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

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Project ID #
PDP_01_McFarland

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Overview

Timeline

- Start date September 1, 2004
- End date May 31, 2010
- 90% Complete

Barriers

Technical Barriers Addressed

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

Budget

- Total project funding
  - DOE share $ 894k
  - Contractor share $ 223k
- Funding for FY08 $498k
- Funding for FY09 $0

Technical Targets

2013 DOE PEC

- Solar-to-Hydrogen Conversion Efficiency >8%
  - Bandgap ~ 1.7-2.2 eV
- Lifetime > 1000 hours

UCSB

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

Relevance

There are no known material systems that are sufficiently efficient, inexpensive, and massively scalable that might realistically be used for the large scale, cost-effective production of hydrogen, or any chemical fuel, from sunlight.

Objectives and Tasks for Total Project

- ***Task #1. With a focus on abundant and non-toxic elements, develop improved materials for solar photon absorption using high throughput methods and new syntheses.***
- ***Task #2. Utilize high-throughput screening to identify candidate materials with a threshold efficiency and stability that , with optimization, might meet the DOE performance and stability targets.***
- ***Task #3. Explore the effects of morphology on the PEC material system efficiency making use of nanostructures to minimize charge carrier path lengths and maximize reactive surface area.***
- ***Task #4. Explore processing and synthesis parameters to optimize efficiency through increased conductivity and minimized 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.***

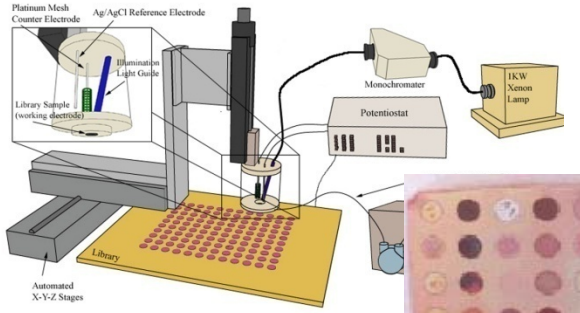
Approach/Selection Criteria

New Candidate Material Discovery: High Throughput Synthesis and Screening

No

Absorption Edge < 2.2 eV ?

Yes

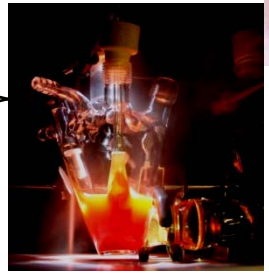


Synthesis of Optimal Compositions and Structures

No

Solar Photon-electron Current Conversion Efficiency > 10%

Yes

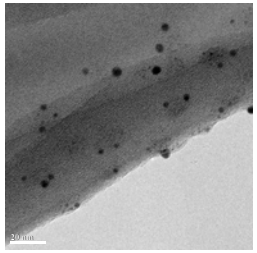


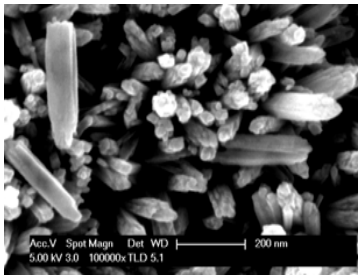
Processing, Surface, Electrolyte, and Electrokinetic Optimization

No

Solar/Hydrogen Efficiency > 8% @ 10000 hours

Yes





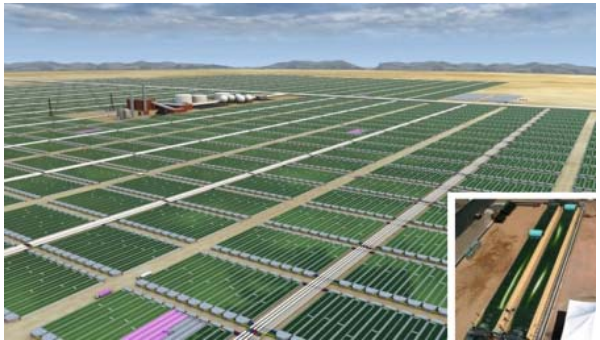
Optimized Large Scale Reactor System Techno-economics

No

Hydrogen Cost Estimate < $5/Kg

Yes

Success!



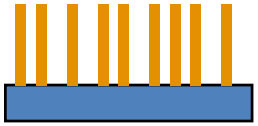
Material-Class Synopsis
Iron Oxide

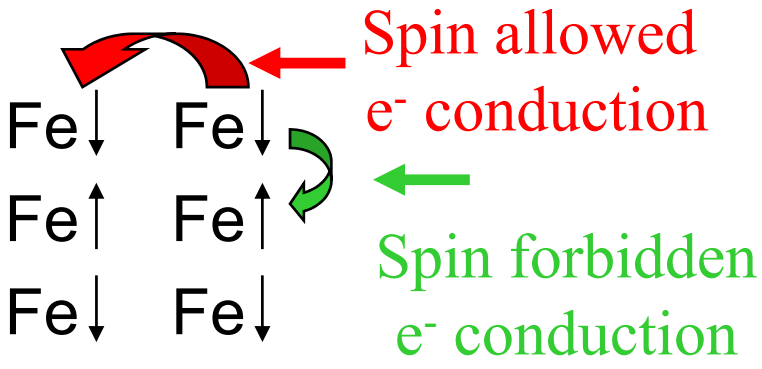
promise

- Bandgap ~ 2 eV (40% solar light absorption).
- Abundant and inexpensive
- High Stability in Electrolytes (pH>3)

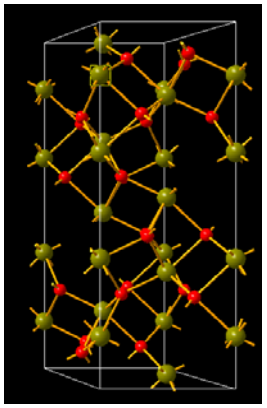
challenges

- Carrier Transport
- Valence Band Edge
- Water Oxidation Kinetics
- Low optical absorption





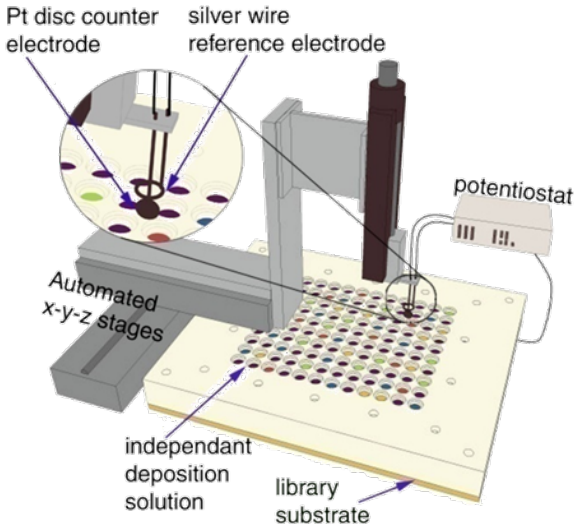
Conduction within (001) planes is 4 order of magnitude higher than parallel to [001].



Technical Accomplishments and Progress

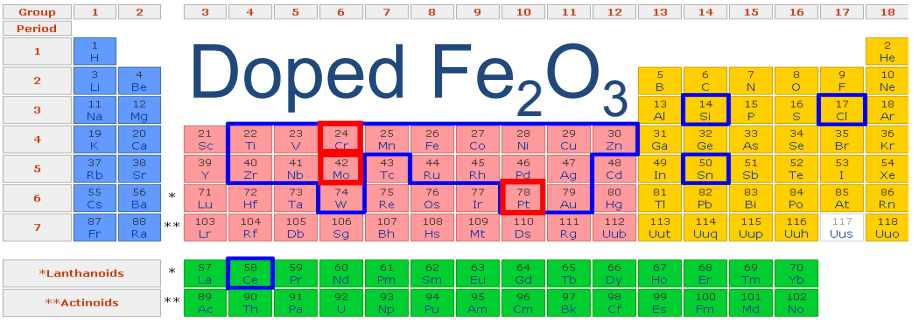
New materials.

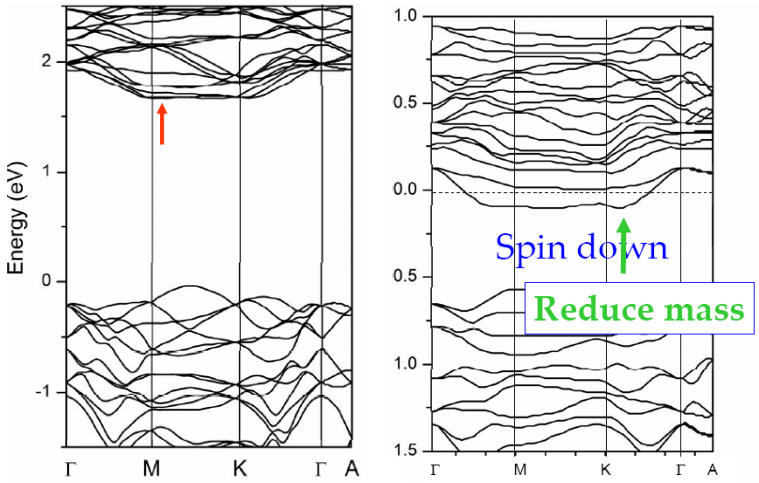
- Theory Guided Synthesis of Doped and Mixed Oxides.
- Comparison of high-throughput syntheses and screening directly with theory provides basis for additional syntheses (proposed Al and mixed donor/acceptors).



FY2007-2008 work

- 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





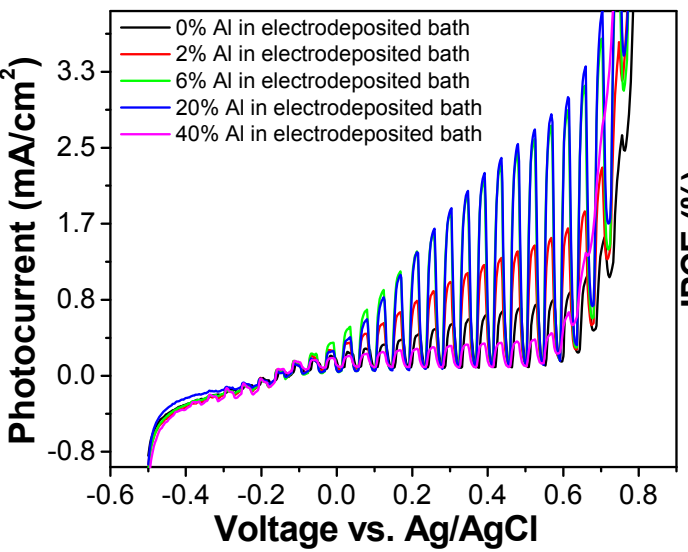
Pure Pt doped iron oxide

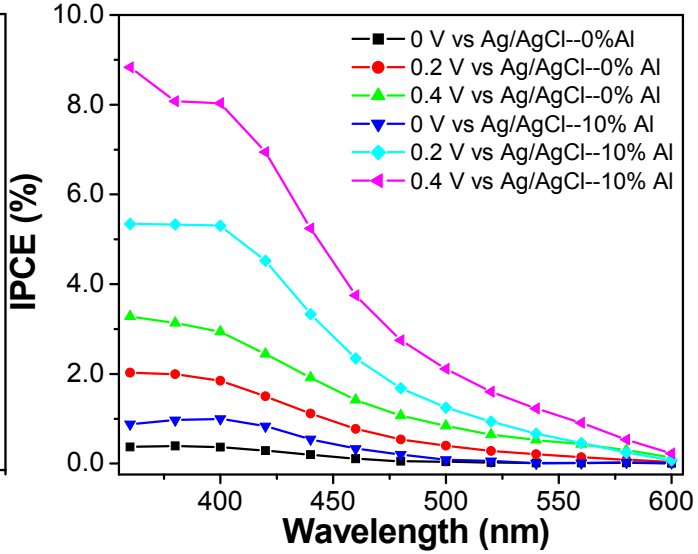
DFT calculations performed by Y. Yan et. al. through NREL collaboration initiated in 2008

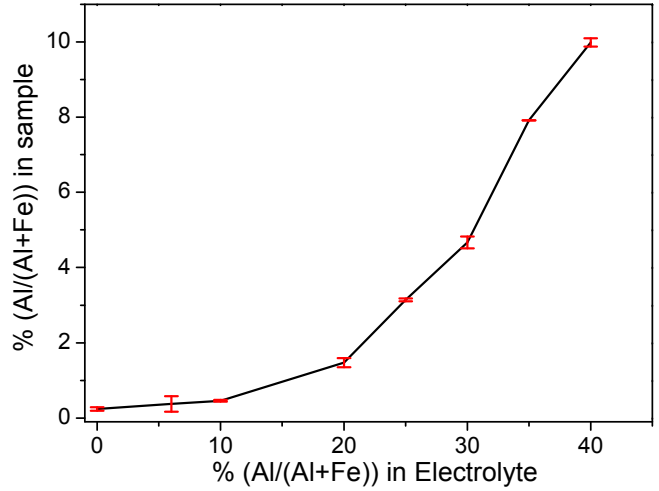
Technical Accomplishments and Progress

New materials.

