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

Eric W. McFarland
Department of Chemical Engineering
University of California, Santa Barbara
June 7, 2010

Project ID # PD034

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start date September 1, 2004
- End date May 31, 2010
- 95% Complete

Barriers

Technical Barriers Addressed

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

Budget

- Total project funding through FY 08
  - DOE share $ 894k
  - Contractor share $ 223k
- Funding for FY09 $0
- Funding for FY10 $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 Investigated in 2010

- ***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.***

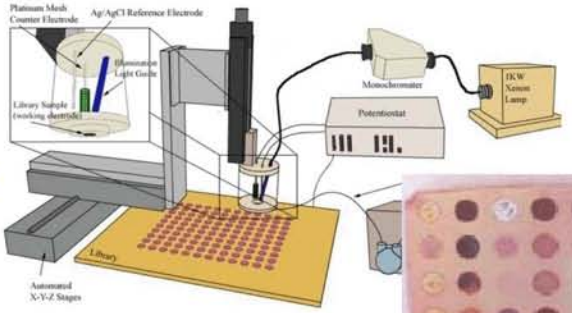
Approach/Selection Criteria

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%

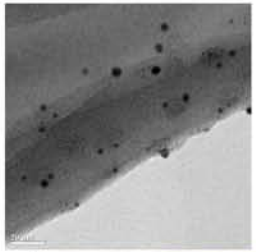
Yes

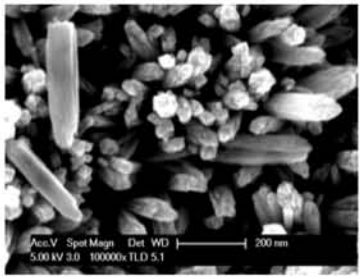
Processing, Surface, Electrolyte, and Electrokinetic Optimization

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

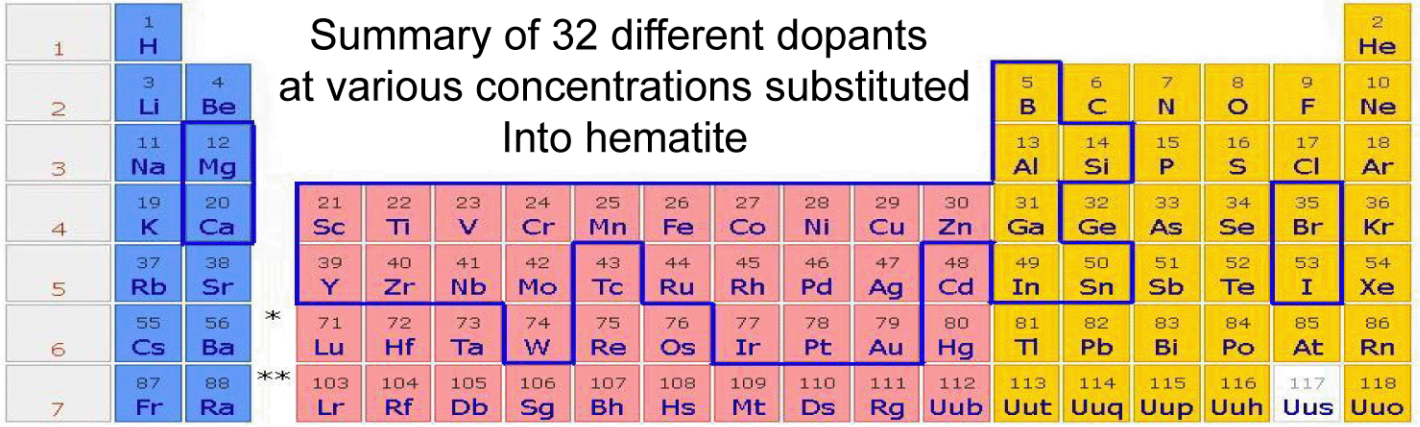
promise

- 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

Summary of 32 different dopants at various concentrations substituted Into hematite

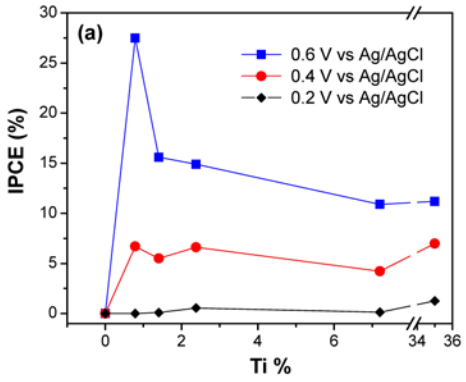


- Higher valence dopants (Pt, Mo, Cr, Ti): increased IPCE by 10x
  → n-doping, increased carriers, increased mobility and conductivity
- Isovalant substitutions with large cation size differences (Al): increased IPCE
  → strain, increased Fe-d overlap, increased hoping conduction
- No significant change in absorbance or effective gap with any dopant.
- Many dopants improved efficiency, but, best zero bias performance still more than an order of magnitude too low; iron oxide will not work for water splitting.

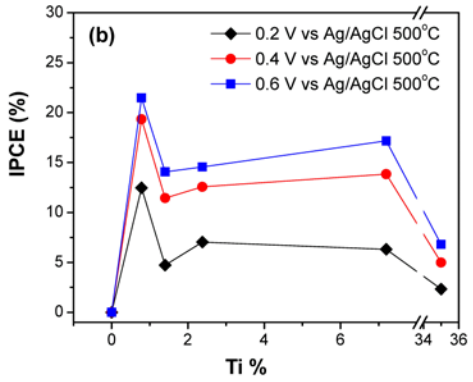
Ti Doped Hematite Thin Films:

Morphologies, Crystallization, and IPCE in 1M NaOH

	Flowrate $Fe(CO)_5$ (sccm)	Flowrate $TiCl_4$ (sccm)	Flowrate Oxygen (sccm)	Hotplate Temp (°C)	min	XPS Ti %
1	40	0	490	500	1	0.00
2	40	10	490	500	1	0.78
3	40	16	490	500	1	1.42
4	40	18	490	500	1	2.38
5	40	20	490	500	1	7.17
6	40	30	490	500	1	35.0

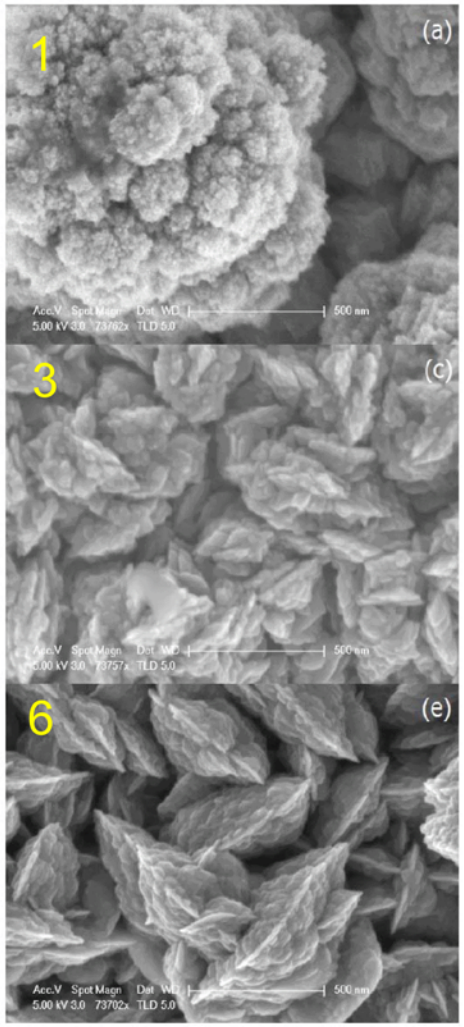


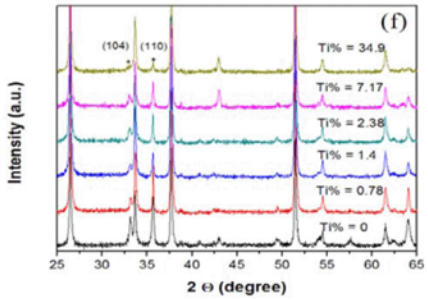
As prepared



After 500 °C

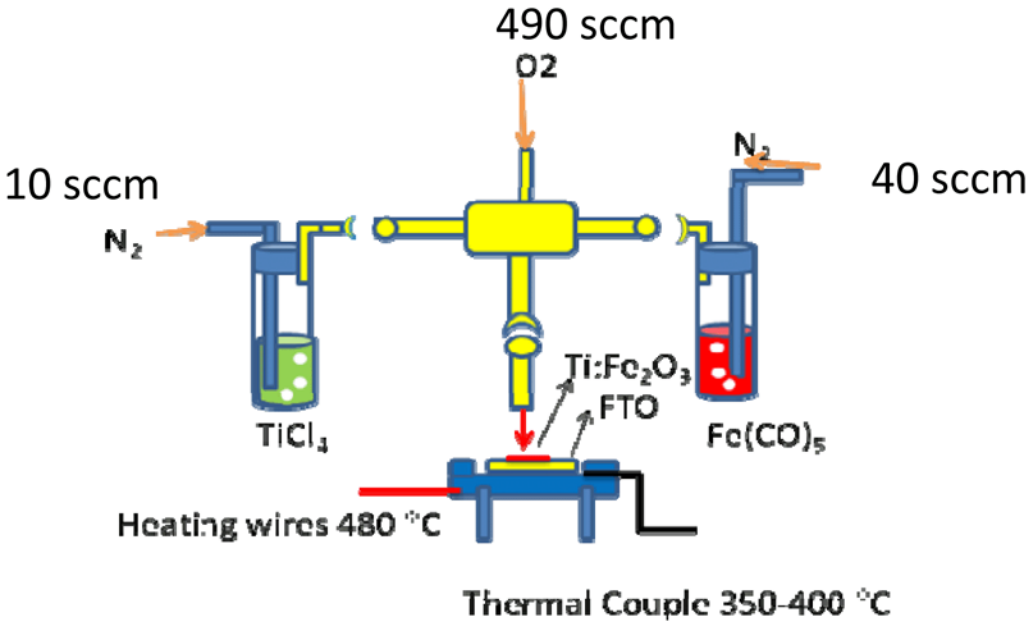
Annealing decreased the trap state density, enhancing the IPCE of hematite at low bias

