Photoelectrochemical Water Splitting

NREL Principal Investigator: John A. Turner

Current staff

Heli Wang, Postdoc
Todd Deutsch, University of Colorado (PhD Student)
John Einspahr, Colorado School of Mines (SS Student)
Jennifer Leisch, Colorado School of Mines (PhD Student)
Ken Menningen, University of Wisconsin (Sabbatical)

Recent Past

Joe Beach, Colorado School of Mines (PhD, Graduated Dec 2001)
Lara Kjeldsen, Colorado School of Mines (MS Student - graduated 2003)
Scott Warren, Whitman College (SS - now at Cornell)
Ken Varner, (SS - North Carolina State)

Others

Vladimir Aroutiounian, University of Yerevan, Armenia (CRDF, ISTC)

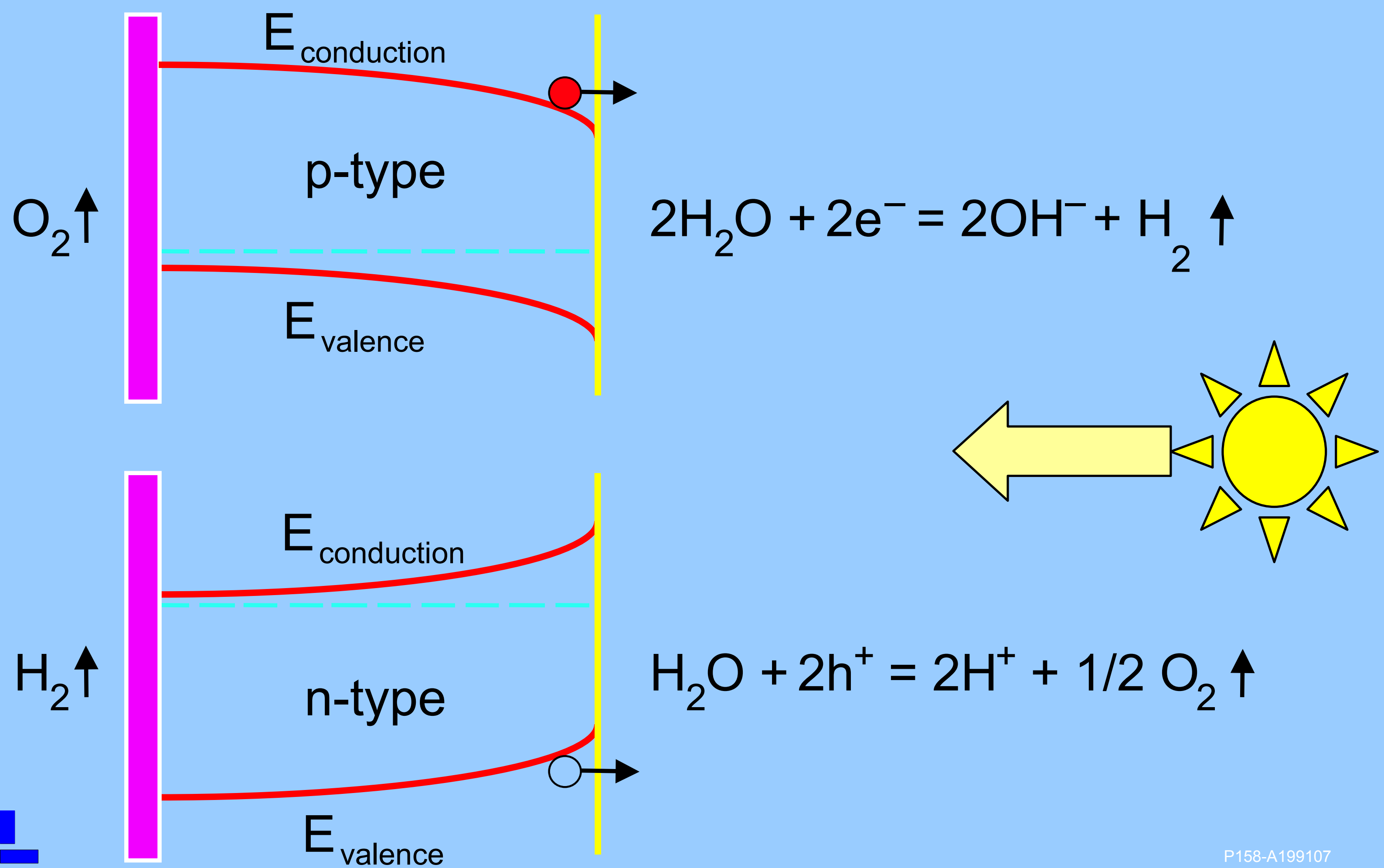
Arturo Fernández, Centro de Investigación en Energía-UNAM, Mexico

Photoelectrochemical Conversion
Goals and Objectives

The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that will split water using sunlight as the only energy input, with a solar-to-hydrogen efficiency of 10% with a 10-year lifetime. Our objectives are:

- Identify and characterize new semiconductor materials that have appropriate bandgaps and are stable in aqueous solutions.
- Study multijunction semiconductor systems for higher efficiency water splitting.
- Develop techniques for the energetic control of the semiconductor electrolyte interphase.
- Developing techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.
- Identify environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.

Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



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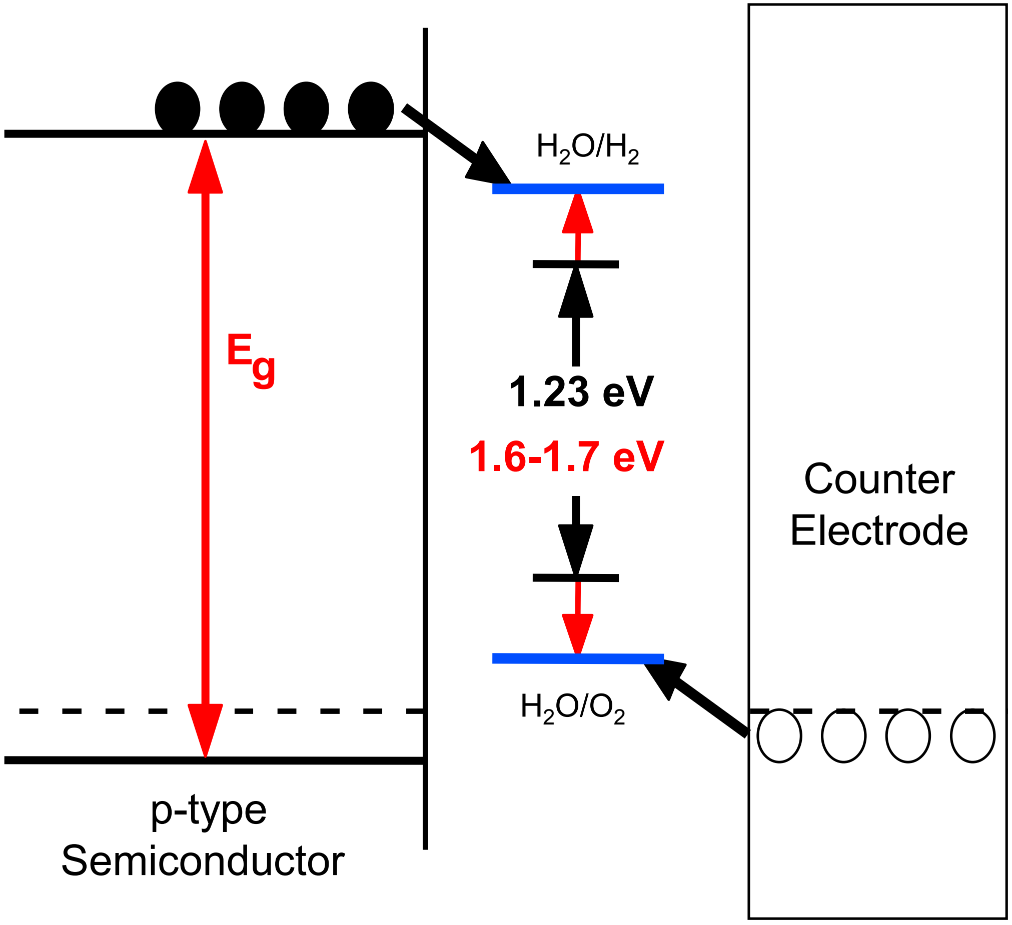
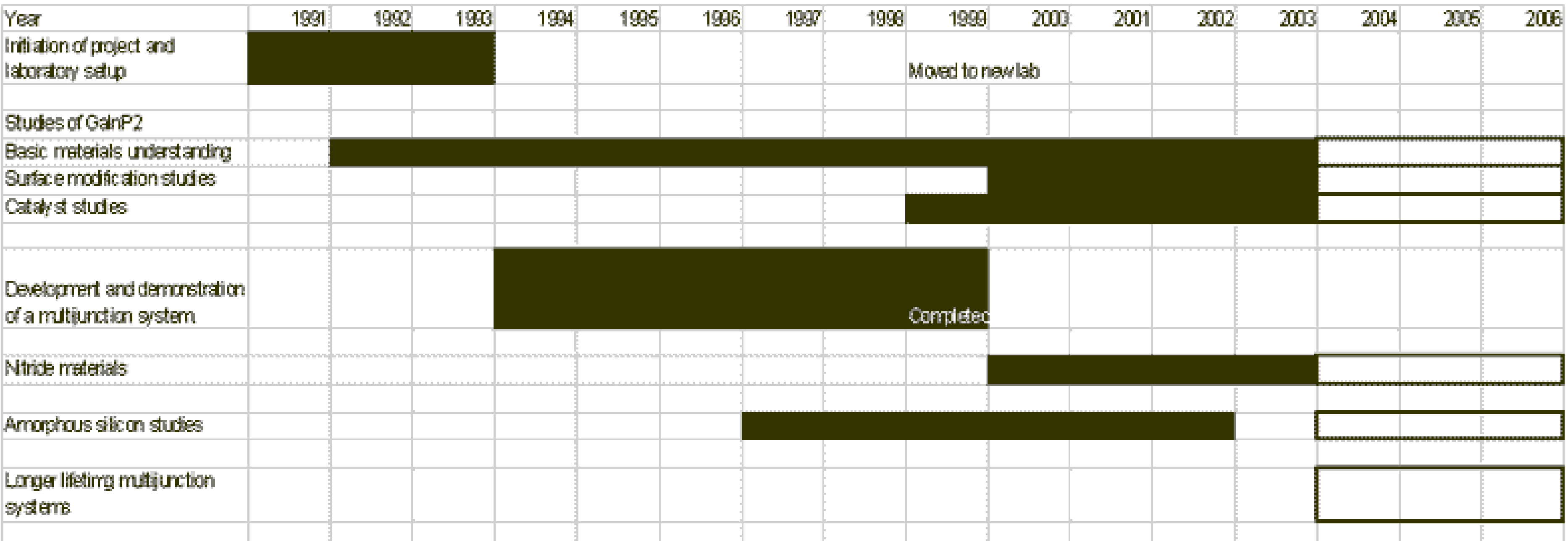
Material and Energetic Criteria



- **Band Gap** (E_g) must be at least 1.6-1.7 eV
- **Band Edges** must straddle H_2O redox potentials
- Fast charge transfer
- **Stable** in aqueous solution