Variable Concentrations of Al Doped α-Fe_2O_3





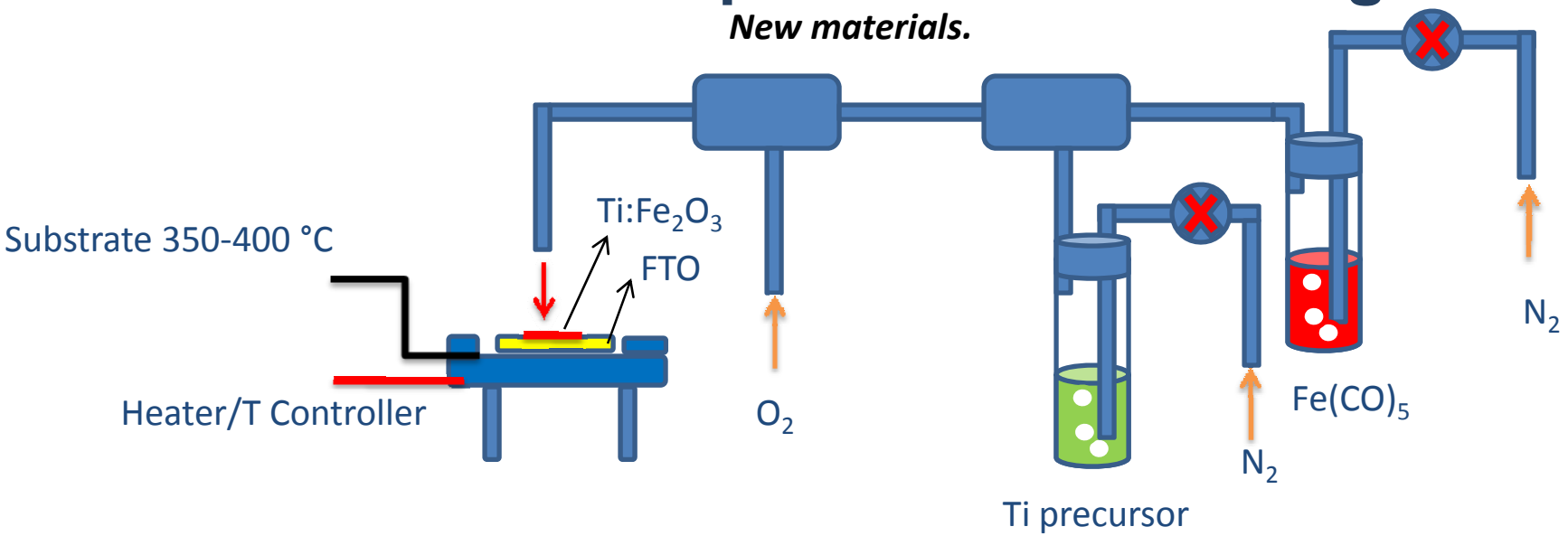


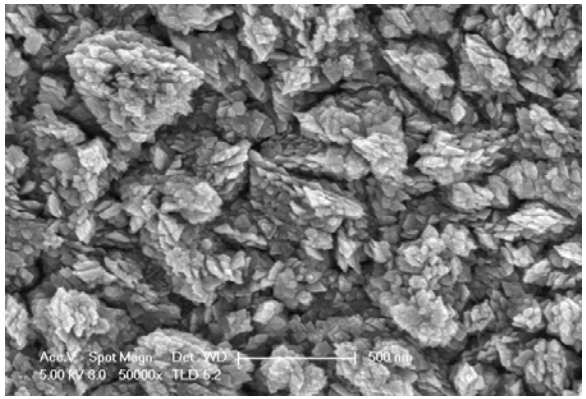
- Best performance obtained ~0.3 -0.5% Al doping
- Higher % Al → phase segregation to the surface

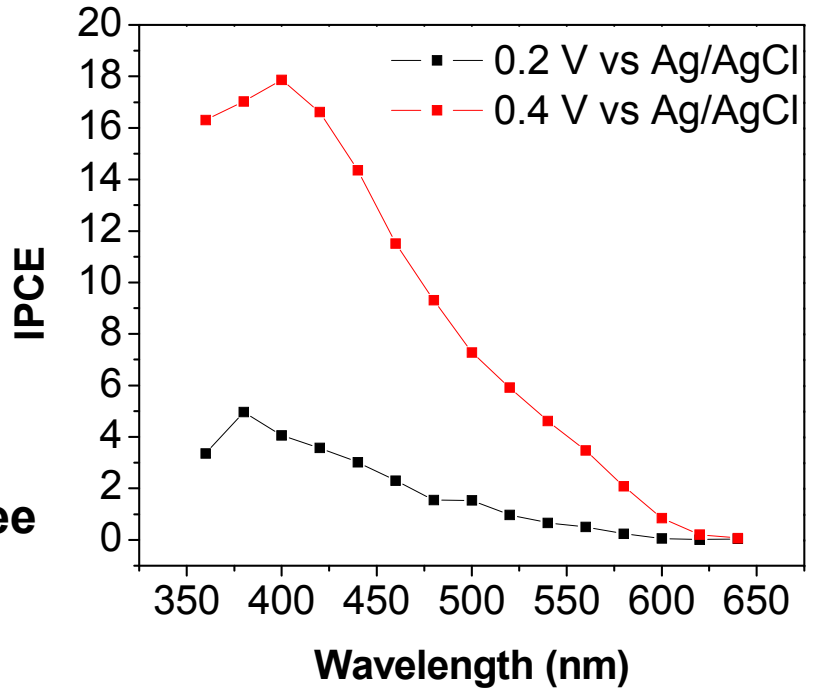
- Iso- valent doping improvement due to lattice contraction ***(predicted by NREL collaborators)***

Technical Accomplishments and Progress

New materials.



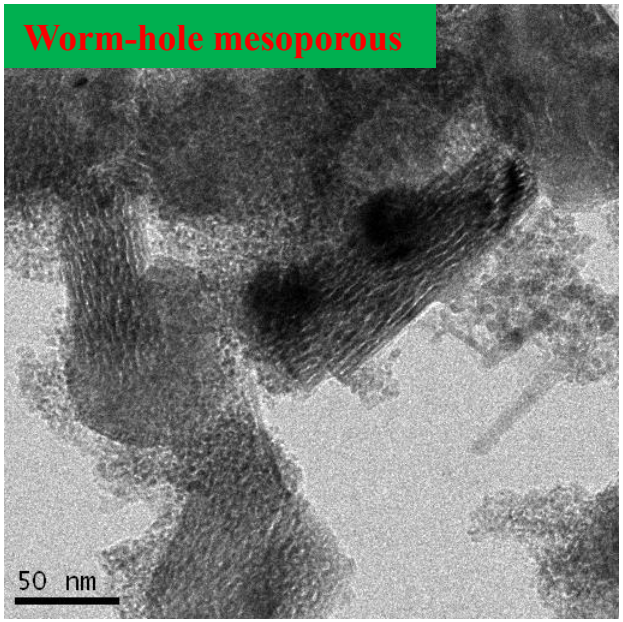


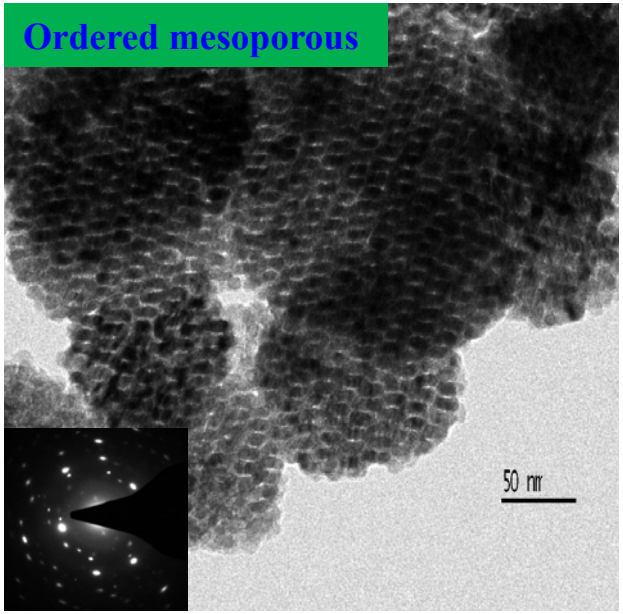


Electrochemical synthesis of Ti:Fe_2O_3 films were disappointing, new water-free synthesis route developed, 3x improvement in IPCE.

Technical Accomplishments and Progress

New Morphologies





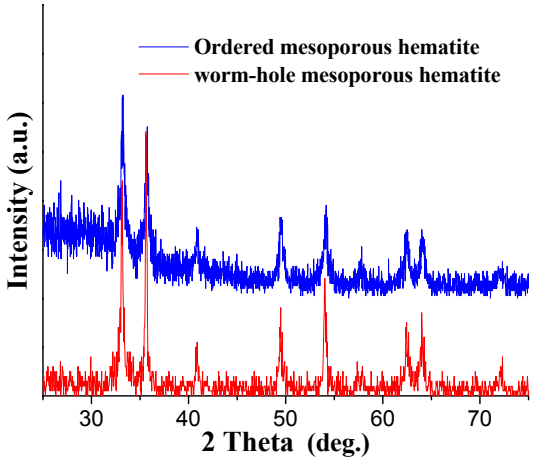
Mesoporous Hematite

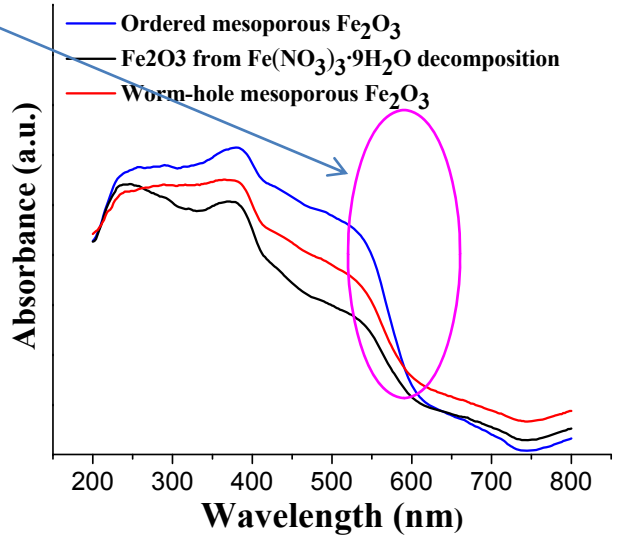
Generalized syntheses developed for high surface area PEC materials: reduced overpotential for the same photon flux;

