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Nanotube Array Photoelectrochemical Hydrogen Production

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Synkera Technologies Inc.

05/10/2011

Project ID # PD062

Overview

Timeline

Project start date: 08/15/08

Project end date: 08/15/11

Percent complete: 87%

Barriers

Photoelectrochemical Hydrogen Production

- AC. Device Configuration Designs

Budget

- Total: $750,000
  - DOE share: $750,000
  - Contractor share: $0
- FY10 Funding: $201,500
- FY11 Funding: $223,725

Partners

- John Turner at NREL is a subcontractor for evaluation of PEC samples
- Synkera has the project lead as the SBIR company

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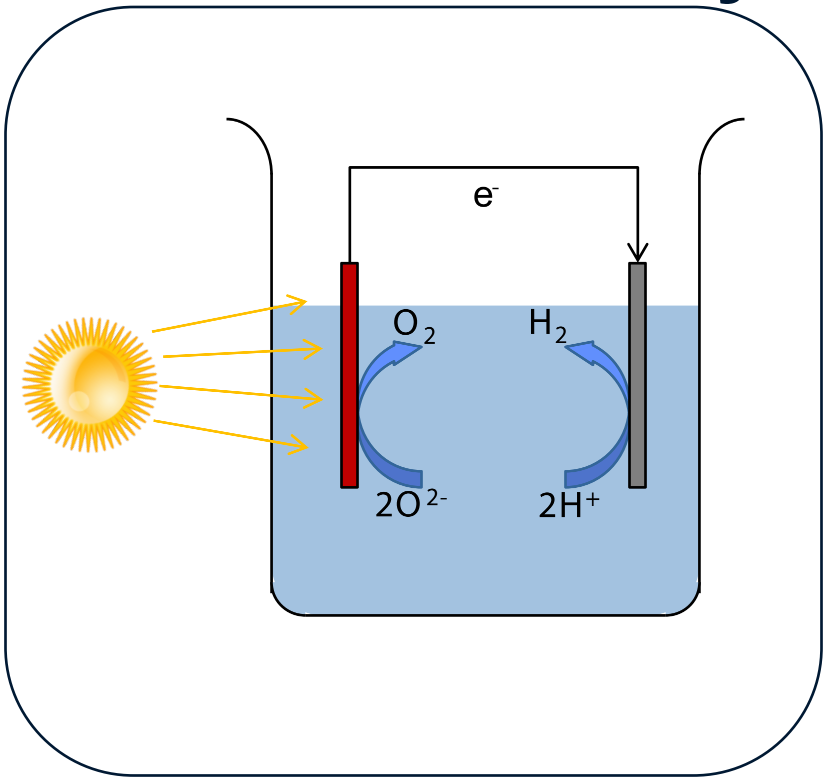
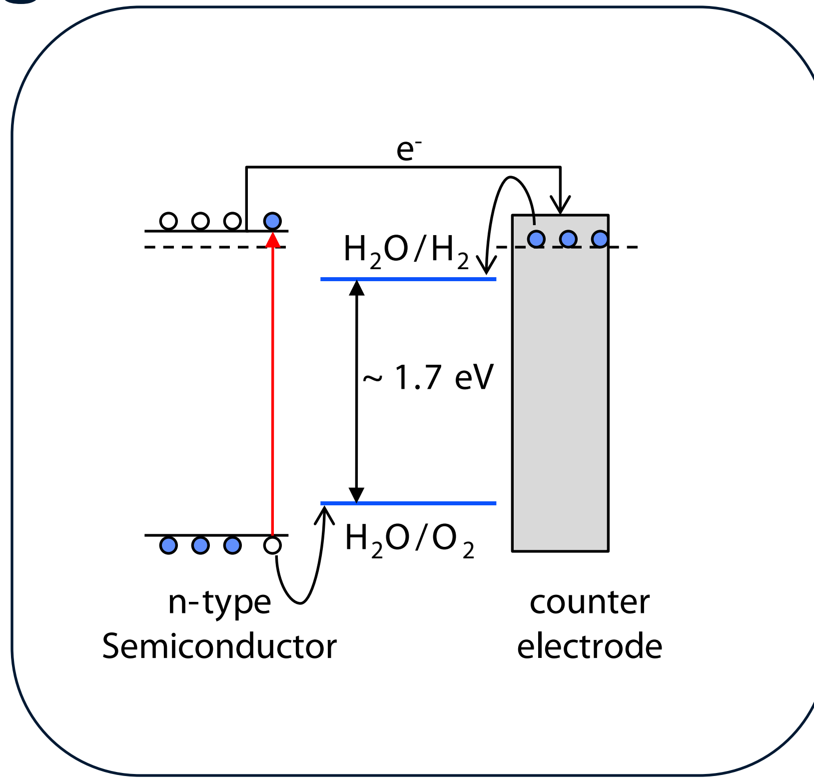
Relevance: Photoelectrochemical (PEC) Hydrogen