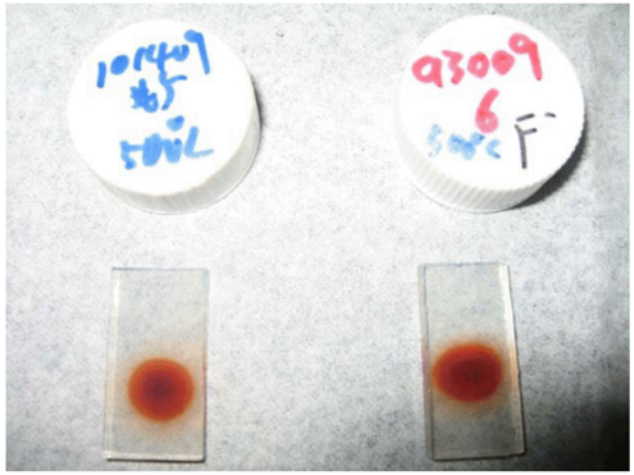


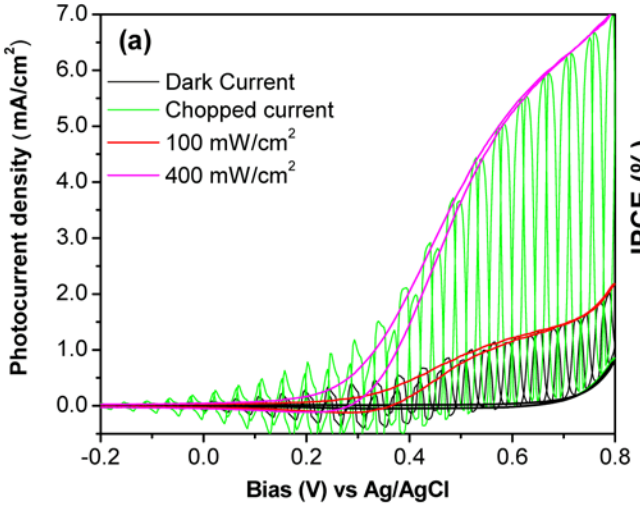


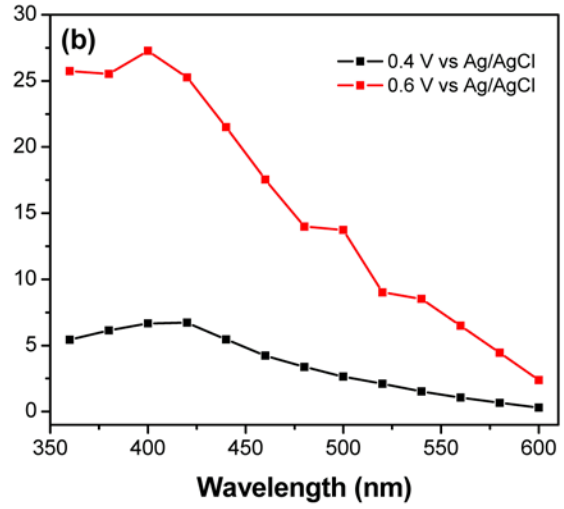
- Feature size increases with Ti%
- Morphologies of doped hematite are different with different Ti%
- All thin films show oriented crystallography

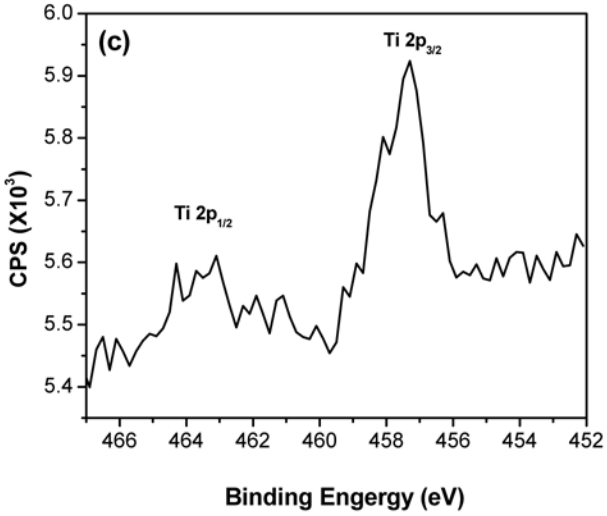
Ti: Doped (Ti%=0.78) Hematite Synthesis and Performance



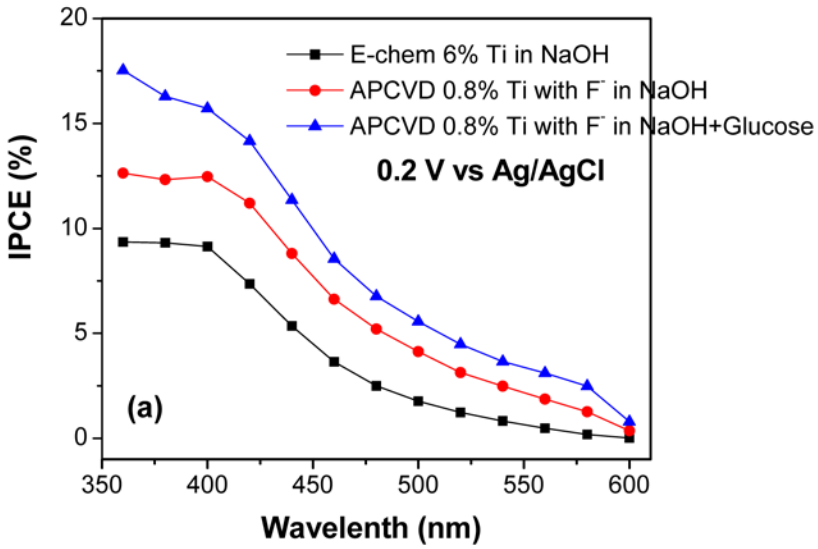


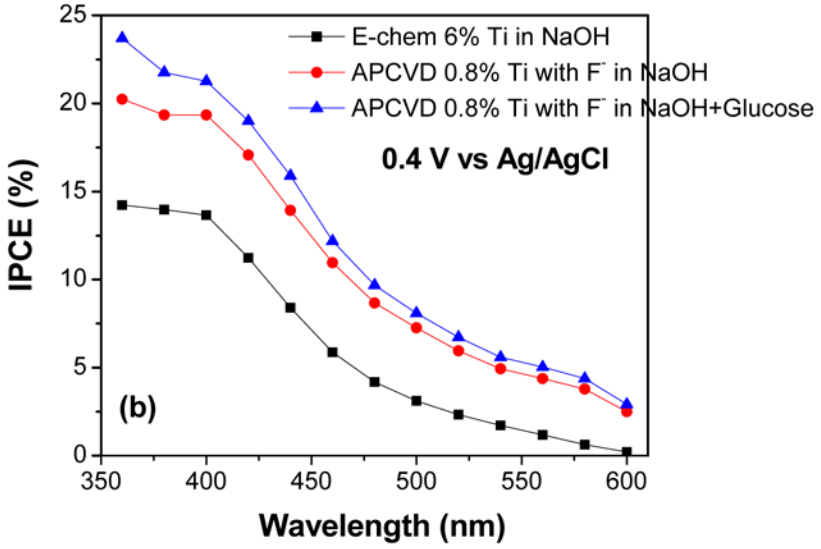


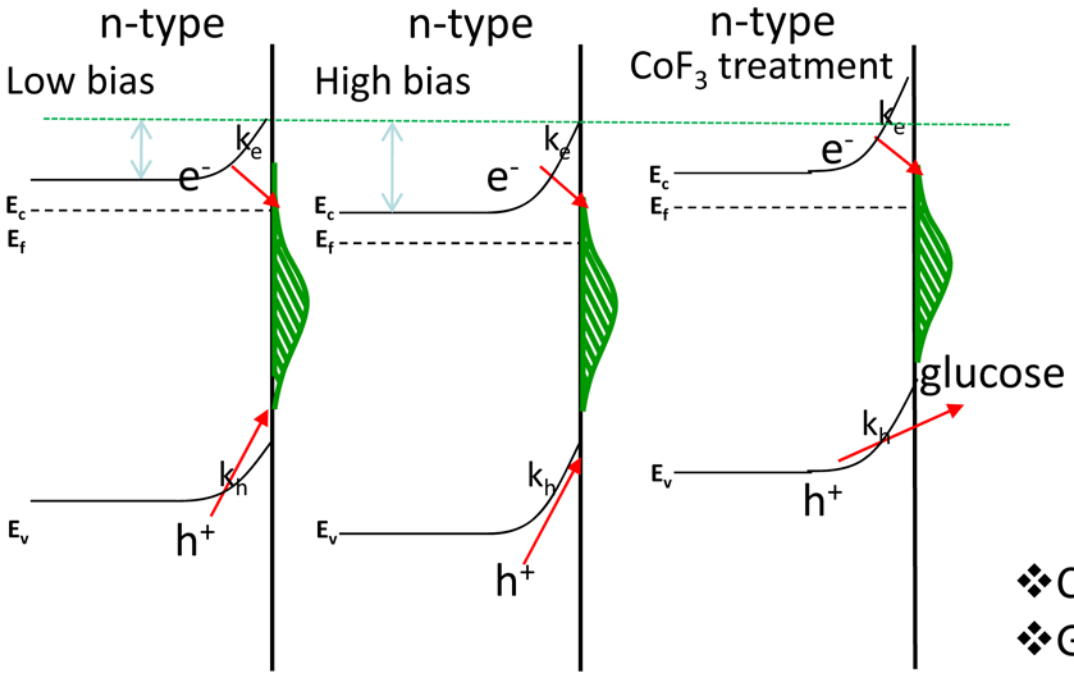


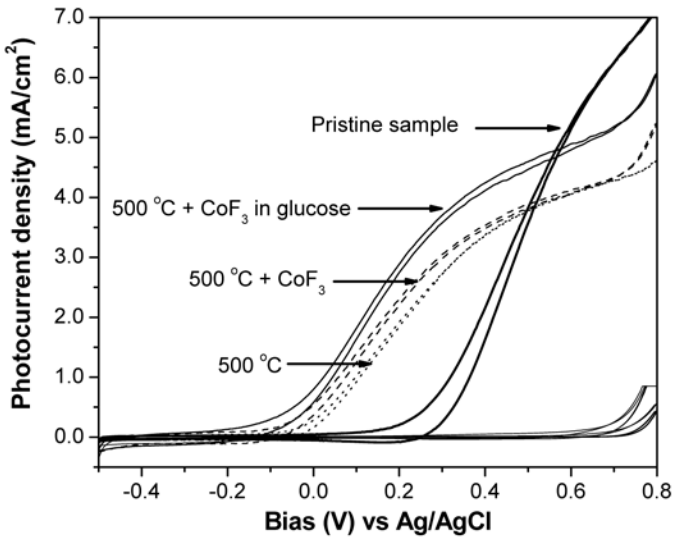


IPCE of CoF_3 Surface Modified Ti:Fe_2O_3 Thin Films Using Glucose as Reductant; Comparison with the Best E-chem Sample





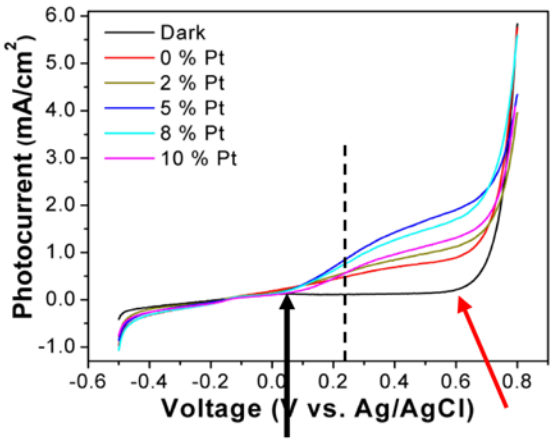




- CoF_3 treatment shifts the bands upward
- Glucose is easier to be oxidized by holes