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

Indirect → direct bandgap transition due to wall effects





Technical Accomplishments and Progress

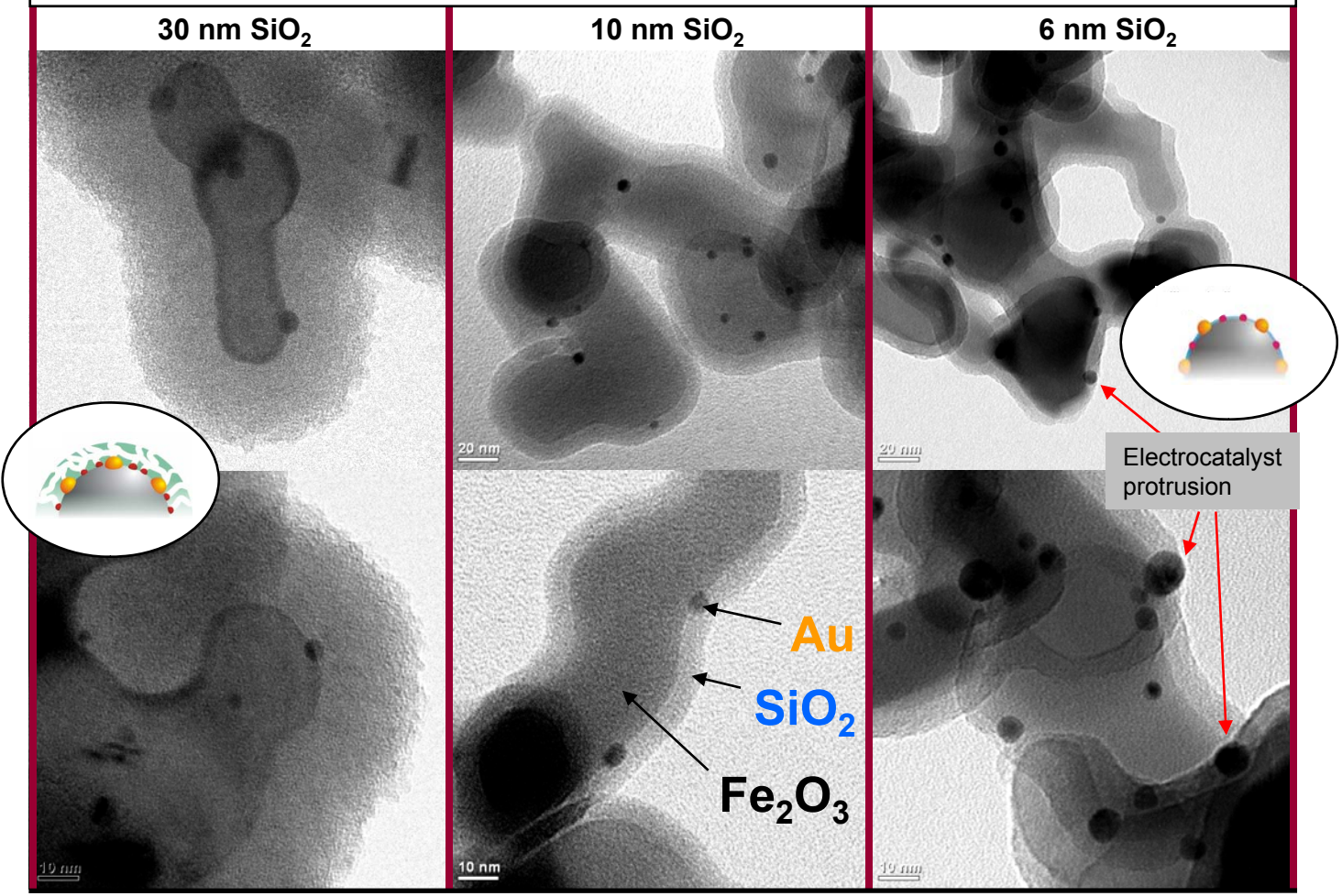
Complete *PEC "Systems"*

Hybrid PEC "Nanoreactors" - semiconductor/metal/oxide heterostructures

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

Au/α-Fe_2O_3@SiO_2

FY2007-2008 work



Broadly applicable synthesis route

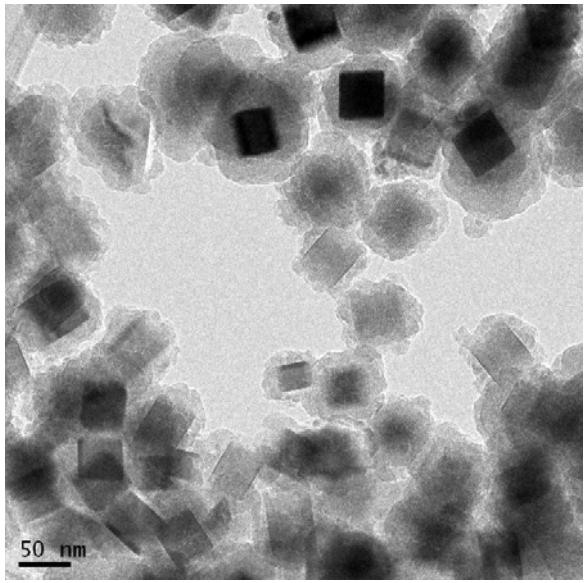
Co-catalyst
- Pt, Au, Ag, Pd, etc.
- Virtually any nanoparticle

Support
- Fe_2O_3, TiO_2, ZnO, SiO_2, Al_2O_3, CeO_2
- Any metal oxide

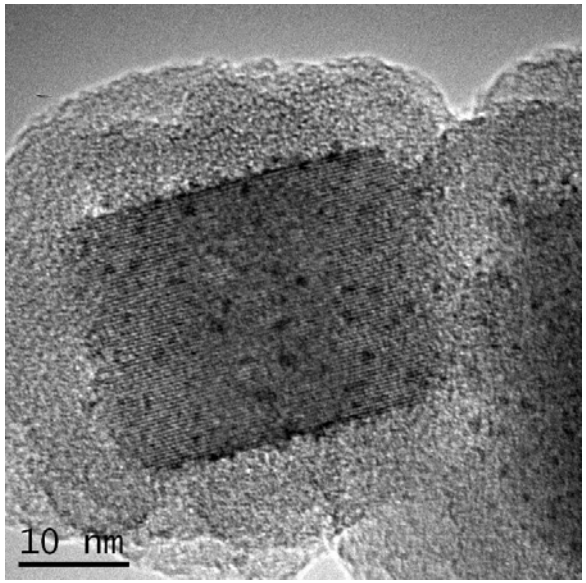
Encapsulant
- SiO_2, ZrO_2, TiO_2, Al_2O_3

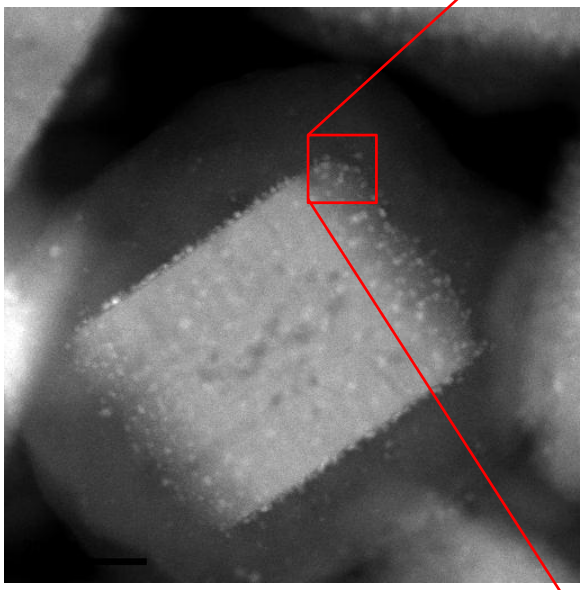
Technical Accomplishments and Progress

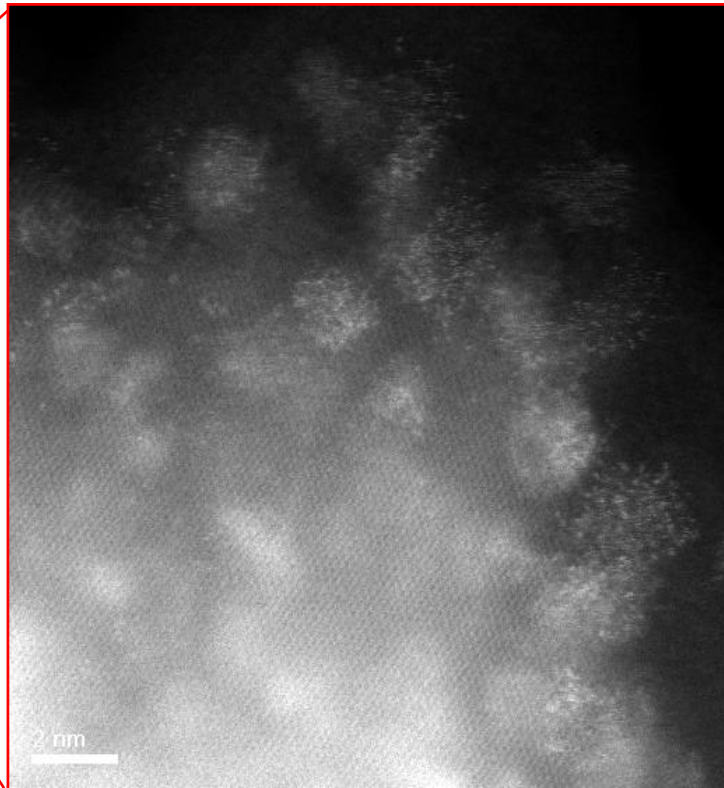
New Morphologies



- Hematite nanocubes synthesized
- Pt nanoparticle electrocatalysts deposited by photoreduction.
- SiO_2 encapsulated for stability.
- Hydrogen production efficiency under evaluation.

