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

Eric W. McFarland
Department of Chemical Engineering
University of California, Santa Barbara
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Project ID # PD034

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

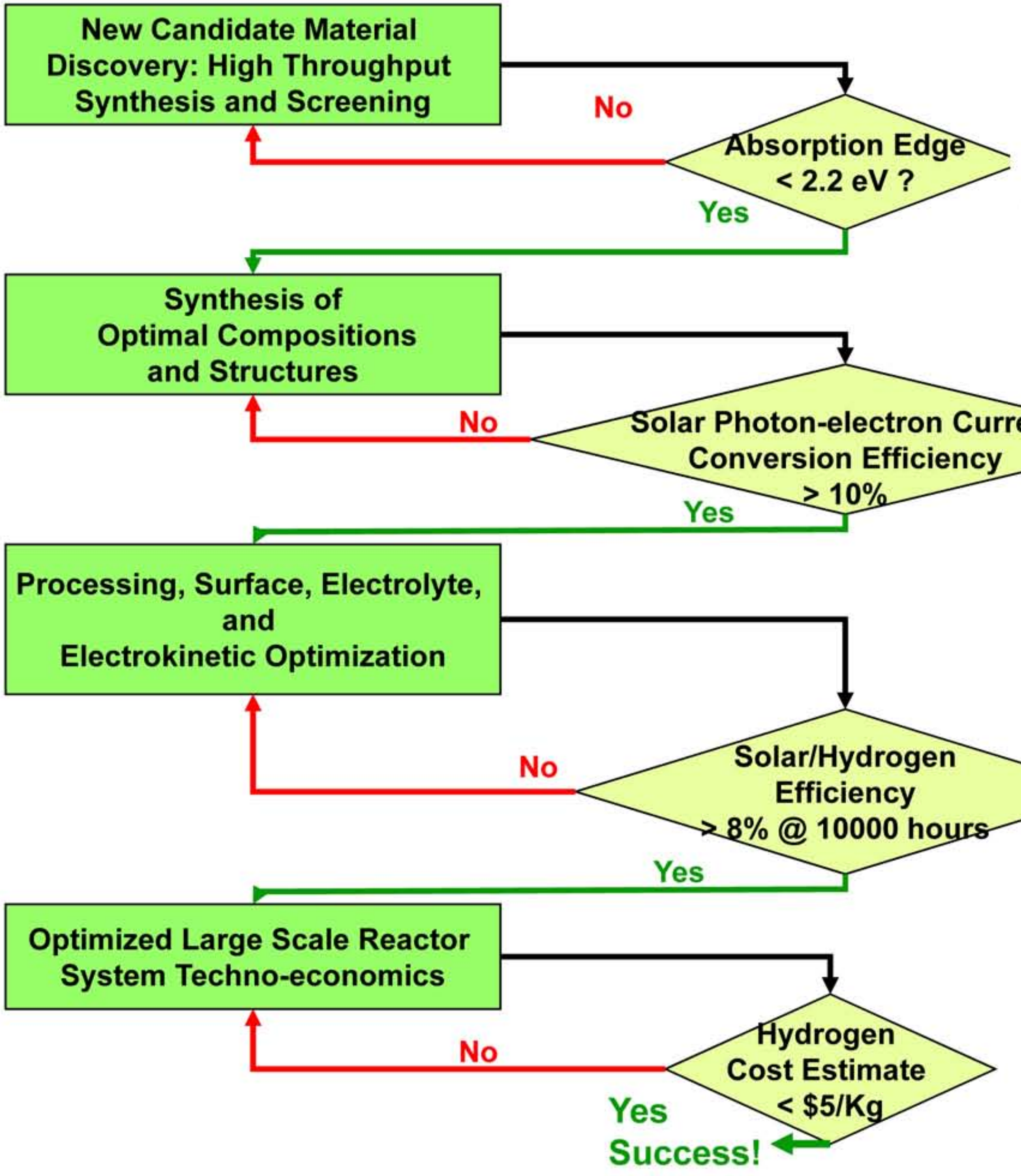
Relevance

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

Absorption Edge < 2.2 eV ?

No

Yes

Synthesis of Optimal Compositions and Structures

Solar Photon-electron Current Conversion Efficiency > 10%

No

Yes

Processing, Surface, Electrolyte, and Electrokinetic Optimization

Solar/Hydrogen Efficiency > 8% @ 10000 hours

No

Yes

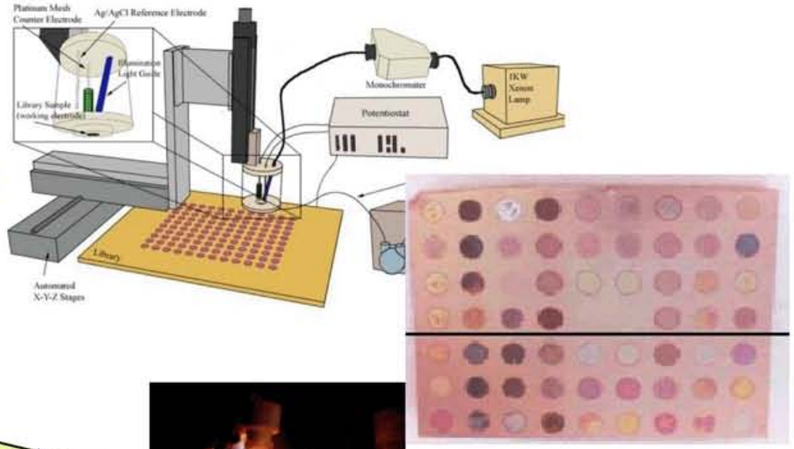
Optimized Large Scale Reactor System Techno-economics

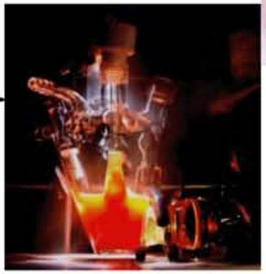
Hydrogen Cost Estimate < $5/Kg

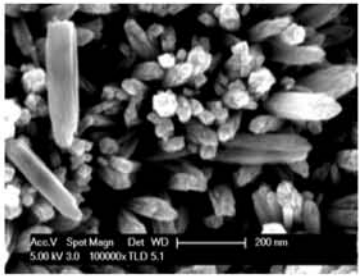
No

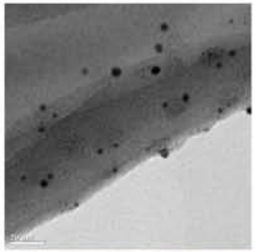
Yes

Success!









Material-Class Synopsis

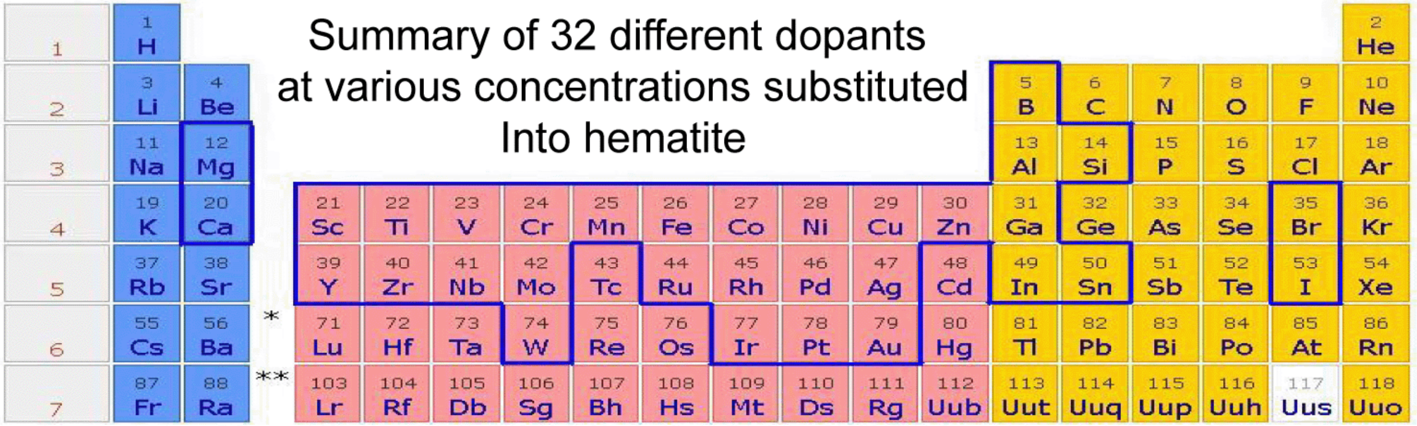
Iron Oxide

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

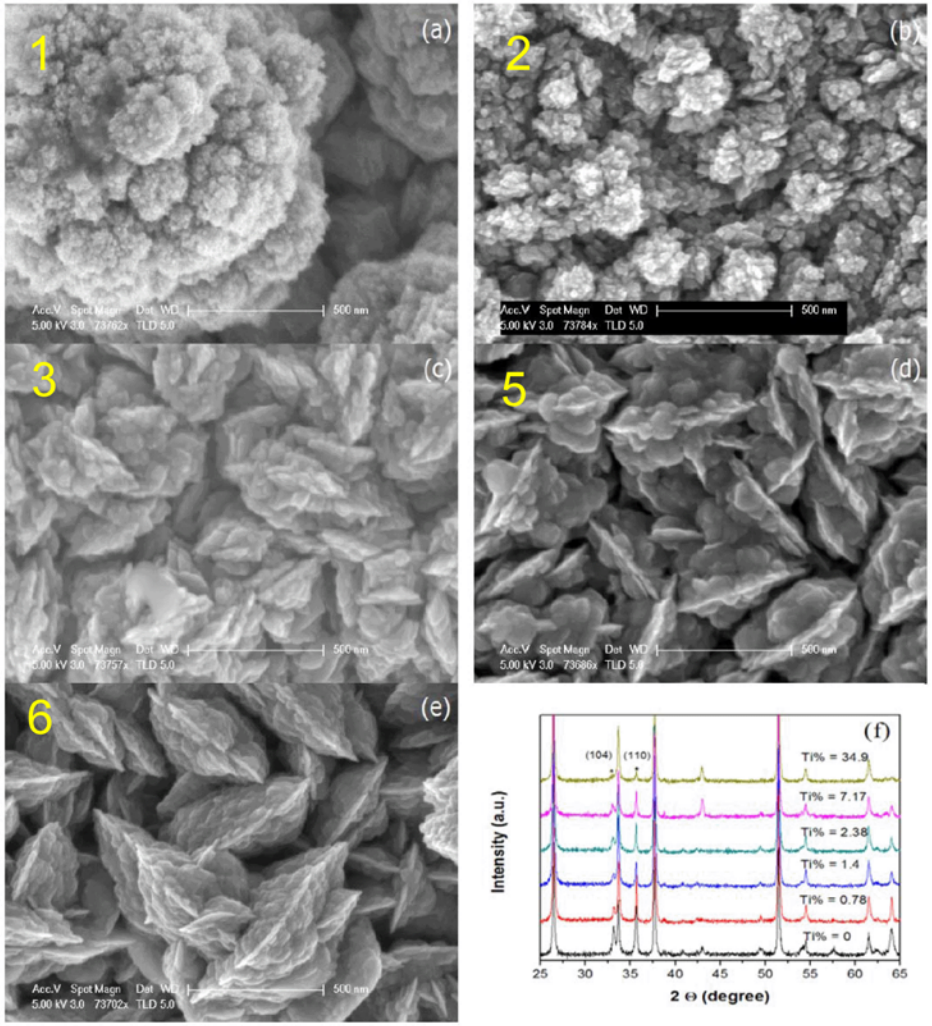
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	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