Requirements of PEC material:

- Band gap must be at least 1.7 eV
- Band edges must straddle H_2O redox potentials
- Must be stable in aqueous solution

John A. Turner, Photoelectrochemical Water Splitting, 2004 DOE Hydrogen , Fuel Cells & Infrastructure Technologies Program Review, 5/24/04.

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Relevance

The project objective is to develop hybrid photoelectrochemical (PEC) devices that meet or exceed the 2018 performance targets.

Synkera is addressing the barrier of PEC **Device Configuration Designs** by creating a hybrid design that combines multiple layers of materials to simultaneously address issues of durability and efficiency. As part of this effort, techniques are being developed that can manufacture devices at commercial scales.

Performance Measure	Units	2013 Target	2018 Target
Usable bandgap	eV	2.3	2.0
Chemical conversion efficiency	%	10	12
Solar to hydrogen efficiency	%	8	10
Plant Durability	hours	1000	5000

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Relevance: Objectives for Previous Year

Key Milestone	% Completed
Conformally deposit ITO inside nanoporous AAO	100
Deposit Pt nanoparticles inside nanoporous AAO	100
Fabricate large area membranes for scale-up	100
Achieve usable bandgap below 2.0 eV	70
Complete fabrication of absorber prototypes	80
Develop large area PEC samples	30
Prototype able to meet all DOE goals	50

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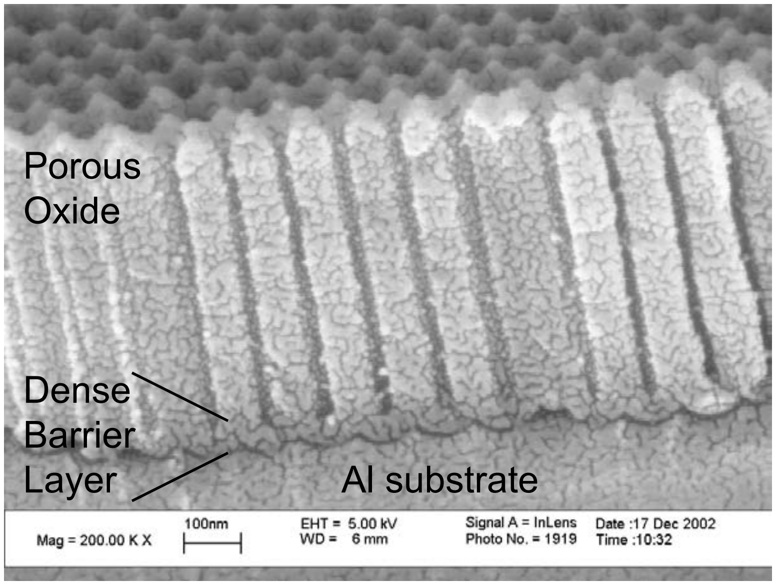
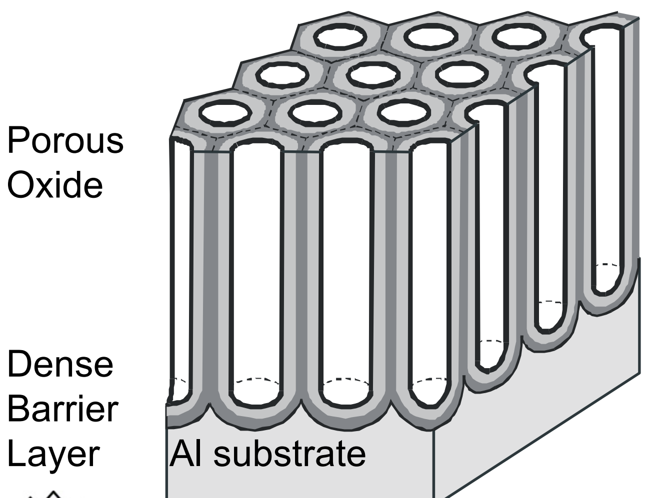
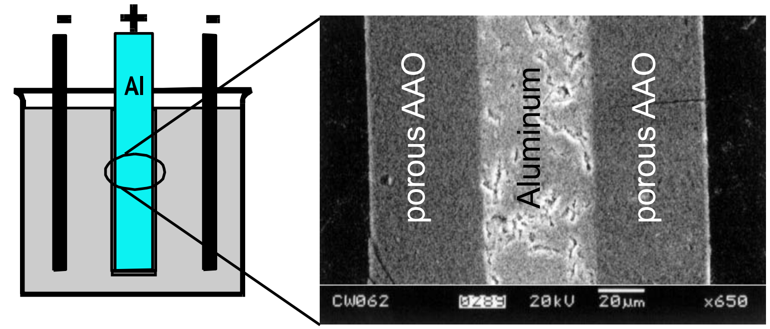
Approach: Anodic Aluminum Oxide as a Scaffold for PEC Materials