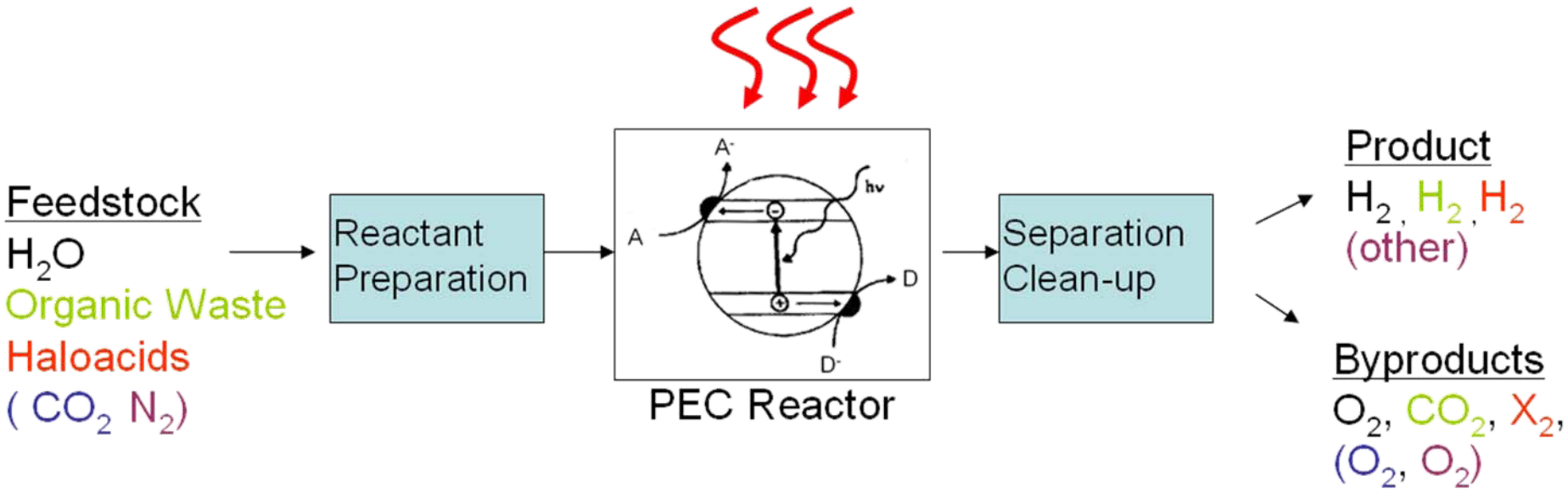


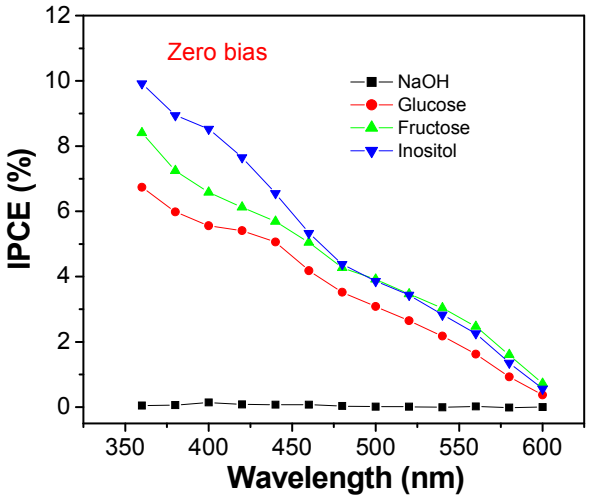


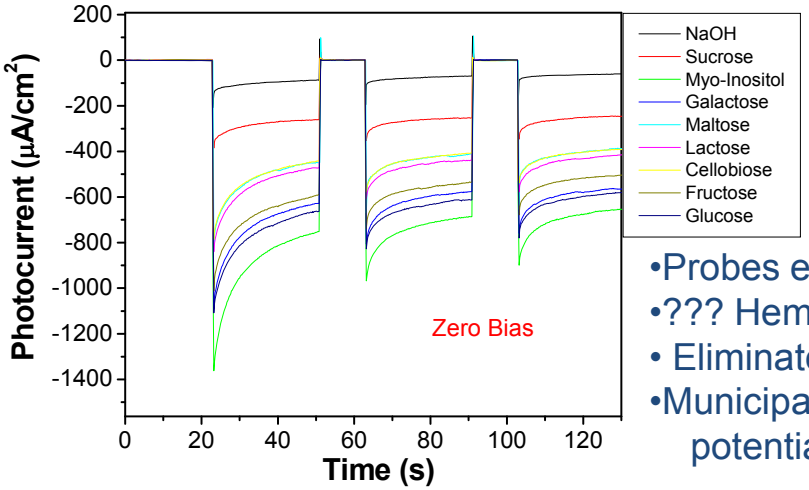


Technical Accomplishments and Progress

Improved Electro-kinetics: Alternative Oxidants



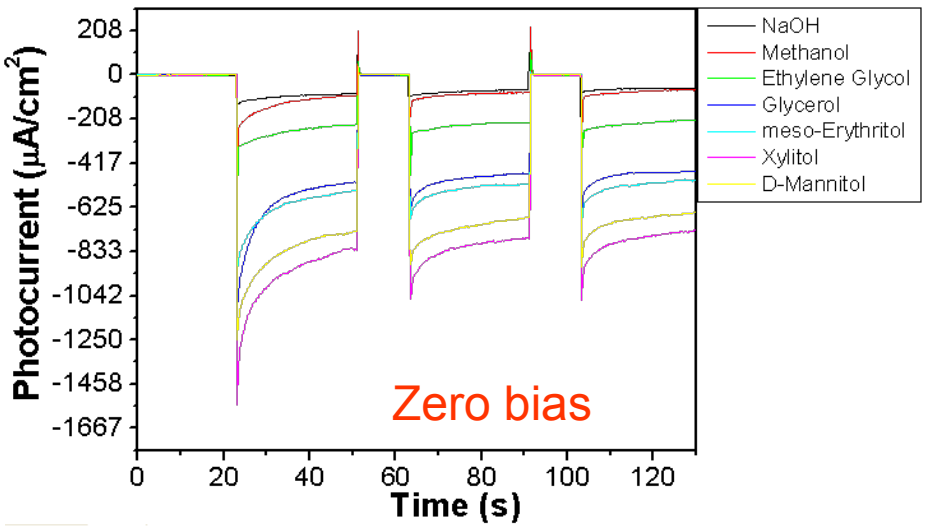


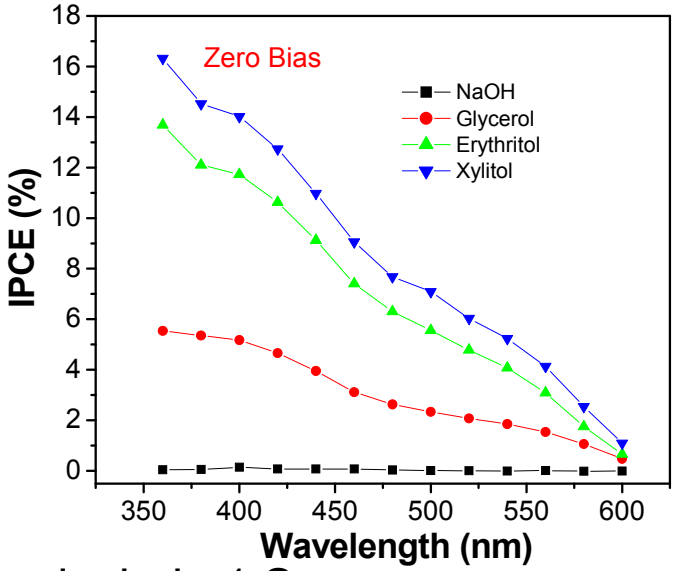


- Probes efficiency in absence of ORR
- ??? Hematite below HER
- Eliminates large ORR overpotential.
- Municipal wastewater and biomass potential feedstocks

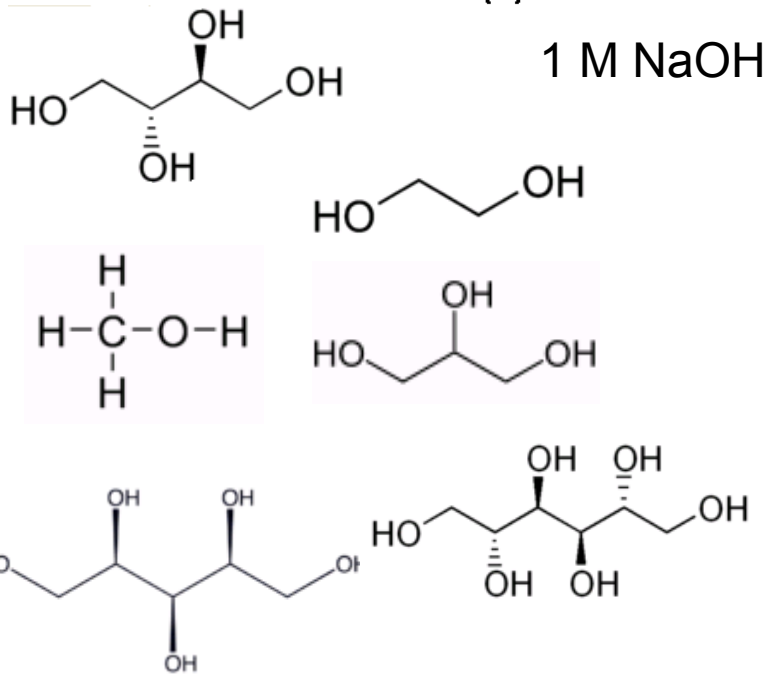
Technical Accomplishments and Progress

Improved Electro-kinetics: Alternative Oxidants on Ti doped Fe_2O_3





1 M NaOH + 0.02 M Poly alcohol 1 Sun



- Poly-alcohols showed an increased performance as compared to methanol
- Increased IPCE ~ 17 % was achieved with Xylitol
- Increased in performance could be obtained if better OER catalyst could be found
- H_2 production and byproducts of redox reaction to be studied

Material-Class Synopsis
Cu Delafossites

promise

- 3B group have direct band gap.
- Effective masses are small, so conduction should be better.
- Alloying group 3A and 3B could be used to reduce the band gap
- Many possible substitutions for the R group in $CuRO_2$

➢ Possibly abundant and inexpensive

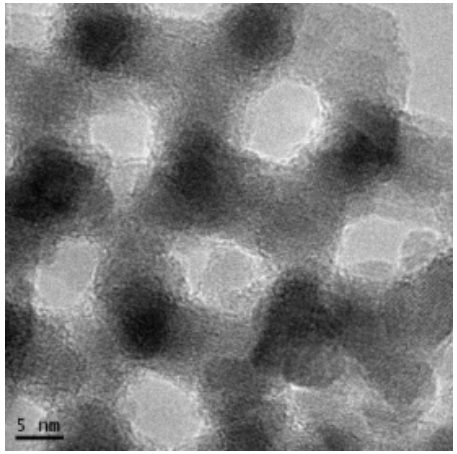
challenges

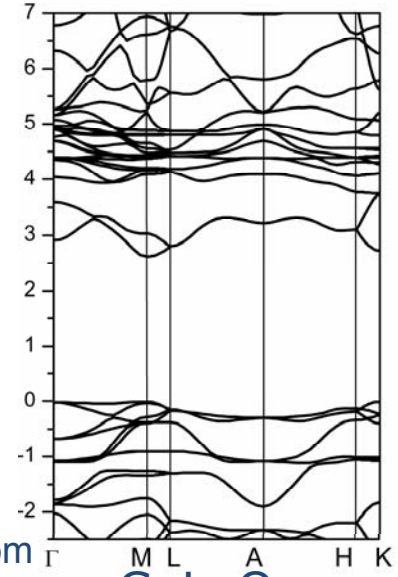
➢ Stability under illumination

➢ High recombination rates

➢ Valence and conduction Band position

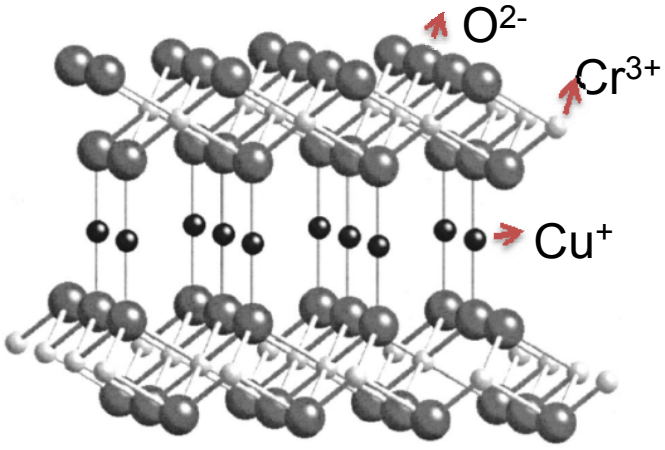
➢ Water Oxidation Kinetics





Inspired by DFT results from NREL, M. Huda et al

$CuLaO_2$



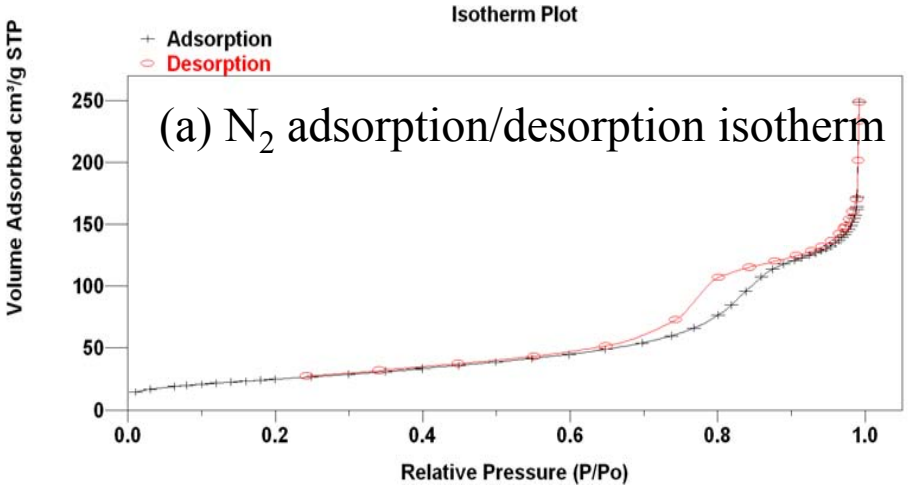
Technology & Barriers:

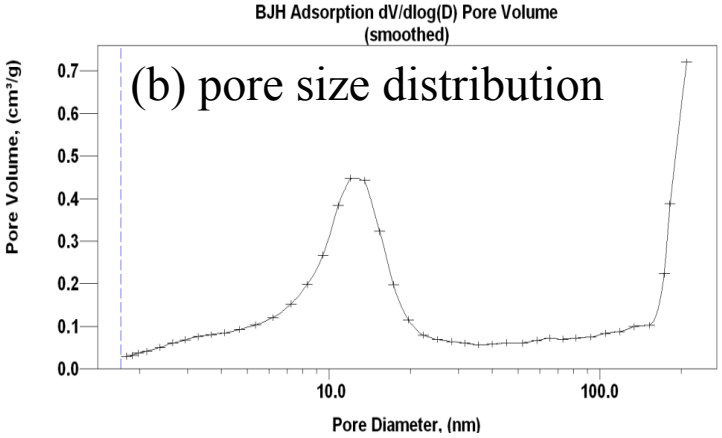
Barrier	Challenges	Strengths
Y. Materials Efficiency	Due to the instability of Cu+ under ambient conditions, photogenerated holes are easily trapped by the Cu+ , which leads to the decomposition of the structure and decrease of the e^-/h^+ transport efficiency.	A narrow bandgap (~1.3 eV) makes the delafossite absorb most of visible light. Doping of divalent ions, e.g. Mg^{2+}, will significantly further increase the electron conductivity.
Z. Materials Durability	Stability of $CuCrO_2$ (bulk and mesoporous) under illumination in strong base solution suffers from its decomposition into spinel $CuCr_2O_4$ and dissolution of copper ions into solution.	The doping with Mg^{2+} significantly increase the electron conductivity in the crystals by a factor of ~1000 upon a doping of 5%. The Mg^{2+} doped mesoporous $CuCrO_2$ has been shown to be stable under a long time illumination (159 hours) from the results of TEM and XPS.
AA. PEC Device and System Auxiliary Material.	Synthesis of mesoporous delafossite structure has some limitation in extending to other materials beside $CuCrO_2$ due to the reaction of metal ions with silica template at high temperature. Further research into less expensive nanoparticles, applicable to other delafossite structures, is also a major key issue.	The silica template applied in the synthesis produced mesoporous nanoparticles with a high surface area , thin wall thickness, and reltively good crystallization. The nanocasting method can be applied in the synthesis of CuLaO2, CuGaO2, CuFeO2, and their sulfide and selenides.
AB. Bulk Materials Synthesis	The obtained material powder is rough and difficult to be redispered in the electrolyte.	Materials are inexpensive and easy to synthesize.

