Throughput Electrochemical Synthesis

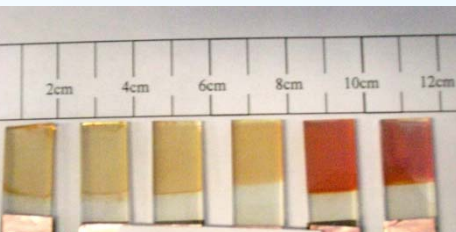
Doped Fe₂O₃

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|--------------|-------|-------|-----------|--------|--------|--------|--------|--------|--------|--------|--------|---------|---------|---------|---------|---------|---------|---------|
| Period 1 | 1 H | | | | | | | | | | | | | | | | | 2 He |
| 2 | 3 Li | 4 Be | | | | | | | | | | | | | | | | 10 Ne |
| 3 | 11 Na | 12 Mg | | | | | | | | | | | | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 4 | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5 | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6 | 55 Cs | 56 Ba | * 71 Lu | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | ** 103 Lr | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Uub | 113 Uut | 114 Uuq | 115 Uup | 116 Uuh | 117 Uus | 118 Uuo |
| *Lanthanoids | | | * 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | | |
| **Actinoids | | | ** 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | | |



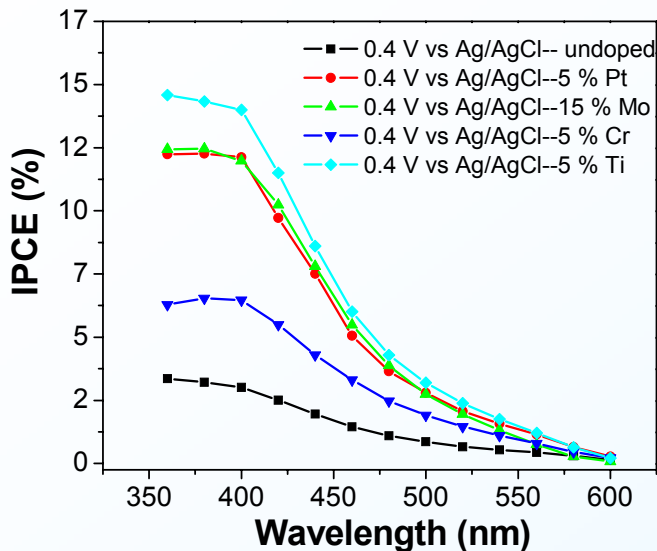
- 23 different dopant species have been tested ($M_xFe_{2-x}O_3$)
- XPS only detected Fe^{3+} for all samples (Pt, Cr, Mo)
- No (catalytic) Pt^0 observed near the surface
- Pt^{4+} , Mo^{6+} , Cr^{4+} enhance the photo-electrochemical performance
- No phase segregation was observed by XRD

A. Kleiman
Y-S. Hu

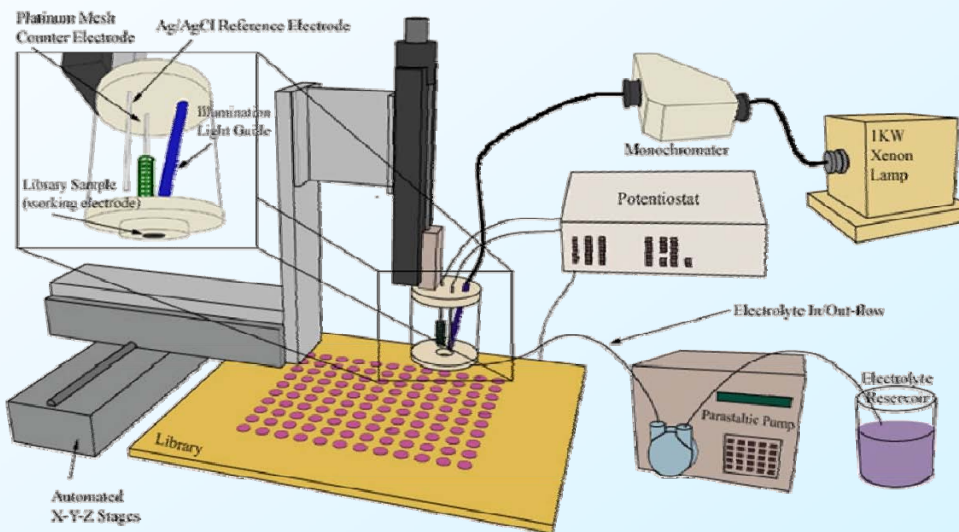
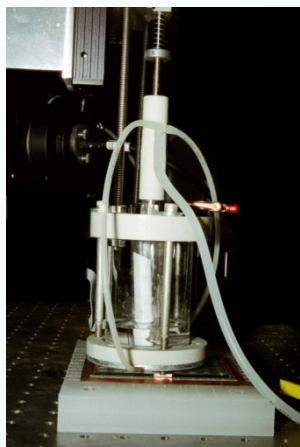
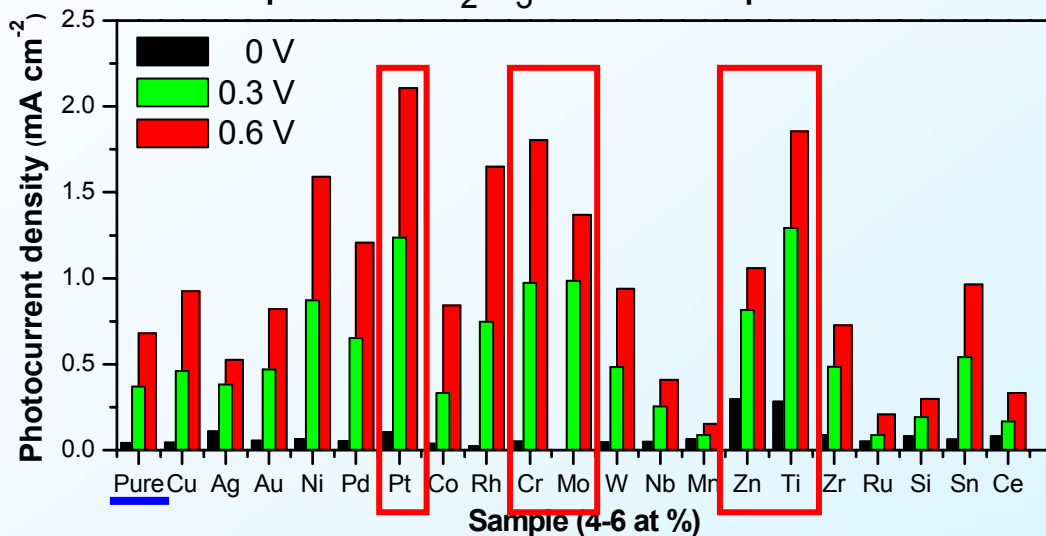


Technical Accomplishments/Progress/Results:

Task #2. High-throughput screening of selected properties, and photoelectrochemical characterization of new host materials.