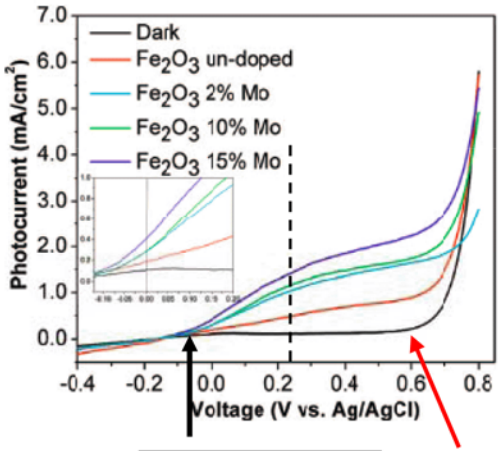
Hematite Performance & Device Quality

E-chem; Pt doped



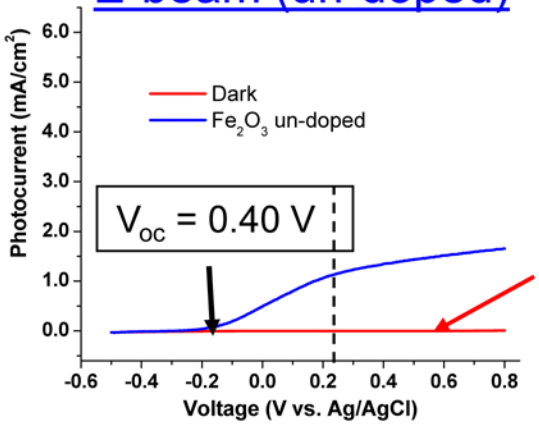
V_{oc} = 0.20 V

E-chem; Mo doped

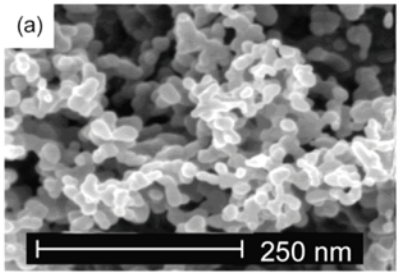


V_{oc} = 0.30 V

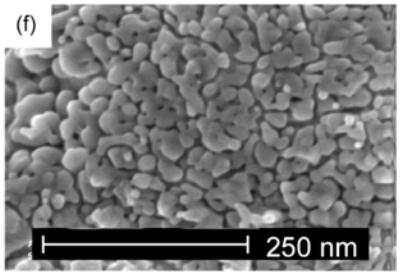
E-beam (un-doped)



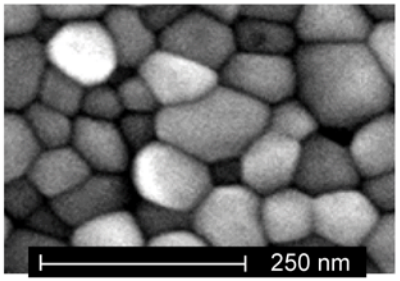
E-chem (un-doped)



E-chem (Mo doped)



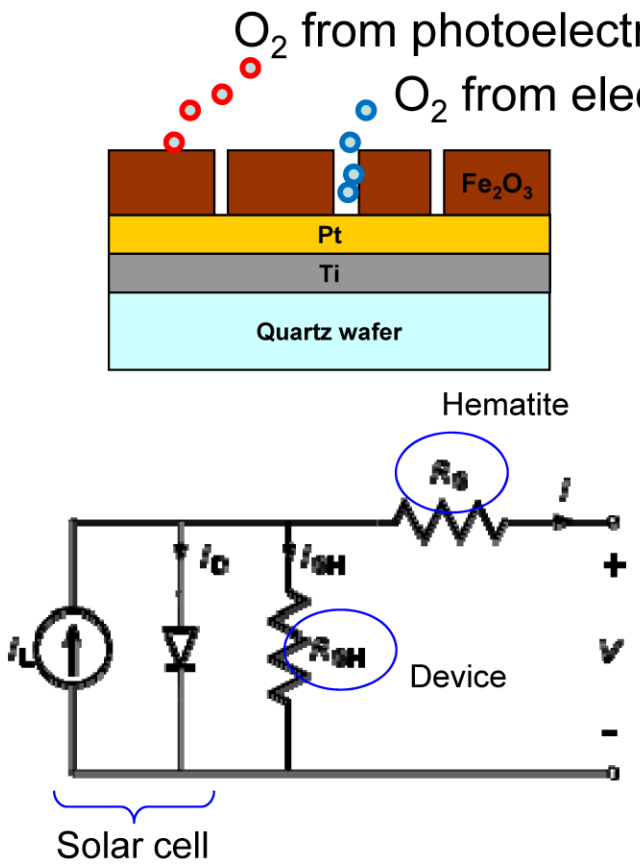
E-beam (un-doped)

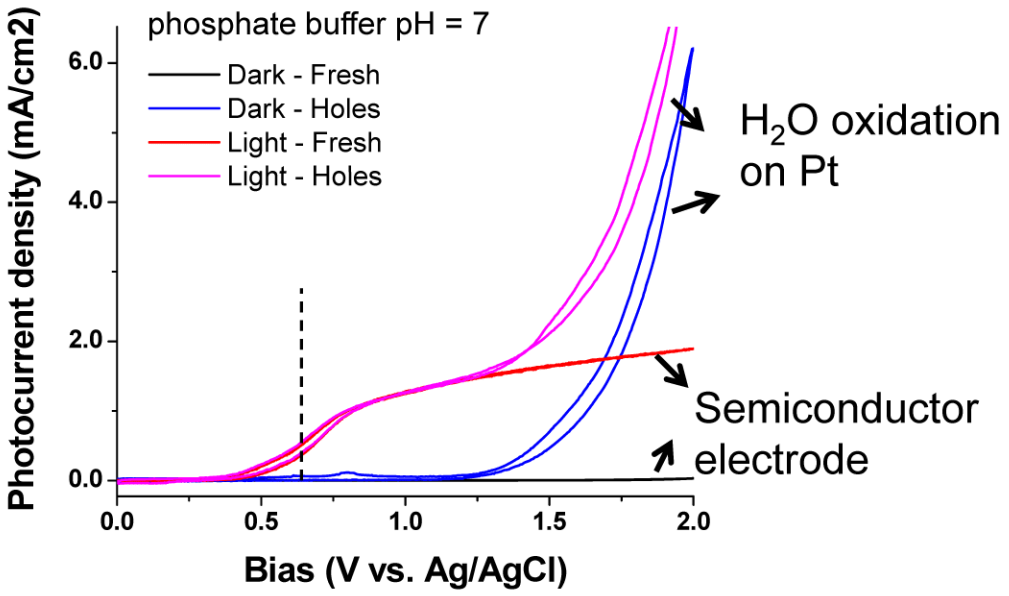


Comparison of onset potential and open circuit voltage of hematite thin films by electrodeposition and electron-beam evaporation (E-Beam) method.

J. Phys. Chem. C, **2008**, 112 (40), 15900–15907
Chem. Mater. **2008,** *20,* 3803–3805

Shunt Resistance and Pinholes – Device Quality





Device quality or intrinsic material properties?

No Significant Decrease In Photoelectrode Efficiency.

❖On semiconductor electrode, no oxidation occurred on 2.0 V vs. Ag/AgCl

❖With pinholes punched on semiconductor electrode, O_2 evolved at 1.2 V vs. Ag/AgCl

Delafossite
Material-Class Synopsis

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

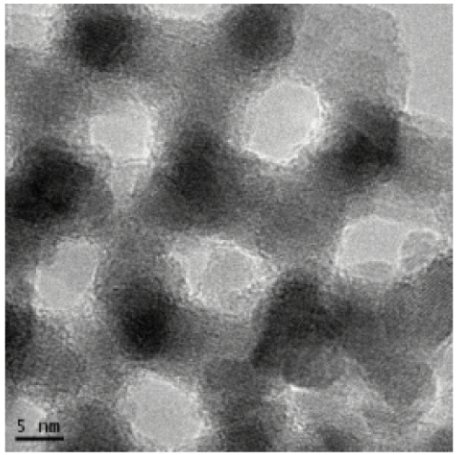
challenges

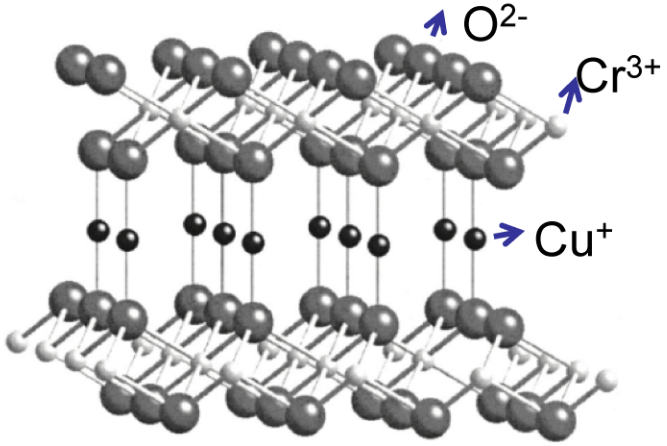
➢ Stability under illumination

➢ High recombination rates

➢ Valence and conduction Band position

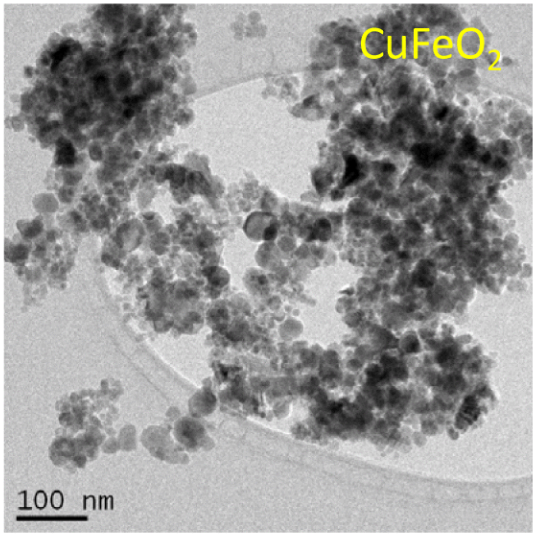
➢ Water Oxidation Kinetics

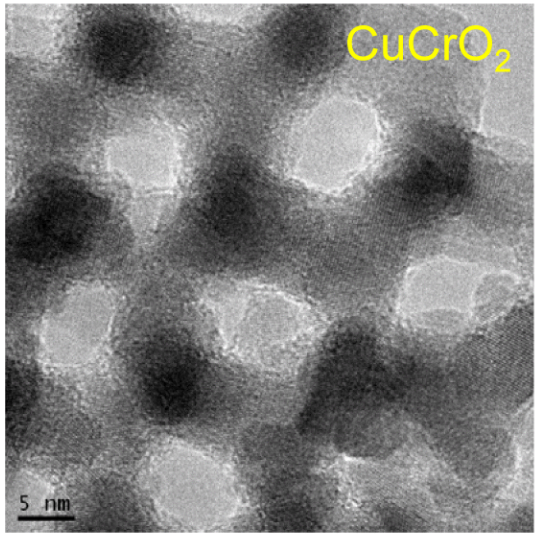


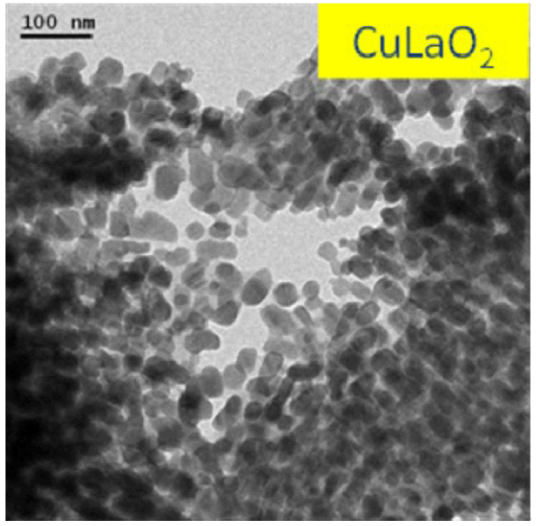


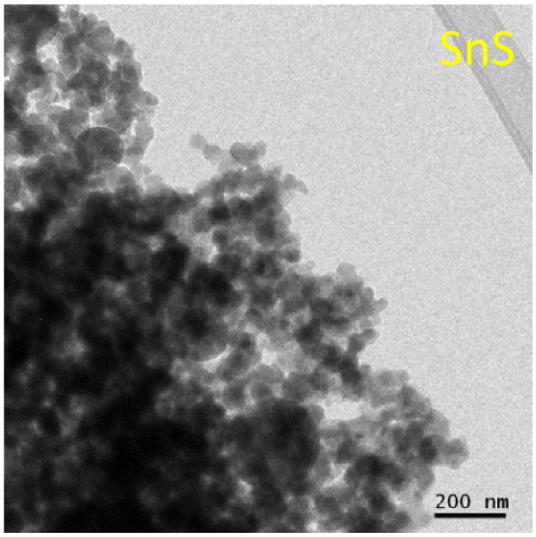
Mesoporous Delafossite and Spinel Structures