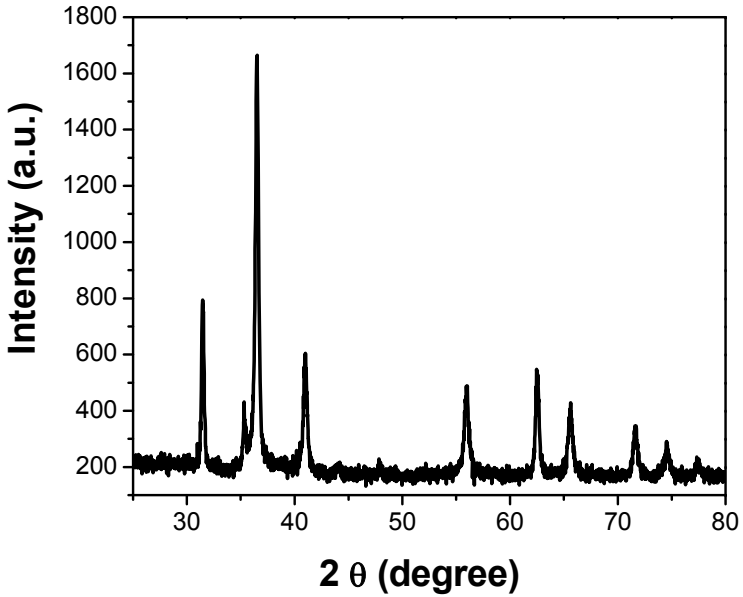
Technical Accomplishments and Progress

New materials.

Mesoporous $CuCrO_2$ delafossite structures, SA=90 m^2/g





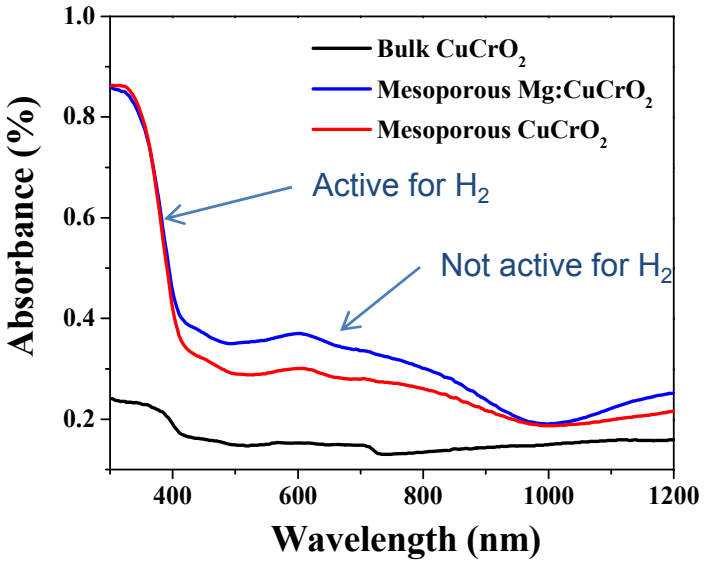


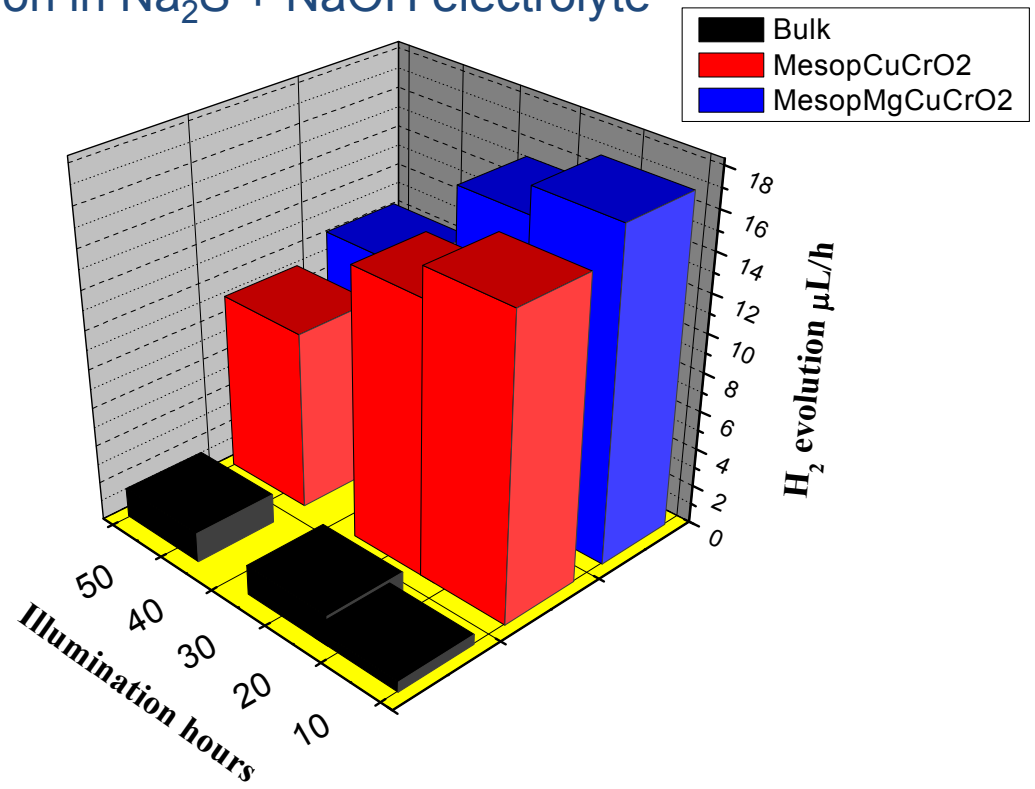
- ***Hydrogen production demonstrated under visible illumination in powders, quantification in progress.***
- ***High conductivity, Doping with Mg^{2+} increases conductivity by a factor of 1000***
- ***Indirect bandgap ~1.3 eV***

Technical Accomplishments and Progress

New materials.

Mesoporous $CuCrO_2$ delafossite structures show activity for hydrogen production in Na_2S + NaOH electrolyte





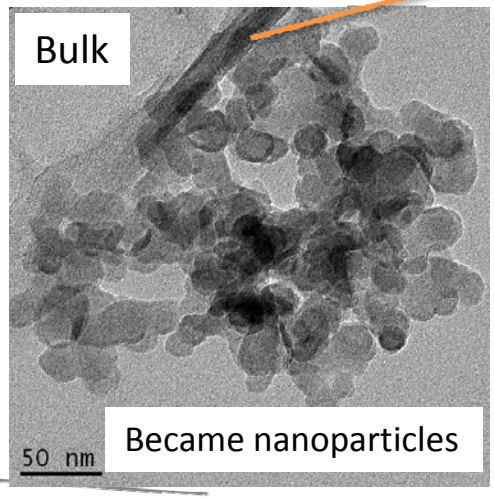
Hydrogen production rate of bulk, mesoporous $CuCrO_2$, and Mg^{2+} doped mesoporous $CuCrO_2$ (5 mg powder in 15 mL NaOH and Na_2S solution). Mesoporous delafossite shows an efficiency > x10 bulk material, however, $\lambda <$ 400nm, required.

Technical Accomplishments and Progress

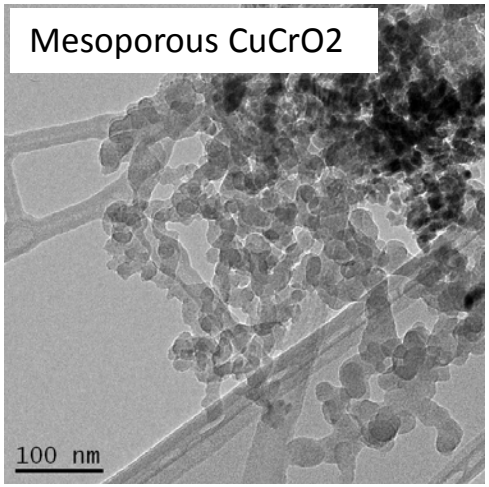
New materials.

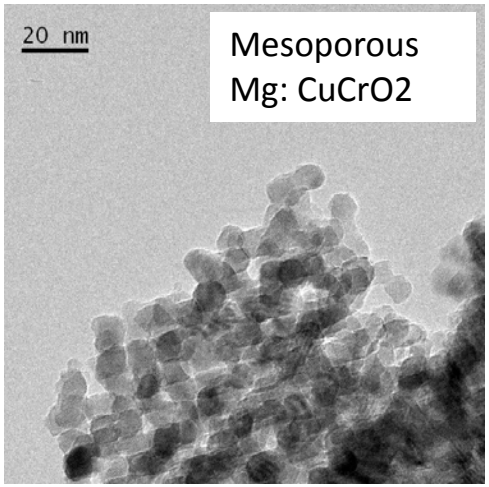
Photocorrosion: Mesoporous $CuCrO_2$ delafossite structures

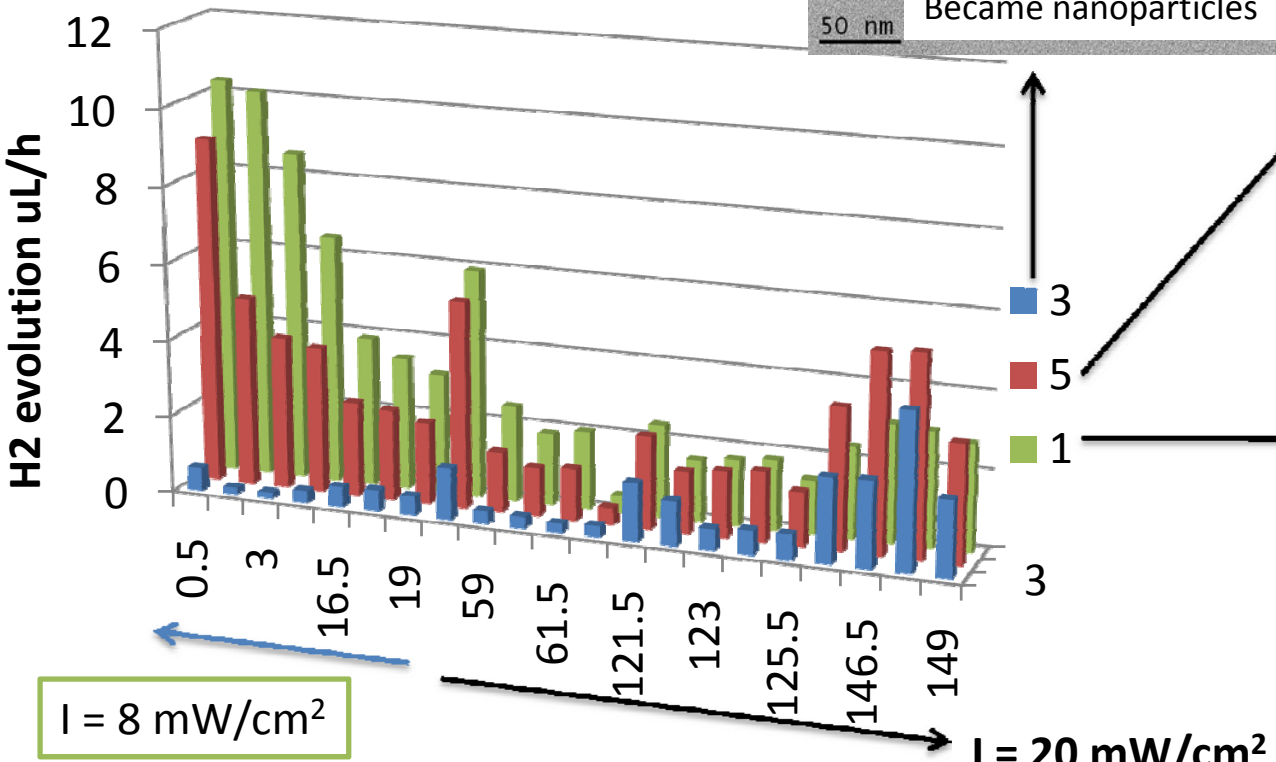
Mg doped $CuCrO_2$ shows the highest chemical stability over 149 hours of illumination.