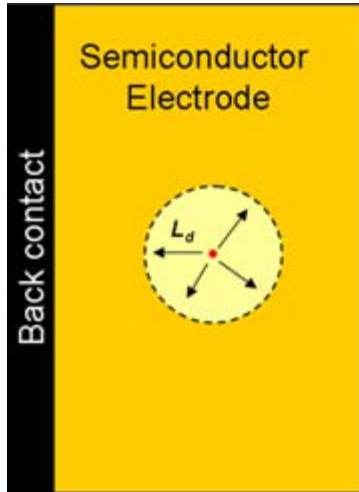
Doped $\alpha\text{-Fe}_2\text{O}_3$ electrodeposited films



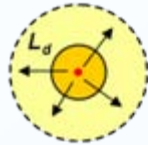
- Pt, Cr, Mo, Ti and Zn have been identified as promising dopants
- Detailed studies have shown the best performing samples are 15% Mo, 5% Pt, 5% Cr and 5% Ti
- The IPCE at 400 nm can be increased up to 400% by doping $\alpha\text{-Fe}_2\text{O}_3$
- Ternary systems $\text{M}_x\text{N}_y\text{Fe}_{2-x-y}\text{O}_3$ are currently being investigated

Technical Accomplishments/Progress/Results:

Task #3. Optimize the morphology of the PEC material system for maximum efficiency;
i) minimize charge carrier path lengths, ii) maximize surface area.

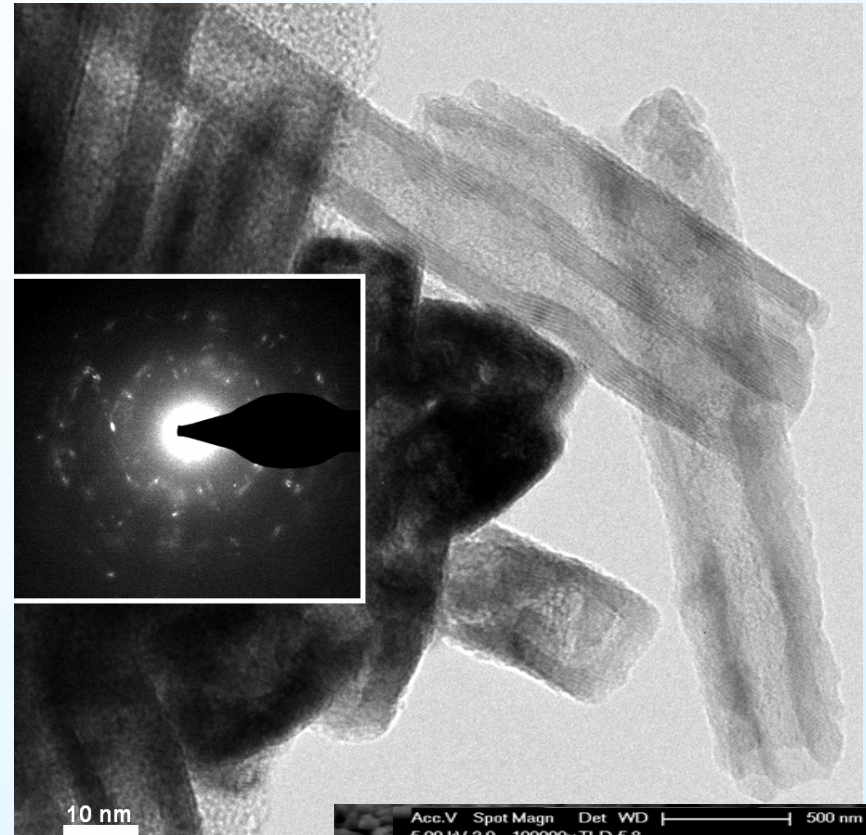


Semiconductor Particle

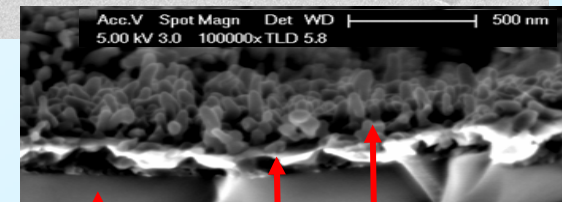


L_d = Free carrier diffusion length
● = Photoexcited carrier
● = Semiconductor particle

- Lower absorption coefficient materials
- Short carrier diffusion lengths
 - $r_{\text{particle}} \sim L_d$
- High SA = low current densities
- indirect \rightarrow direct (surface provides k)



- Hydrothermal synthesis \rightarrow β -FeOOH
- Thermal Dehydration, crystalline hematite.
- Substitutional doping, unsuccessful.
- Post synthesis diffusion (Ti), improved PEC performance.



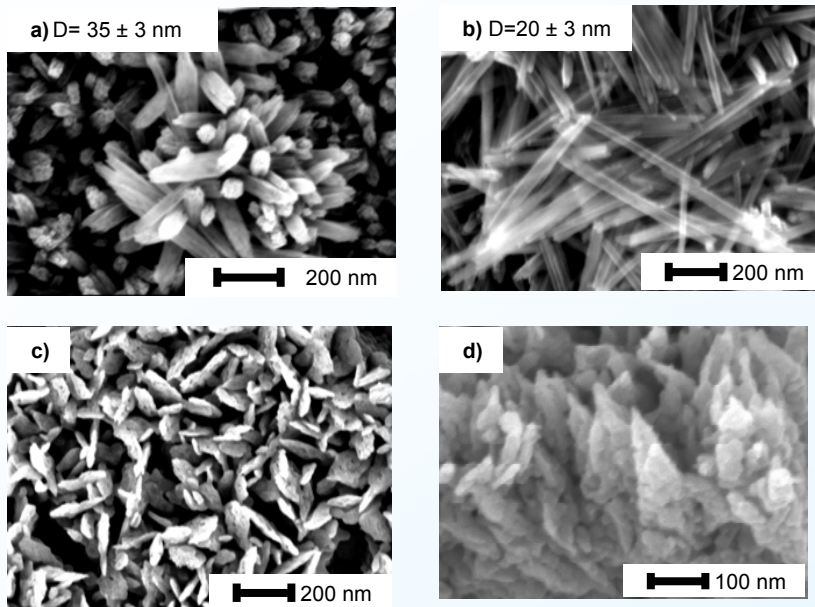
Quartz substrate Ti/Pt nanorods

A. Kleiman

Technical Accomplishments/Progress/Results:

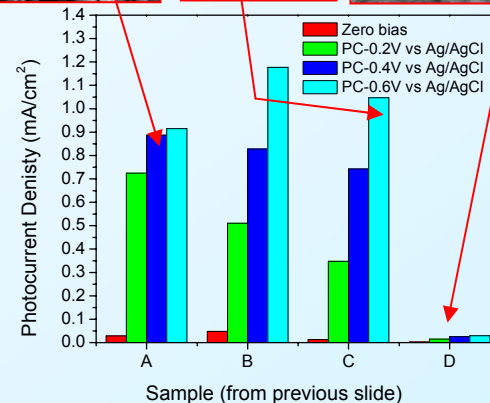
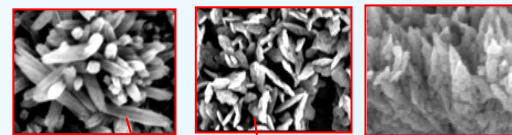
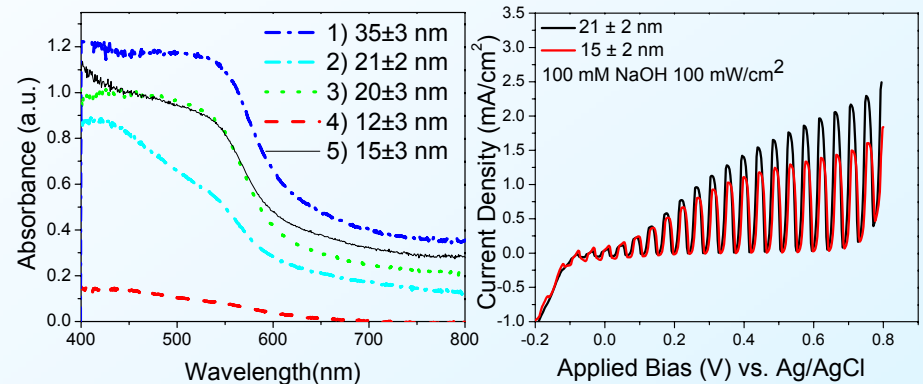
Task #3. Optimize the morphology of the PEC material system for maximum efficiency; i) minimize charge carrier path lengths, ii) maximize surface area.