All must be satisfied simultaneously

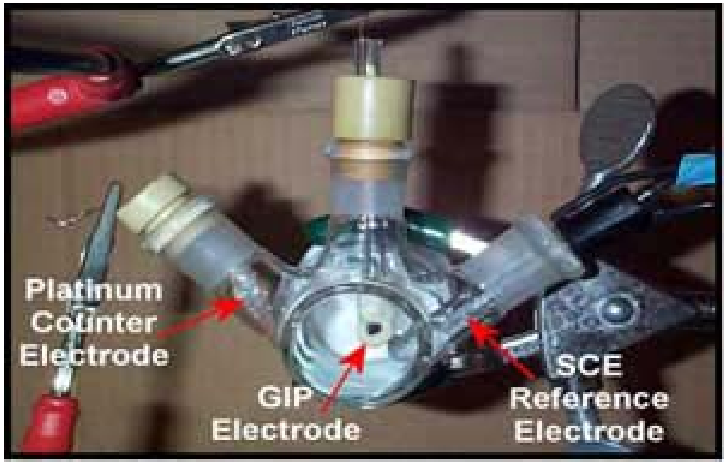
Timeline: 1991 to present



Cumulative Federal Funding: $4500K (~0.75 FTE + postdoc, average)

Project Status

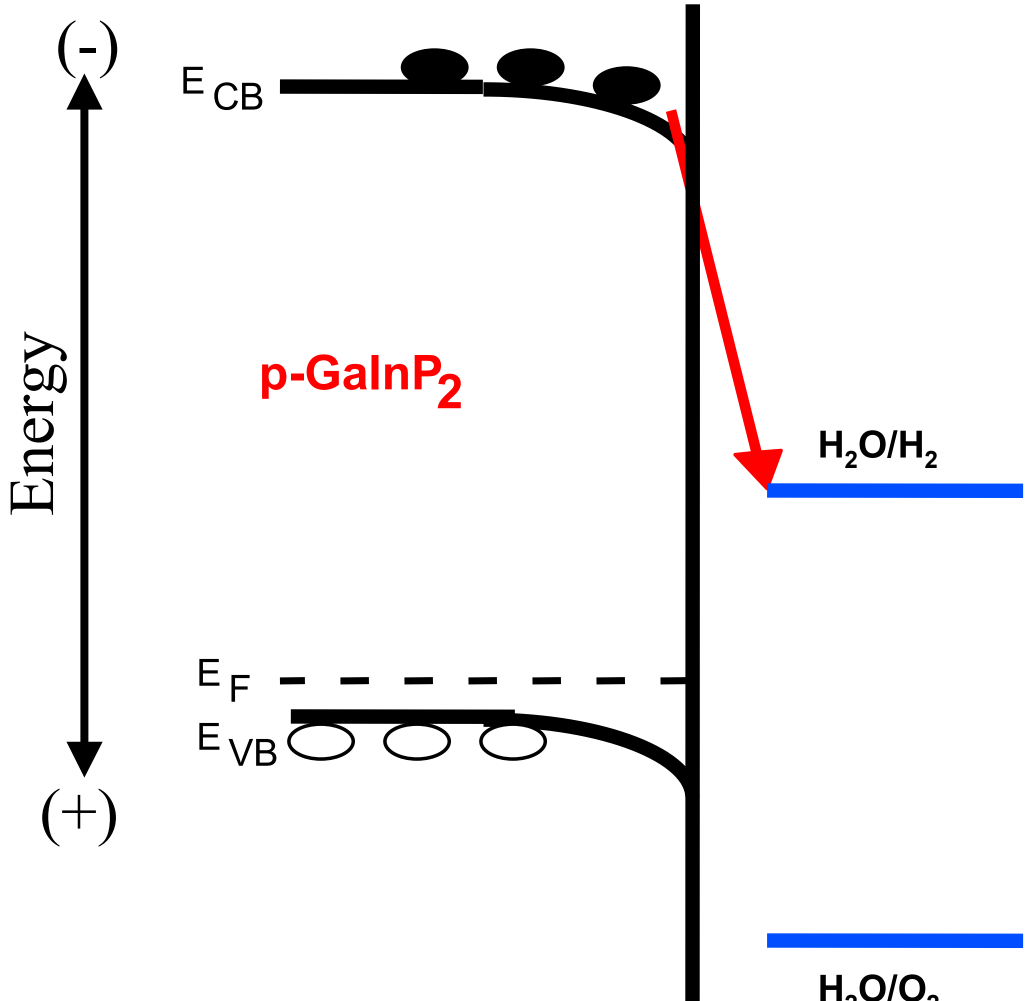
- Current status:
  - 12.4% efficiency multi-junction system, 20 hour lifetime.
  - H_2 Cost: >$13/kg



- Targets:
  - 10% solar-to-hydrogen efficiency, 10-year lifetime
  - H_2 Cost: $3/kg

Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions

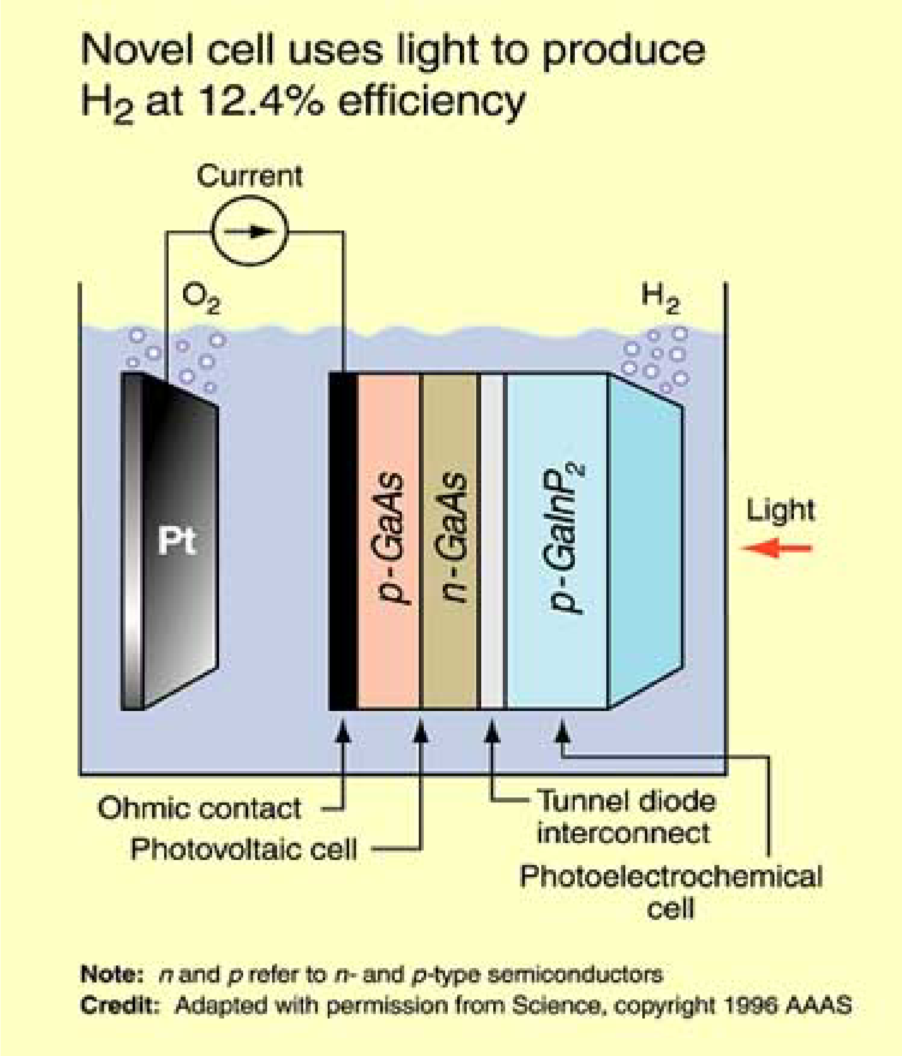


Eg = 1.83 eV

Band edges are 0.2-0.4 V too negative

Band edges are pH sensitive

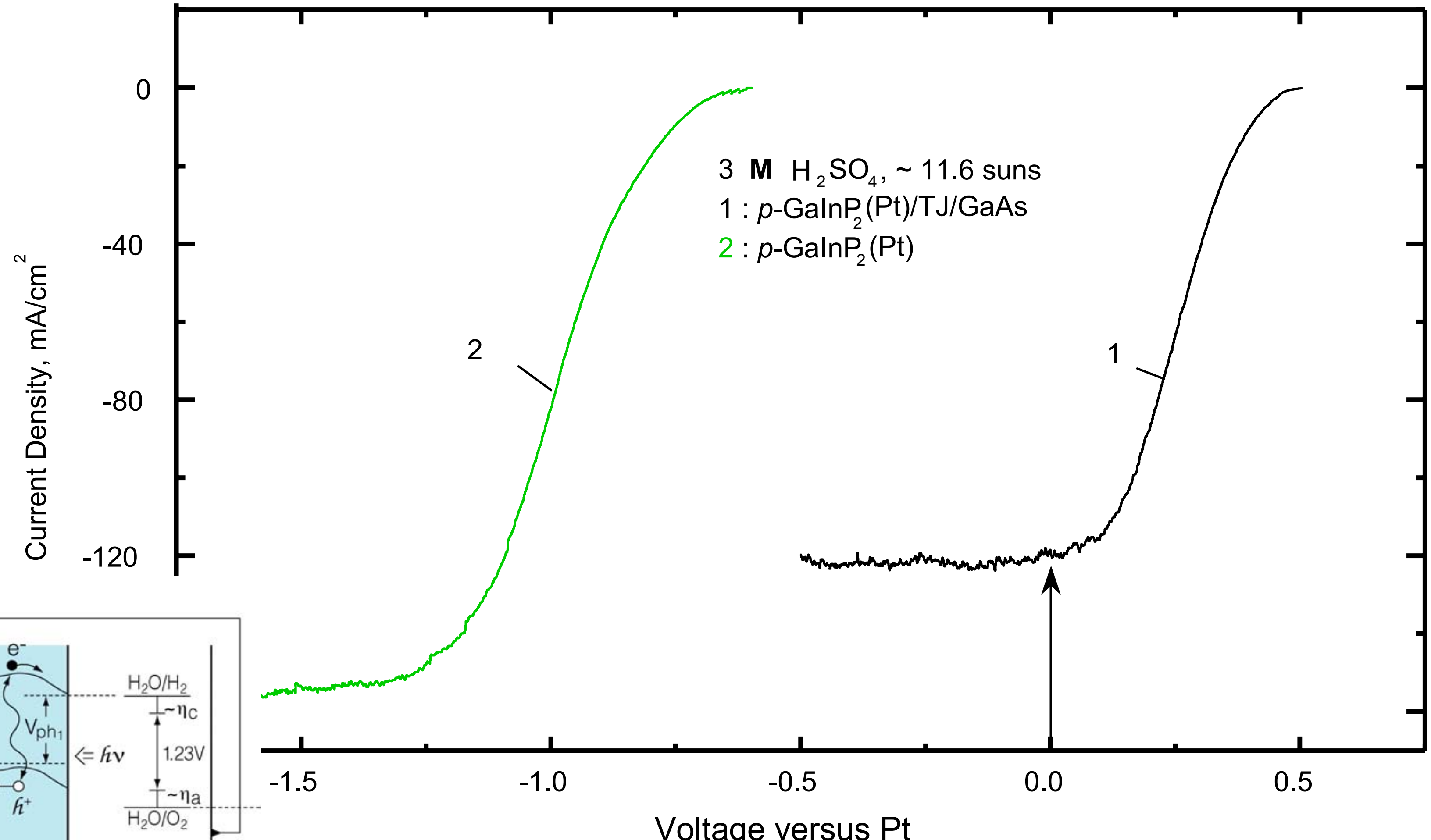
World Record Photoelectrolysis Device <u>Science</u>, April 17 1998.