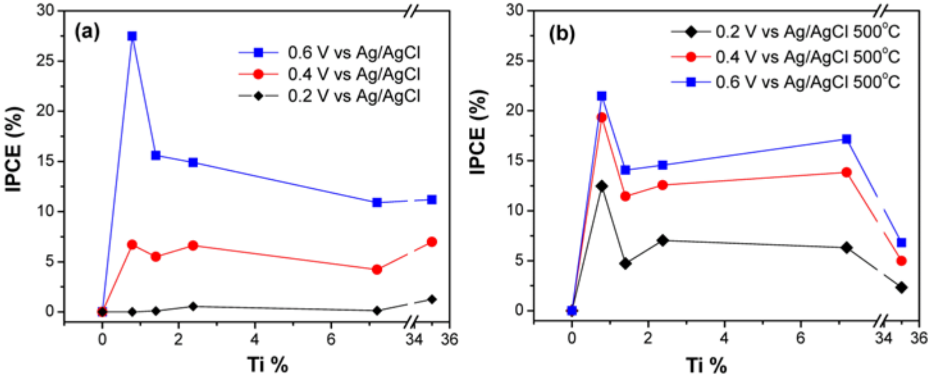
- Higher valence dopants (Pt, Mo, Cr, Ti): increased IPCE by 10x
  → n-doping, increased carriers, increased mobility and conductivity
- Isovalant substitutions with large cation size differences (Al): increased IPCE
  → strain, increased Fe-d overlap, increased hoping conduction
- No significant change 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