Synthesis of Iron Oxide Nanorods



- The morphology of iron oxide nanorods can be changed by modification of the growth conditions
- Nanorods from 11 to 50 nm in diameter can be synthesized, as well other nanostructured hematite.

Characterization



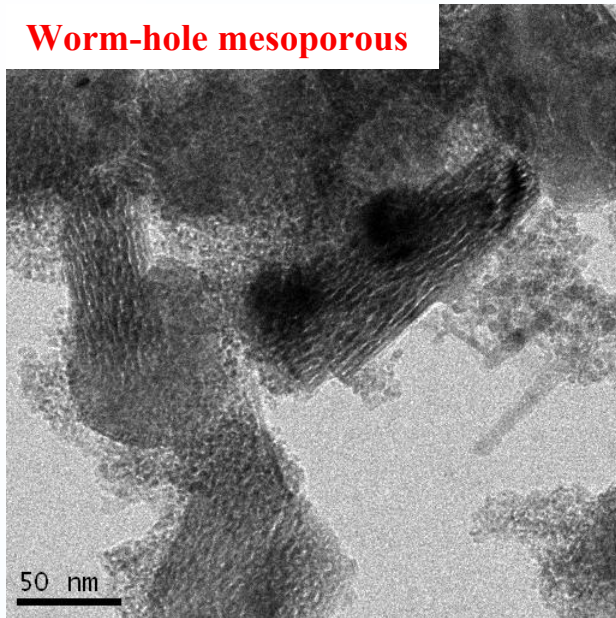
- Large variation in properties of nanorods.
- Performance is dependant on nanorod, size, shape and thickness
- Further studies are underway to understand the synthesis parameters on the performance of α -Fe₂O₃ nanorods

A. Kleiman

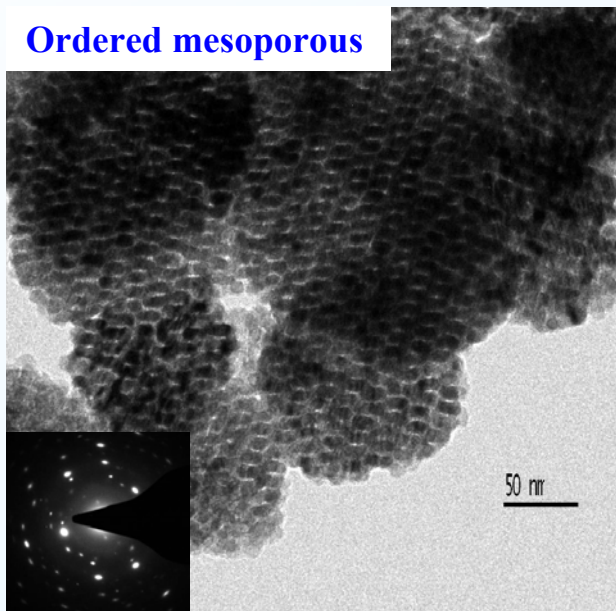
Technical Accomplishments/Progress/Results:

Task #3. Optimize the morphology of the PEC material system for maximum efficiency;
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Worm-hole mesoporous

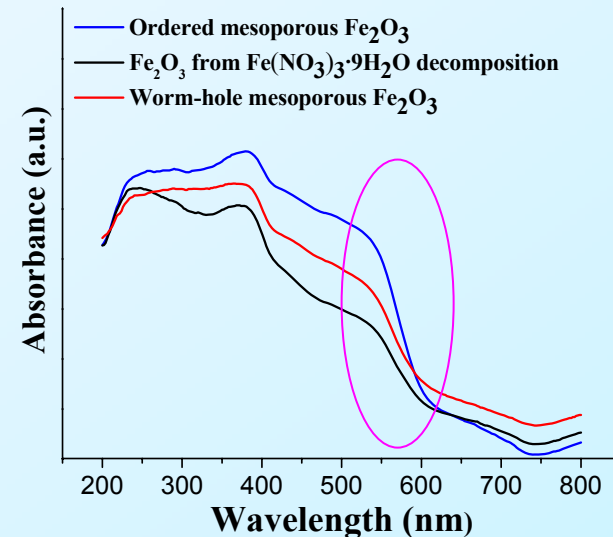
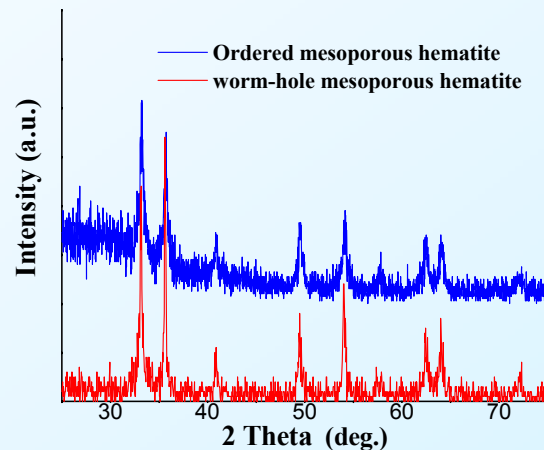


Ordered mesoporous



Mesoporous Hematite

- **High surface area: reduced overpotential for the same photon flux**
- **Short charge transport length**
- **Large internal fields: separation of holes and electrons**
- **High pore volume: capability of heterogeneous nanoparticles, e.g. Pt, Au NPs**
- **Both nanoparticles and mesoporous nanoparticles have high surface area and short transport length**

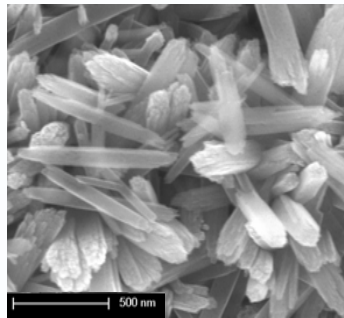


P. Zhang, A. Forman

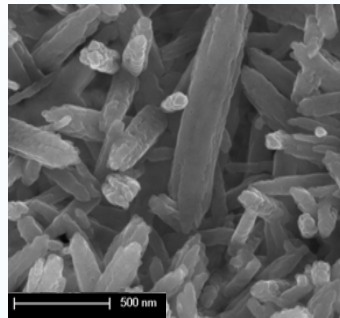
Technical Accomplishments/Progress/Results

Task #4. Explore processing and synthesis parameters to optimize the conductivity and minimize charge trapping and surface recombination of selected materials