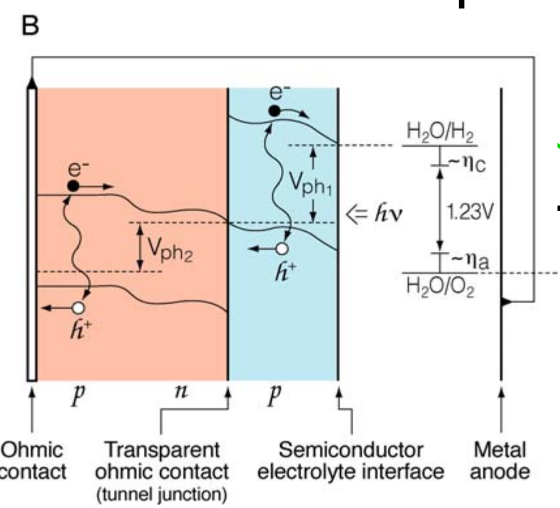


- Direct water electrolysis.
- Unique tandem (PV/PEC) design.
- 12.4% Solar-to-hydrogen

Experimental Cell

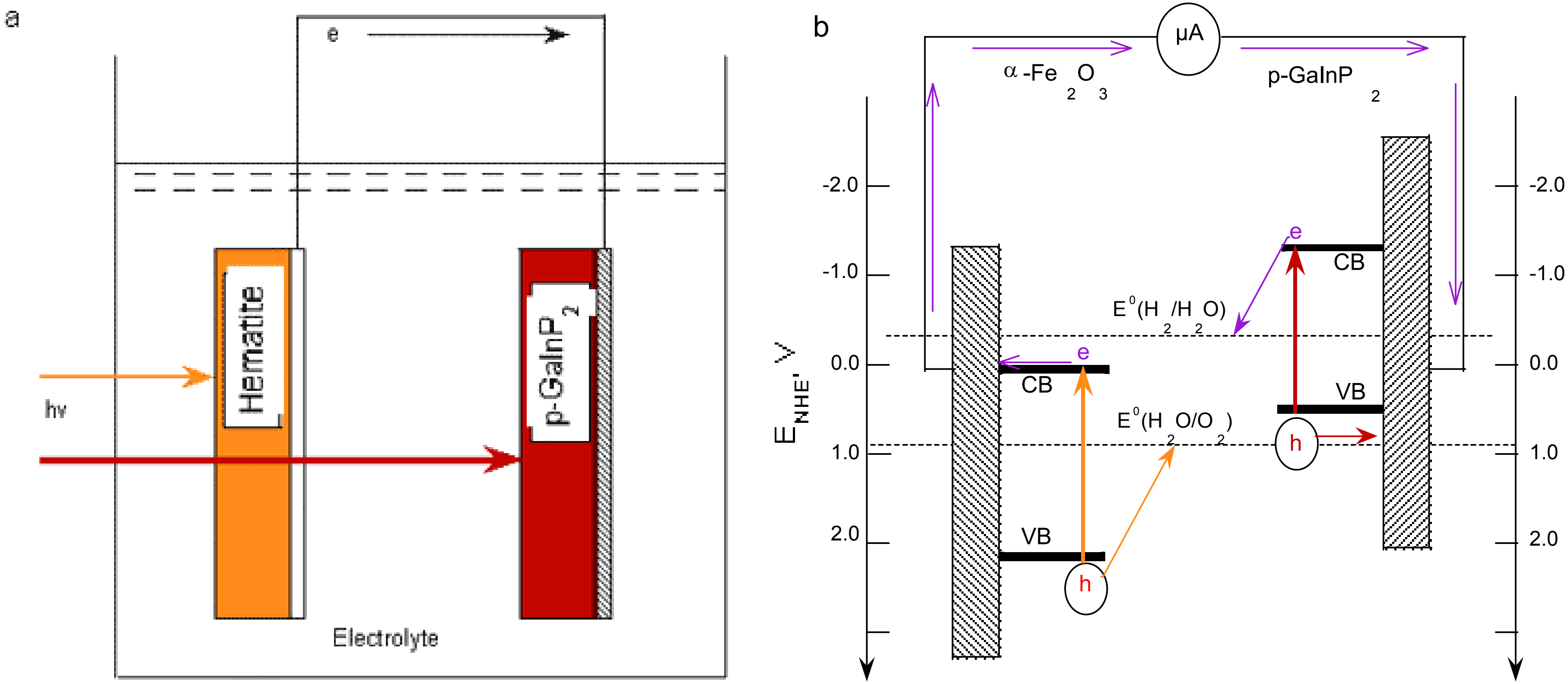
Comparison of *p*-$GaInP_2$ and PEC/PV device





The GaAs integrated PV cell compensates for the energetic mismatch – but expensive

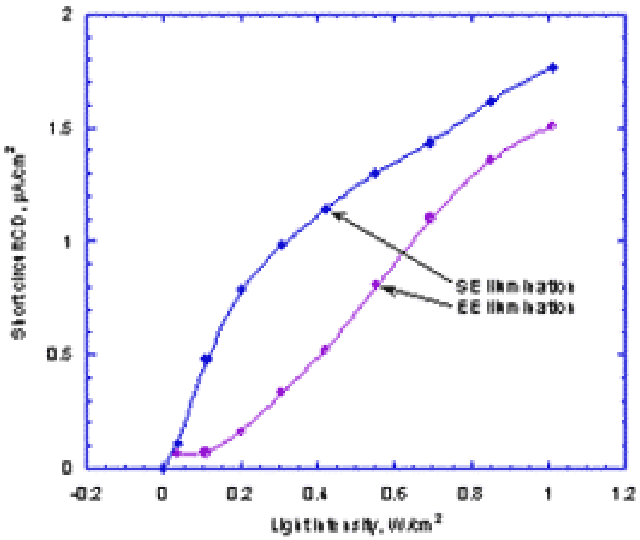
Additional Approaches for Bandedge Mismatch and Stability Issues

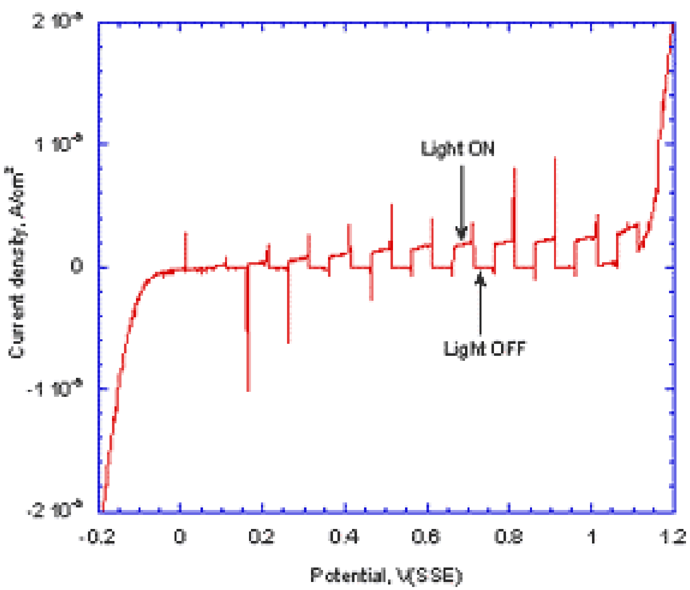


Lower cost Fe_2O_3 electrode is a possibility, but…..

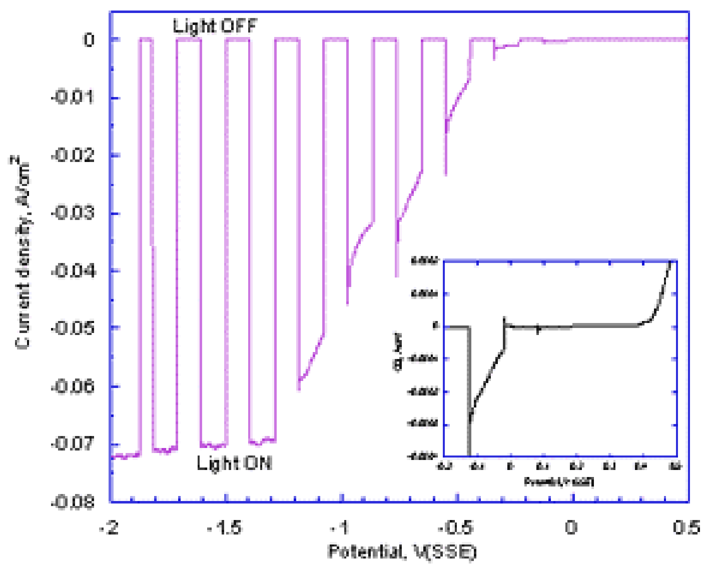
….While the System splits water, the efficiency is very low.

The photocurrent is limited by response of the iron oxide. Work is continuing in collaboration with other researchers (as part of our IEA efforts) to discover better materials.





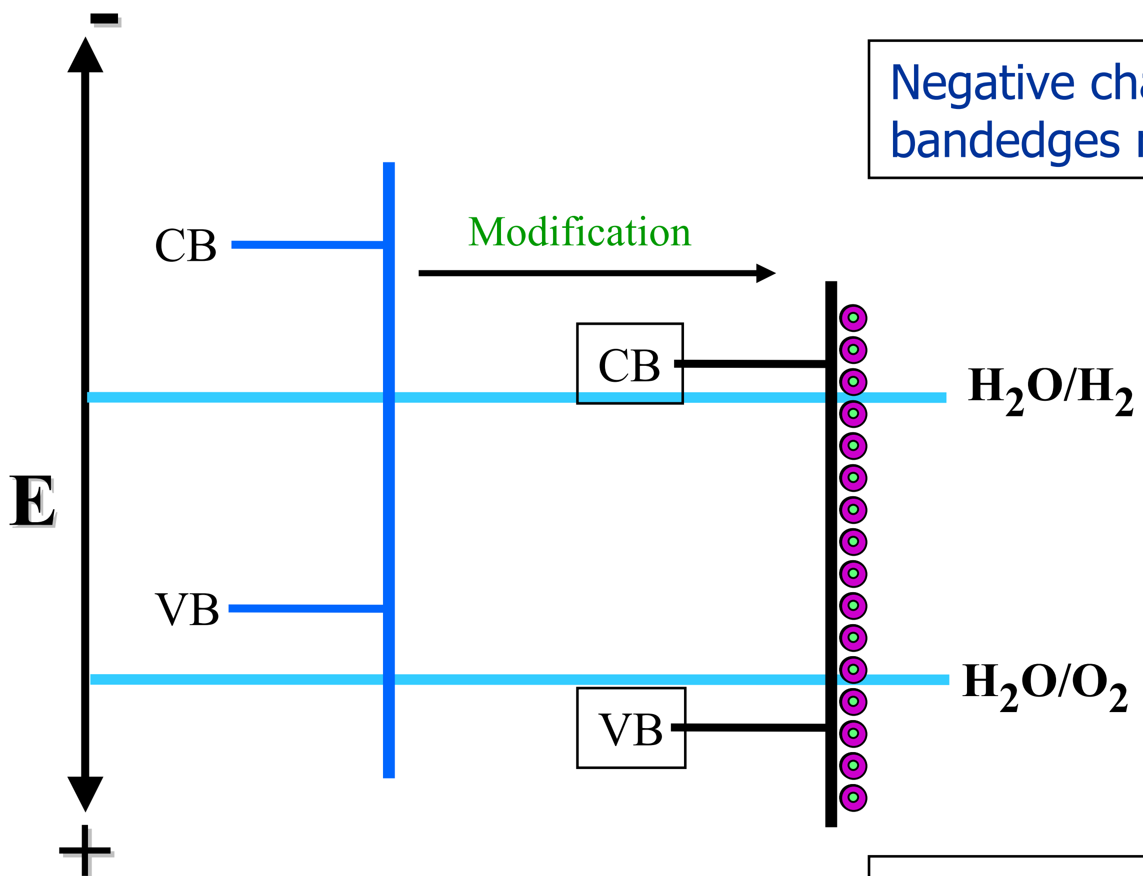
Hematite nanorods in 0.5 M KNO_3 ~1 W/cm^2



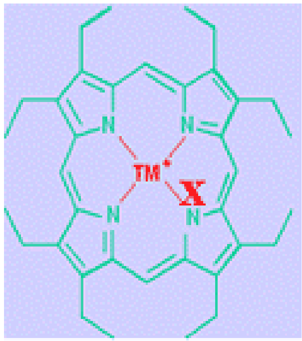
$GaInP_2$ in 0.5 M KNO_3 ~1 W/cm^2

Band Edge Engineering

The goal is to shift the band edges by surface modification to provide the proper energetic overlap.