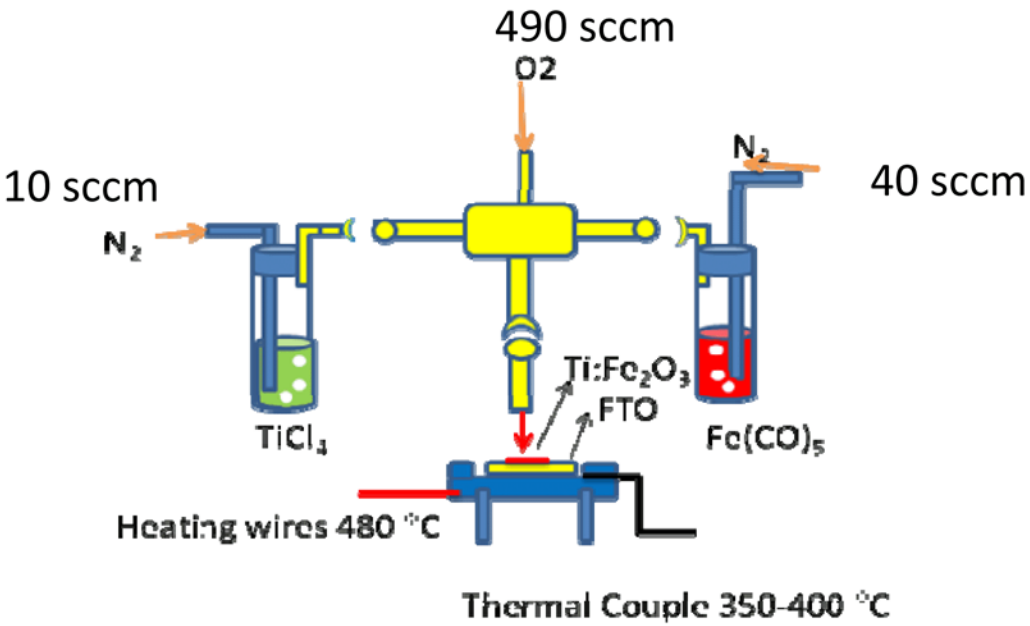
As prepared

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



490 sccm

O2

10 sccm

N_2

N_2

40 sccm

$TiCl_4$

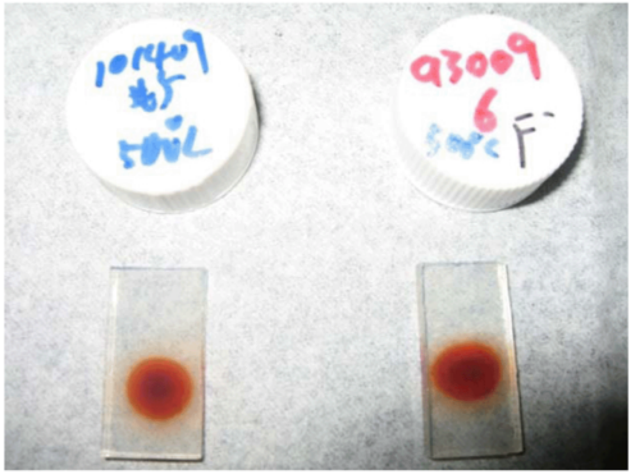
$Ti:Fe_2O_3$

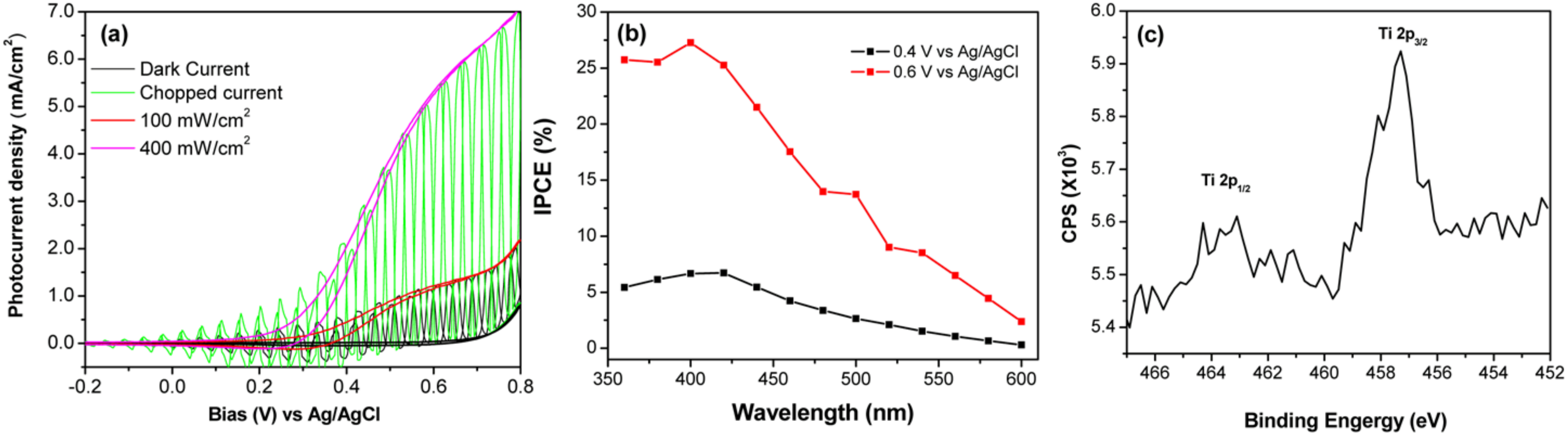
FTO

$Fe(CO)_5$

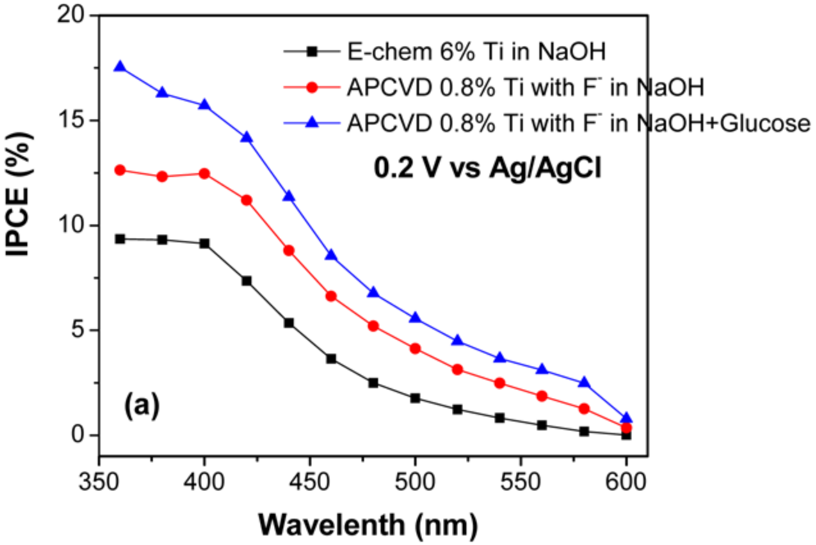
Heating wires 480 °C

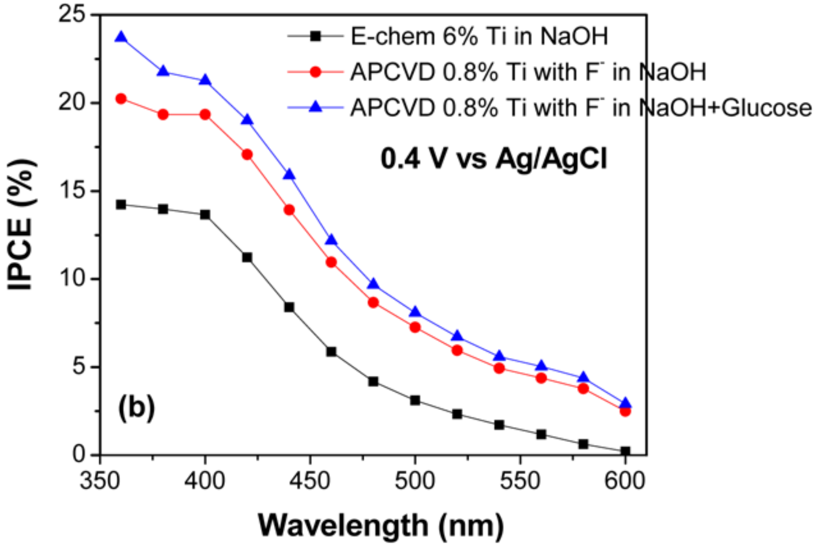
Thermal Couple 350-400 °C

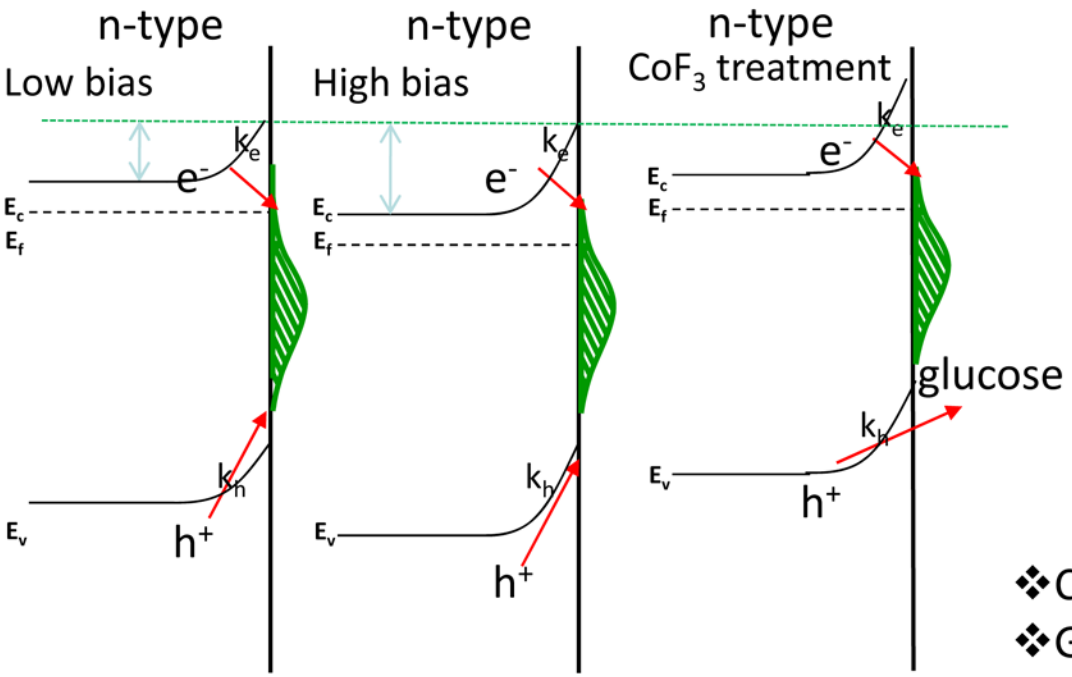


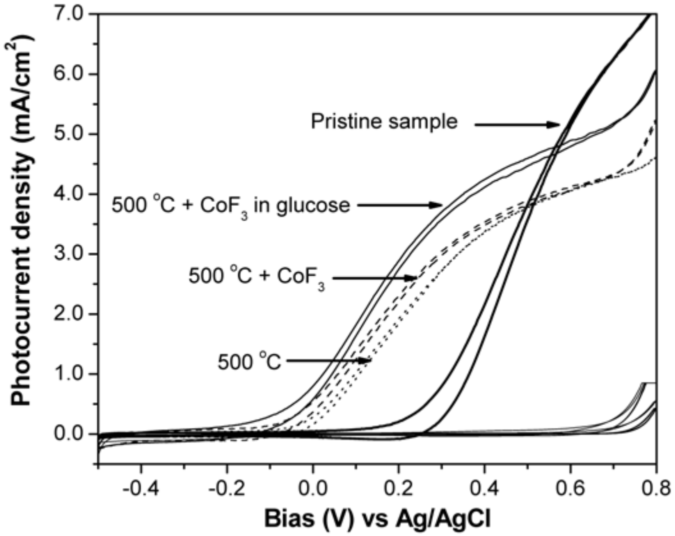


IPCE of CoF_3 Surface Modified $Ti:Fe_2O_3$ Thin Films Using Glucose as Reductant; Comparison with the Best E-chem Sample





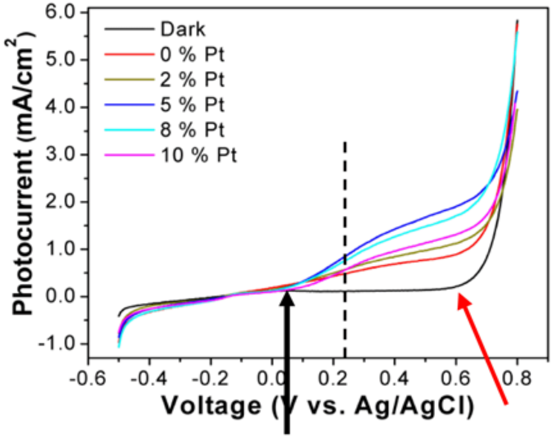




- ❖ CoF_3 treatment shifts the bands upward
- ❖ Glucose is easier to be oxidized by holes

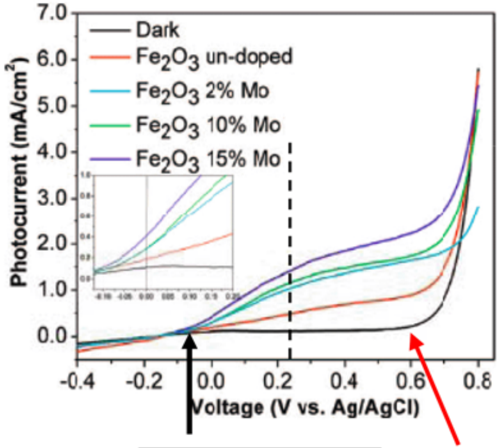
Hematite Performance & Device Quality

E-chem; Pt doped



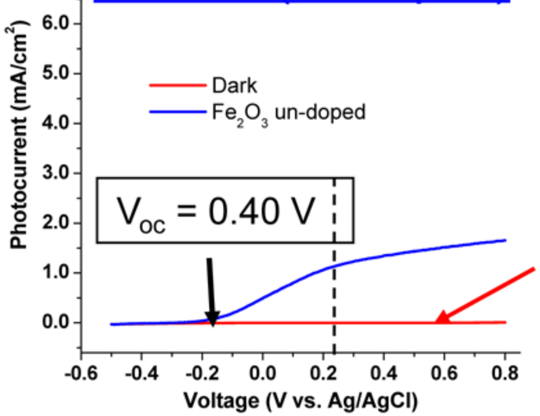
V_{oc} = 0.20 V

E-chem; Mo doped



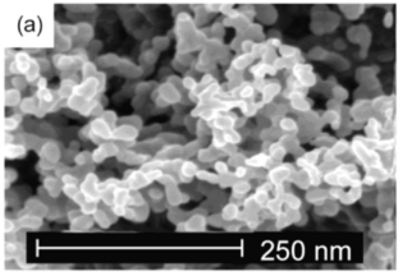
V_{oc} = 0.30 V

E-beam (un-doped)

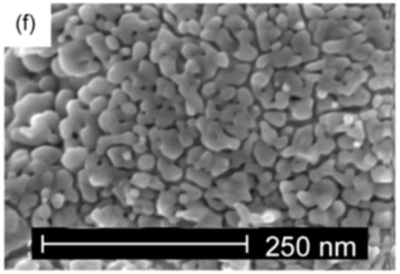


V_{oc} = 0.40 V

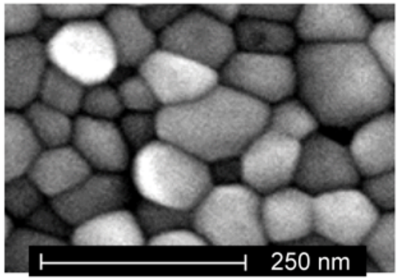
E-chem (un-doped)



E-chem (Mo doped)



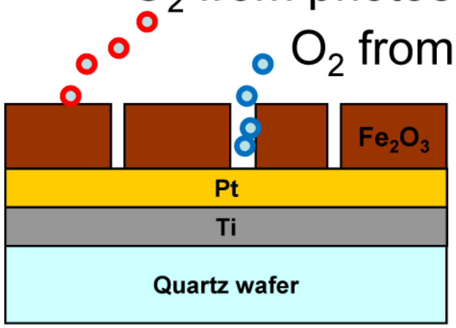
E-beam (un-doped)



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

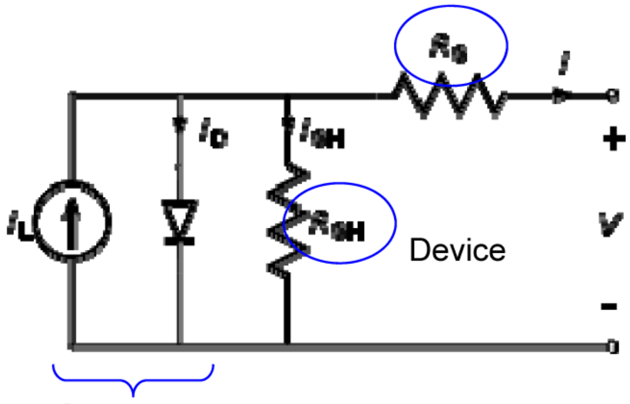
J. Phys. Chem. C, **2008**, 112 (40), 15900–15907
Chem. Mater. **2008,** *20,* 3803–3805

Shunt Resistance and Pinholes – Device Quality



O_2 from photoelectrolysis

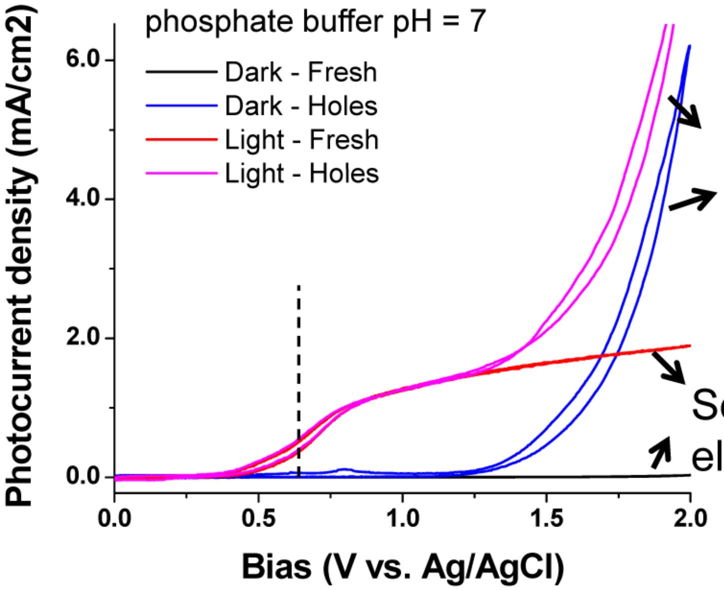
O_2 from electrolysis on Pt and hematite