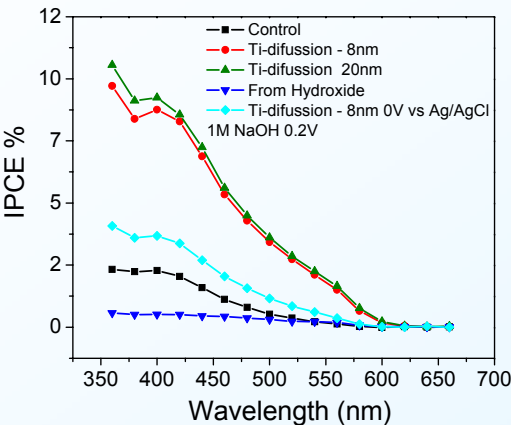
Surface Diffusion of Ti in NR's



Control



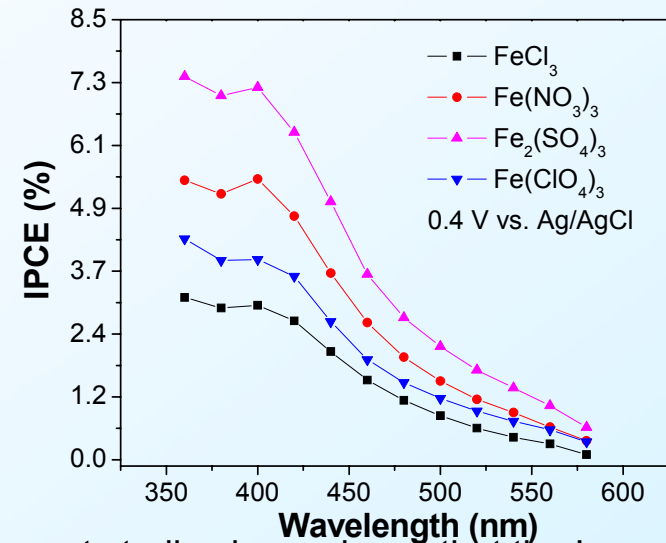
Ti-diffusion sample



- The thermal treatment conditions (Green vs. Red) are important for performance enhancement.
- Titanium diffusion has the ability of greatly improving the nanorod performance.

$$IPCE(\%) = \frac{\#electrons}{\#incident\ photons} = \frac{j_p(\lambda)}{I_0(\lambda)} * 100$$

Electrochemical Synthesis: Effect of Precursor

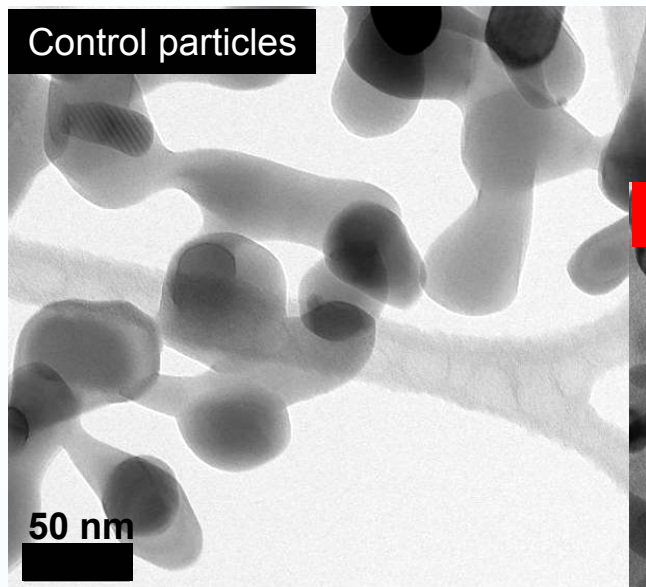


- Recent studies have shown that the Iron precursor used for electrochemical deposition has a great impact on the performance of the sample.
- Prior work with doping has been made with the FeCl₃ precursor and currently the effect of different precursors and the impact on structure and electronic properties are under investigation.

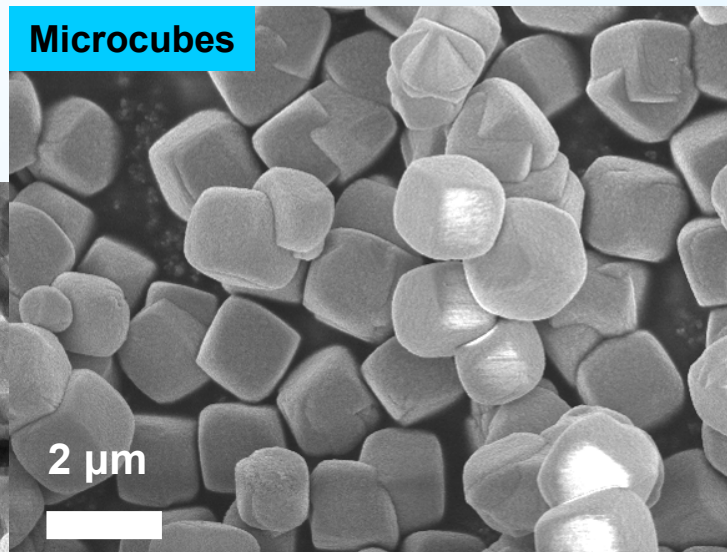
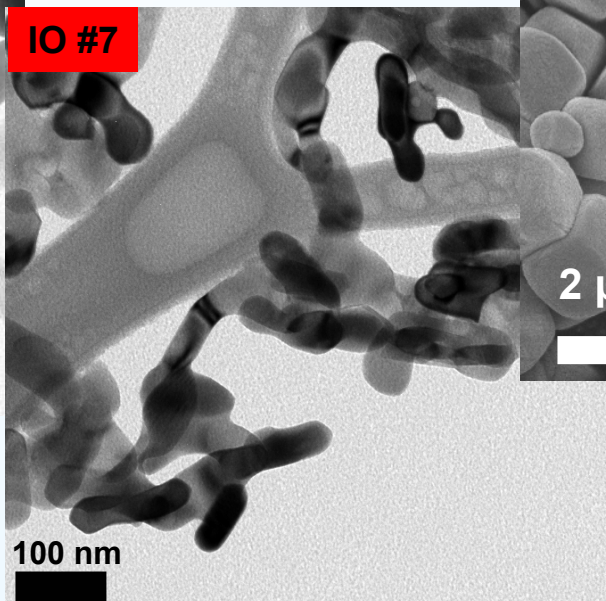
A. Kleiman
Y-S. Hu

Technical Accomplishments/Progress/Results:

Task #4. Explore processing and synthesis parameters to optimize the conductivity and minimize charge trapping and surface recombination of selected materials



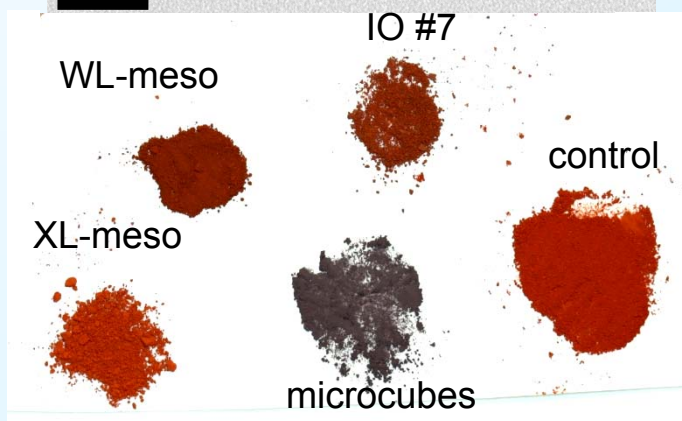
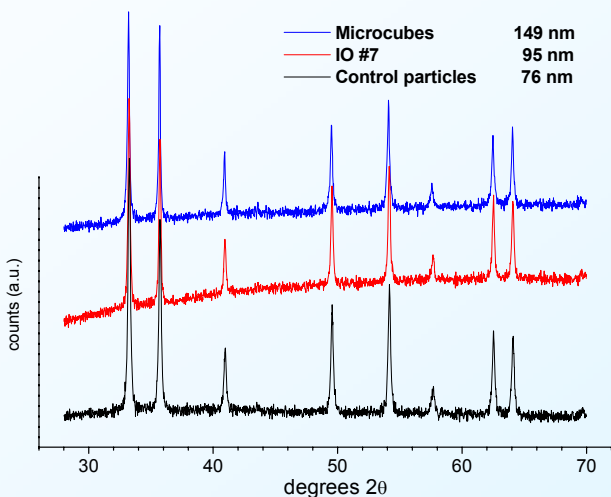
➤ **All hematite is not created equal!**