Cu metal nanorod







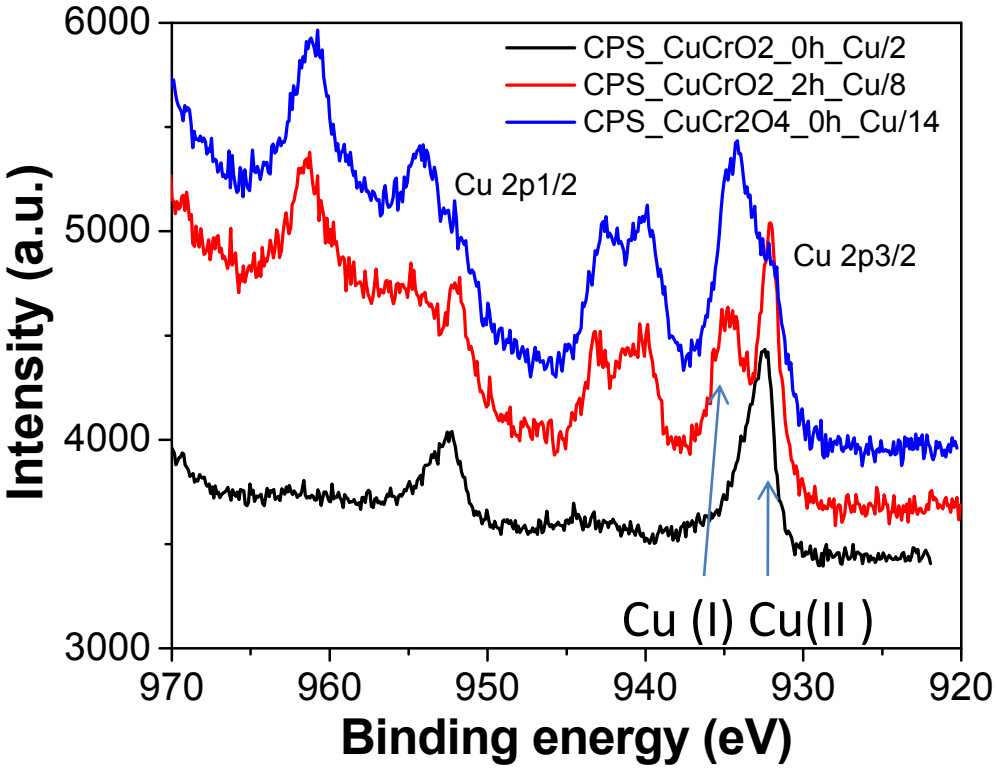
Technical Accomplishments and Progress

New materials.

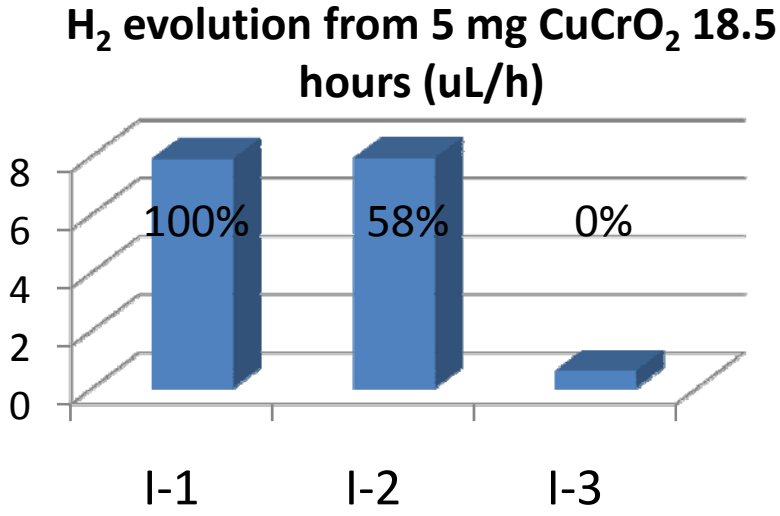
XPS results on Photo-oxidation of Cu^{+} in bulk and mesoporous delafossite structures

Cu+ oxidized into Cu2+ according to XPS, such reaction is proposed:

$2CuCrO_2 + H_2O \rightarrow CuCr_2O_4 + CuO + H_2$



XPS of control and illuminated delafossite



Stability for Cu(II) → Cu(I)

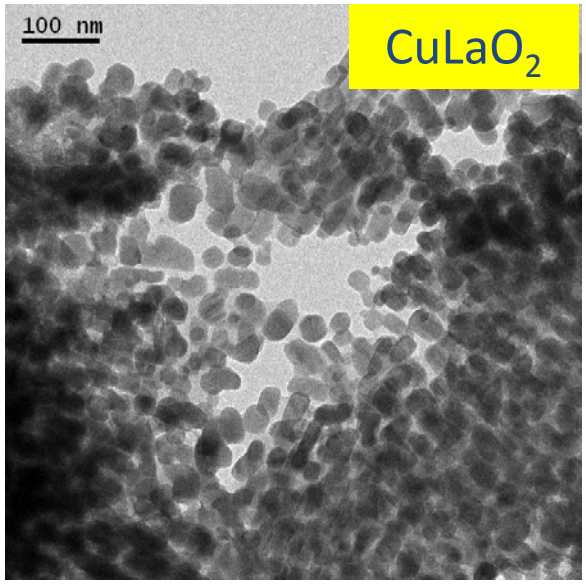
I-1: Mg:$CuCrO_2$, remained 100% Cu(II)

I-2: Mesoporous $CuCrO_2$, remained 58%

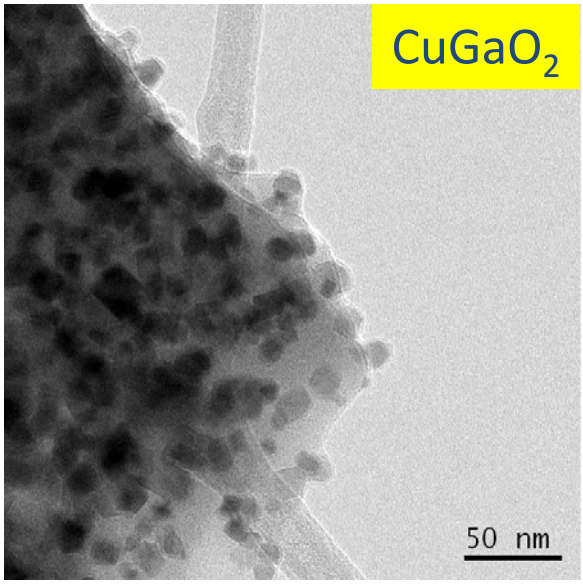
I-3: Bulk $CuCrO_2$, remained 0%

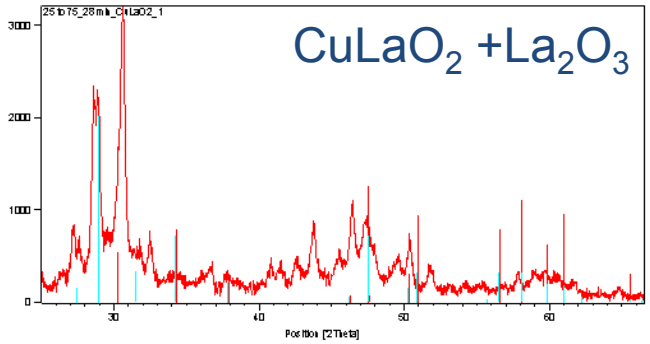
Technical Accomplishments and Progress

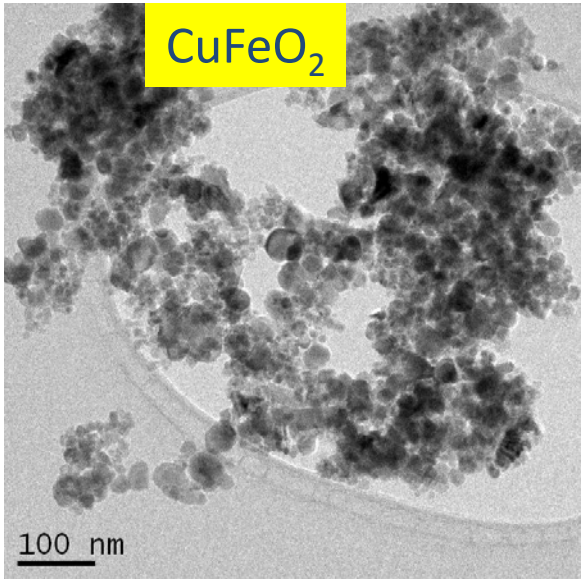
New materials.



- Recent success in synthesis of several new Delafossites, though not all pure phase materials.
- Have set-up necessary systems to rapidly create other combinations in the same class.
- PEC performance screening in progress.

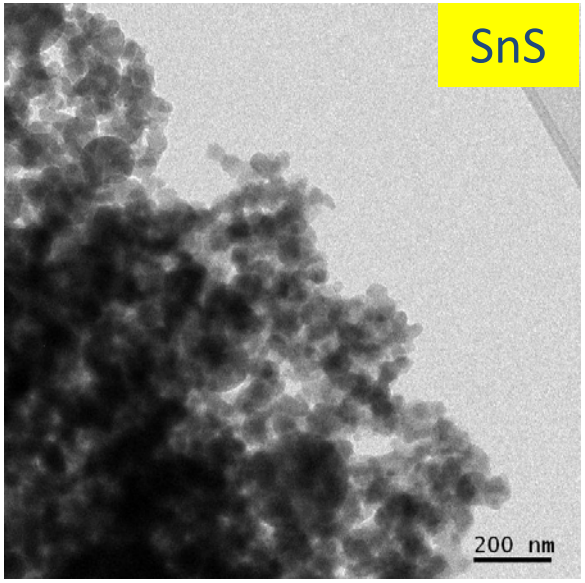




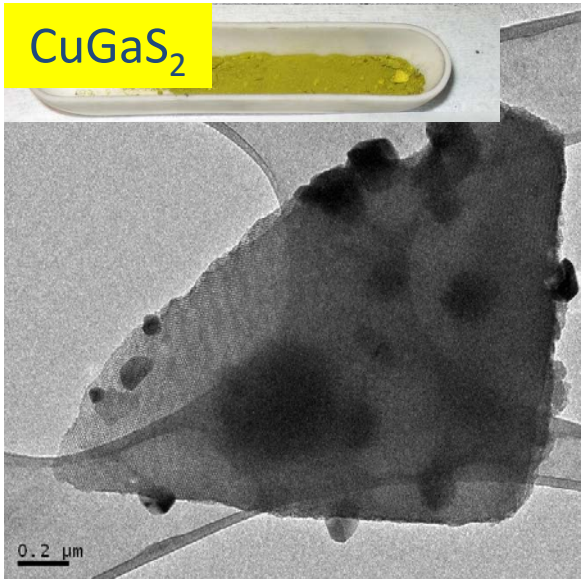


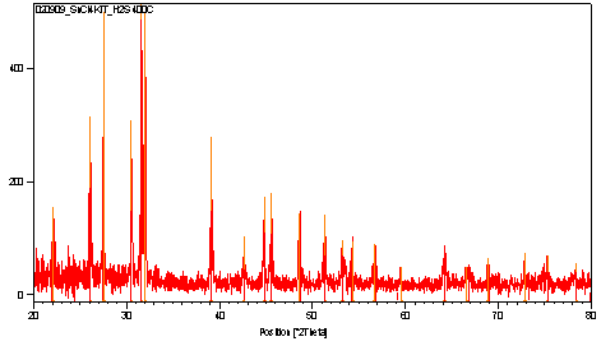
Technical Accomplishments and Progress

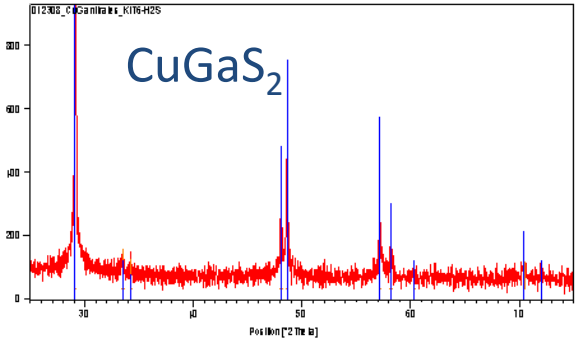
New materials.