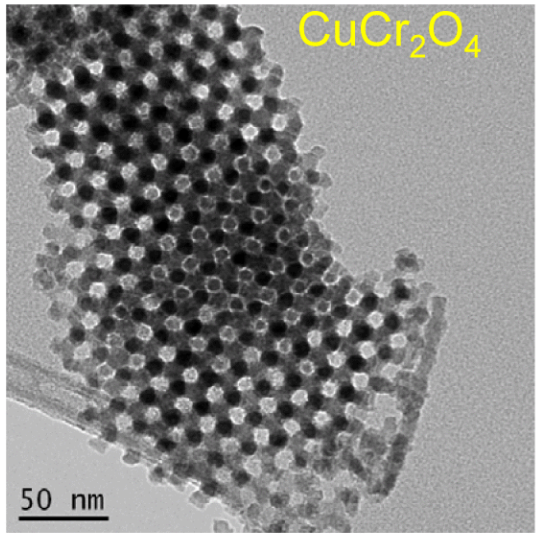
----variety of new materials synthesized

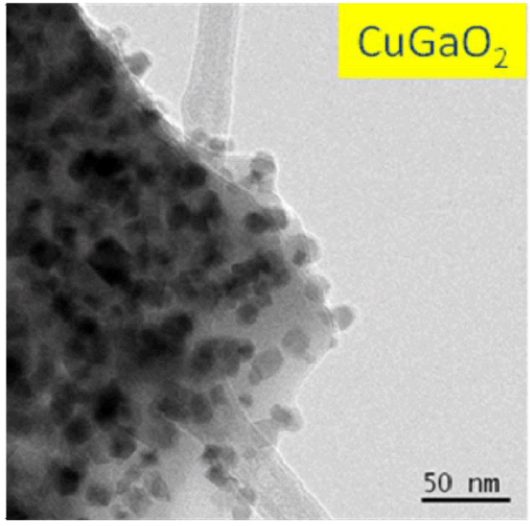








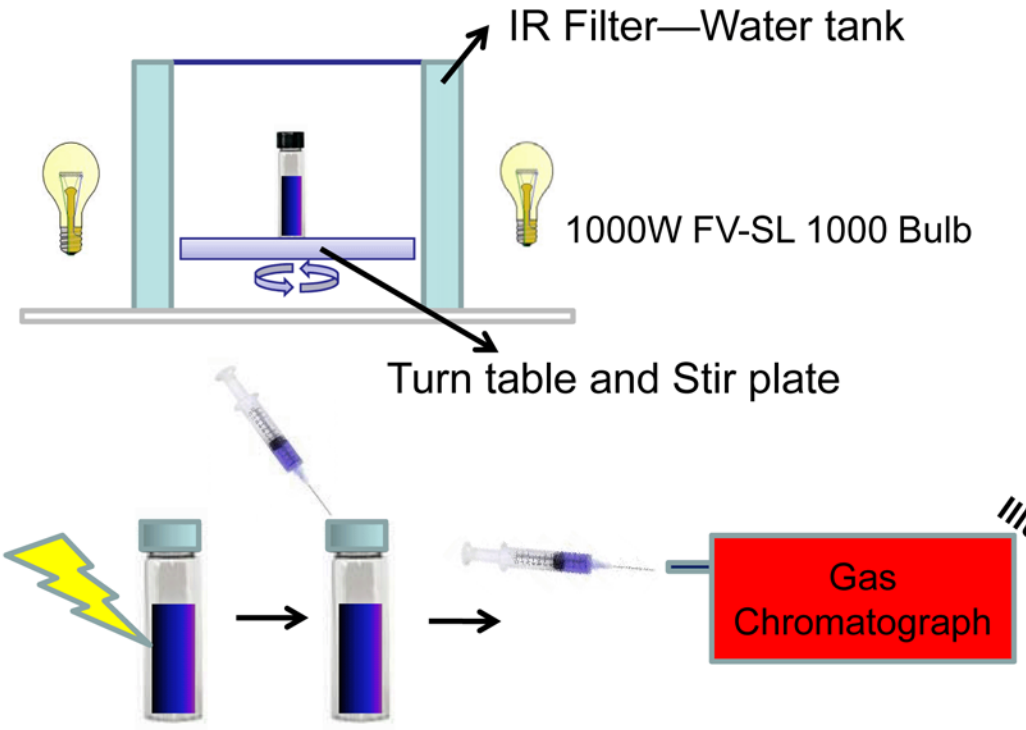


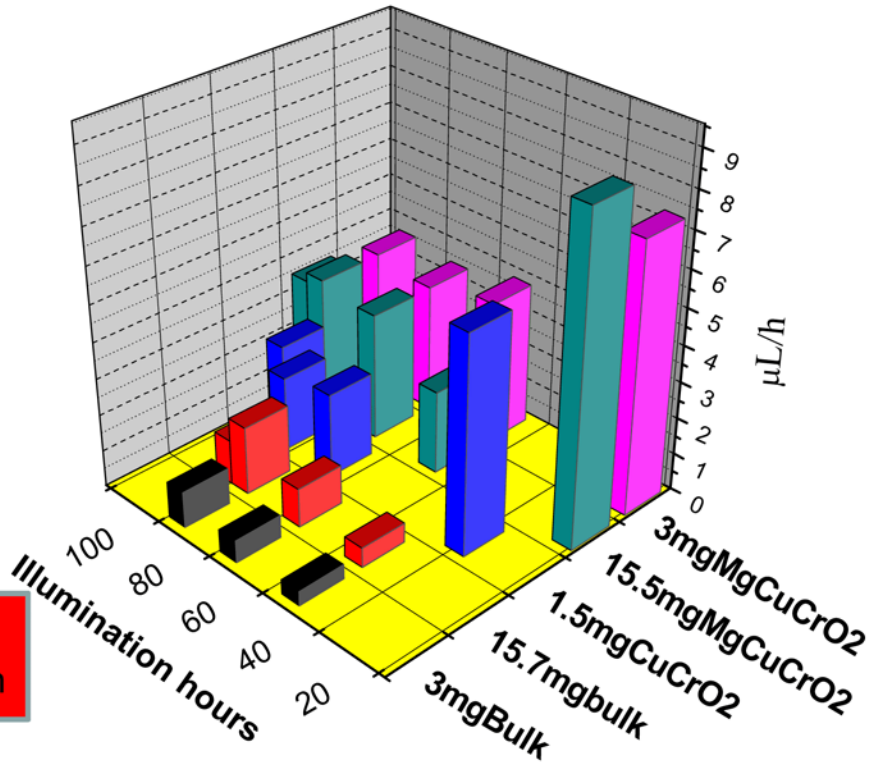


$CuCrO_2$, Ar, 1000 ˚C SA=90.1 m^2/g

$CuCr_2O_4$, Air, 950 ˚C, SA = 68.8 m^2/g

PEC Hydrogen Production From Slurry Delafossite: Schematics and Results





- Mg:$CuCrO_2$ and $CuCrO_2$ are still active after 100 hours reaction.
- Mesoporous structures are more active than bulk $CuCrO_2$
- Although improvements noticed, all IQE < 0.1%

BET Surface area:
Bulk: 0.298 m^2/g
Mesoporous: 63.3 m^2/g
Mg Doped Mesoporous: 53.7 m^2/g

Material-Class Synopsis
Phosphides

promise

- Bandgap ~ 0.8 – 2.0
- Several known with very high internal quantum efficiency (e.g. GaP, InP).
- Intrinsically good opto-electronic properties

challenges

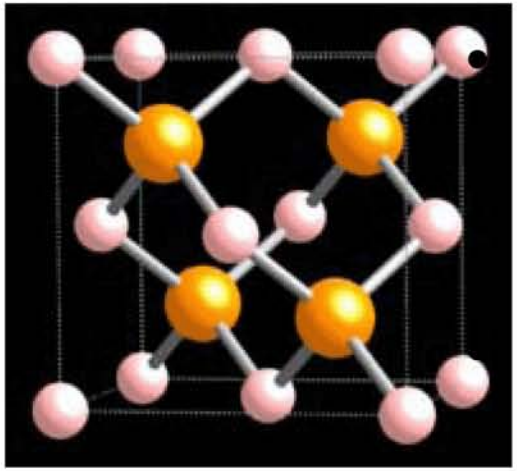
- Stability
- Valence Band Edge
- Water Oxidation Kinetics

Approach to Phosphides

- Investigate InP as model system to understand and improve stability.
- Create high-throughput methods for making mixed oxides then use subsequent processing to form phosphides.
- Investigate alternative redox couples for energy conversion and storage in which phosphides are stable.

Phosphides

(start with an efficient material and make it more stable)

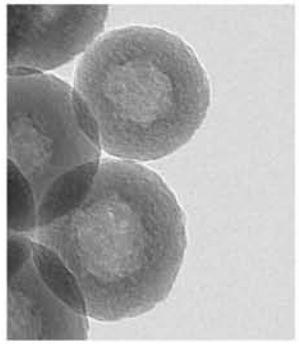


Easy to make

- (1a)M_xO_y +H_3PO_4 @500ºC in Air; ***OR***
- (1b) $Na_6\,[H_xM_yO_z] + NH_4HPO_4 \rightarrow MPO_x + NH_4OH + NaOH + H_2O$
- (2)Reduction in H_2 @ 600 – 900º C