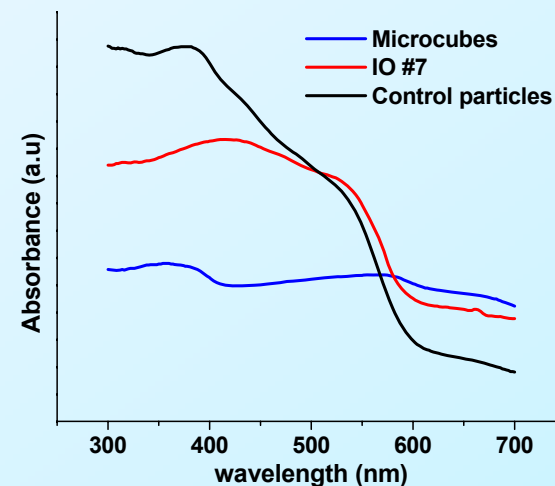
P. Zhang
A. Forman

XRD

— Microcubes 149 nm
— IO #7 95 nm
— Control particles 76 nm



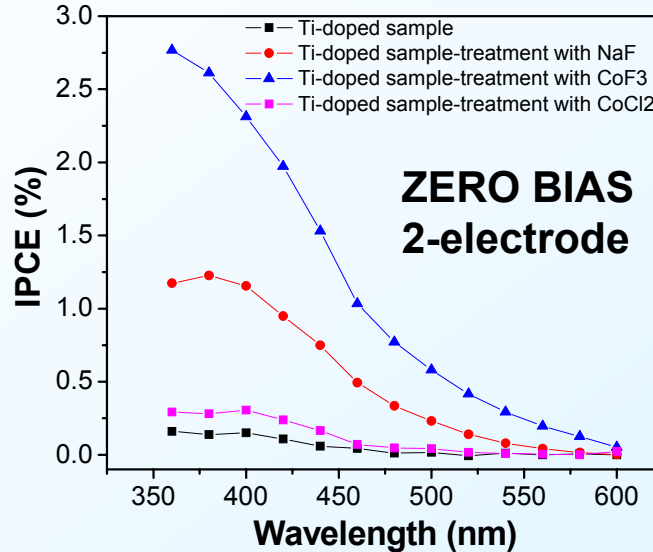
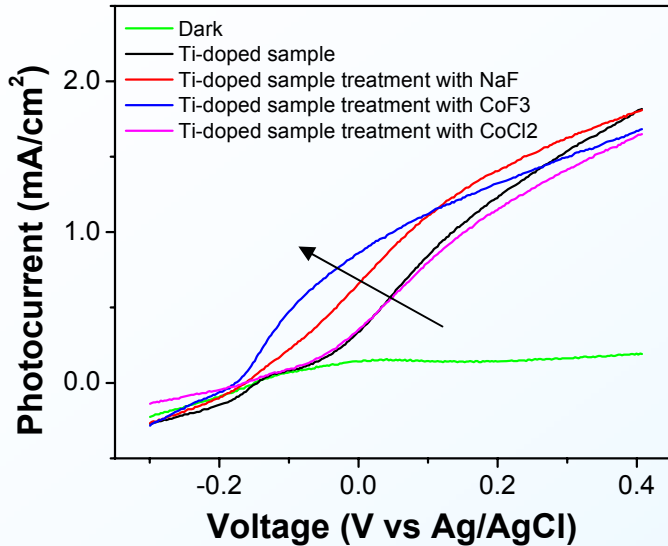
UV-Vis



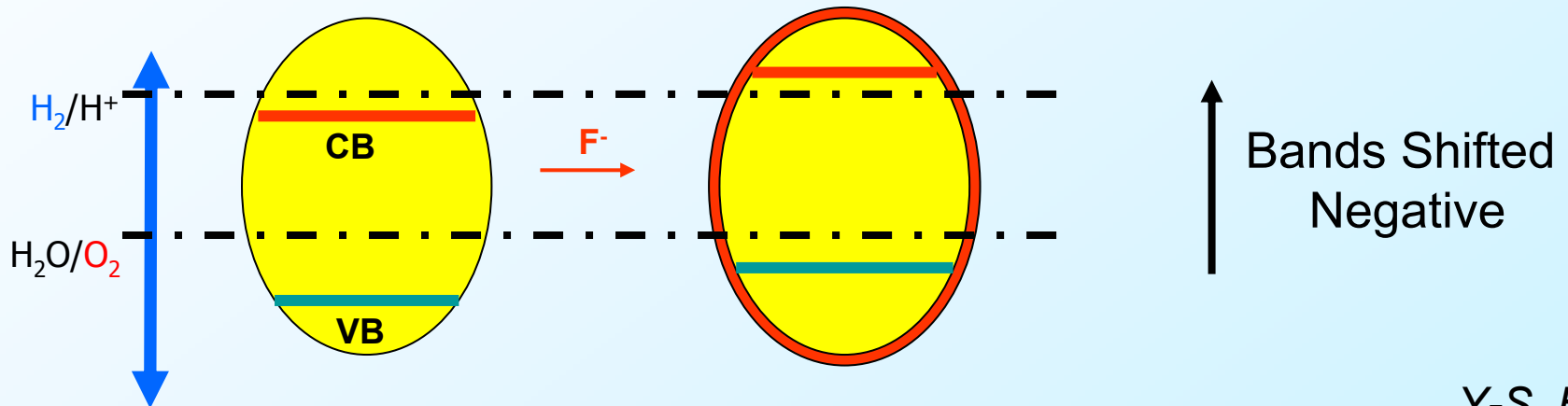
Technical Accomplishments/Progress/Results:

Task #4. Explore processing and synthesis parameters to optimize the conductivity and minimize charge trapping and surface recombination of selected materials

Electronegative surface species shifts conduction band electron energy relative to H_2/H^+ redox level



F^- , and not Co, is responsible for the change.