- Recent success in synthesis of new sulfides.
- H_2S furnace able to process safely multiple samples.
- PEC performance screening in progress.

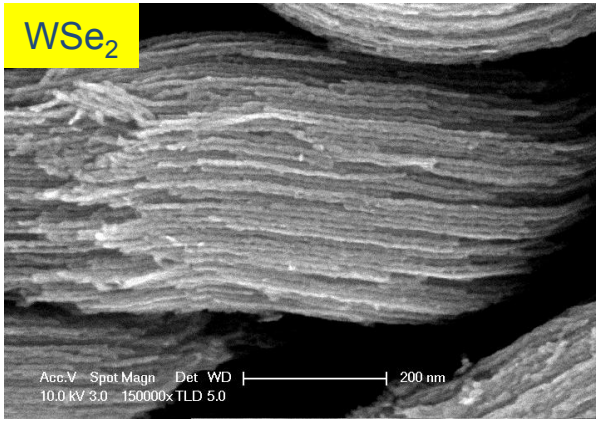


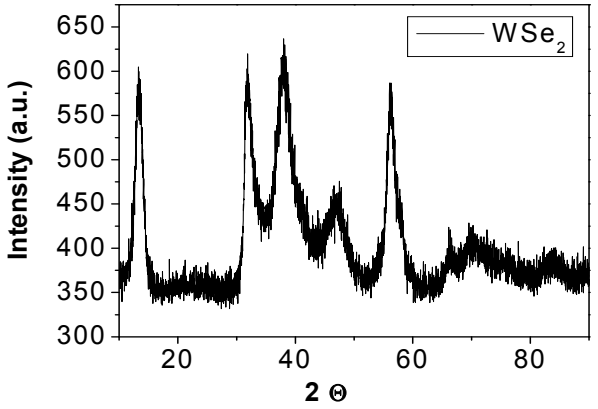




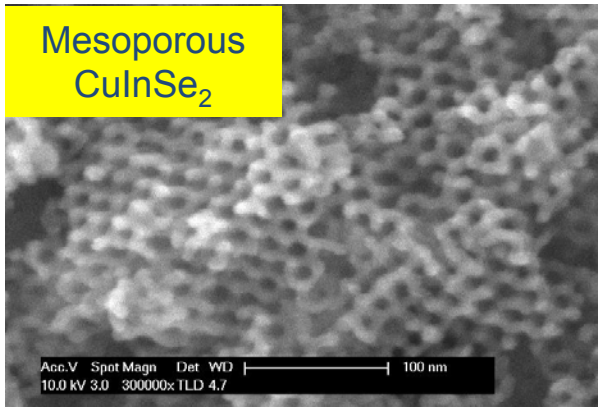
Technical Accomplishments and Progress

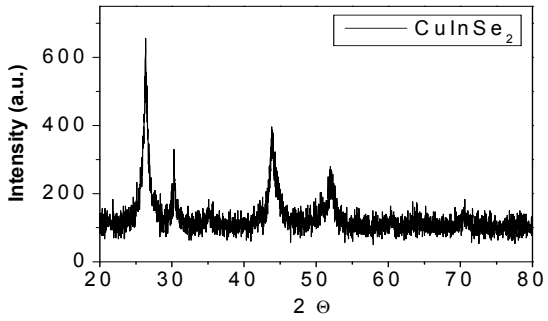
New materials.

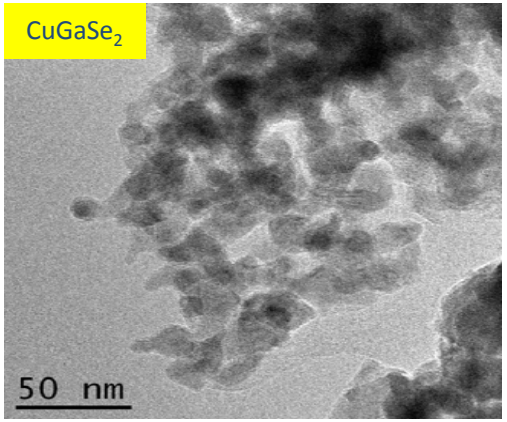


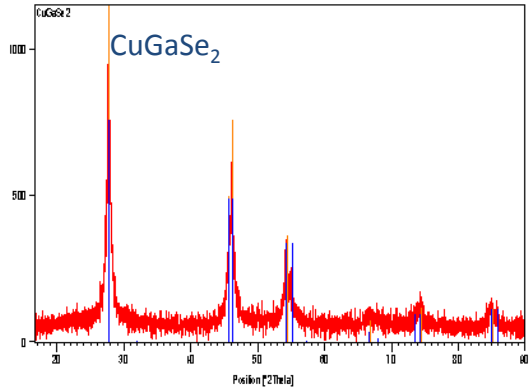


- Recent success in synthesis of <u>new selenides</u> by wet chemical route amenable to scale-up.
- PEC performance screening in progress.





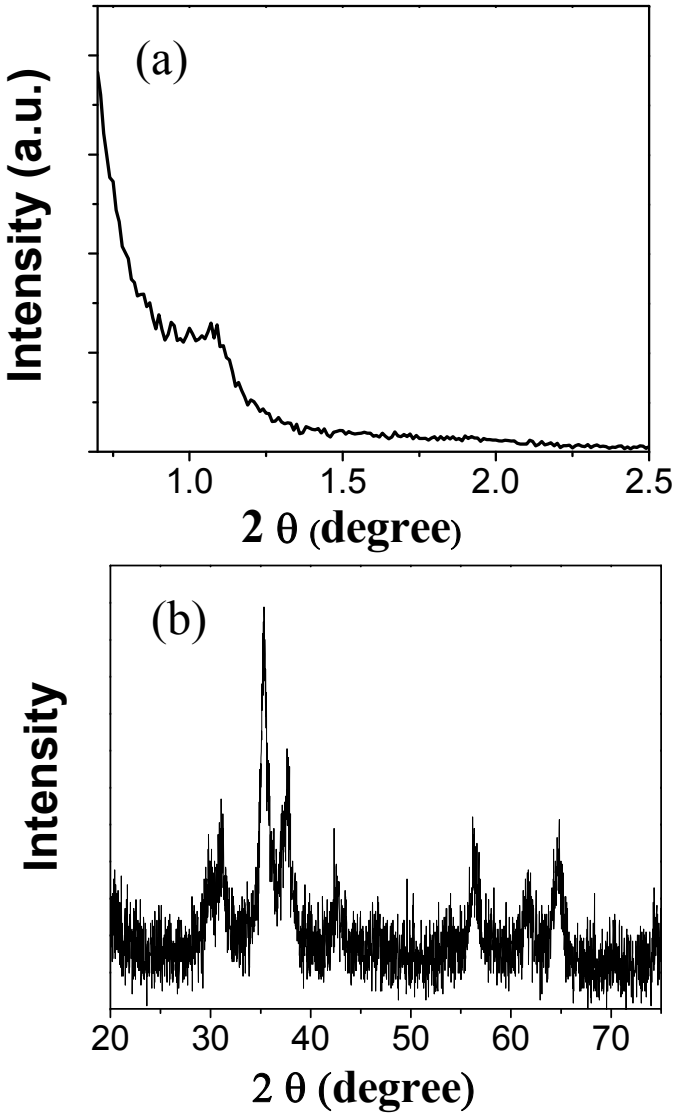


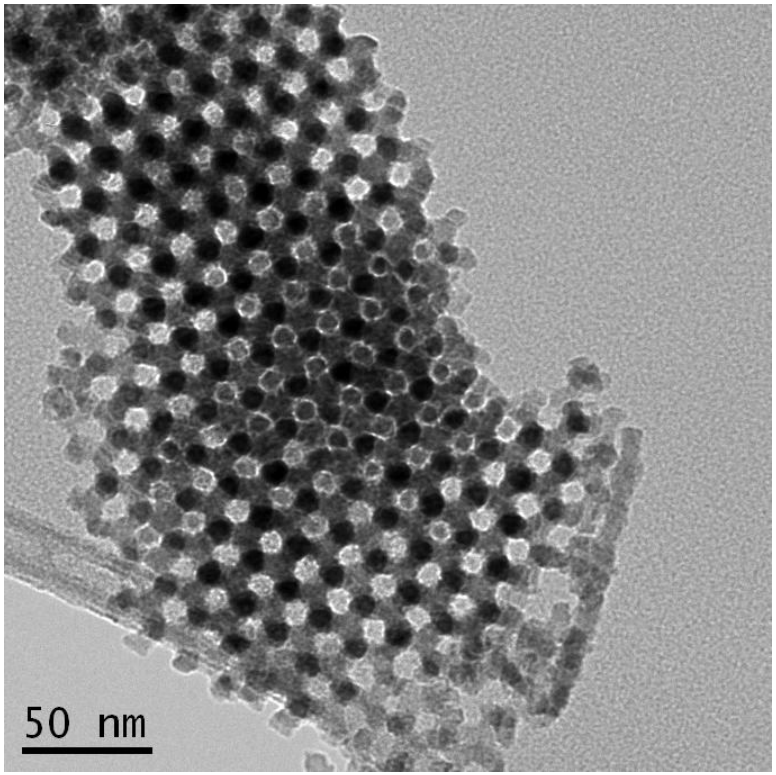


Technical Accomplishments and Progress

New materials.

Mesoporous $CuCr_2O_4$ spinel structures active as powders for hydrogen production in Na_2S + NaOH electrolyte only under UV illumination



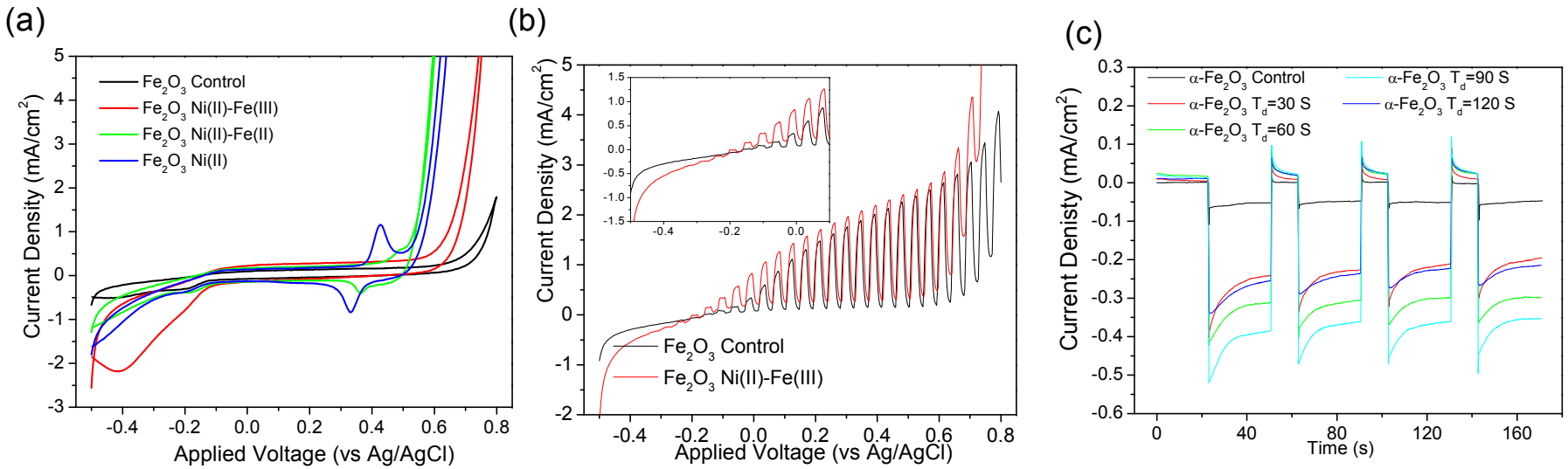


Mesoporous $CuCr_2O_4$ spinel active as powders for hydrogen production in Na_2S + NaOH electrolyte only under UV illumination

Technical Accomplishments and Progress

Improved Electro-kinetics

Electrodeposition of NiFe Electrocatalysts



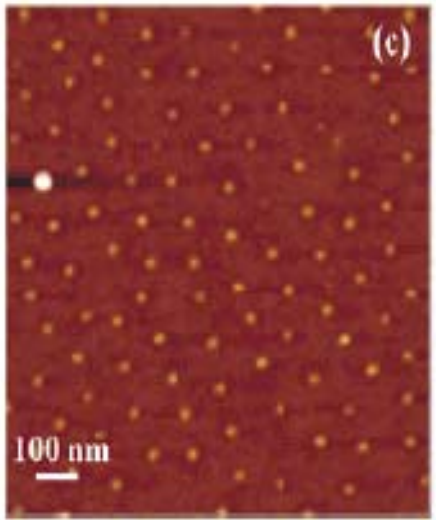
Sample	mV onset vs Ag/AgCl	α	Io [A/cm²] α
Fe_2O_3 Control	650	0.68	2.1-E7
NiFe (III)	560	0.59	7.4E-7
NiFe (II)	490	0.39	2.0E-7
Ni	490	0.44	2.1E-7

- NiFe(III) improved the PEC performance by as much as 4.5 times as compared to the control sample.
- NiFe(II) and Ni had a decrease in the PEC performance
- The optimum loading for the NiFe(III) electrocatalyst corresponded T_{dep} ~90 sec.