Hematite

Device

Solar cell



H_2O oxidation on Pt

Semiconductor electrode

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

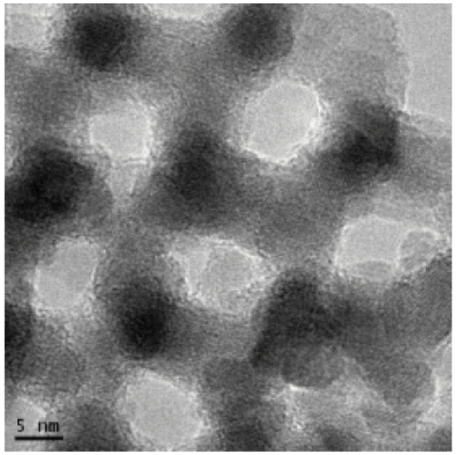
Delafossite Material-Class Synopsis

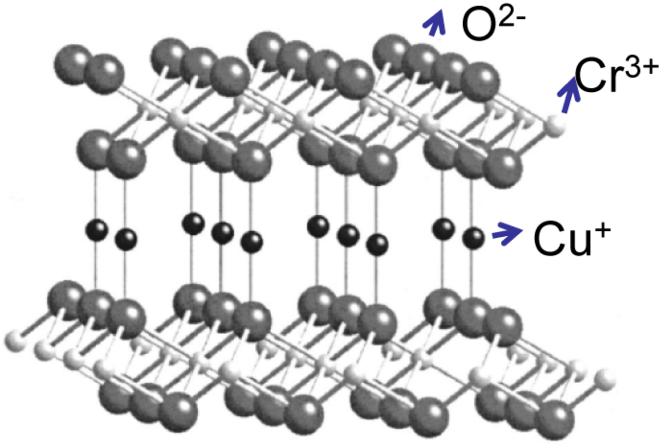
promise

- **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

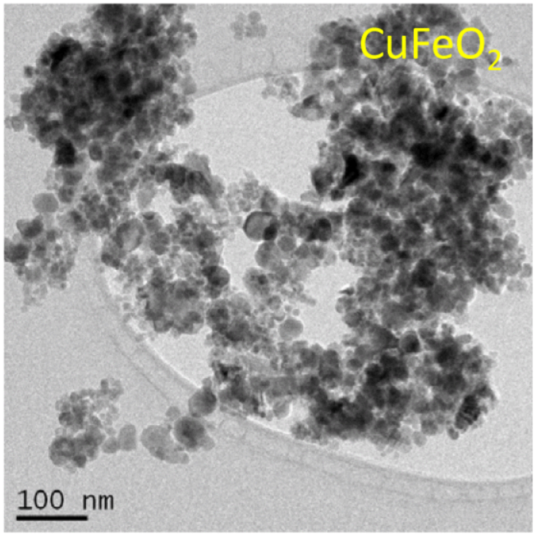
- ➢ **Stability under illumination**
- ➢ **High recombination rates**
- ➢ **Valence and conduction Band position**
- ➢ **Water Oxidation Kinetics**

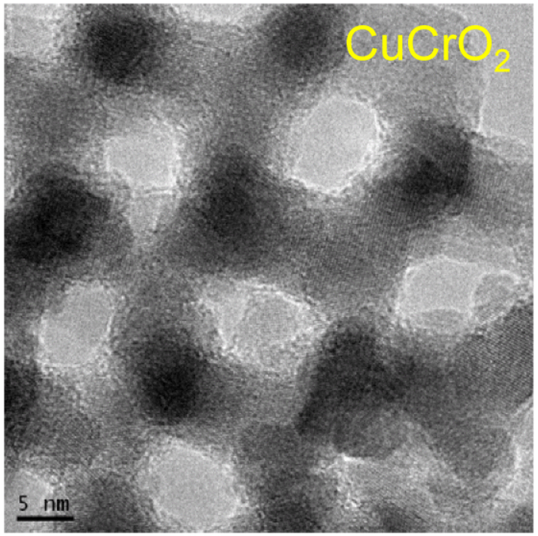


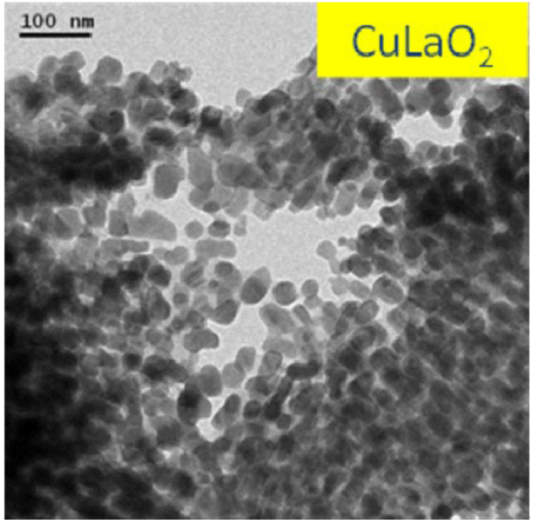


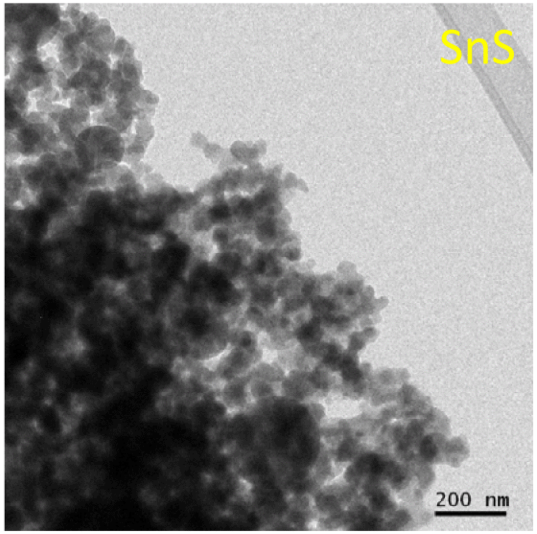
Mesoporous Delafossite and Spinel Structures

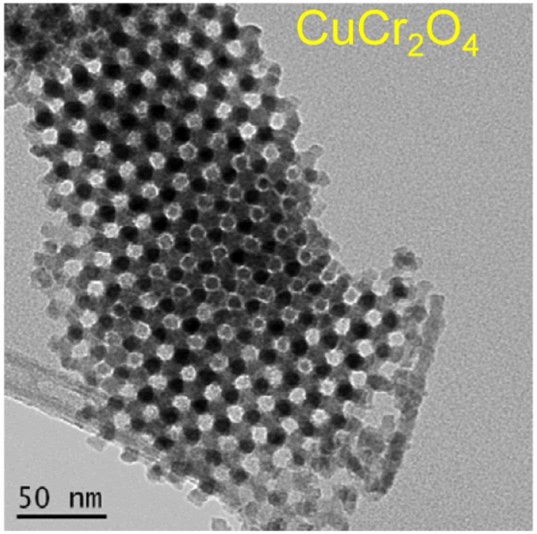
----variety of new materials synthesized

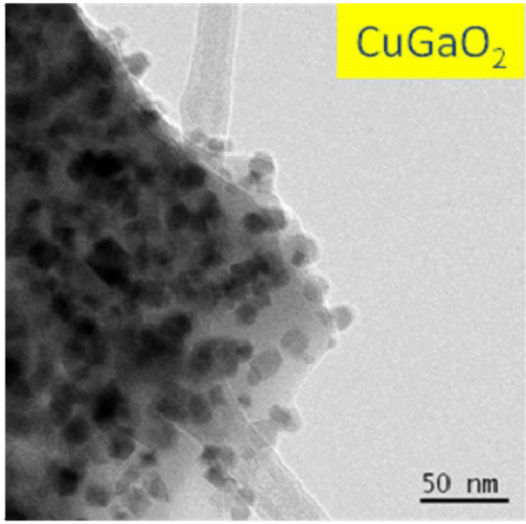






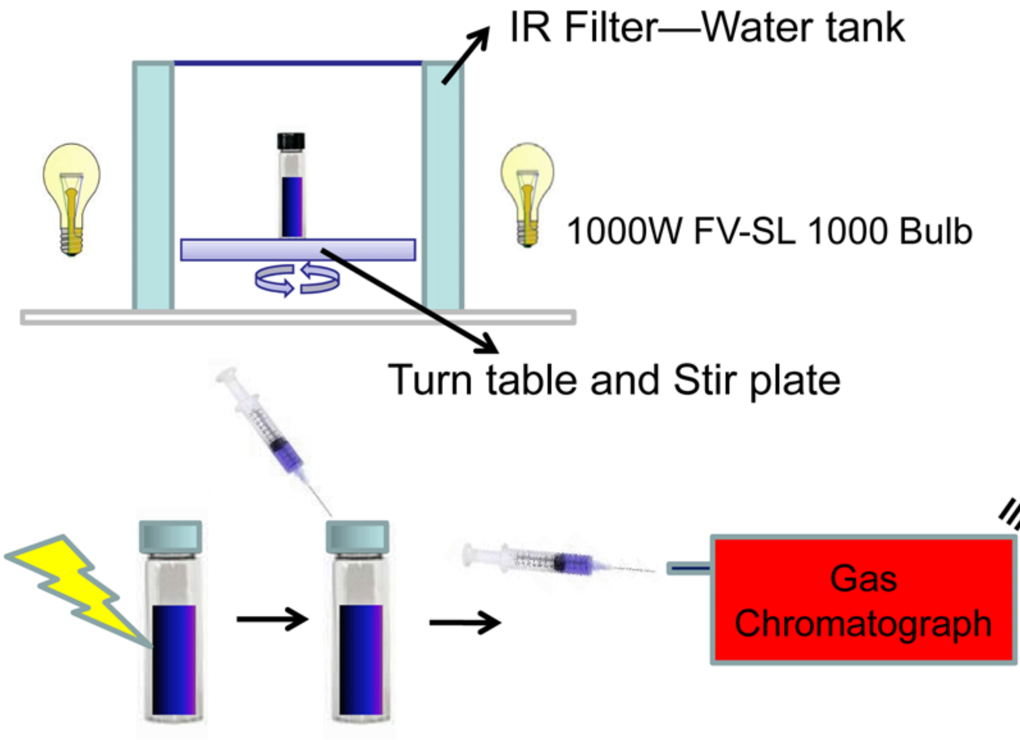


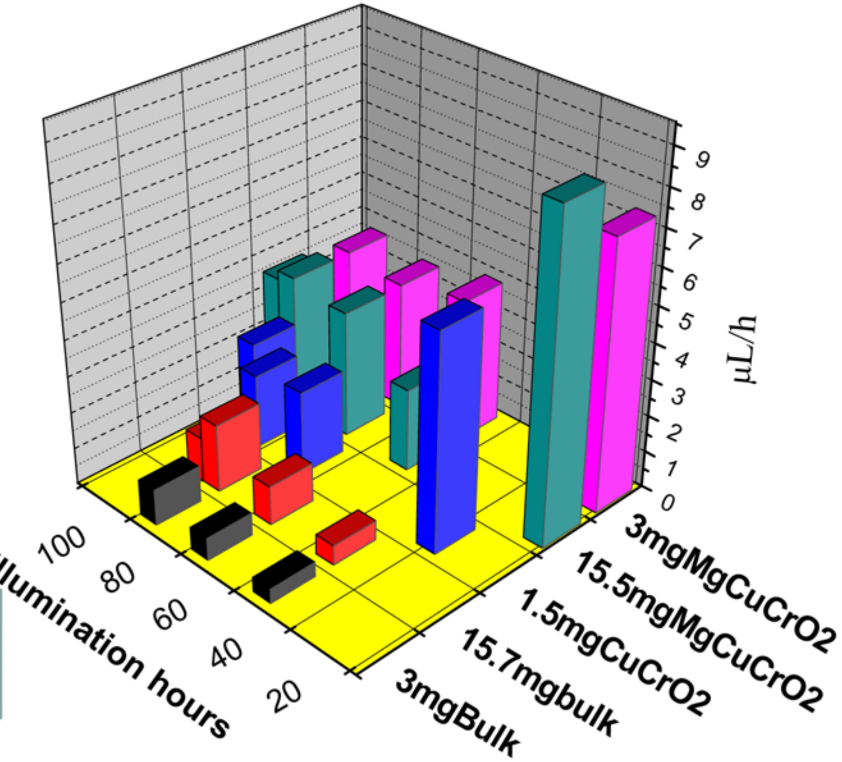




$CuCrO_2$, Ar, 1000 °C SA=90.1 m^2/g
$CuCr_2O_4$, Air, 950 °C, SA = 68.8 m^2/g

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

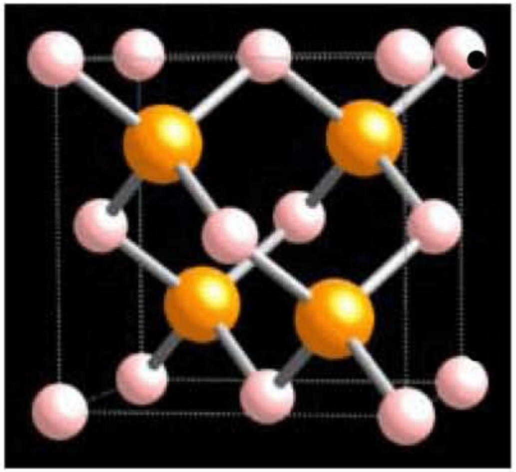
- Stability
- Valence Band Edge
- Water Oxidation Kinetics

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.