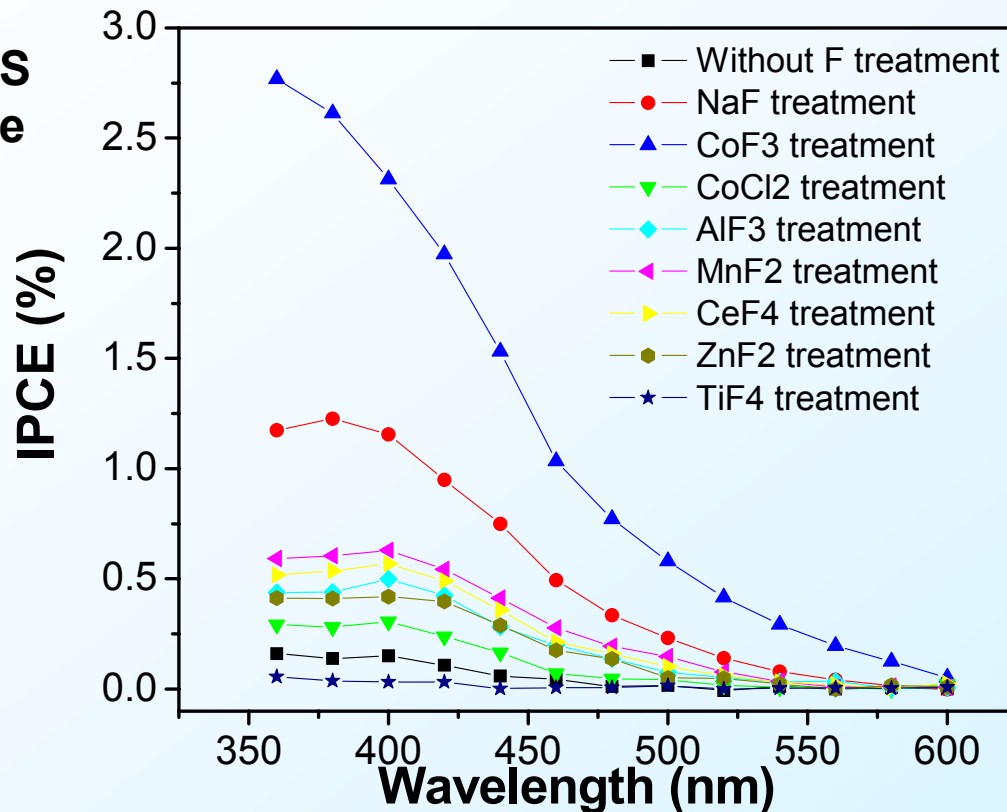


Technical Accomplishments/Progress/Results

Task #4. Explore processing and synthesis parameters to optimize the conductivity and minimize charge trapping and surface recombination of selected materials

Improved IPCE for water splitting with Zero Bias
in 1M NaOH on Ti doped Fe₂O₃ with F⁻ surface treatment

**ZERO BIAS
2-electrode**

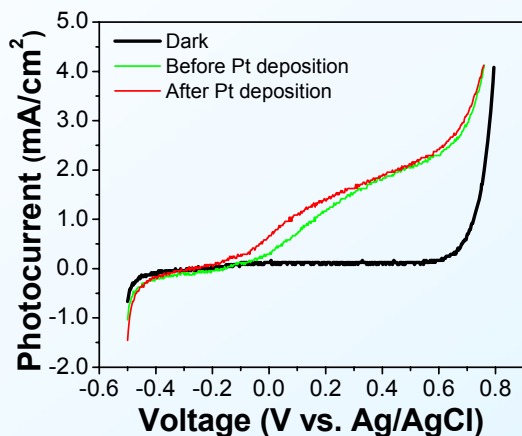
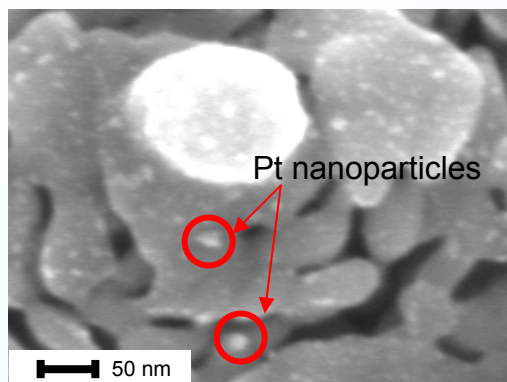


- Improve hematite conduction by doping with Ti
- Shift conduction band edge with electronegative surface preparation

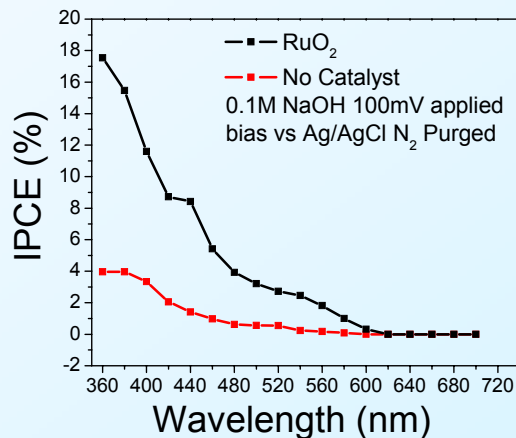
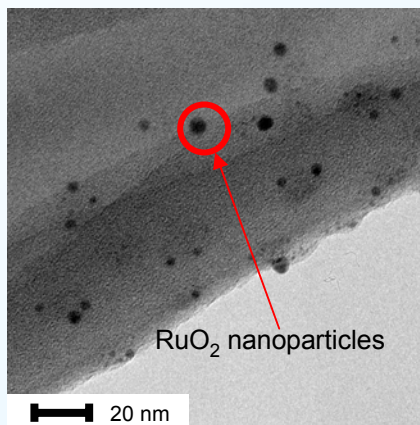
Technical Accomplishments/ Progress/Results:

Task #5. Identify and minimize electrokinetic limits by synthesis of appropriate electrocatalysts compatible with the host, electrolyte, and reactant/product properties.

Electrodeposition of Pt



Electrodeposition of RuO₂



- Improve OER limited electrokinetics by use of oxidation catalysts.
- High activity nanoparticles
- Deposition by electro/photo deposition
- Library exploration of specific materials underway.

A. Kleiman
Y-S. Hu
A. Forman

Technical Accomplishments/ Progress/Results

Task #6. Develop a complete, "photoelectrochemical unit", combining material absorption, charge transport, stability, and electrokinetic design features.

Identify suitable host absorber

Optimize synthesis conditions

Optimize morphology

Optimize electrokinetics

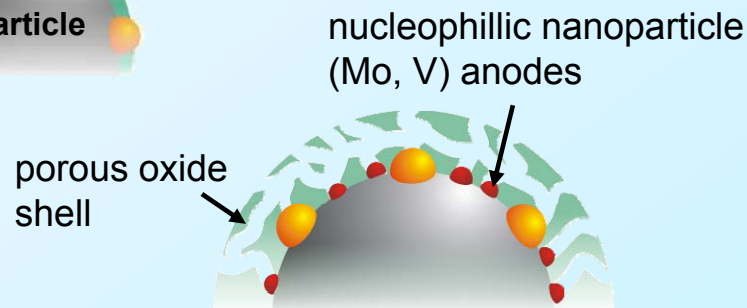
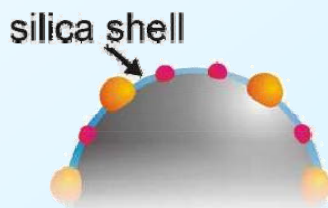
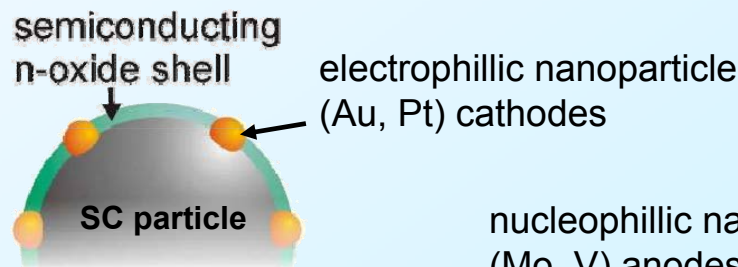
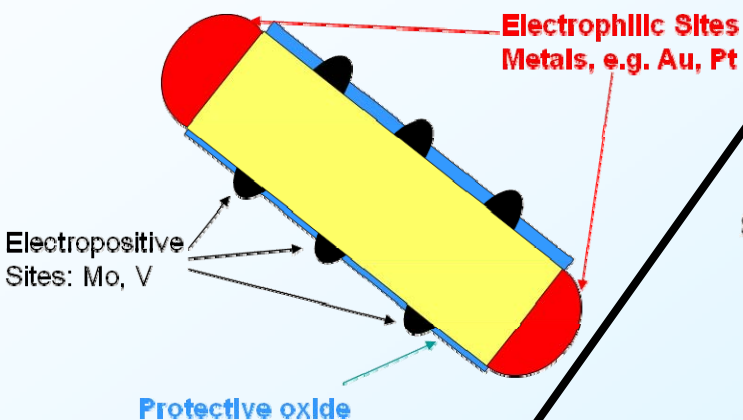
Stabilize structure