Easy to break

- Anodic dissolution:
  - $Zn_3P_2 + 6H_2O \xrightarrow{H^+} 2PH_3 + 3Zn(OH)_2$



- **Strategy → keep them safe**

1)Core/shell structure
2)Noble Metal surface enhancement

FeP

InP

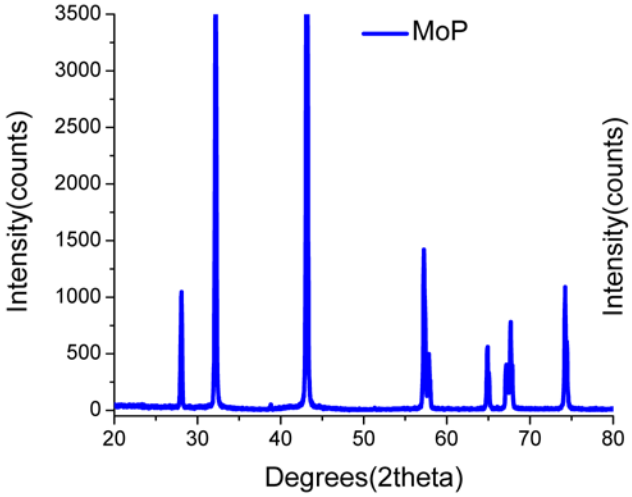
Zn_3P_2

Ni_2P

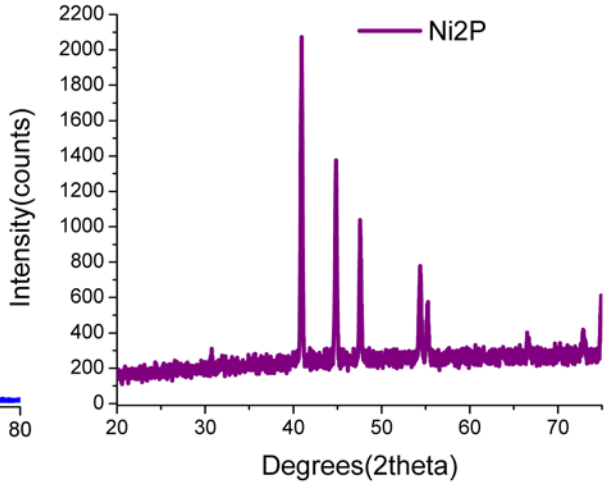
WP

MoP

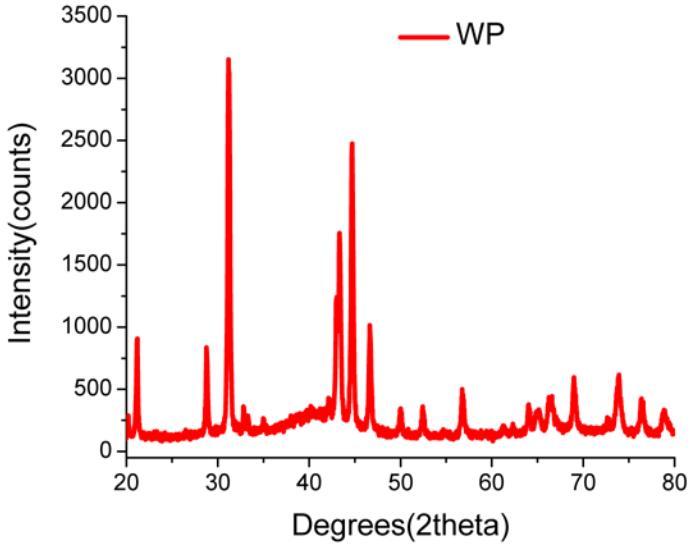
X-Ray Diffraction of Powder Phosphides From Metal Oxides



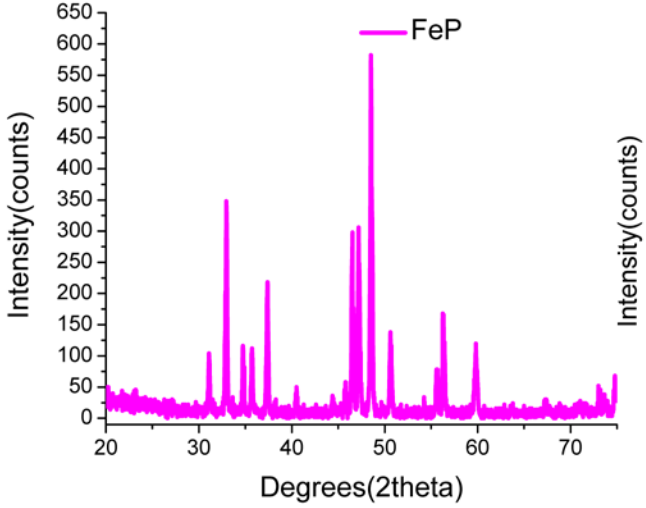
Single Phase MoP



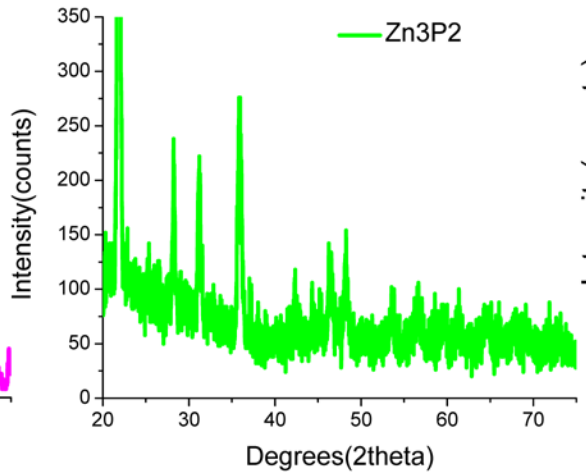
Nearly phase-pure Fe_2P (>5% NiP)



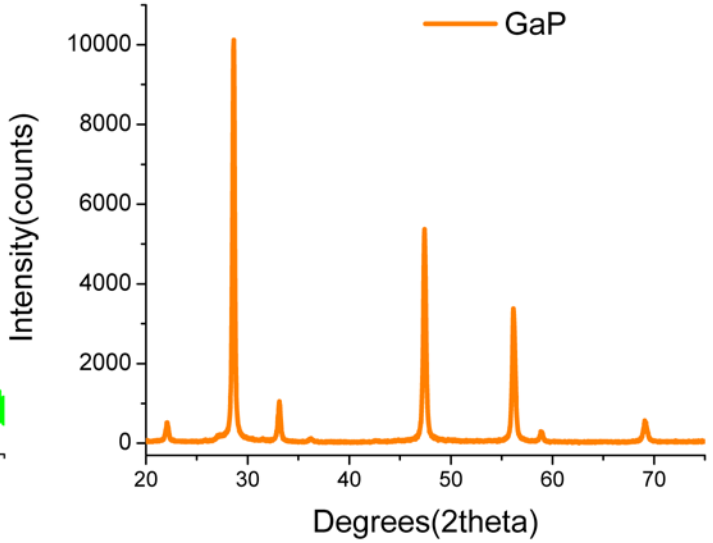
Single Phase MoP



Nearly phase-pure FeP (>5% Fe_2P)



Mixed ZnP2 and ZnP4



Single Phase GaP

Materials Engineering: Mixed Metal Phosphides

Modified Synthesis:

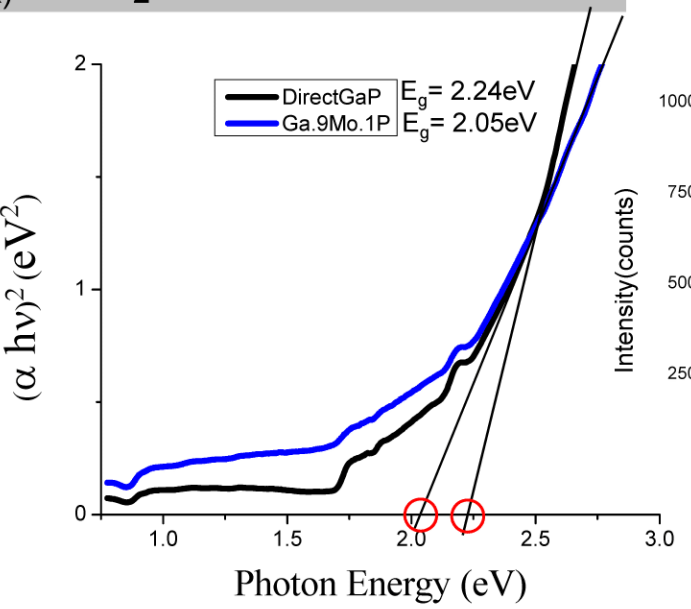
Alloy Ga (oxide) + M in air ~30h **

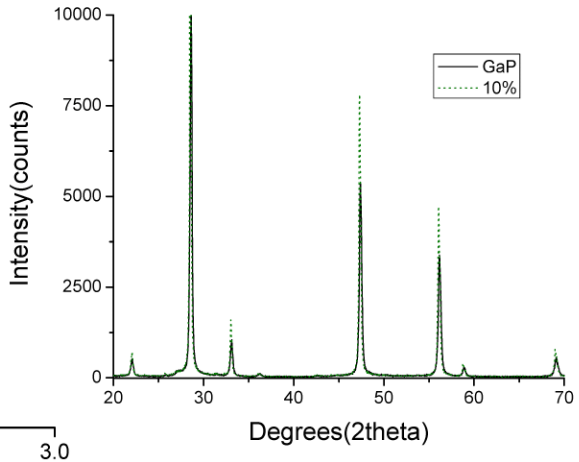
$Ga_xM_{(1-x)}O_x + H_3PO_4 \rightarrow Ga_xM_{(1-x)}PO_x$ [@500ºC in Air ~20h)

$Ga_xM_{(1-x)}PO_x + H_2 \rightarrow Ga_xM_{(1-x)}P + H_2O$

GaP

$Ga_{.9}Mo_{.1}P$





Goal:

(1)Narrow GaP band gap (2.24eV) for efficient capture of solar spectrum.

(2)Improve stability over narrower single metal phosphides (Fe, W, Mo, etc.)

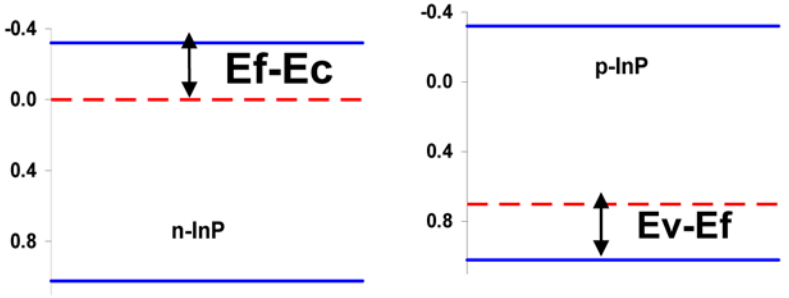
Work to Come: Investigation of the parameter space that includes partial Ga substitution by metals including Fe, Mo, W, Zn, Ni; and partial P substitution by Sb.