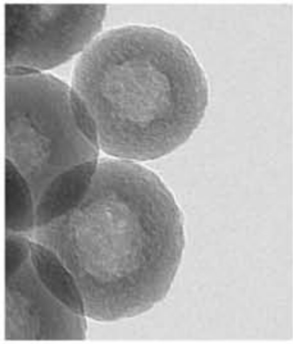
Phosphides

(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

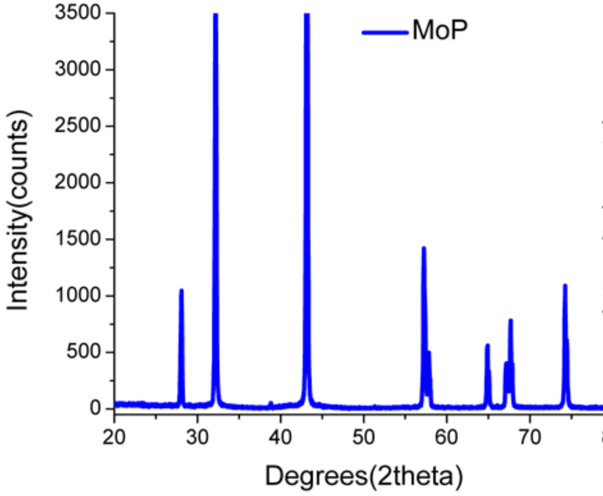
Zn_3P_2

Ni_2P

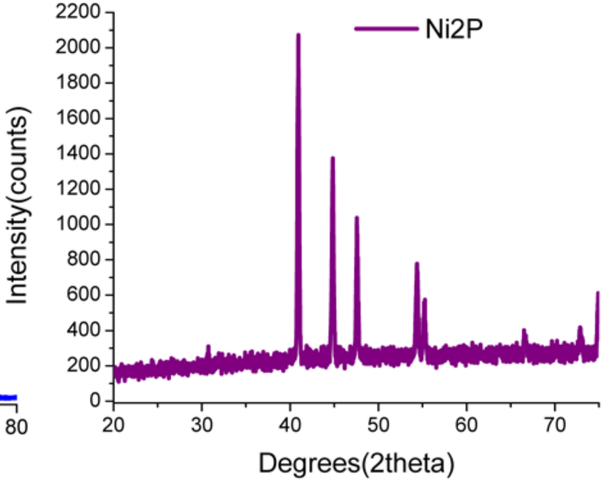
WP

MoP

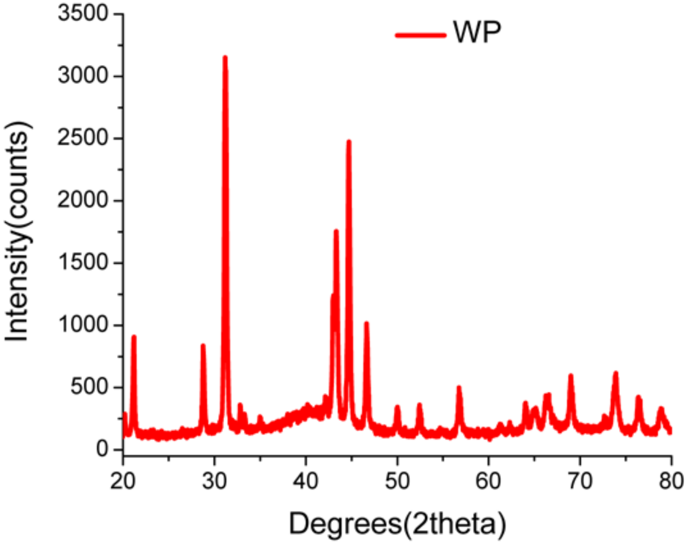
X-Ray Diffraction of Powder Phosphides From Metal Oxides



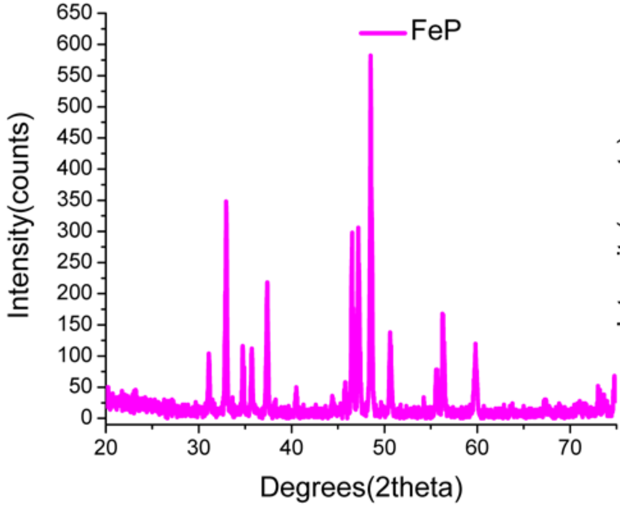
Single Phase MoP



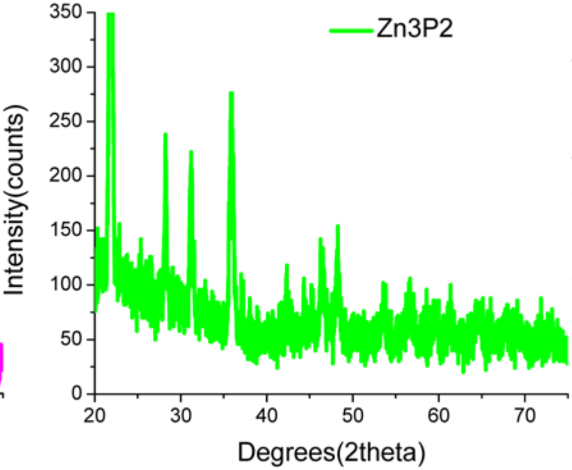
Nearly phase-pure Fe$_2$P (>5% NiP)



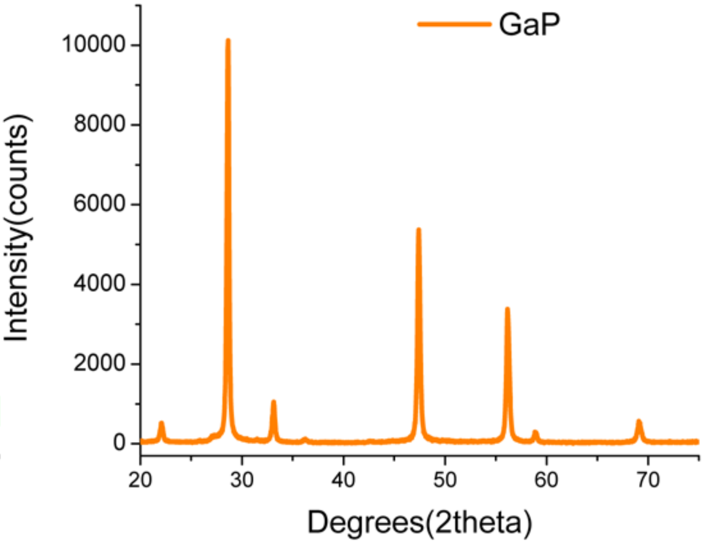
Single Phase MoP



Nearly phase-pure FeP (>5% Fe$_2$P)



Mixed ZnP2 and ZnP4



Single Phase GaP

Materials Engineering: Mixed Metal Phosphides

Modified Synthesis:

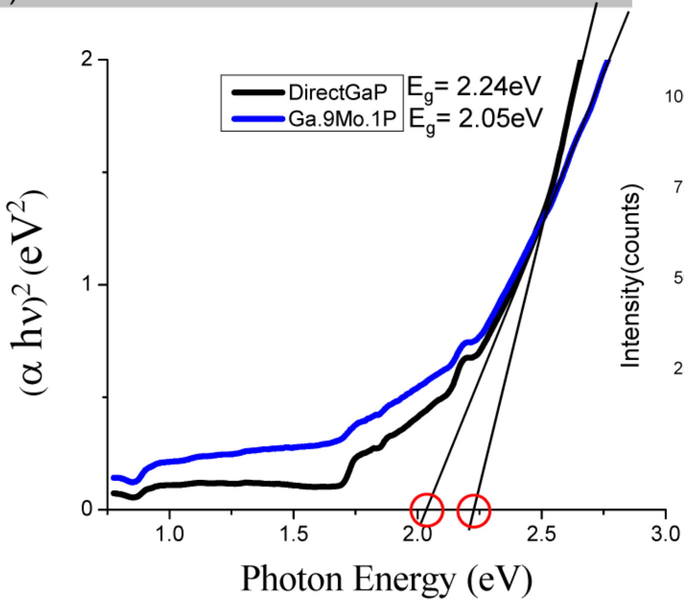
Alloy Ga (oxide) + M in air ~30h **

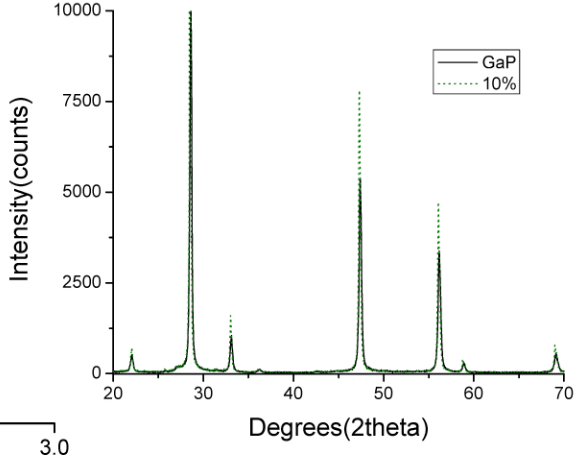
$Ga_xM_{(1-x)}O_x + H_3PO_4 \rightarrow Ga_xM_{(1-x)}PO_x$ [@500ºC in Air ~20h)

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

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.)

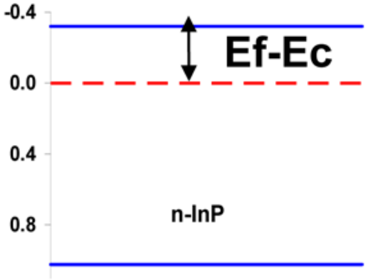
Work to Come: Investigation of the parameter space that includes partial Ga substitution by metals including Fe, Mo, W, Zn, Ni; and partial P substitution by Sb.