An Ideal
"PEC Unit"?

Encapsulant coatings

- Protect against corrosion
- Kinetic enhancement
- Stabilize co-catalyst particles
- Heterostructures
- etc...

Hybrid PEC "Nanoreactors"



A. Forman

Technical Accomplishments/ Progress/Results:

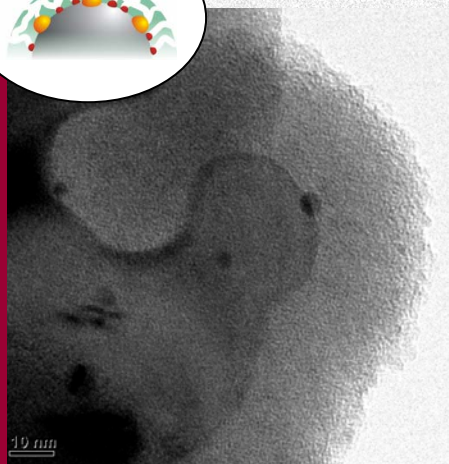
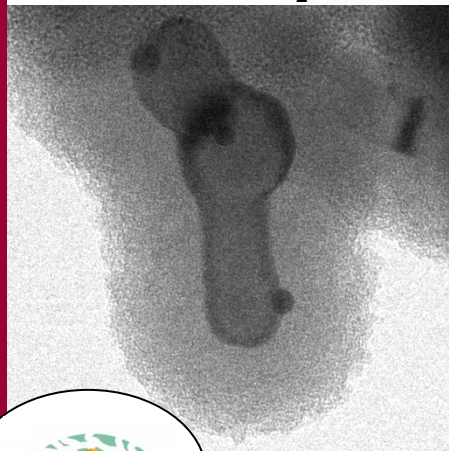
Task #6. Develop a complete, “photoelectrochemical unit”, combining material absorption, charge transport, stability, and electrokinetic design features.

Hybrid PEC “Nanoreactors” - semiconductor/metal/oxide heterostructures

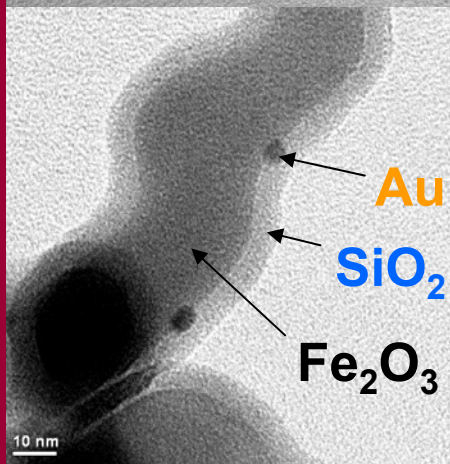
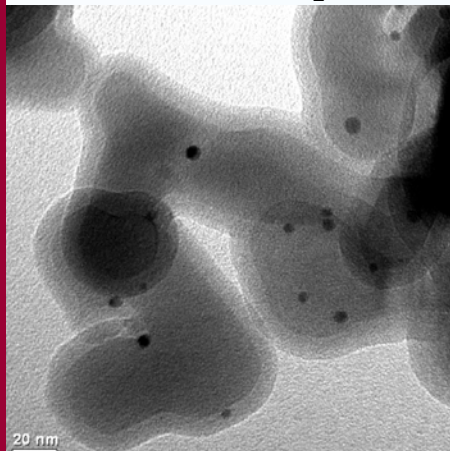
Low cost, scalable, solution phase synthesis of: **co-catalyst/SC@encapsulant**

Au/ α -Fe₂O₃@SiO₂

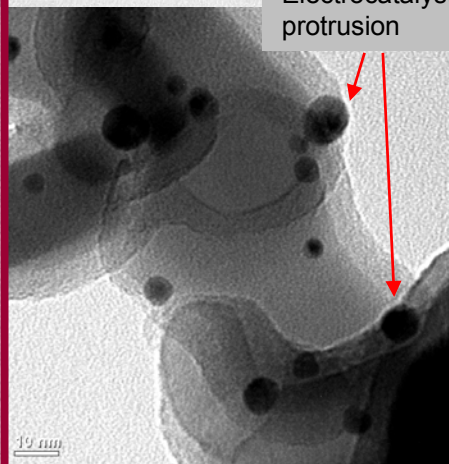
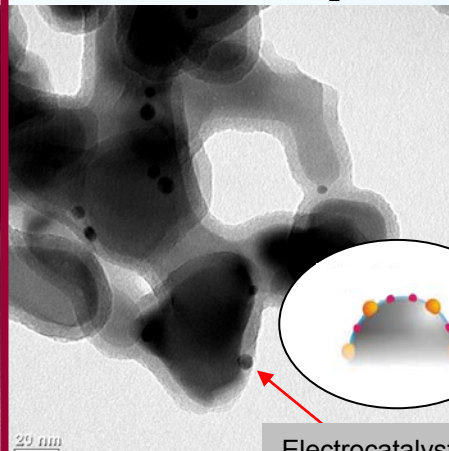
30 nm SiO₂