- High quality self-organized material with regular nanoporous lattice
- Uniform & aligned arrays of cylindrical nanopores
  - Pore diameter: 5 - 300 nm
  - Pore density: 10^{12} -10^{8} cm^{-2}
  - Thickness: 0.1 - 300 µm
- Formed by anodic oxidation of Aluminum
- Scaleable, manufacturing-friendly
- Platform for nano/microfabrication

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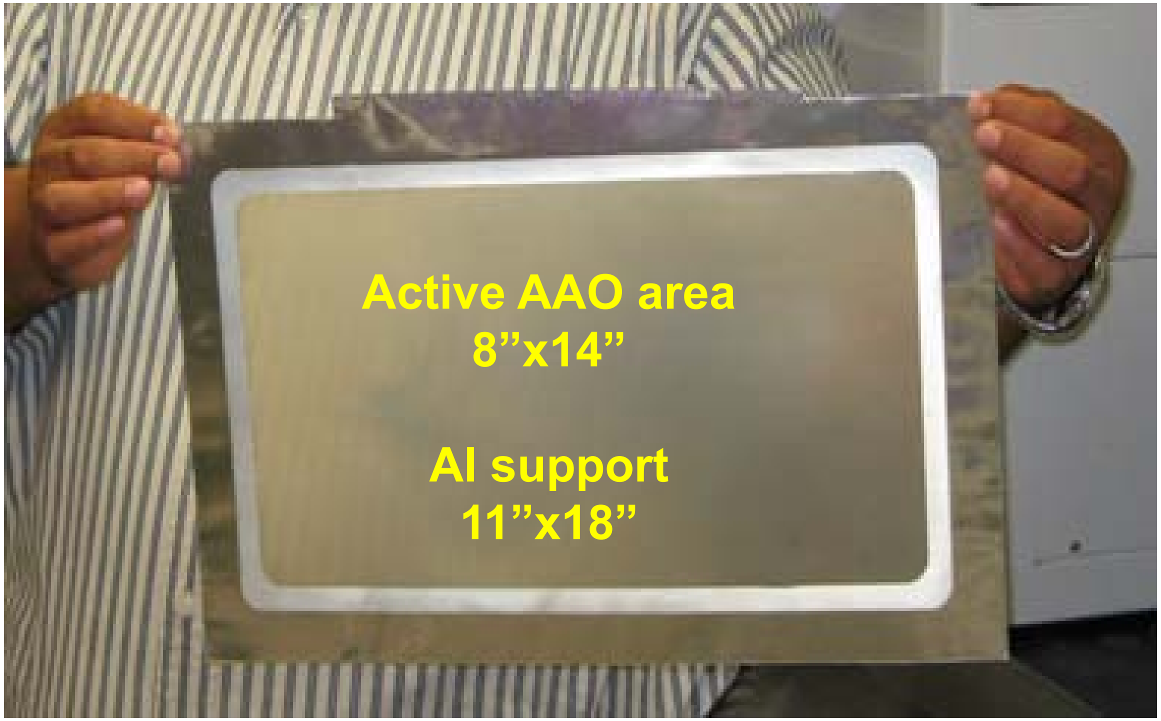
Approach: AAO a Scalable Material