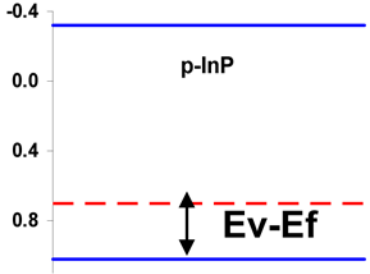
Variation of Fermi level position vs. Ev and Ec with doping density for p and n-InP

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

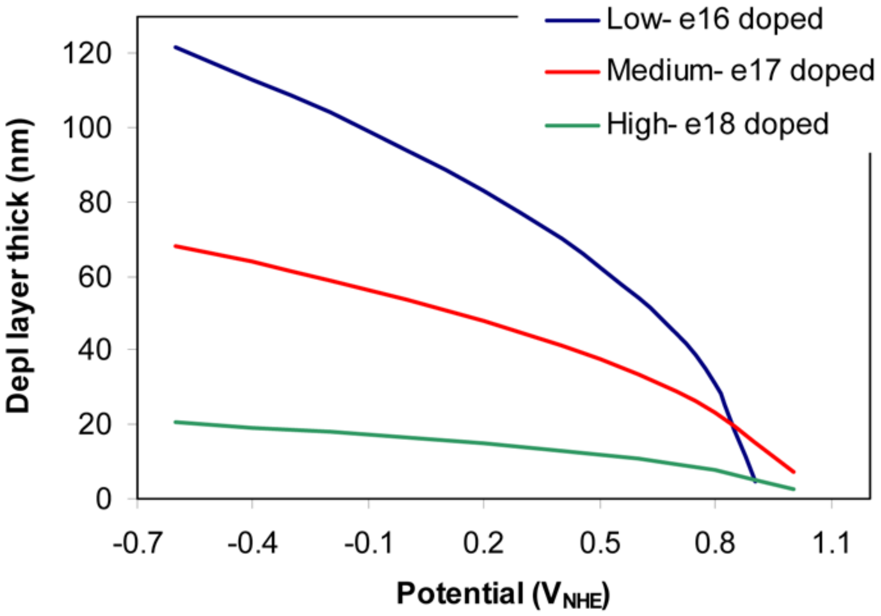
$N_c = 5.57 \times 10^{17}$ /cm^3

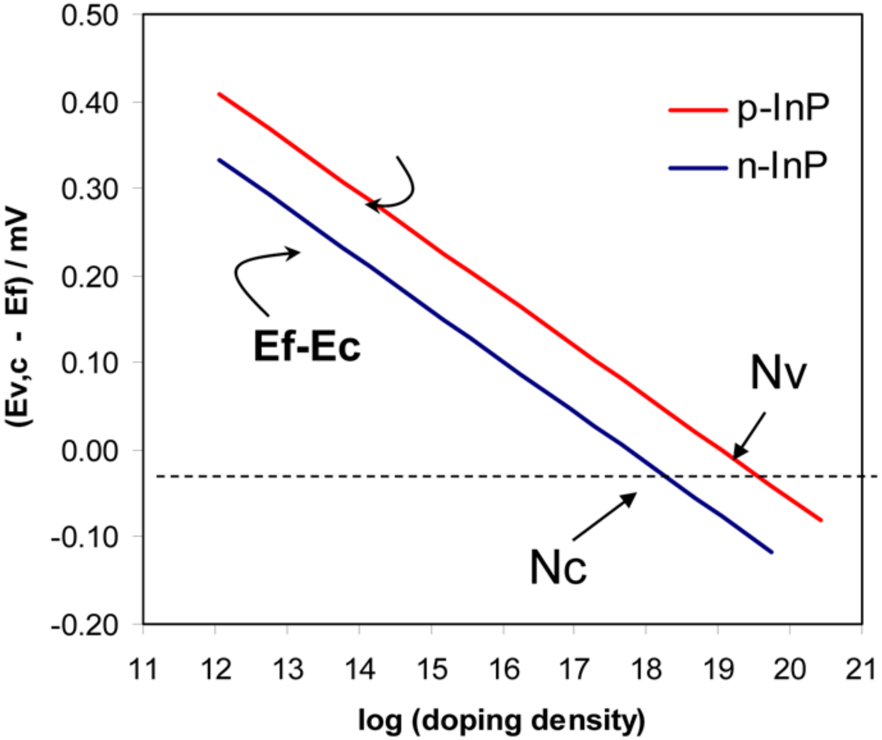
T ↑ ⇨ slope ↑





P-InP depletion layer thickness





Pt Deposition on p-InP Surface

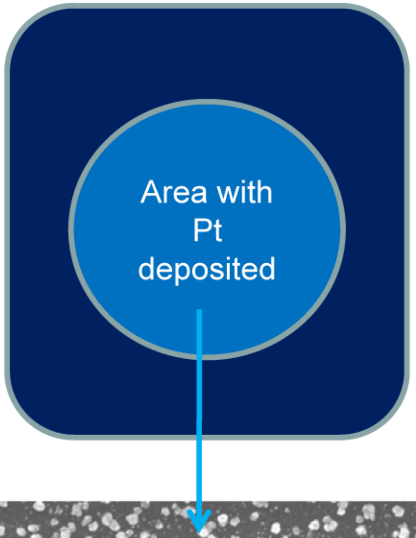
1.6mM H_2PtCl_6, 45 mW/cm^2 -0.35 V vs. Ag/AgCl

→ Pt nanoparticles

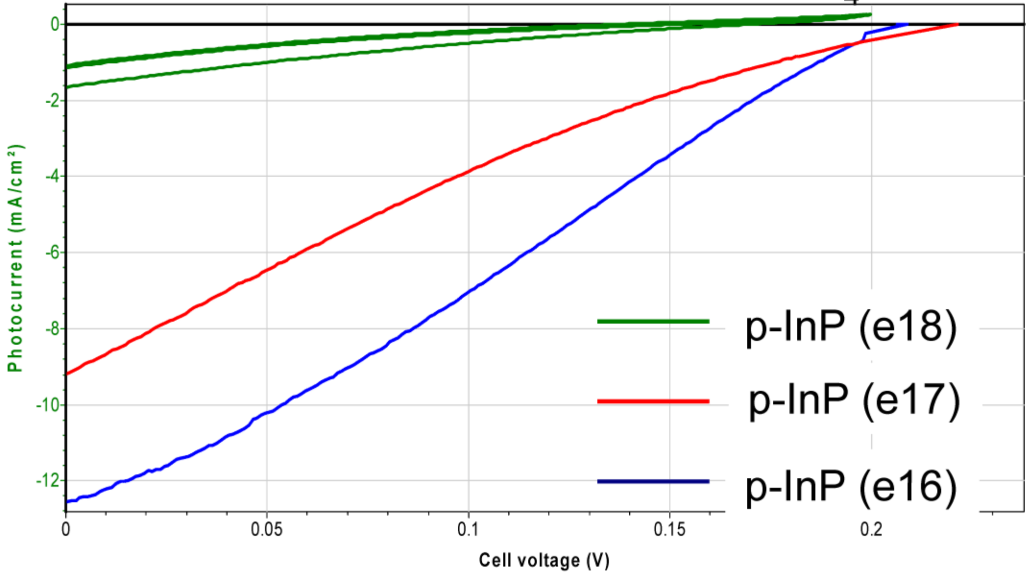
→ p-InP

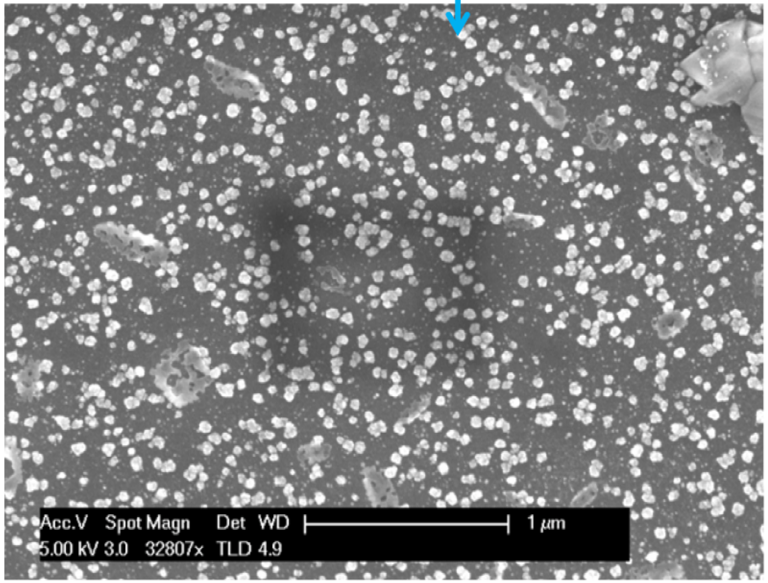
→ AuZn Ohmic contact, 30+100 nm

→ Pt layer 500 nm



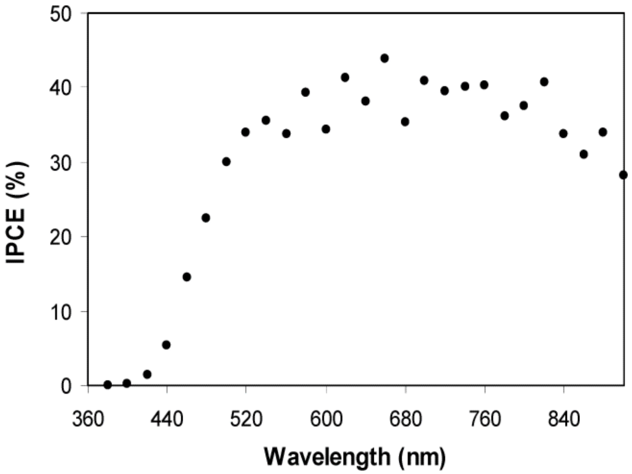
Current-Potential (I-V) response of p-InP (with various doping densities) with photoelectro-deposited Pt and Au/Zn contact recorded in 0.5 M HI/NaClO$_4$