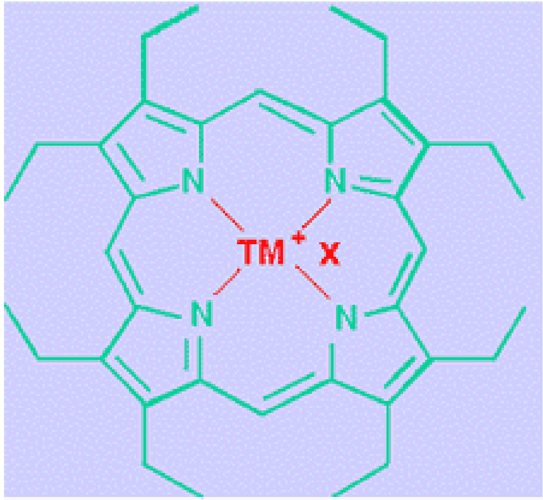
Negative charges move the bandedges negative.



Positive charges move the bandedges positive.

The work involved two series of Metallo-Porphyrins

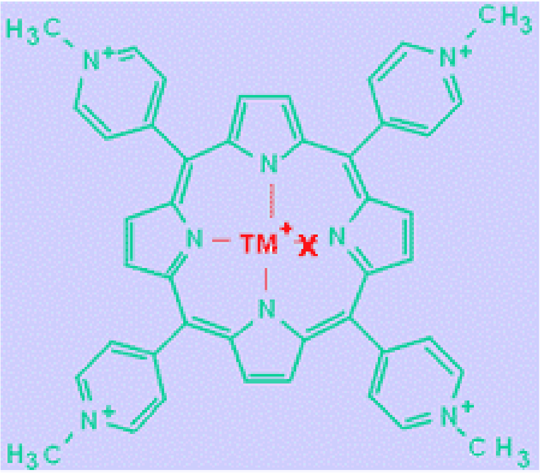
Insoluble



Octaethyl Porphyrin

~OEP~

Soluble



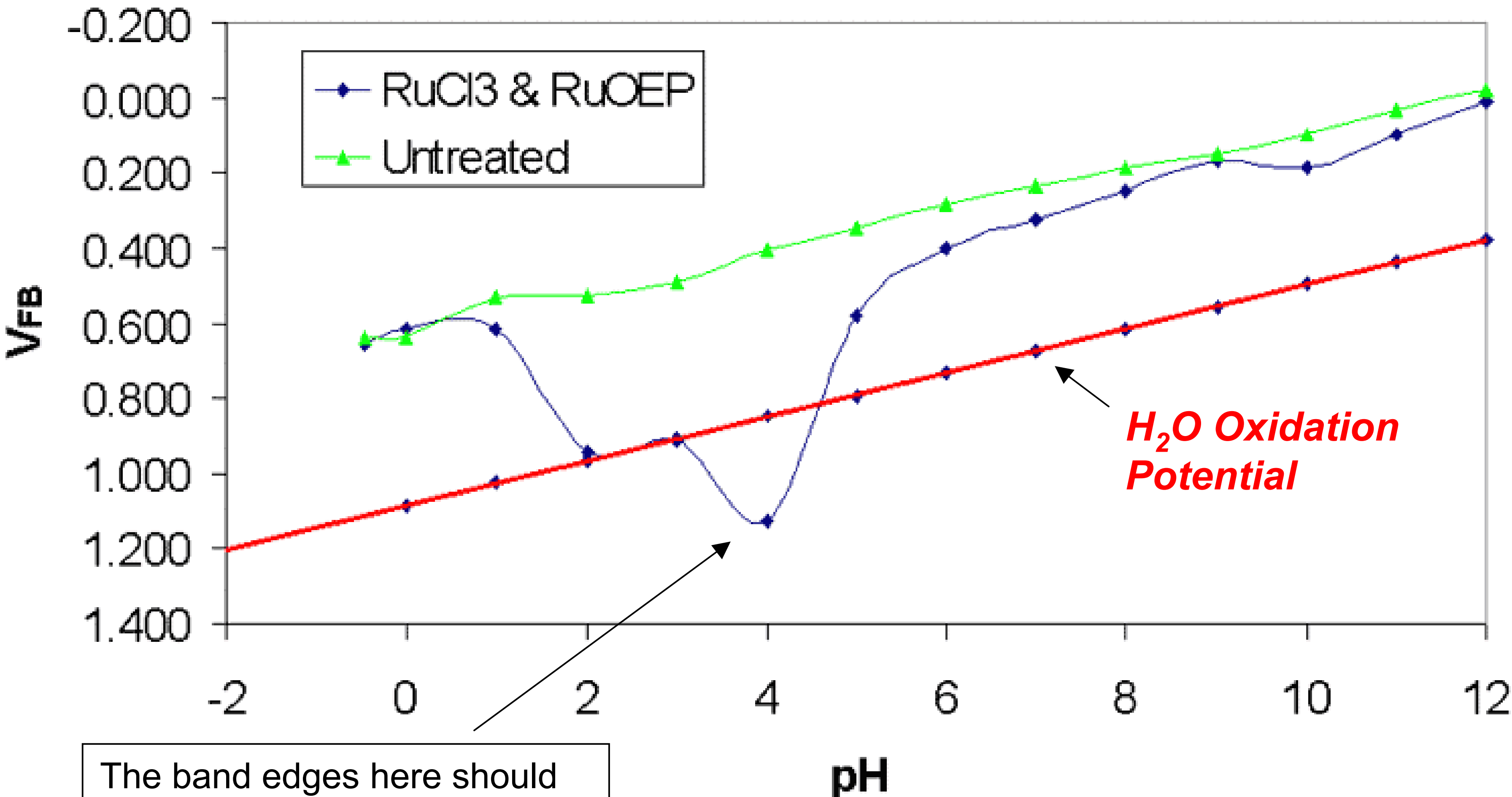
Tetra(N-Methyl-4-Pyridyl)porphyrin

~TMPyP(4)~

Transition metal in center of porphyrin *may* combine favorable properties of band edge shifting and charge transfer.

Band Edge Engineering - $GaInP_2$

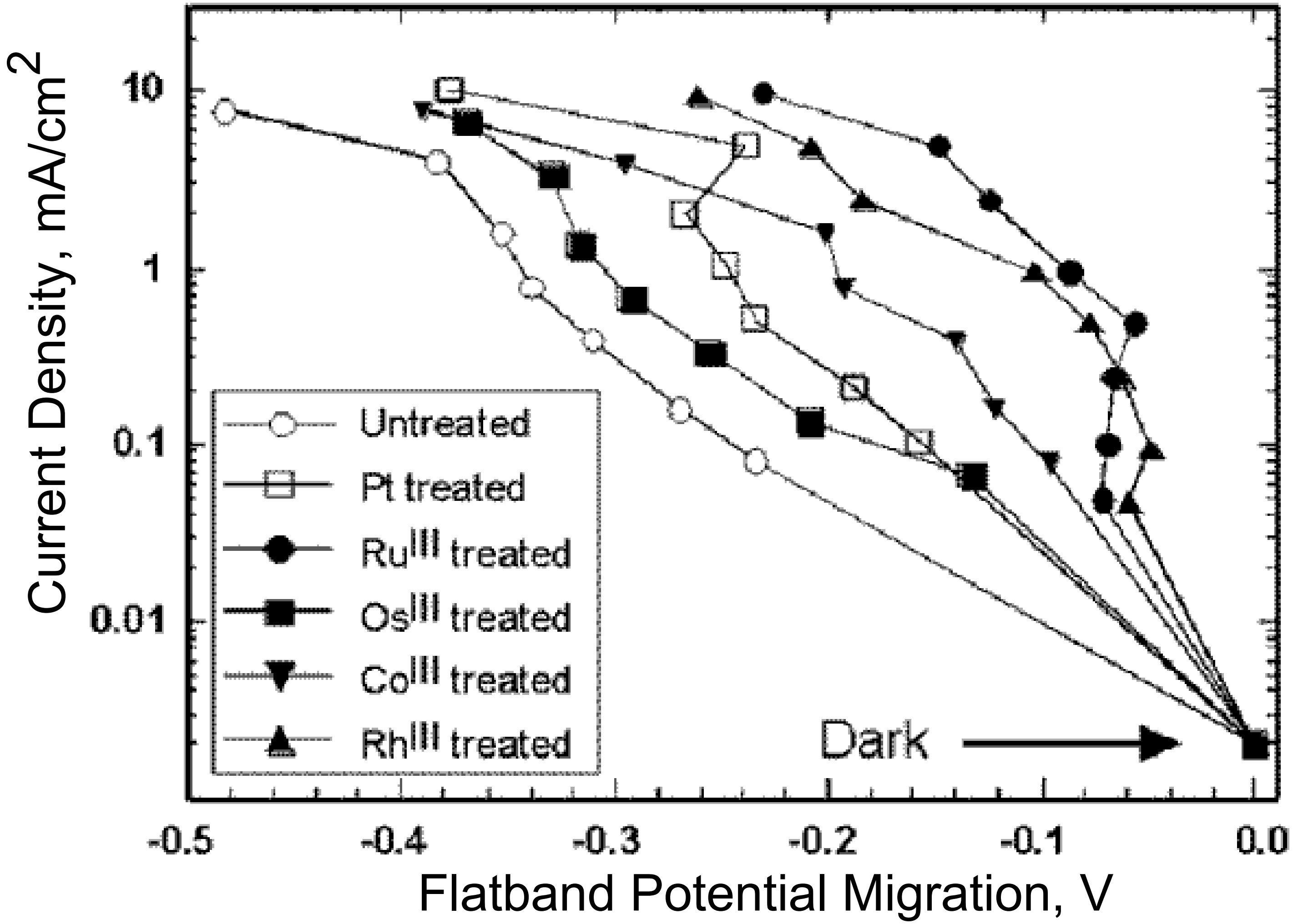
V_{FB} vs. pH for $RuCl_3$ + RuOEP Treated $GaInP_2$ Electrode