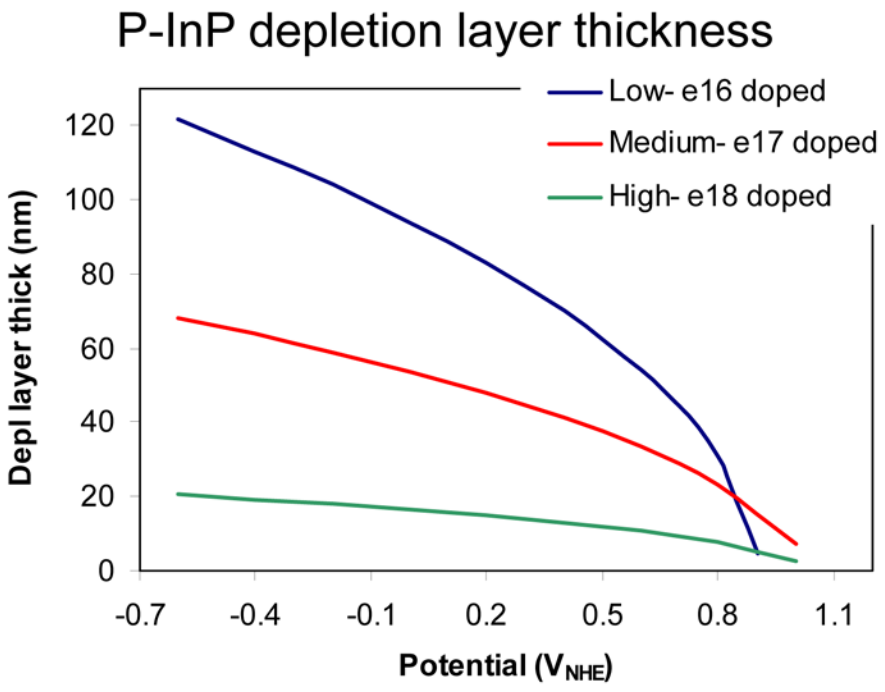
Variation of Fermi level position vs. Ev and Ec with doping density for p and n-InP

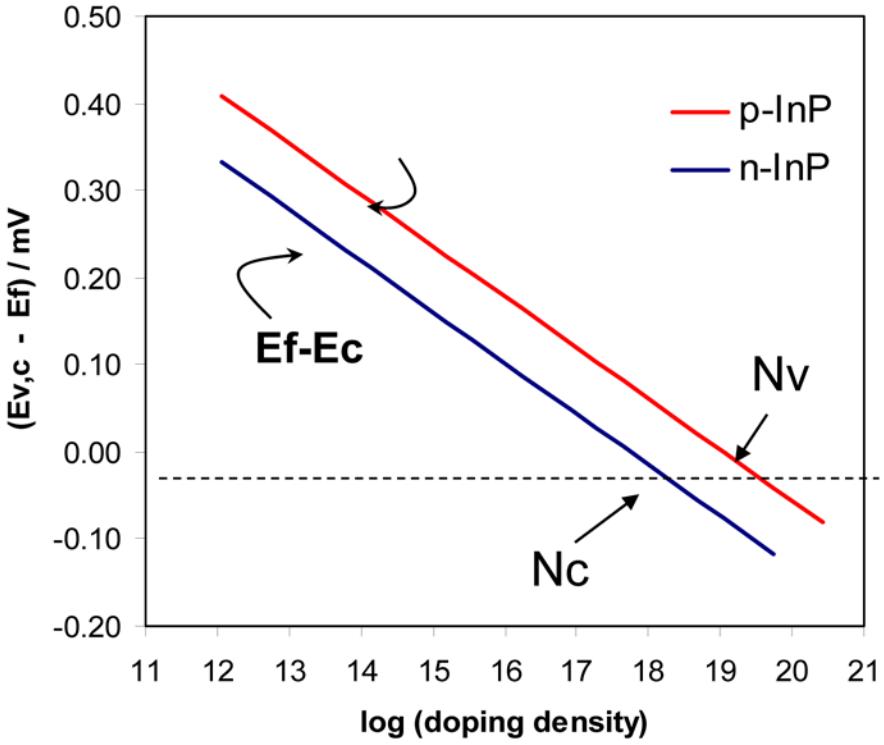
$N_v = 1.11 \times 10^{19}$ /cm^3

$N_c = 5.57 \times 10^{17}$ /cm^3

T ↑ ⇒ slope ↑

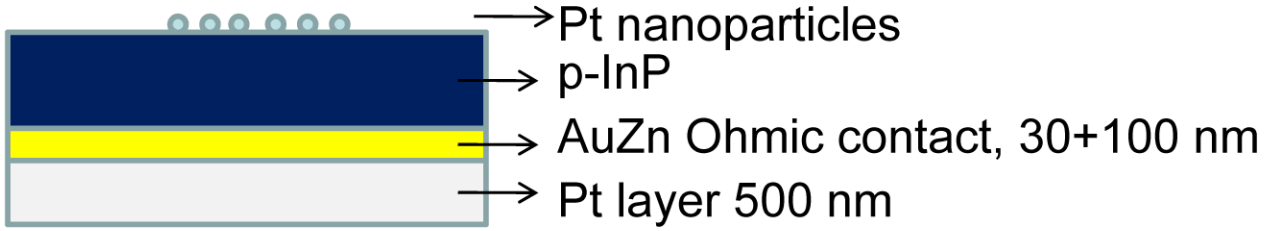


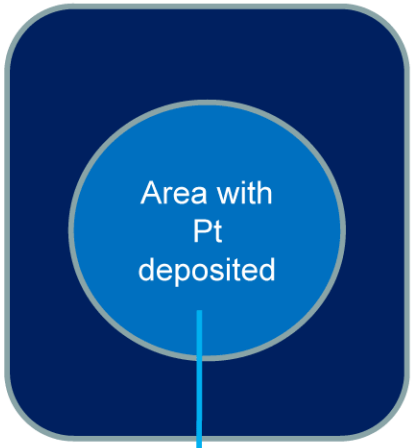




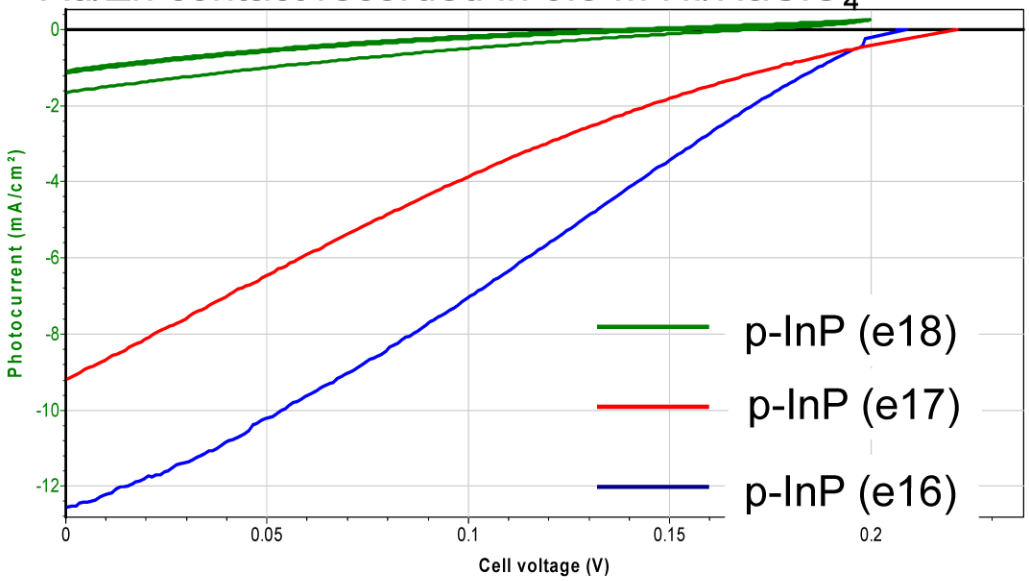
Pt Deposition on p-InP Surface

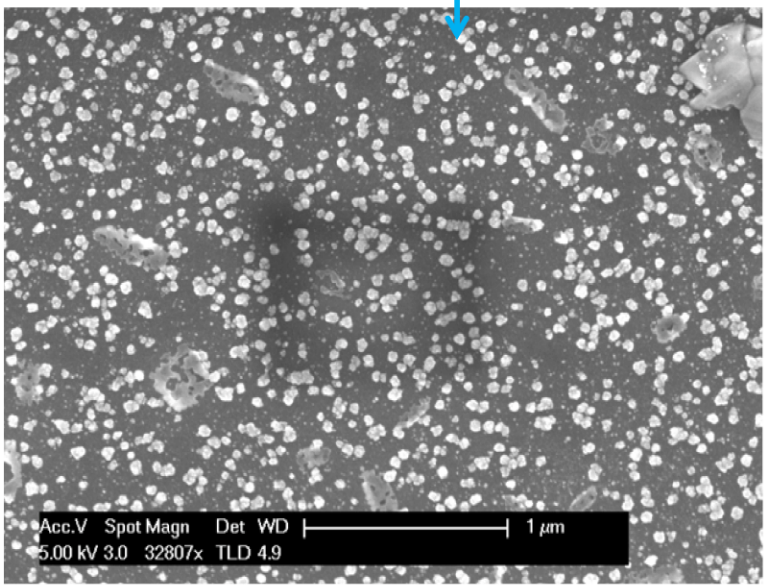
1.6mM H_2PtCl_6, 45 mW/cm^2 -0.35 V vs. Ag/AgCl





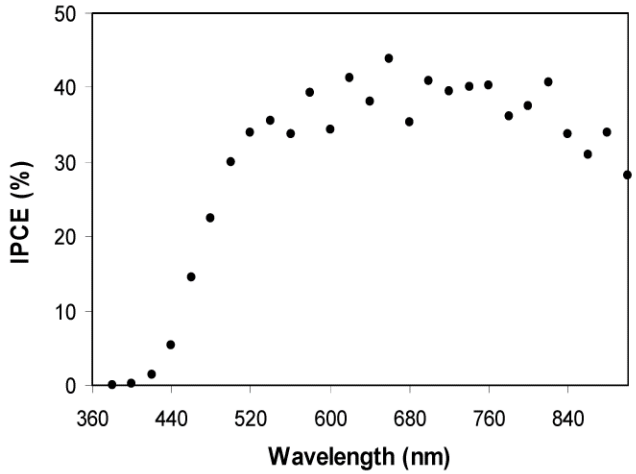
Current-Potential (I-V) response of p-InP (with various doping densities) with photoelectro-deposited Pt and Au/Zn contact recorded in 0.5 M HI/$NaClO_4$



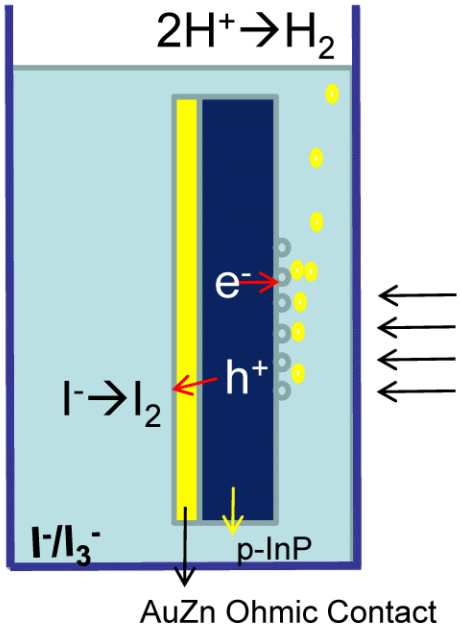


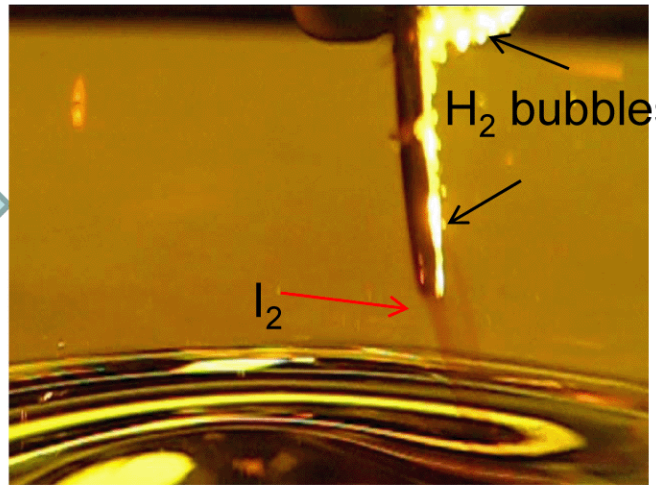
3X10^{16} (Zn/cm^3) p-InP has the best performance

PEC Performance of Low Doped (E16) p-InP with Ohmic Contact in 0.5 M HI/$NaClO_4$ under Zero Bias