10 nm SiO₂



6 nm SiO₂



Broadly applicable synthesis route

Co-catalyst

- Pt, Au, Ag, Pd, etc.
- Virtually any nanoparticle

Support

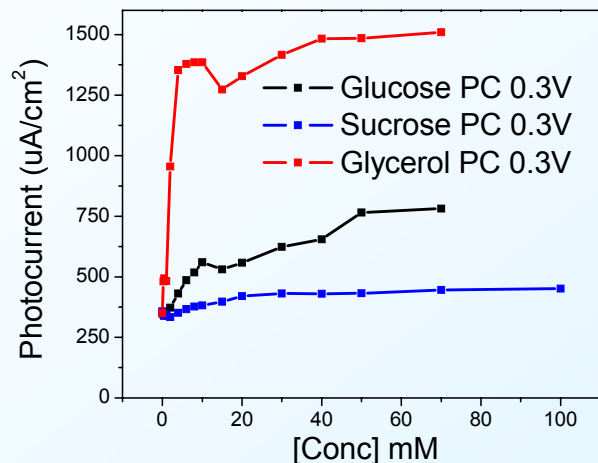
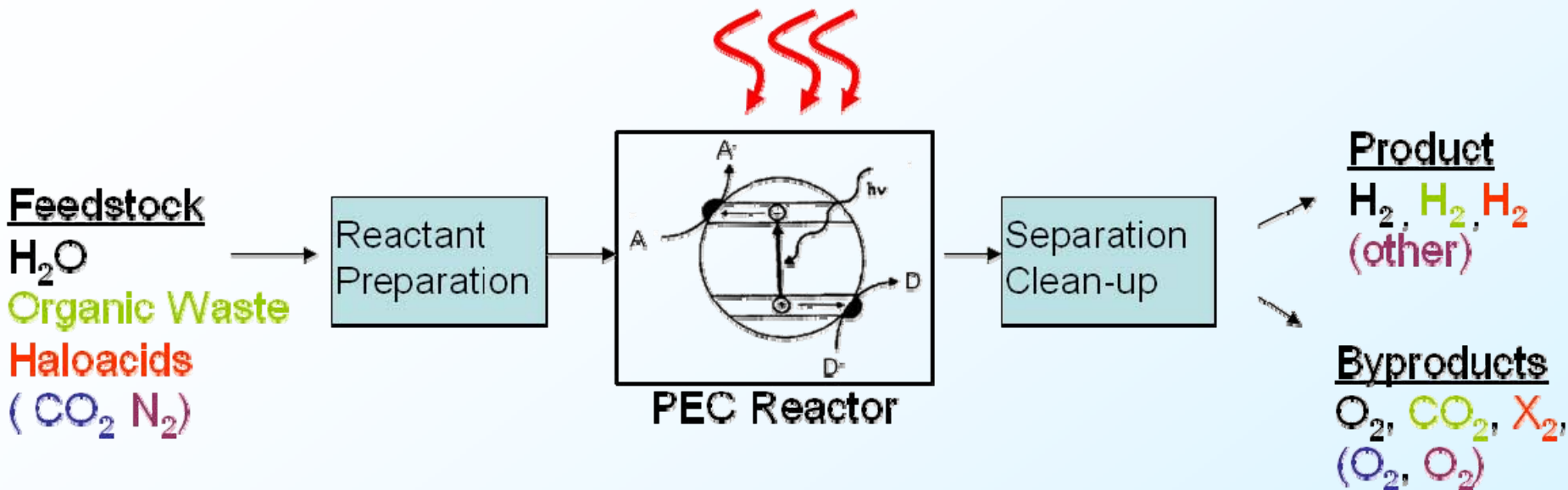
- Fe₂O₃, TiO₂, ZnO, SiO₂, Al₂O₃, CeO₂
- Any metal oxide

Encapsulant

- SiO₂, ZrO₂, TiO₂, Al₂O₃

Technical Accomplishments/ Progress/Results:

Tasks #7, #8, and #9: Evaluate conceptual model reactor systems, theoretical and practical economic potential of alternative redox reactions, estimate hydrogen production costs.



$$\text{Efficiency}(\%) = \frac{j_p(1.23 - E_{app})}{\text{incident energy}} * 100$$

| Best Overall Energy Efficiency | | |
|--------------------------------|---------|---------|
| | 100 mV* | 500 mV* |
| NaOH | 0.3% | 1.4% |
| NaOH+ Glucose | 0.4 | 2.8% |

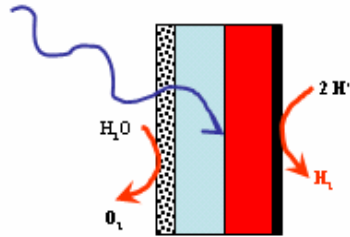
Undoped hematite

*2 electrode bias voltage

Technical Accomplishments/ Progress/Results:

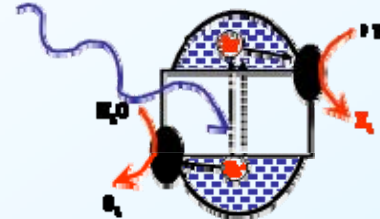
Tasks #7, #8, and #9: Evaluate conceptual model reactor systems, theoretical and practical economic potential of alternative redox reactions, estimate hydrogen production costs.

Structural Photoelectrode Reactors



- Requires high absorbance material to minimize thickness.
- Direct gap materials
- Requires solid electrical continuity.
- Fabrication methods limited.
- No large scale similar processes ever built.
- Separates H₂/O₂
- Entire system must be replaced after corrosion.
- Known Economics: Electrodes could always be metalized to make electricity as a PV – why bother, e- are more valuable than H₂. Costs known ~ \$5/W
- Requires a membrane and extremely clean water.

Slurry Reactors with Bulk Particulates



- Absorbance not critical, depth of unit scales linearly.
- Nanoparticulates allow both direct and indirect gap materials.
- Maximal surface/volume → lowest current density and overpotential.
- Requires no direct electrical contact to the photoreceptor.
- Large number of synthetic possibilities.
- Large scale slurry phase photoreactors have been built.
- May require separation of H₂/oxidation products
- May replace corroding particulates without disassembly.

Project Summary

- **A systematic methodology for improving PEC performance has been demonstrated:**
 - Improving conductivity by high throughput exploration of dopants.
 - Optimization of synthesis route and morphology.
 - Shifting relative positions of bands relative to hydrogen redox level.
 - Highest, zero-bias, water splitting photocurrent for Fe_2O_3 demonstrated, IPCE ~2% at 425nm.
- **General synthetic methodologies have been developed to produce ultrahigh surface area nanostructured PEC materials in bulk quantities to minimize carrier path lengths.**
 - Need to balance surface area and path length, recombination and separation.
- **Methods and processes generally applicable to any PEC host, however, at present, of the oxides, Fe_2O_3 , shows a promise as a cost effective single gap PEC material.**
 - Hematite performance to date, not high enough, however, we believe there is significant room for improvement.
 - Must demonstrate, IQE of individual PEC unit >90%. In progress.
 - Further work on New Hosts in progress.
- **Established New 2008 Technology Transfer/Collaborations:**
 - NREL Theory Group (Y.Yan, M.Huda, A.Walsh, M.Al-Jassim)
 - Physical Optics Corporation
 - Materials Modification, Inc.

Future Work



DOE Hydrogen Program

- **Tasks #1 and #2:** *New materials still needed – HT-synthesis of other hosts (sulfides, Cu based mixed oxides). Continued optimization of hematite: theory guided, multi-atom (cation) substitutions of $\alpha\text{-Fe}_2\text{O}_3$.*
- **Task #3.** *Detailed characterization of nanostructured PEC materials; i) direct measurement of IQE, ii) carrier lifetimes (femtosecond spectroscopy). Improve carrier separation by heterostructure fabrication. Fabricate mesostructures from materials identified in Tasks 1+2.*
- **Task #4.** *Broad exploration of post-processing modification for band-position tuning. Combine with task 3 to identify factors maximizing lifetime. Surface passivation and surface state quenching with selective, ultra-thin silica coatings; ultra-thin surface coating with additional oxides (e.g. TiO_2 , ZrO_2 , MnO_2).*
- **Task #5.** *High throughput synthesis of appropriate electrocatalysts on planar Fe_2O_3 substrates compatible with electrolyte, and reactant/product properties.*
- **Task #6.** *Develop a complete, “photoelectrochemical unit”, combining material absorption, charge transport, stability, and electrokinetic design features.*
- **Tasks #7, #8, and #9:** *Construct conceptual model reactor systems for the theoretical and practical economic evaluation of photoelectrode vs. slurry-colloidal reactor systems and the potential of alternative redox reactions, estimate hydrogen production costs in each.*