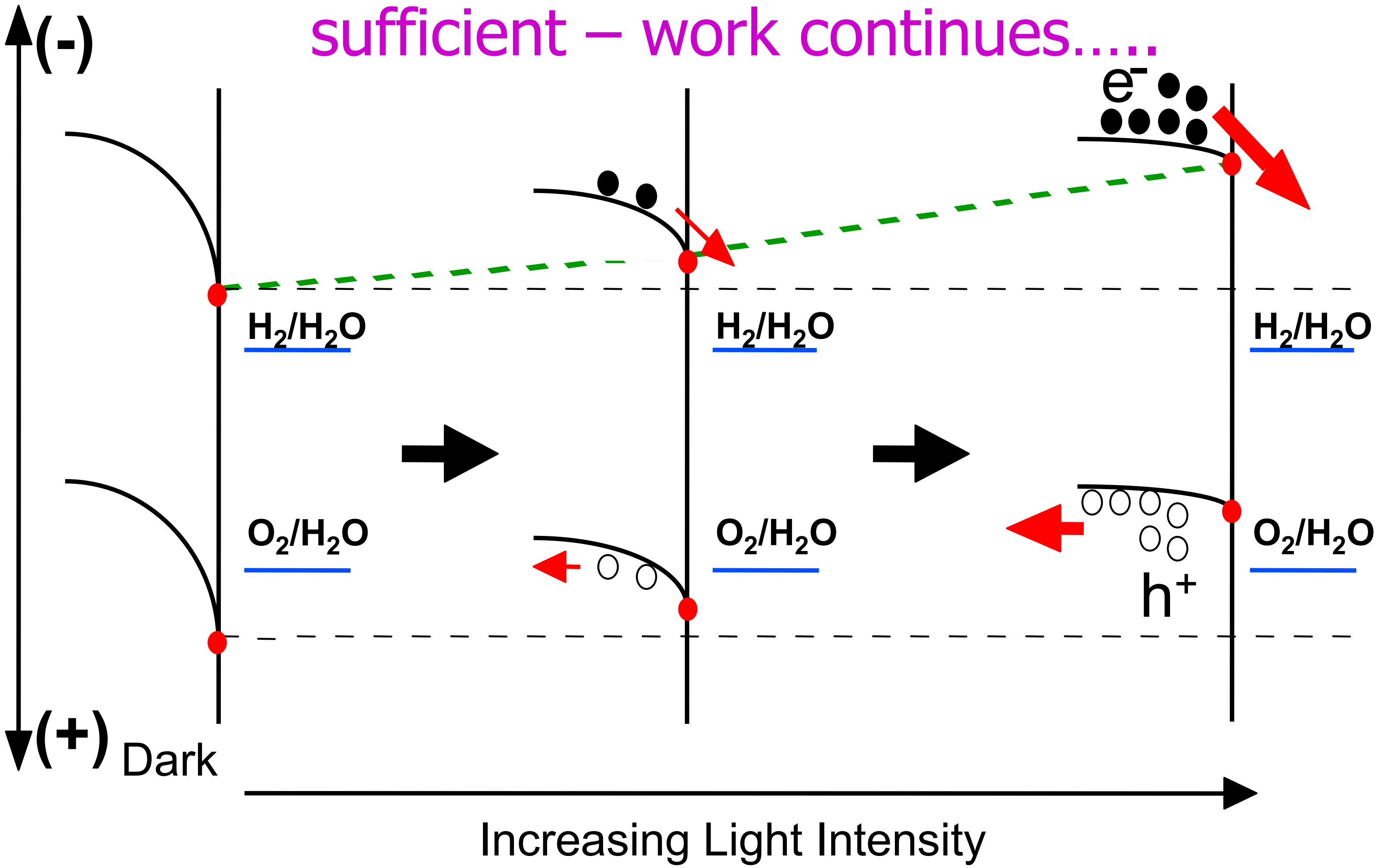
The band edges here should be able to split water…..but no water splitting observed.

Metal Ion Catalysis

All show bandedge migration

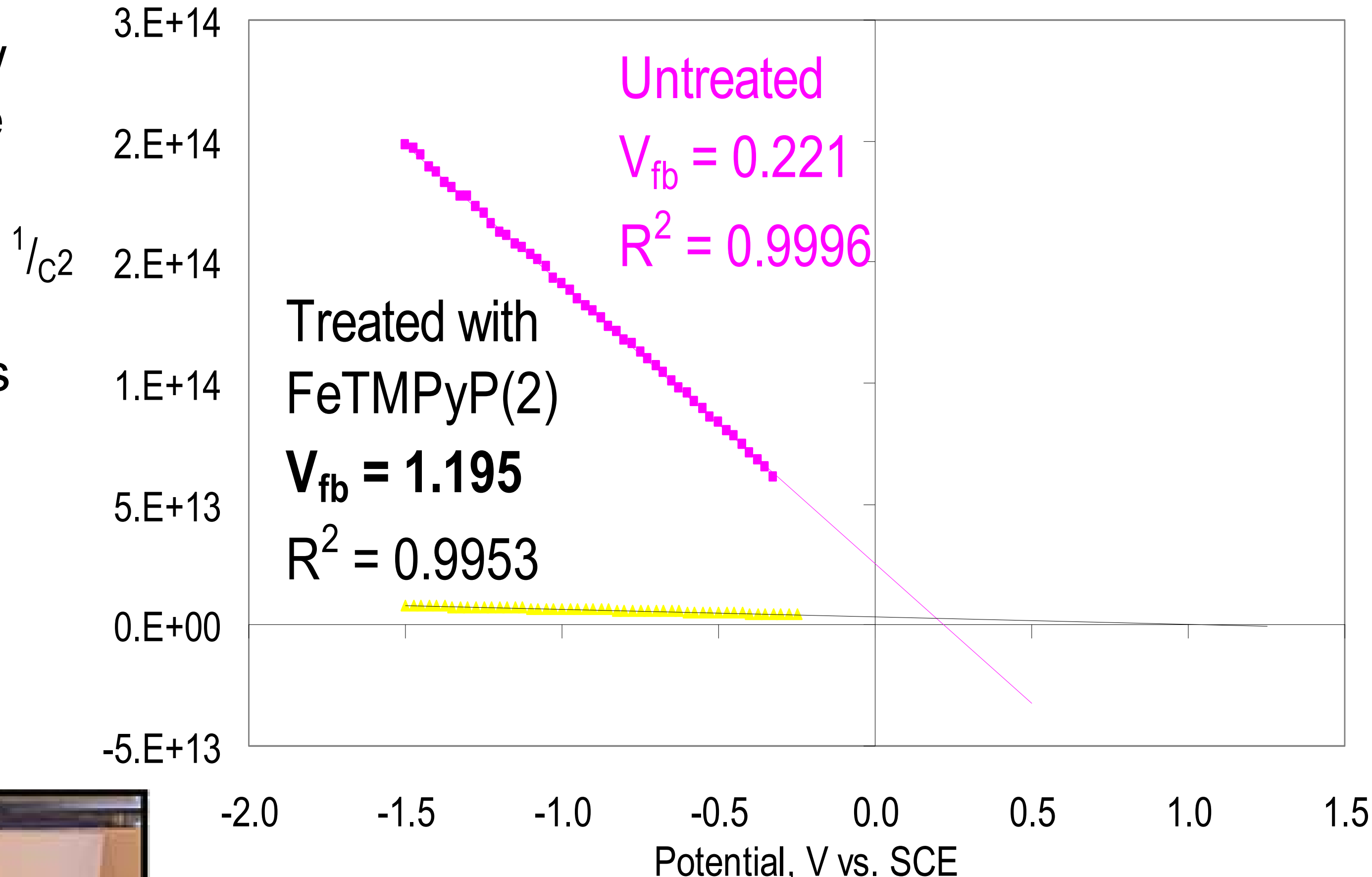


Band edge migration is due to negative charges accumulating at the surface – catalysis is not sufficient – work continues…..

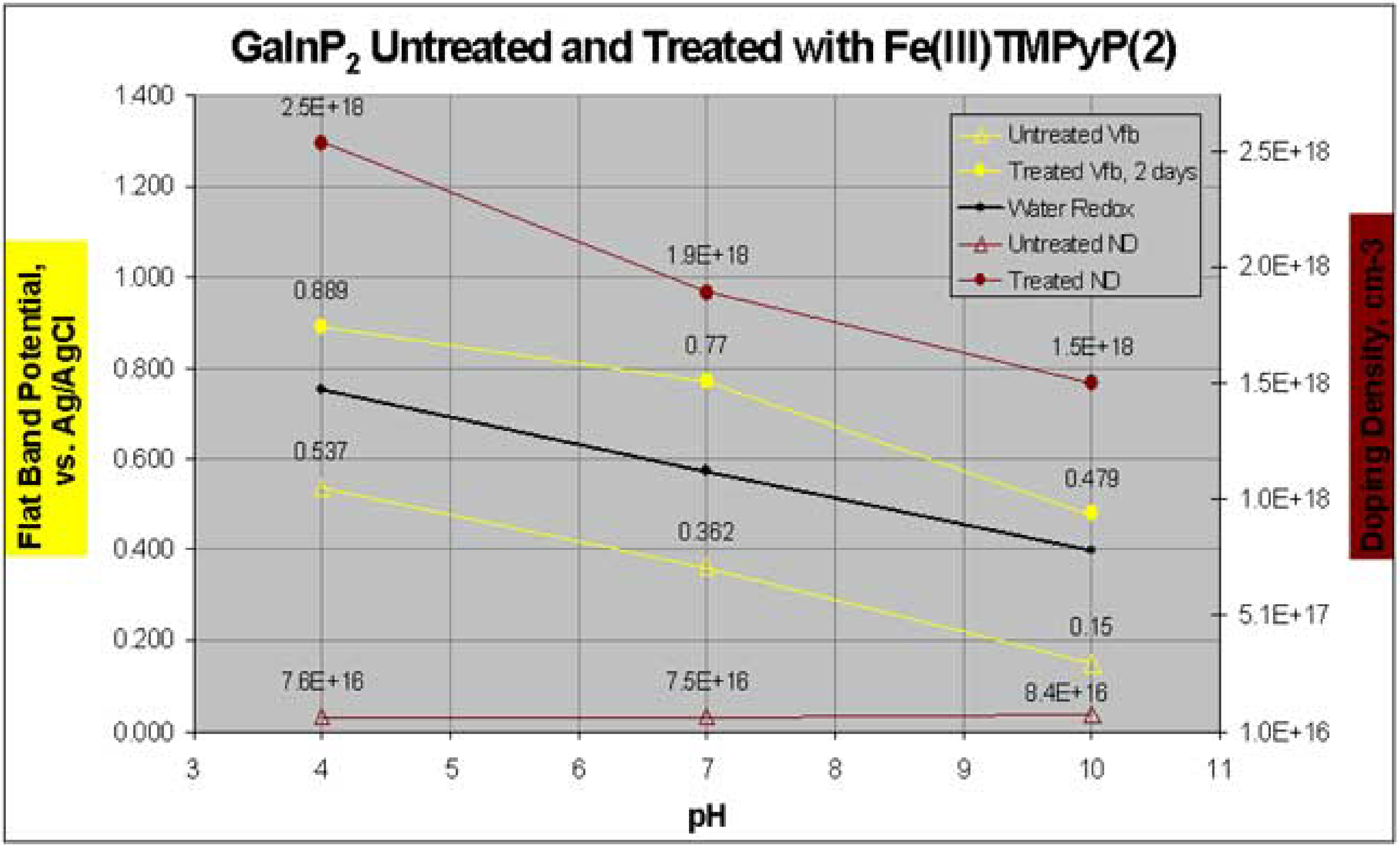


Mott-Schottky Plot of Fe(III)TMPyP(2), pH 7

The soluble porphyrins show large band edge shifts, but why the large change in slope…indicates a higher doping density…?