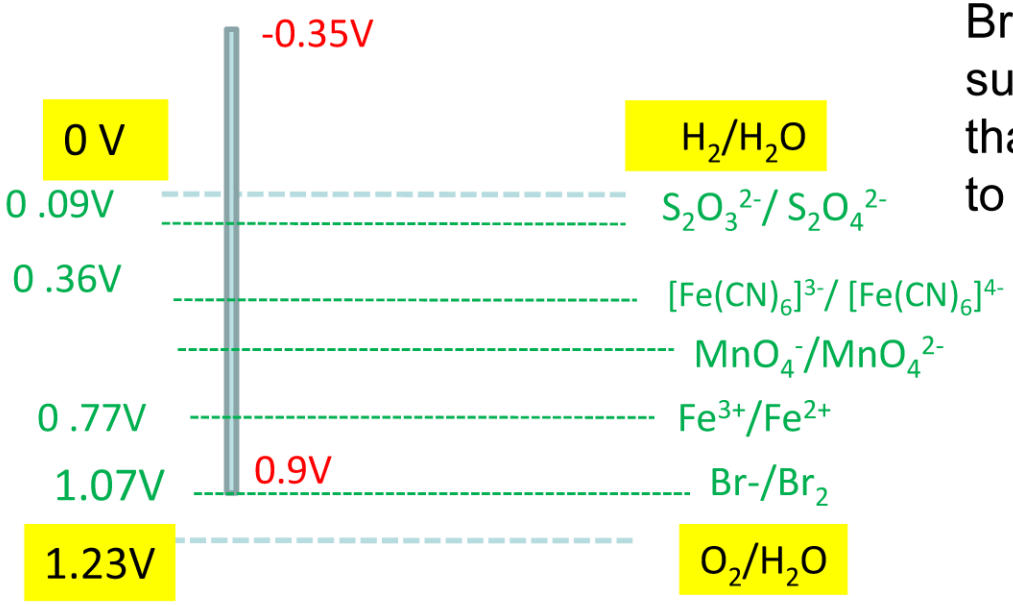
❖Zero bias (2 electrode IPCE for hydrogen production from HI ~40% across abs. band.



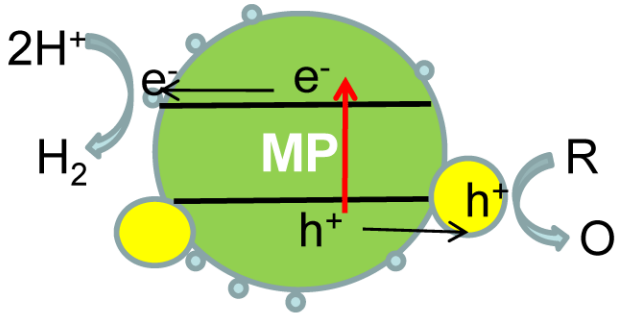


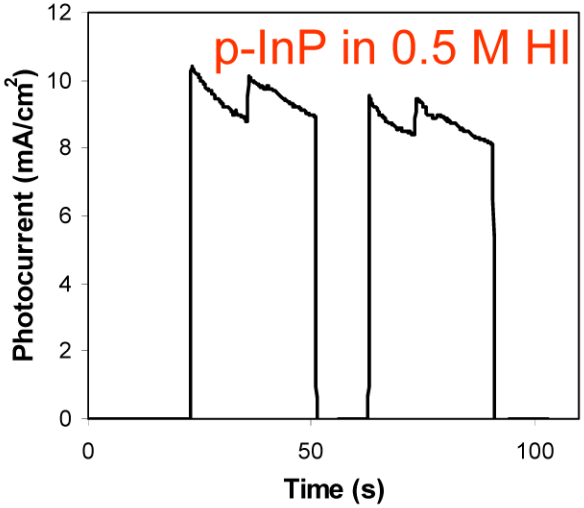
❖ Direct H_2 bubbling was observed on free sample.

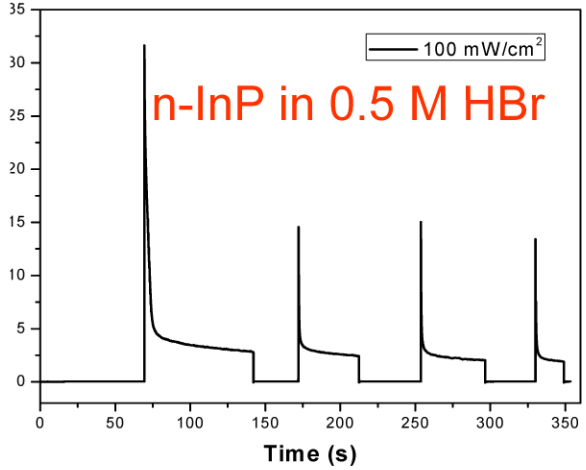
Candidates of Redox Couples and Proposals for Slurry System Using p-InP



Br^- and I^- dissolve many noble metals, such as Au. Thus, other candidates that allow presence of Au-Zn layer are to be sought.







Alloy nanoparticles

Pt Nanoparticles

- n-InP active for HBr splitting
- p-InP active for HI splitting

Schematic Diagram of Fuel Production from Biomass including Solar H_2/Br_2 Recycling System

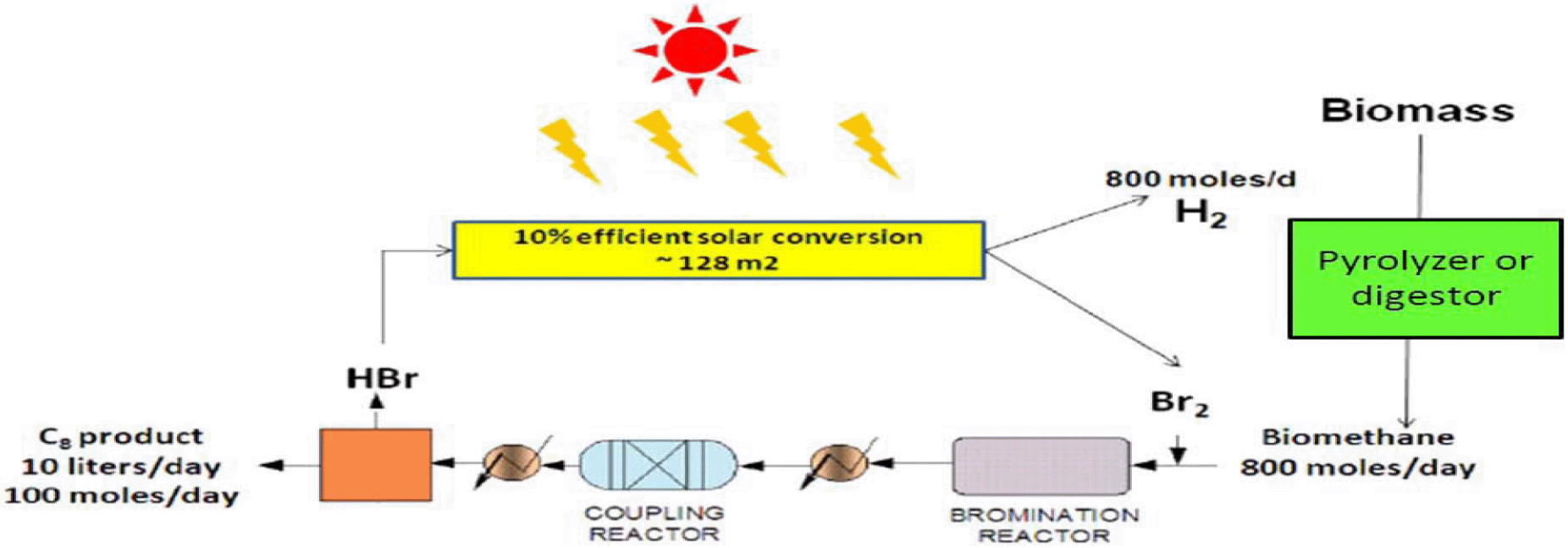


Figure 1. Project Design Schematic[1]

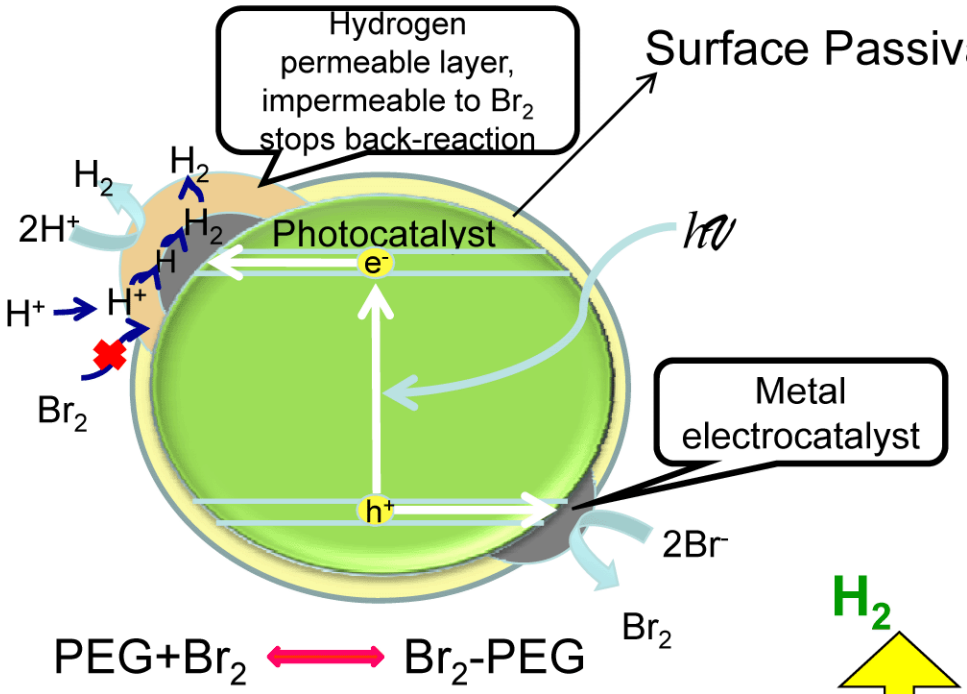
Renewable Energy

1. Biomass → Methane
2. Methane + $Br_2(l)$ → Gasoline +HBr(l)
3. HBr + Sunlight → $H_2(g)$ + $Br_2(l)$

Reasons

- Higher conversion efficiency
- Less energy wasted
- $H_2(g)$ produced

Photoelectrochemical (PEC) Nanoreactor Design



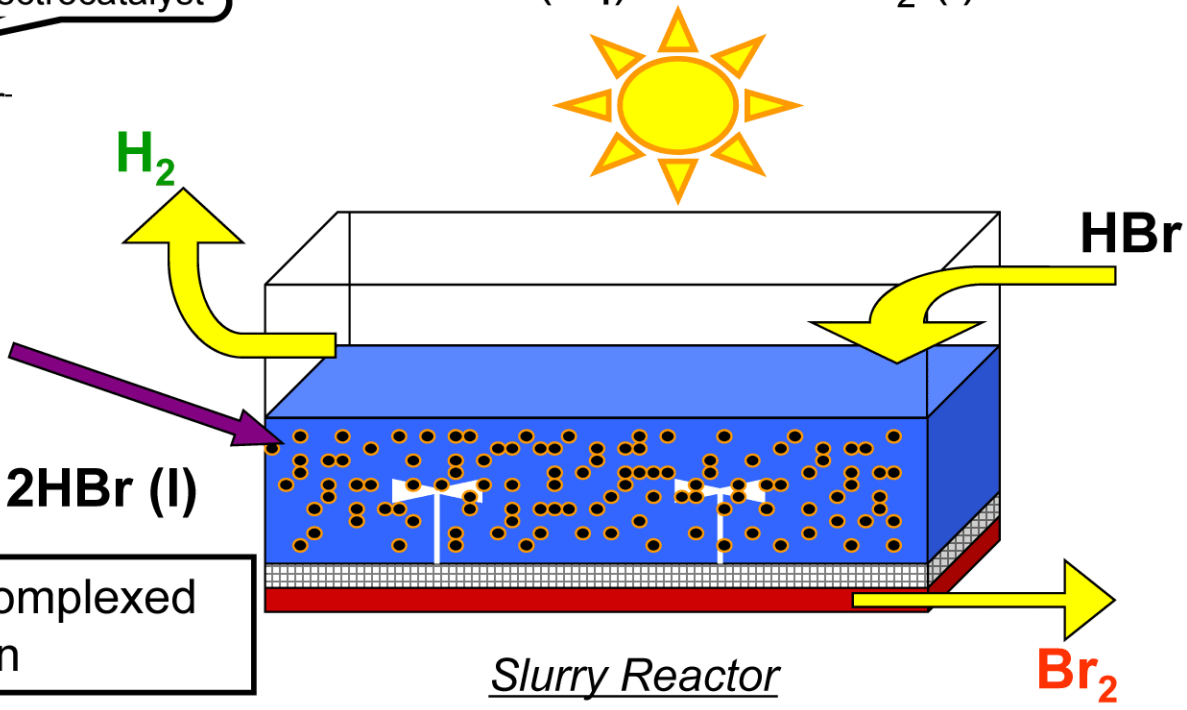
Electrochemical Reactions

Cathodic:

$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

Anodic:

$2Br^-(aq) \rightarrow 2e^- + Br_2 (l)$



PEC Nano-particle

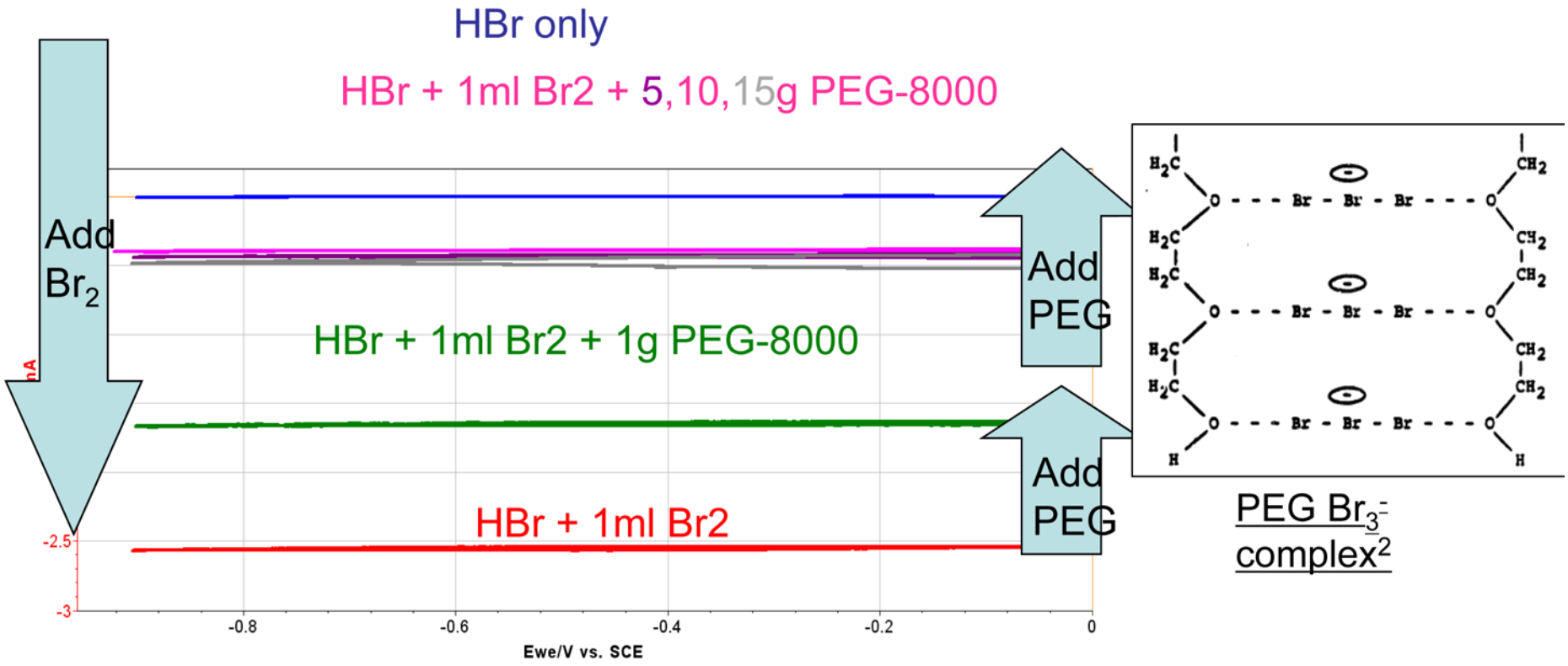
Slurry Reactor

Back-Reaction :

$Br_2(l) + 4H^+(aq) + 4e^- \rightarrow 2HBr (l)$

Complexing agent + Br_2 → Complexed Br_2 for easy extraction

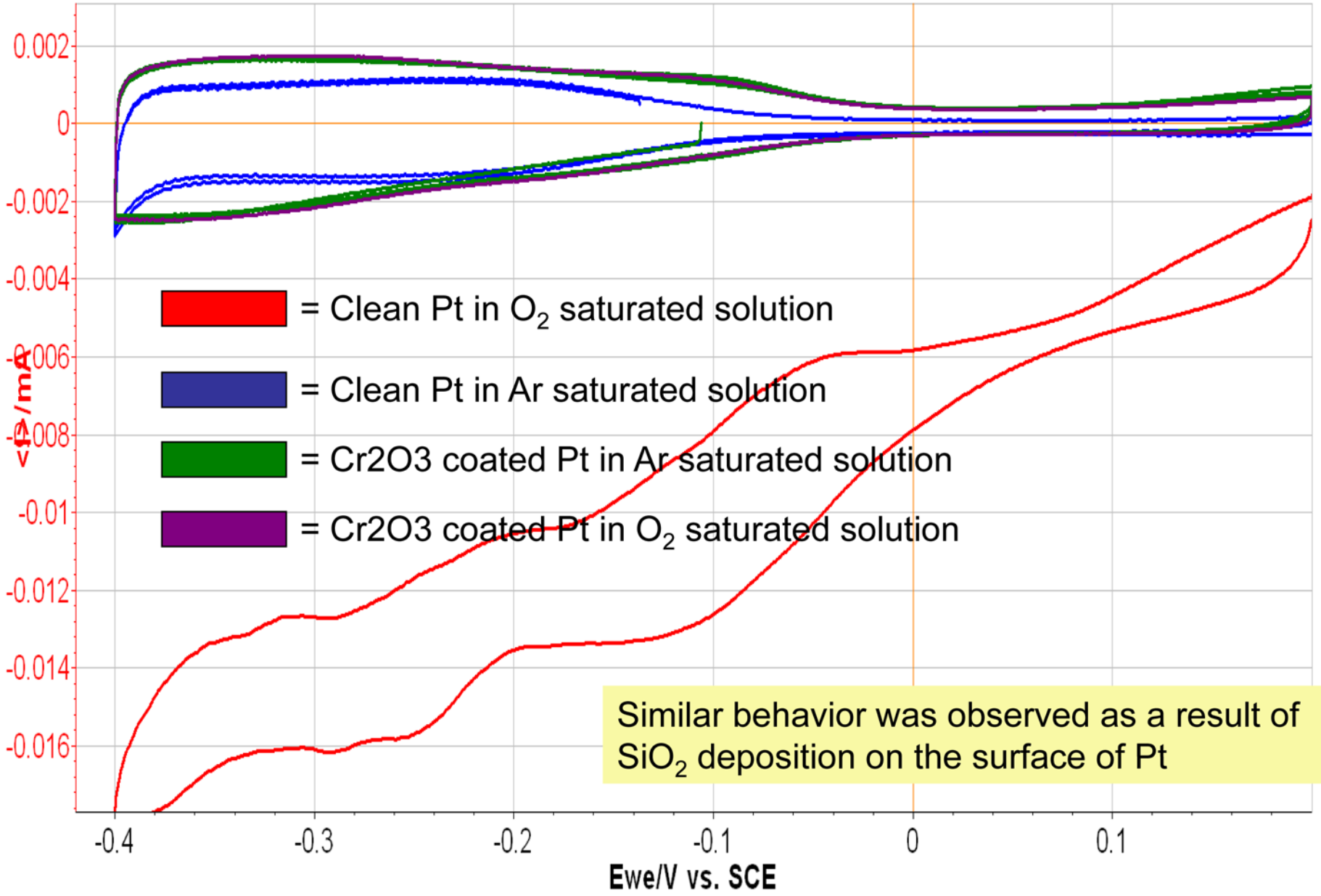
Back-Reaction Range, Various Conditions



❖Cyclic Voltammetry (scan #5), 3M HBr, two-compartment electrochemical cell glassy carbon working electrode, complexing agent: PEG-8000, scan range: 0 to -0.9V

❖Addition of PEG significantly restrains the back reaction of Br-/Br_2

Pt vs. Cr_2O_3 coated Pt in 0.5M Na_2SO_4, pH = 3.6
Cr_2O_3 layer has eliminated O_2 reduction



Similar behavior was observed as a result of SiO_2 deposition on the surface of Pt

Summary

- **New PEC Materials (Tasks 1-2)**
  - **Oxides:**
    - **Iron Oxide: We have substituted over 32 different "dopants" at several concentrations into hematite. Significant improvements were often observed, however, none of the magnitude required to give reason to pursue iron oxides further.**
    - **Theory inspired synthesis and characterization of $CuMO_2$ Delafossite type oxides was completed for M=Cr,Fe,Ga,La. All had poor PEC performance.**
    - **No oxide semi-conductor has yet been shown to be a practical candidate for hydrogen production by PEC.**
  - **Non-oxides:**
    - **Initial work with phosphides shows InP to have extremely high IQE and IPCE for hydrogen production using oxidants other than water.**
    - **Initial syntheses of new phosphides from oxides in format for high-throughput testing promising.**

- **Surface Passivation and Electrokinetics (Tasks 3-6)**
  - **Surface integrity (cracks and pinholes) less of a concern than other factors.**
  - **Pt electrocatalysts may be photoreduced on p-type phosphides after synthesis.**
  - **Passivation of phosphide surface with stable oxides permeable to hydrogen may be used to block back reaction.**

- **New Systems and Technoeconomics (Tasks 7-9)**
  - **Intial exploration of hydrogen production from HX haloacids coproduced with biogasoline in a biomethane process using X_2 halogens as a methane activating agent is promising and allows use of more efficient PEC materials.**

Future Work

- ***Synthesis and Screening of New Materials and Structures:***
  - ***2010 Focus Phosphides***
  - ***High-throughput screening and selected physical, electronic, and photoelectrochemical characterization of phosphides made from oxides.***
  - ***Solution phase synthesis of p-n junctions, $Cu(M)O_2$ /TiO_2***
- ***New Redox Systems:***
  - ***Develop slurry based system stable in HBr for production of H_2 and Br_2***
  - ***Integrate into biomethane based fuel producing system.***

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 ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE NREL