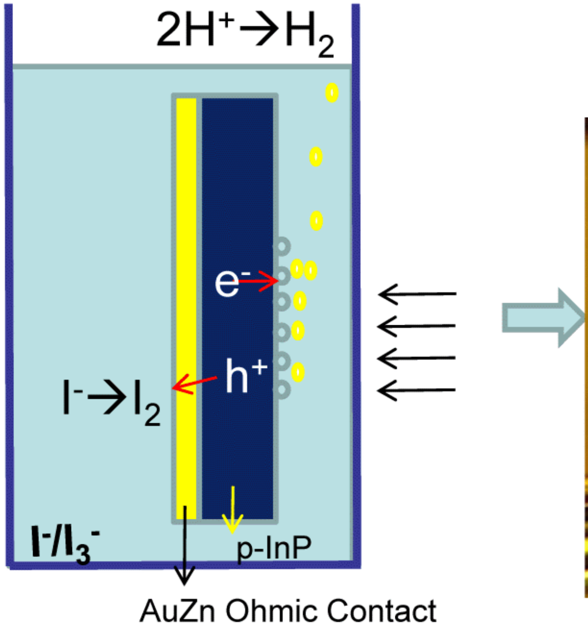


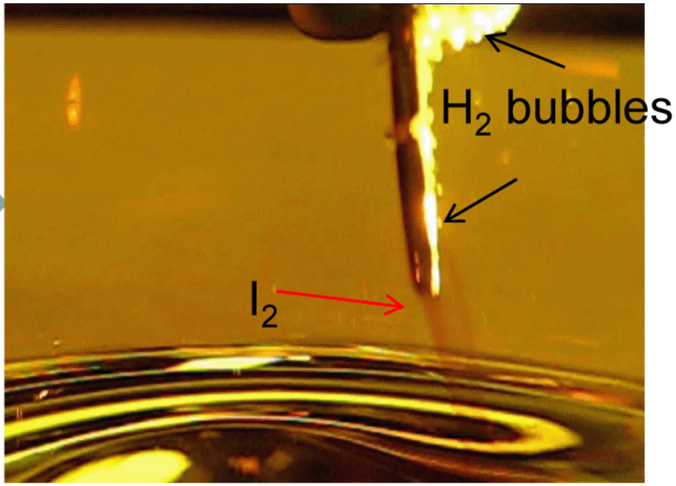
3X10^{16} (Zn/cm^3) p-InP has the best performance

PEC Performance of Low Doped (E16) p-InP with Ohmic Contact in 0.5 M HI/NaClO$_4$ under Zero Bias



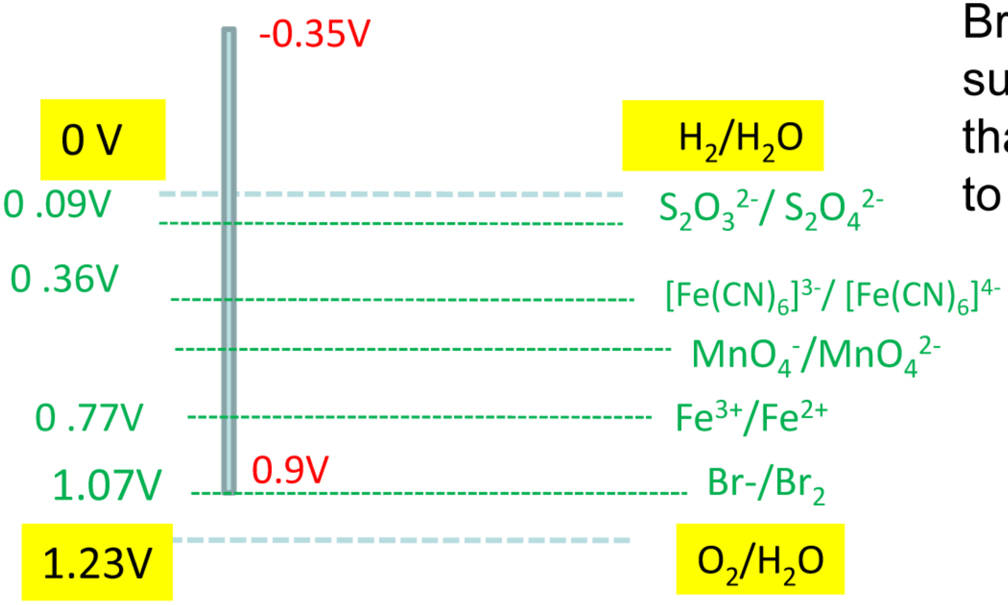
- ❖Zero bias (2 electrode IPCE for hydrogen production from HI ~40% across abs. band.





- ❖ Direct H_2 bubbling was observed on free sample.

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



-0.35V

0 V H_2/H_2O

0 .09V $S_2O_3^{2-}/ S_2O_4^{2-}$

0 .36V $[Fe(CN)_6]^{3-}/ [Fe(CN)_6]^{4-}$

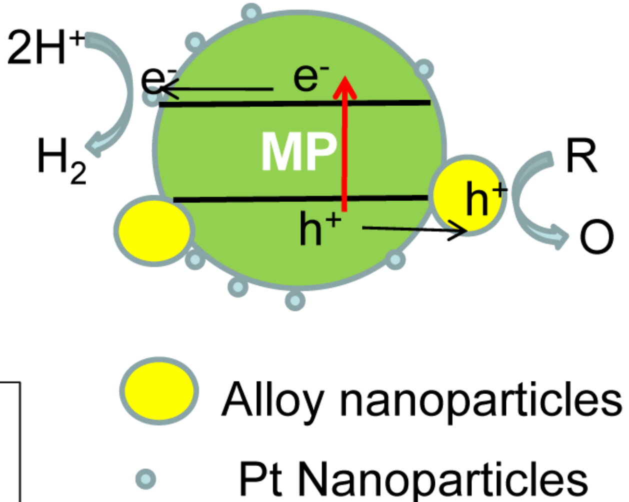
MnO_4^-/MnO_4^{2-}

0 .77V Fe^{3+}/Fe^{2+}

1.07V 0.9V Br-/Br_2

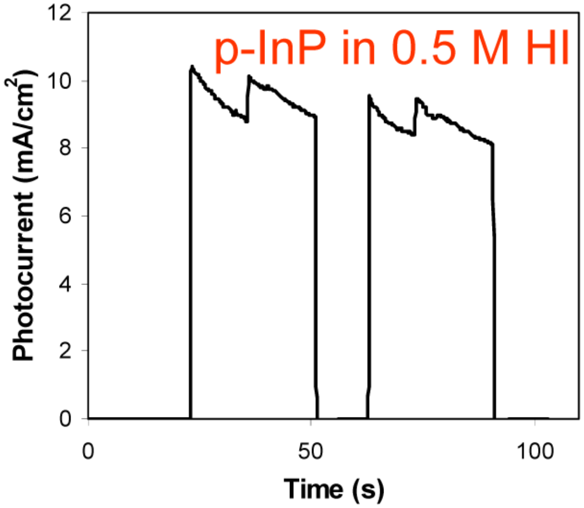
1.23V O_2/H_2O

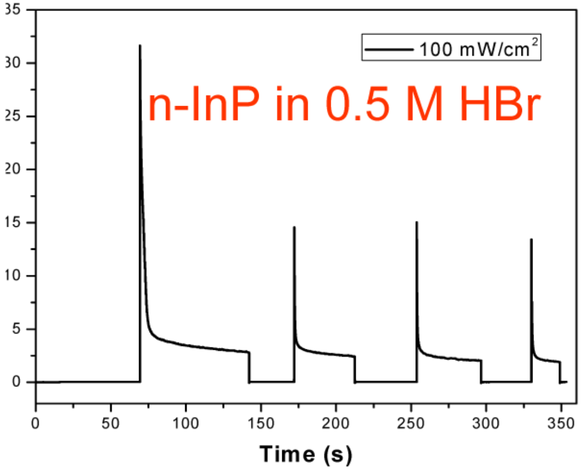
Br^- and I^- dissolve many noble metals, such as Au. Thus, other candidates that allow presence of Au-Zn layer are to be sought.



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

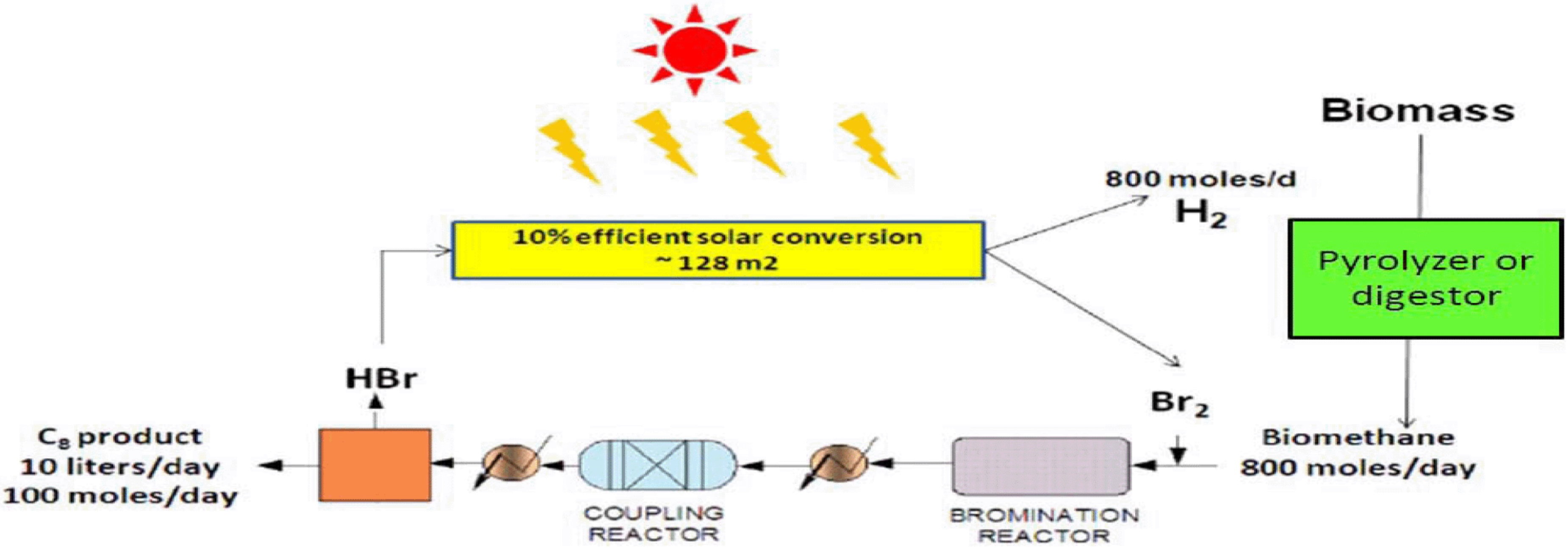


Figure 1. Project Design Schematic[1]