pH testing shows even more interesting behavior



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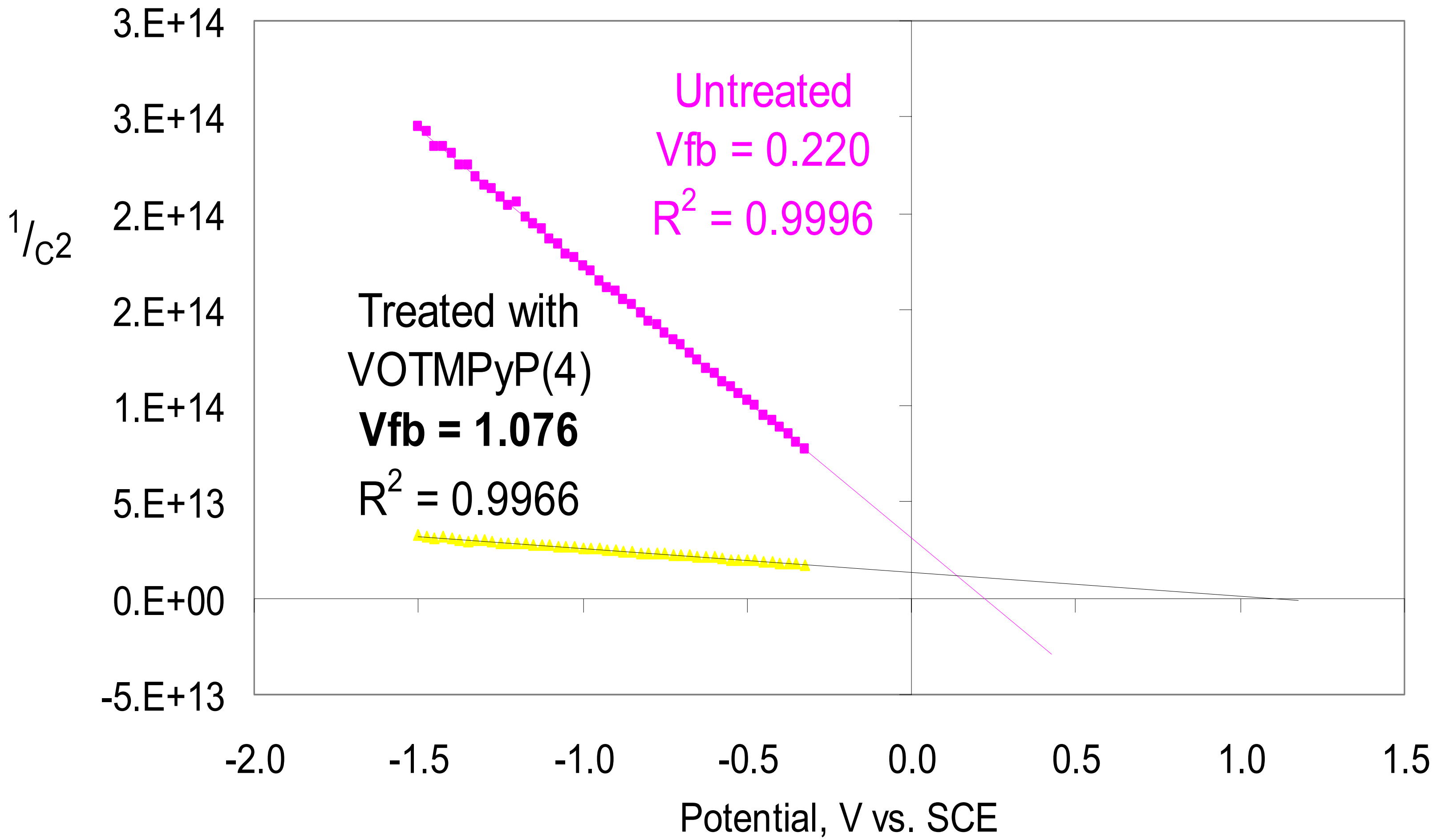
Mott-Schottky Plot for VO(IV)TMPyP(4), pH 7

This phenomenon is not unique to the iron system.
Electron density is being drawn from the near surface of the semiconductor, but the mechanism is unclear…



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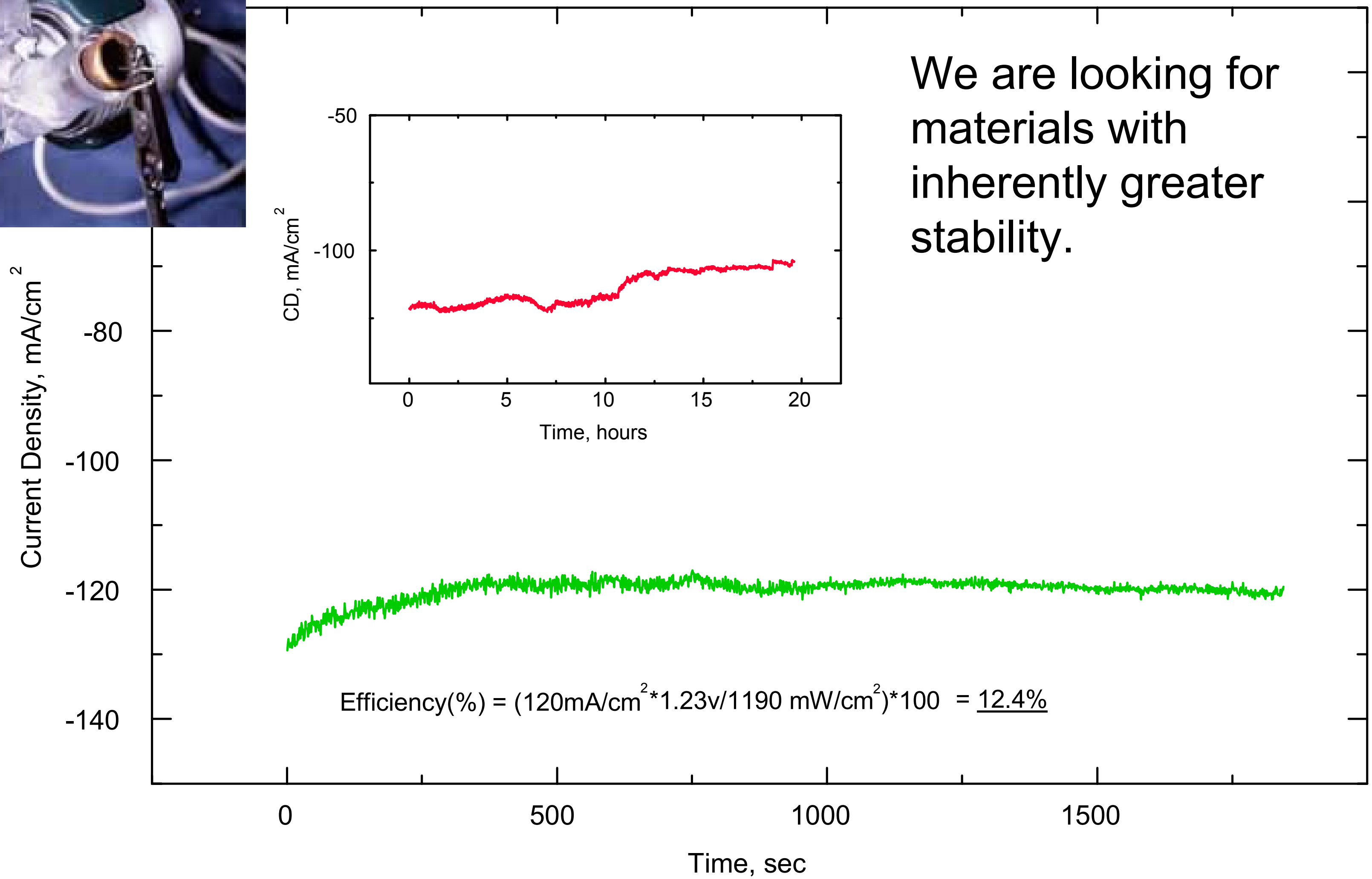
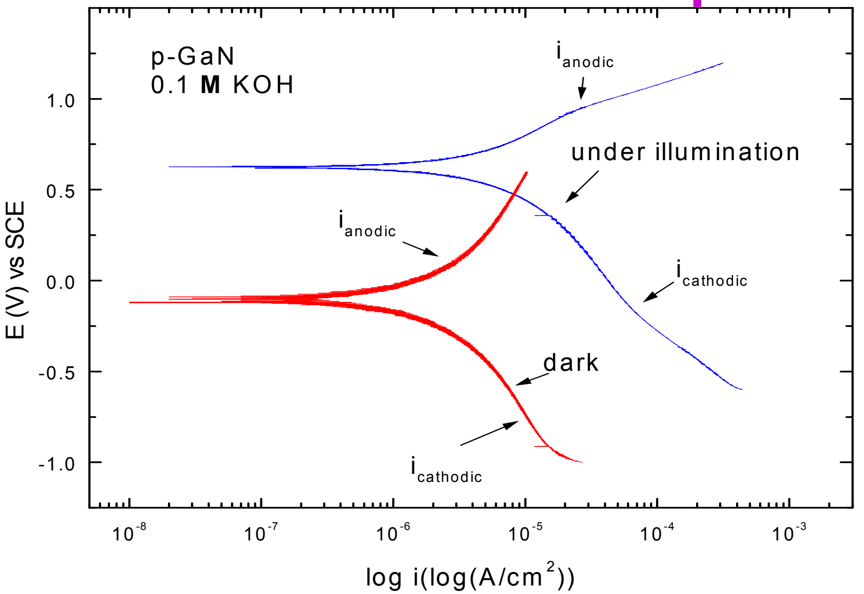
Photocurrent time profile for PEC/PV Water-Splitting device, showing current decay due to corrosion.