World’s largest nanoporous AAO membrane produced at Synkera

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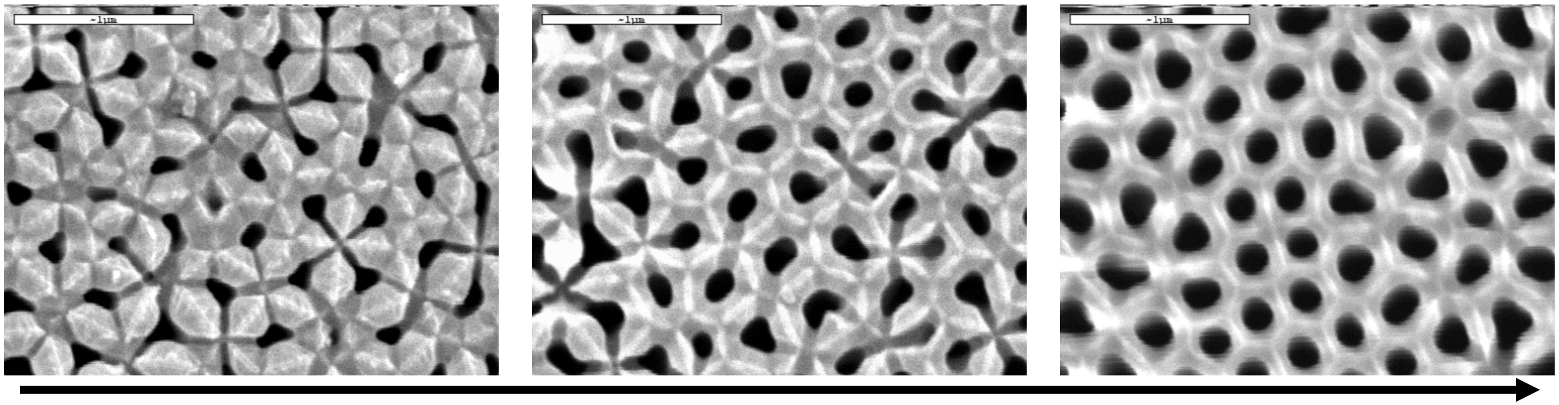
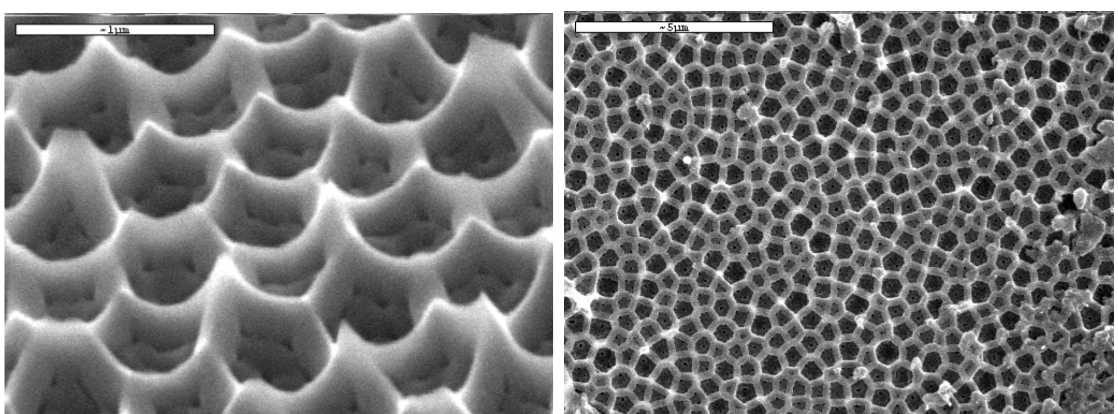
Engineered Nanotemplates for PEC

Synthesis of anodic aluminum oxide with large pore sizes.