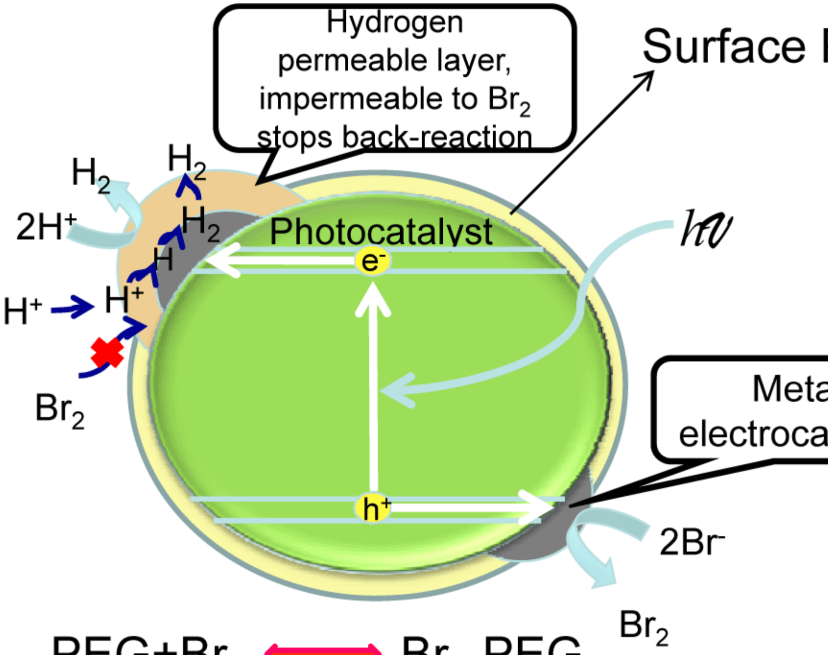
Renewable Energy

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



PEG+Br_2 ⟷ Br_2-PEG

Electrochemical Reactions

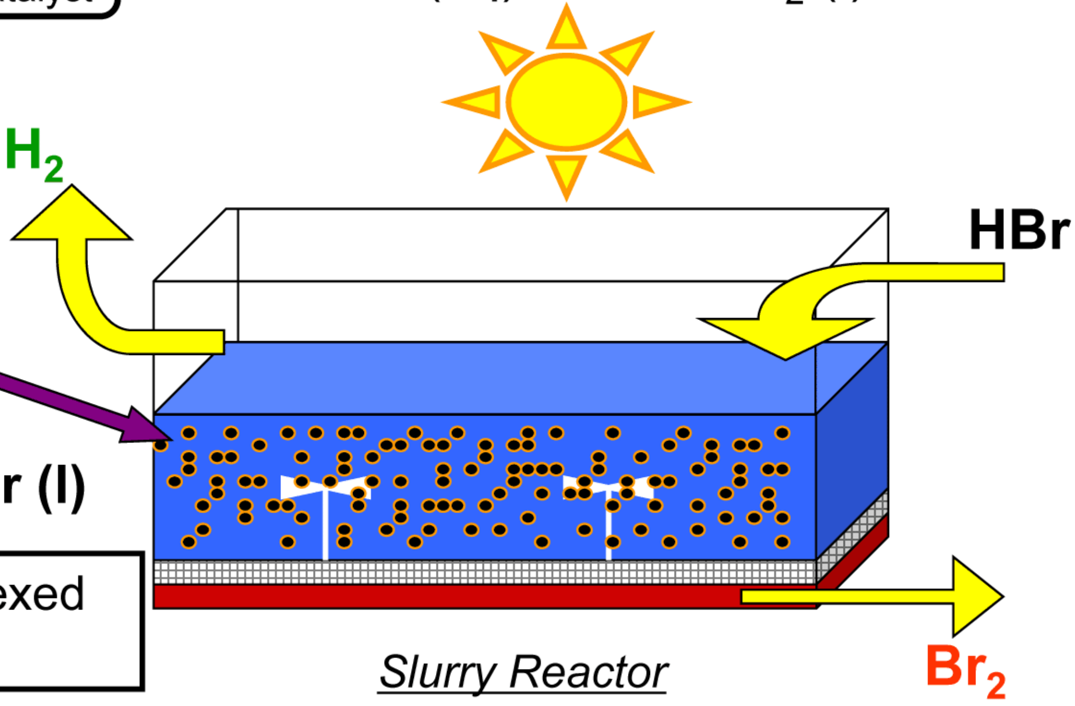
Cathodic:

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

Anodic:

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

PEC Nano-particle



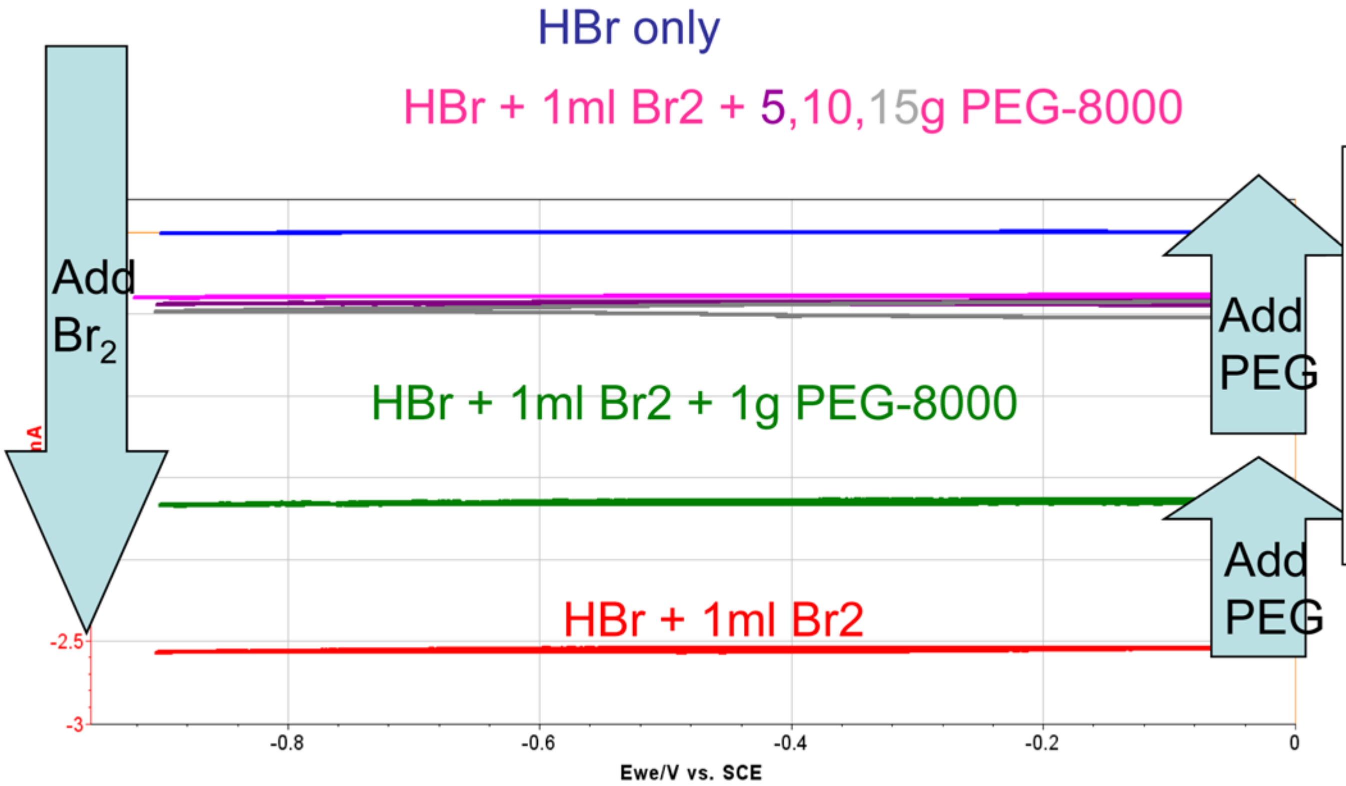
Slurry Reactor

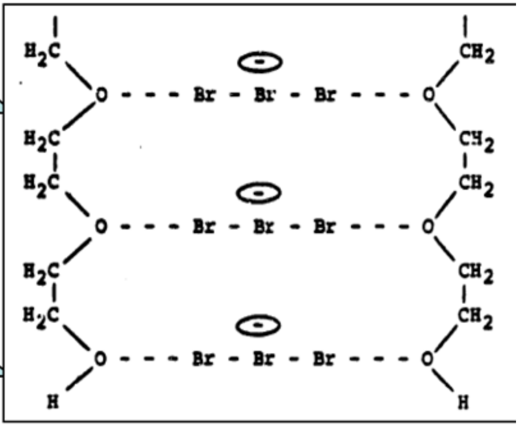
Back-Reaction :

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

Complexing agent + Br_2 → Complexed Br_2 for easy extraction

Back-Reaction Range, Various Conditions

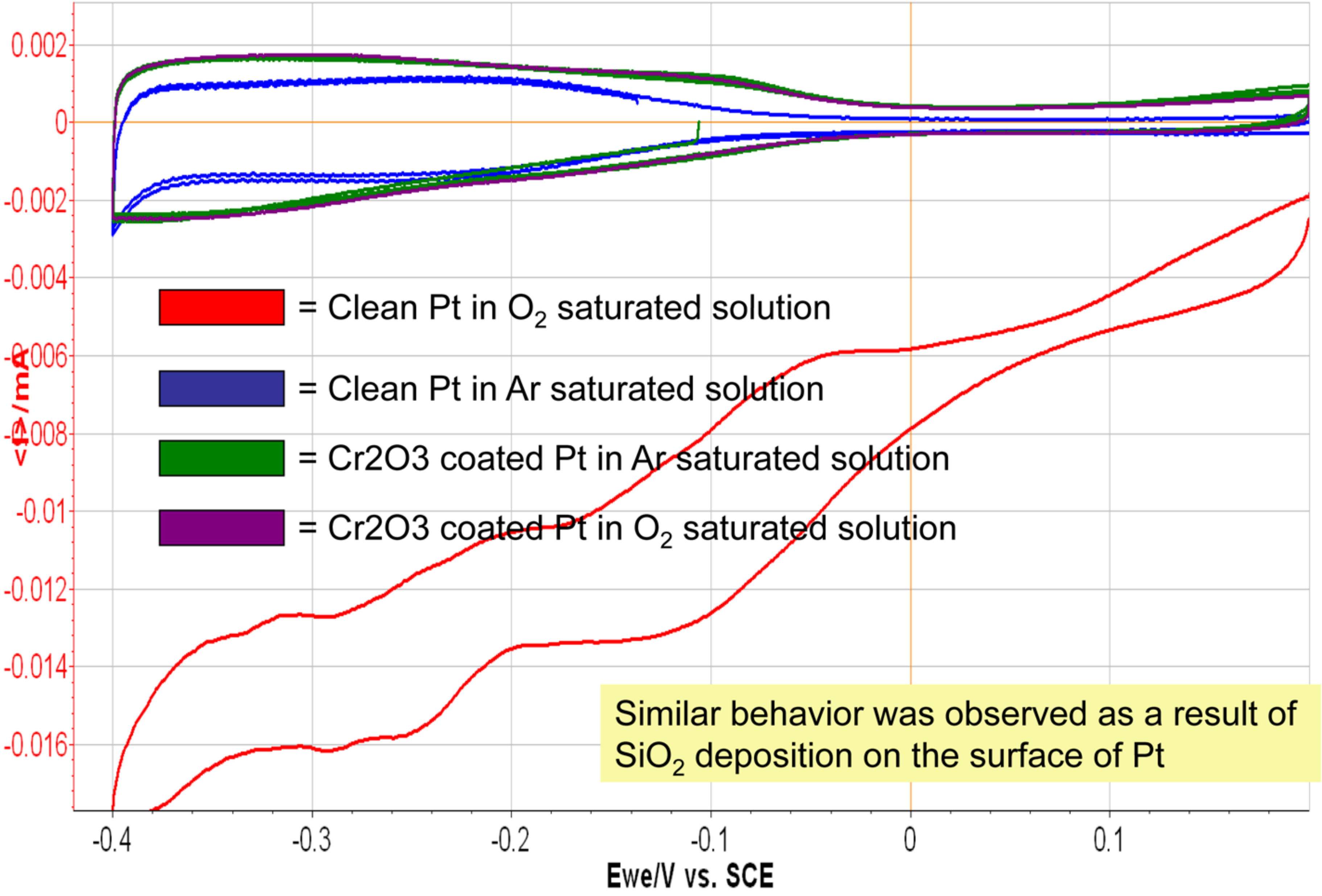




PEG Br_3^- complex[2]

- 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)

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