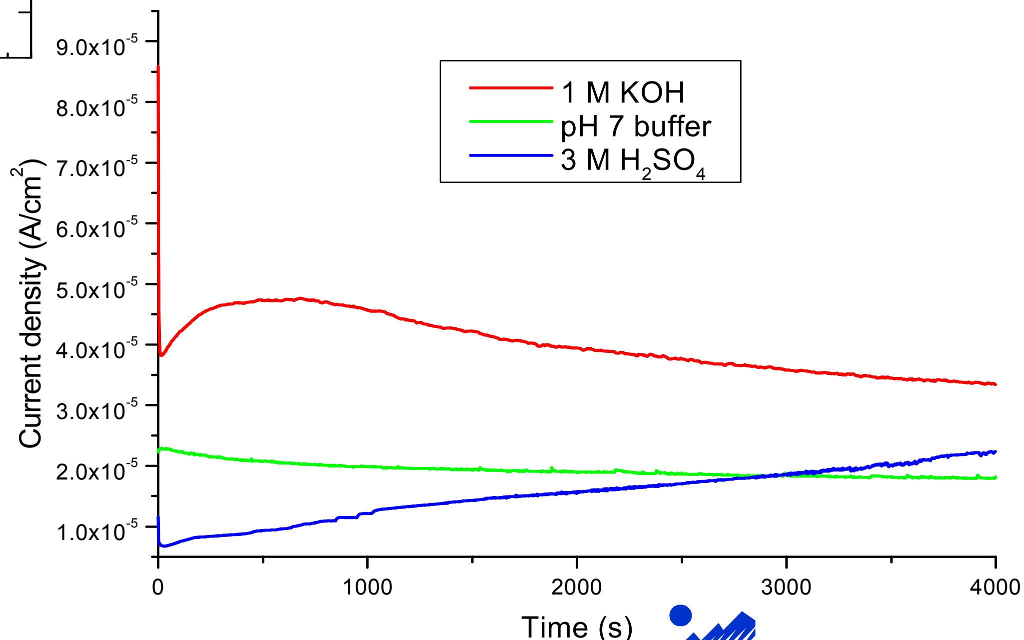


One possibility is nitride materials, an example of which is p-GaN



It shows excellent stability…

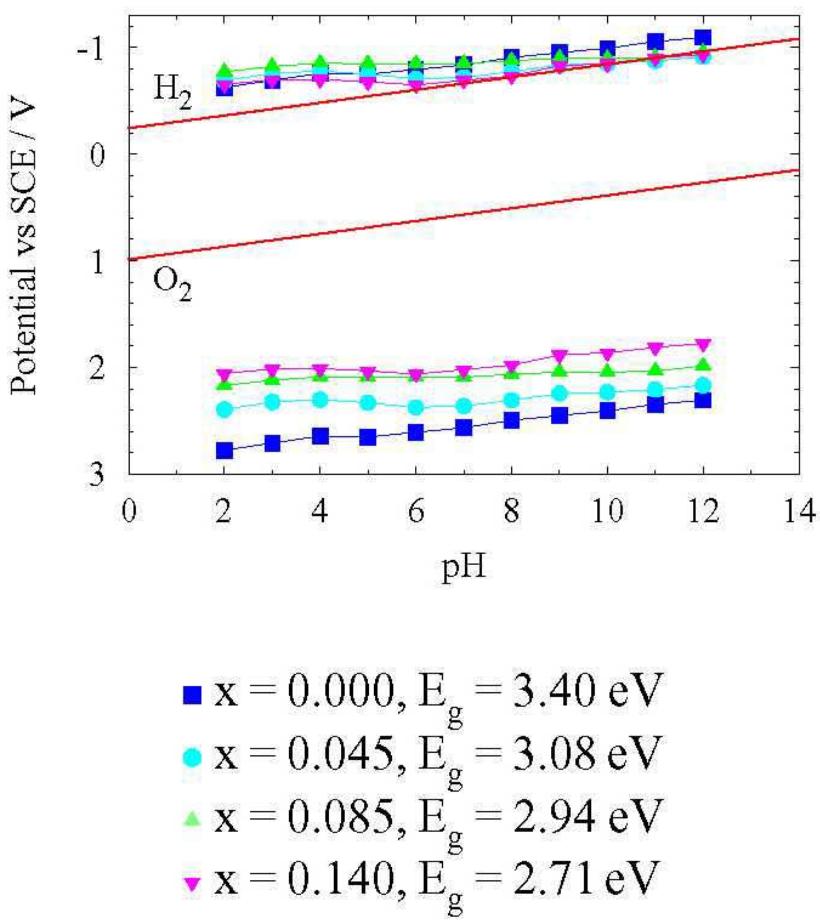
…and water splitting capability



But…3.0eV bandgap

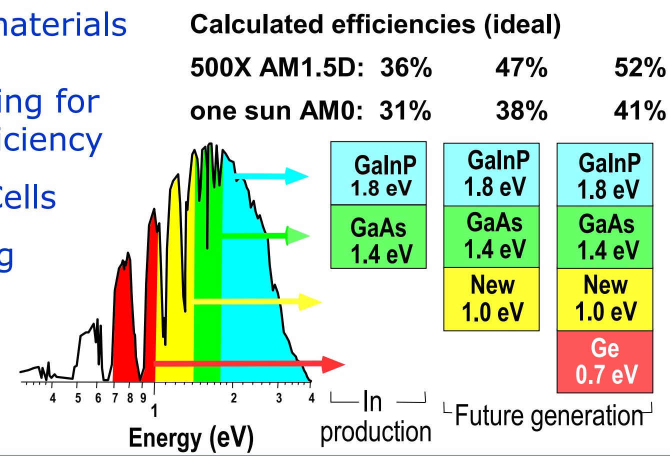
Adding indium lowers the bandgap

The band edge potentials of n-$In_xGa_{1-x}N$



These materials are also interesting for high efficiency

- Solar Cells
- Lighting



- Indium changes E_g much more than Φ_{fb}.
- Change in Φ_{fb} due to indium may be pH dependent.
- n-$In_xGa_{1-x}N$ should split water at low pH.

Other material possibilities include…..

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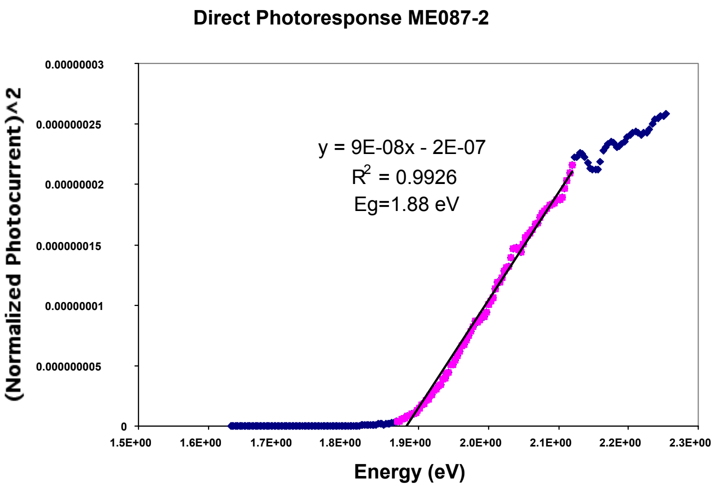
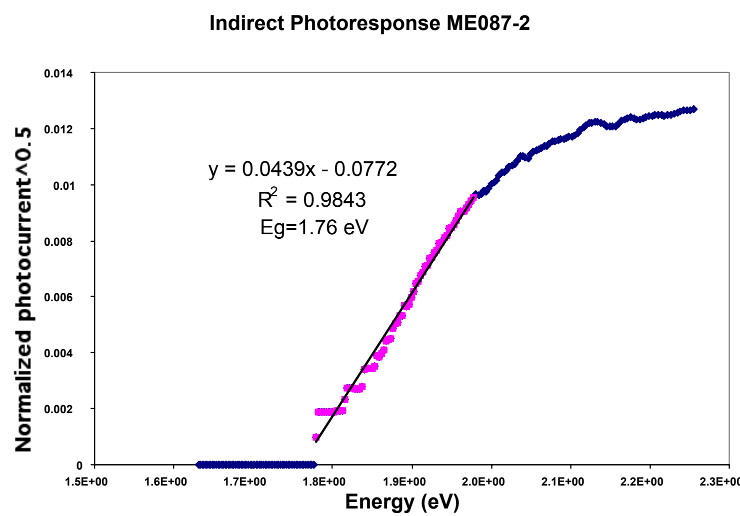
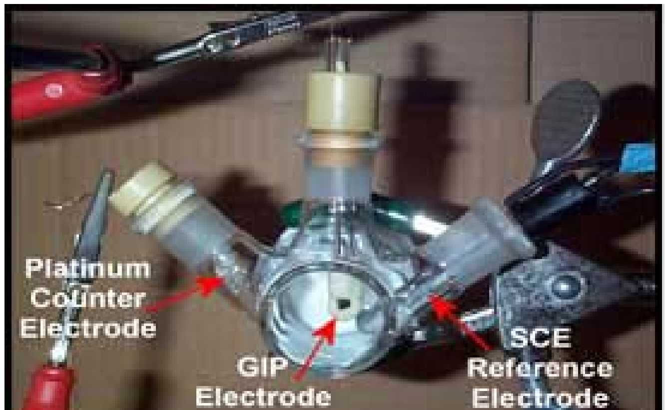
New materials - Preliminary Investigation of GaAsPN for PEC Water Splitting Systems

with Professor Carl Koval *University of Colorado at Boulder*





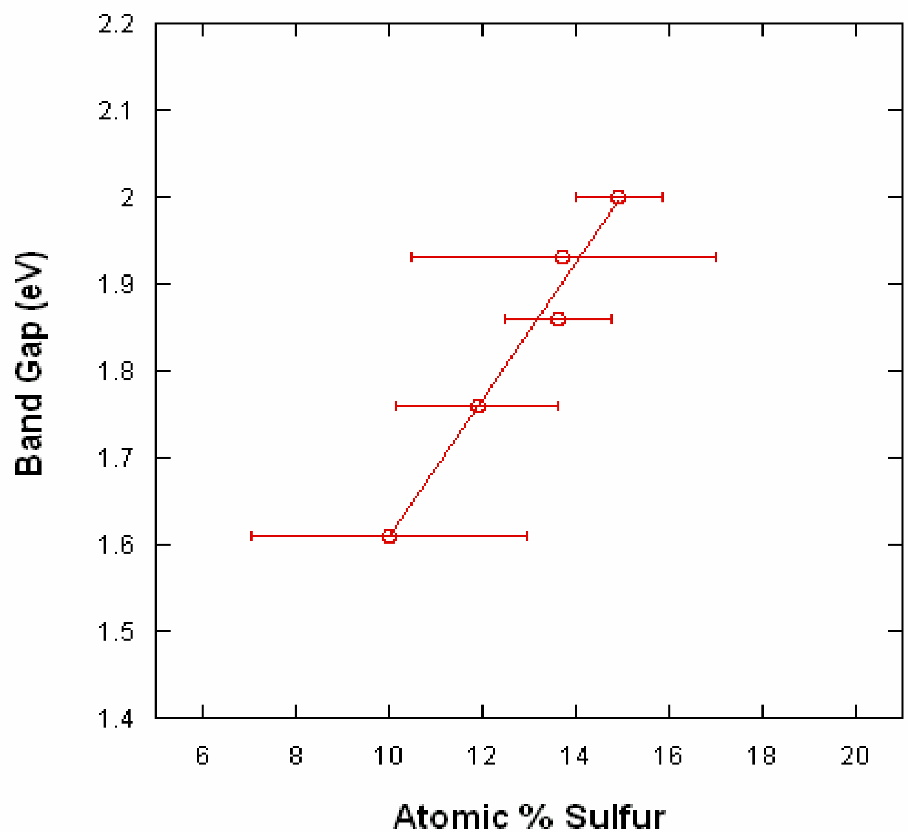
Electrode	Direct Eg	Indirect Eg
ME085-2	1.74 eV	1.69 eV
ME085-3	1.75 eV	1.67 eV
ME086-1	1.66 eV	1.59 eV
ME086-2	1.69 eV	1.58 eV
ME087-1	1.88 eV	1.75 eV
ME087-2	1.88 eV	1.76 eV

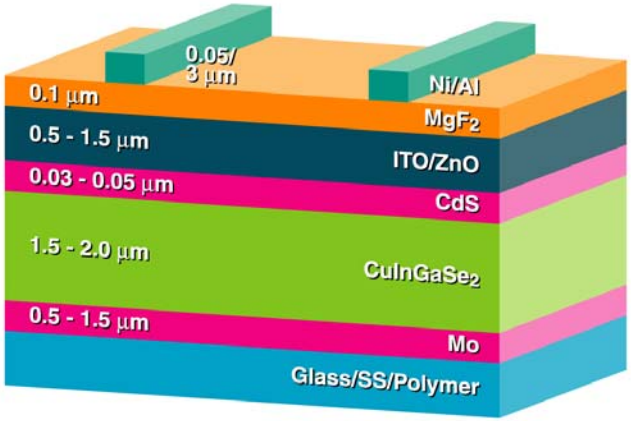


A long shot, but could be low cost….