Increasing Etch Time

Anodic aluminum oxide with minimally reflective surface.



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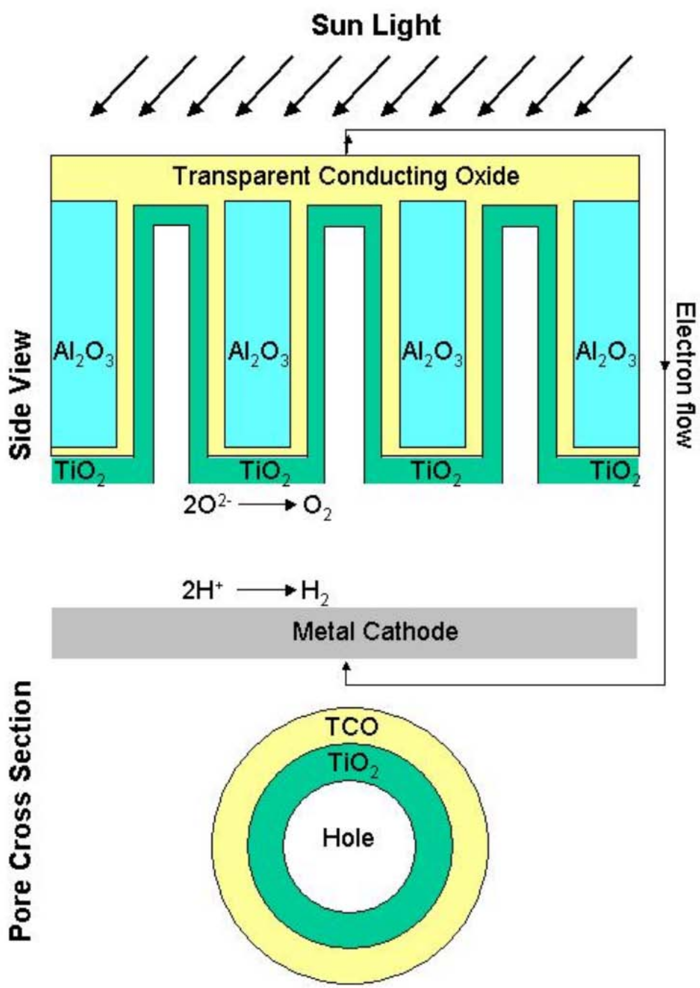
Approach: Nanorod Arrays for PEC Hydrogen (Phase I design)



- Based on AAO nanotemplate
- Short distance to conductors allows for efficient electron-hole separation
- Small pore size will reduce gas bubble formation
- TiO_2 is doped to reduce the band gap, but conductivity through TCO is unaffected
- Fabricated using atomic layer deposition (ALD)