Electrochem. Comm. 2009 (in Press)

Technical Accomplishments and Progress

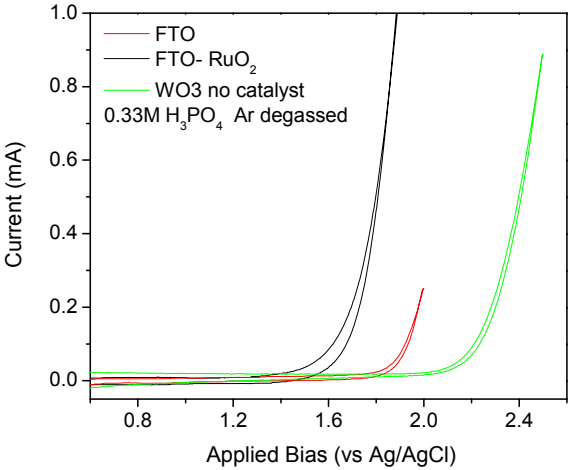
Improved Electro-kinetics



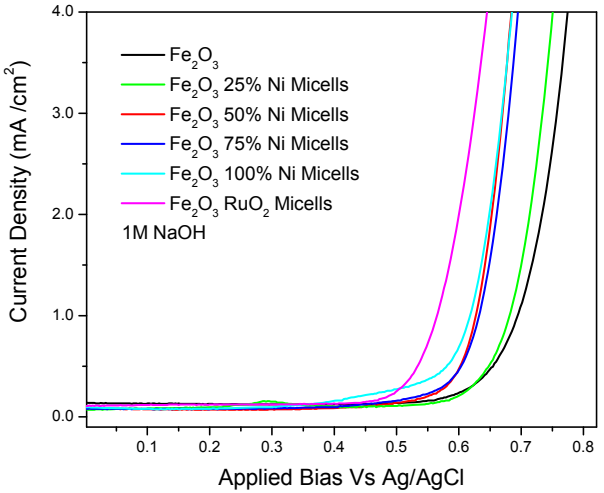
12928 ■ J. AM. CHEM. SOC. 2003, *125*, 12928−12934

Dark IV curves

a)

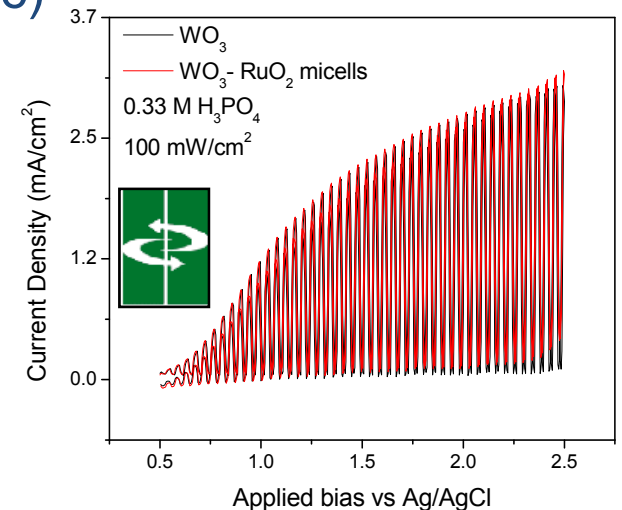


b)

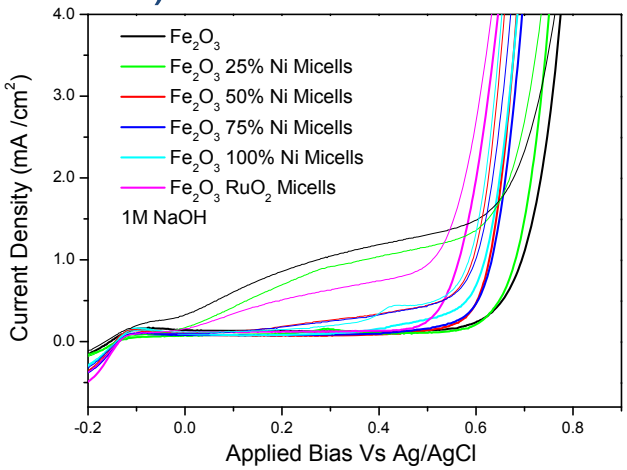


PEC performance

c)



d)

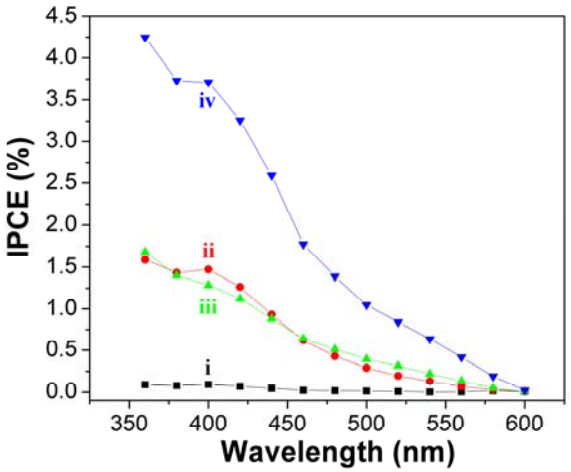


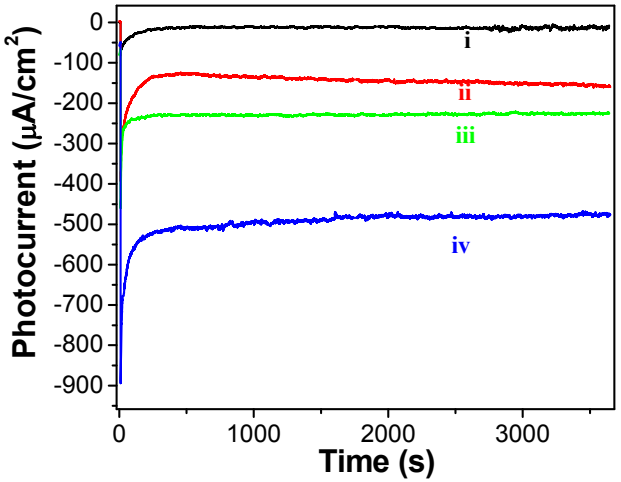
- WO_3 is greatly hindered by Oxygen Evolution reaction (a)
- Fe_2O_3 is greatly improved by NiFe or RuO2 electrocatalyst deposition
- No improvement observed by: RuO_2 nanoparticles deposition on WO_3(c) or electrocatalyst deposition on Fe_2O_3 (d)

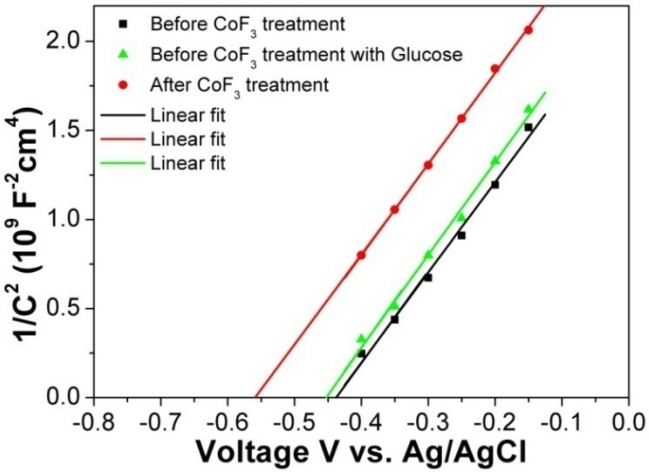
Technical Accomplishments and Progress

Processing and synthesis

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







i: Ti-doped sample without CoF_3 treatment in NaOH solution

ii: Ti-doped sample **with** CoF_3 treatment in NaOH solution

iii: Ti-doped sample without CoF_3 treatment in NaOH+Glucose solution

iv: Ti-doped sample **with** CoF_3 treatment in NaOH+Glucose solution

- Record efficiency for a True Zero bias hematite photoelectrode
- New method applicable to Fe_2O_3 to shift the VB/CB

Chem. Comm. 2009 (in press)

Summary

- **New PEC Materials**
  - **Theory guided synthesis and characterization of additional doped iron oxides supports theoretical predictions that the Mott-Insulator symmetries must be broken to improve conductivity. HTE of Al doped hematite identified 0.3-0.5 % as optimal, IPCE increased 4-5x over controls . Initial results of donor/acceptor doping predicted by theory, disappointing.**
  - **Theory inspired synthesis and initial characterization of new, $CuMO_2$ Delafossites completed for M=Cr,Fe,Ga,La. Now attempting electrode configurations.**
  - **Several new oxides ($CuCr_2O_4$), sulfides (SnS, $CuGaS_2$), and selenides (WSe_2,$CuInSe_2$, $CuGaSe_2$) synthesized, PEC characterization in progress.**

- **Optimization of Material Performance**
  - **Surface modification with F to shift conduction band-edge of Ti-doped hematite produced record zero bias (two electrode) efficiency for hematite ~ 1% at 450 nm.**
  - **NiFe electrocatalysts have shown an improvement of ~ 4X on the performance**
  - **Biomass analogues have been successfully photo decomposed with increased performance 15 times or higher than NaOH.**
- **New Structures**
  - **Developed generalized synthesis routes to integrated absorber/catalyst/coating PEC systems. Will defer further work to focus on new absorber material identification.**

Future Work

(focus on finding and optimizing solar spectrum absorber consisting of earth abundant materials)

- ***Synthesis and Screening of New Materials:***
  - ***Iron based oxides (to make go/no-go decision on iron oxides in 2009)***
    - ***High-throughput investigation of Fe-Ti up to 40% Ti.***
    - ***Thin-Film doped iron oxides using organometallic pyrolysis (Si, Ti,C, doping guided by theory)***
  - ***Copper based oxides***
    - ***Complete screening of delafossite oxides materials***
      - ***Attempt pure phase $Cu(Fe)O_2$, $Cu(La)O_2$***
      - ***Delafossite synthesis as films to allow electrochemical analysis.***
  - ***Begin initial exploration of Sulfides, Phosphides, and Selenides***
    - ***Solution synthesis of $Cu(Ga)Se_2$, $Cu(La)S_2$, SnS , WSe_2 , SnP***
    - ***Develop High-Throughput Synthesis Methods.***
  - ***High-throughput screening and selected physical, electronic, and photoelectrochemical characterization of new host materials.*** **Quantitative analysis of photocurrents and photovoltages and indirect measurement of hydrogen production activity and flatband potential. Selected use of Mott-Schottky analysis and direct bulk H_2 yields.**
  - **Detailed analysis of selected candidates including carrier lifetime analysis by femtosecond transient absorption spectroscopy; internal quantum efficiency (IQE) characterization, and Raman.**
- ***New Structures***
  - ***Thin films and Mesoporous supports (ITO, WO3, TiO2) with nanometer scale doped iron oxide inclusions.***
  - ***Solution phase synthesis of p-n junctions, $Cu(M)O_2$ /TiO_2***

Collaborations

- DOE H_2 Program
  - Directed Technologies (Participated in PEC System Analysis)
  - Standard PEC testing group discussion
  - Yanfa Yan, NREL (Theoretical Calculations)
  - Eric Miller, University of Hawaii (Electrocatalysts for WO_3)
  - Clemens Heske, UNLV (Characterization of Fe_2O_3)
  - Tom Jaramillo, Stanford (round-robin testing)

- M. Gräztel, Ecole polytechnique fédérale de Lausanne (Fe_2O_3)

UCSB UNLV University of Nevada, Las Vegas STANFORD UNIVERSITY EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE NREL