New Materials - Band Gap Requirements for Electrodeposited CIGSSe

- Dependence on sulfur content noted.
- However, this is convoluted by varying concentrations of other elements

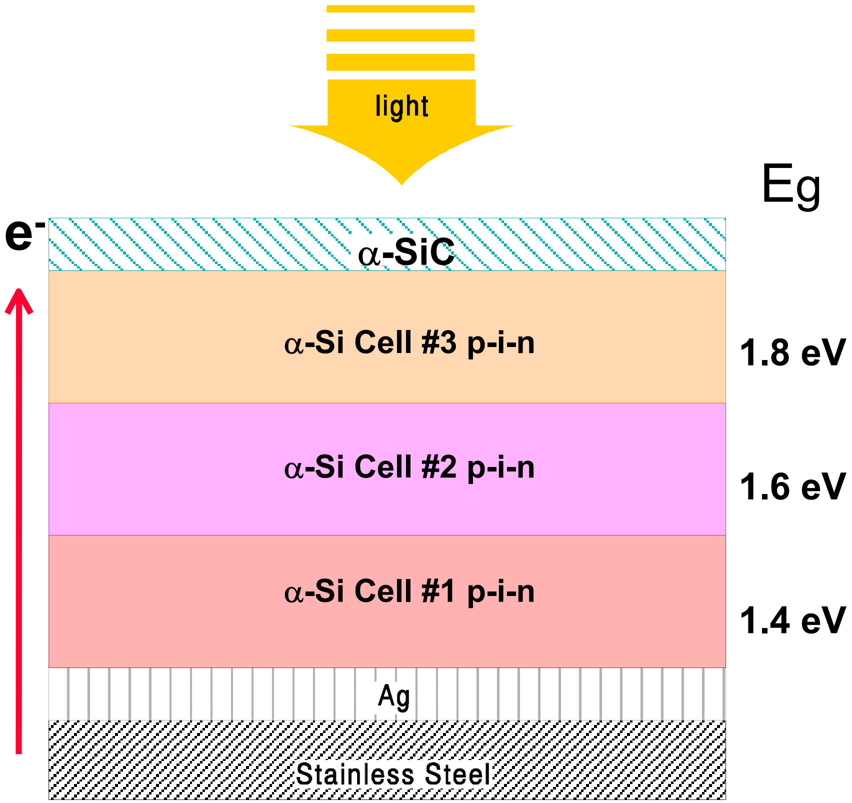


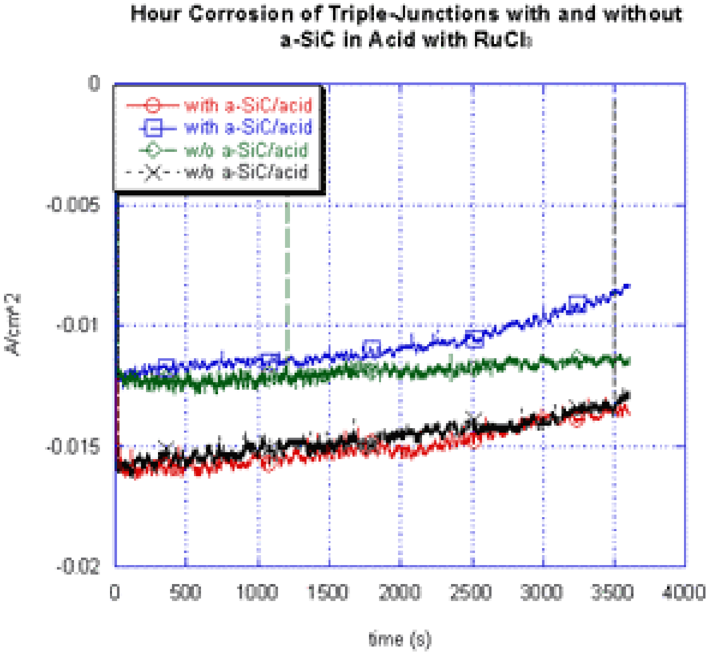


Possible low-cost thin-film material

Results for a-Si samples with Metal-ion Catalysts.

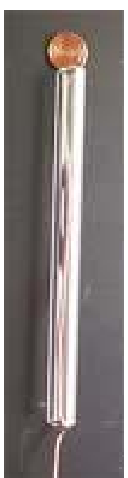
Another possible low-cost thin-film material





Summary of ongoing work for FY2003 in blue

- GaInP$_2$ - NREL (fundamental understanding)
- GaPN - NREL (high efficiency, stability)
- InGaN - SVT Associates, NREL, (high efficiency, stability)
- CuInGaSeS - UNAM (Mexico), NREL (Low cost)
- Multi-junction Amorphous Silicon - University of Toledo and ECD (Low cost)
- Energetics
  - Band edge control
  - Catalysis
  - Surface studies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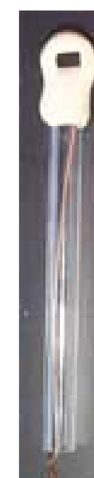

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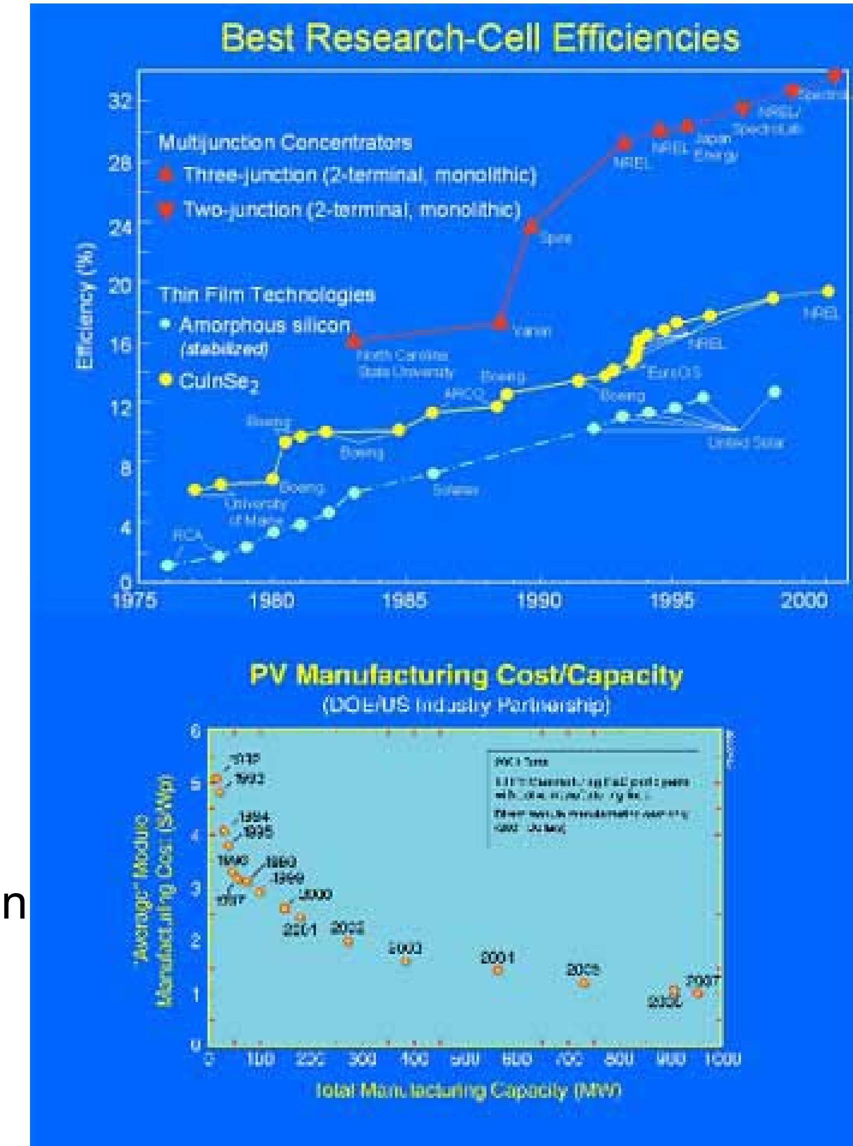
Plans for future work

- Continue materials research, discovery and development.
  - $In_xGa_{1-x}N$
  - GaPN
  - a-Si
  - CuInGaSSe
  - a-SiN (coating for stability)
  - Others…
- Energetics
  - Band-edge engineering
    - Development fundamental understanding of surface interaction
    - Try treatment on other materials
  - Catalysis
  - Surface studies



Collaborations and Interactions

In the US

Colorado School of Mines
University of Colorado
University of Wisconsin (Whitewater)
GM, Astropower (proposed)
Others working in this area: FSEC, Duquesne

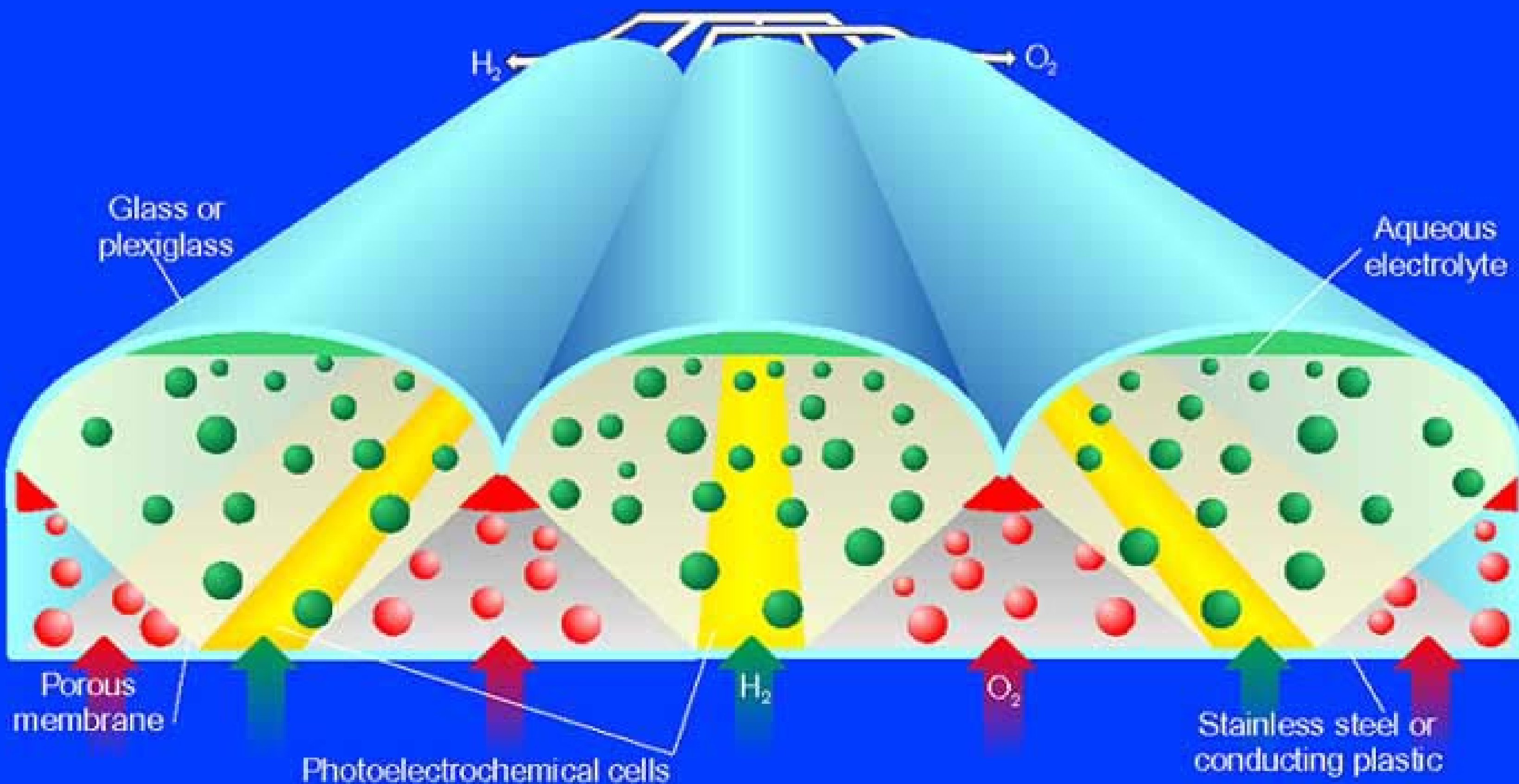
Outside of the US

Switzerland, Mexico, Armenia, Sweden, Japan

Plans

- Continue materials development.
  - Nitrides
  - CuGaInSSe
  - a-Si
- Band-edge engineering
  - Development fundamental understanding of surface interaction.
  - Try treatment on other materials
- Increase industry interactions

Conceptual Design of a Photoelectrochemical Water Splitting System with Light Concentration



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