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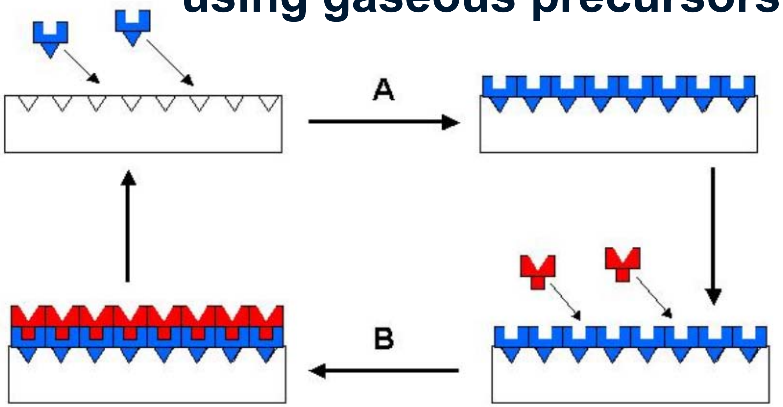
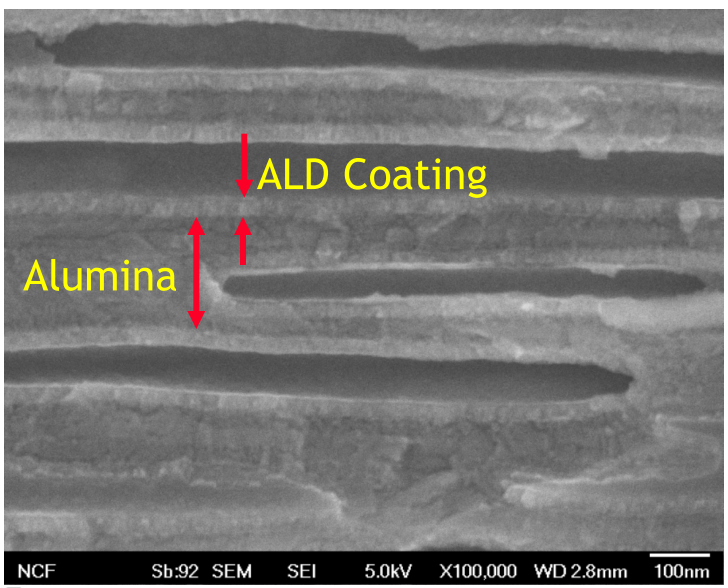
Approach: Fabrication by Atomic Layer Deposition

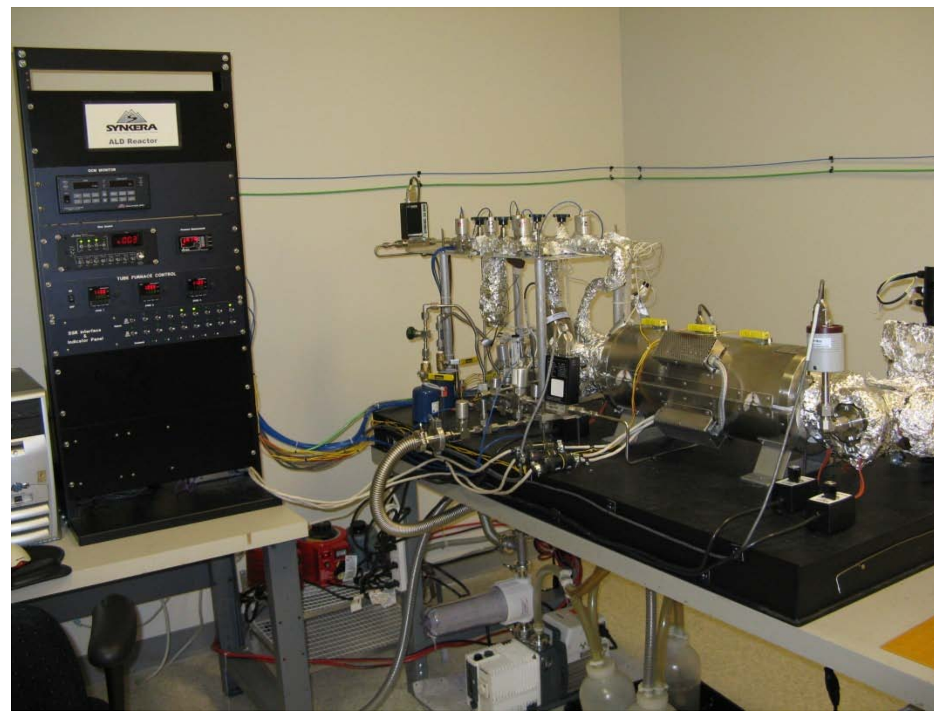
ALD consists of sequential self-limiting surface reactions using gaseous precursors applied in ABAB… fashion.



ALD inside AAO



Synkera ALD Reactor



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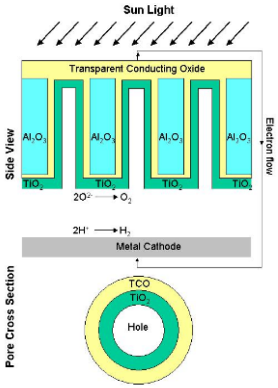


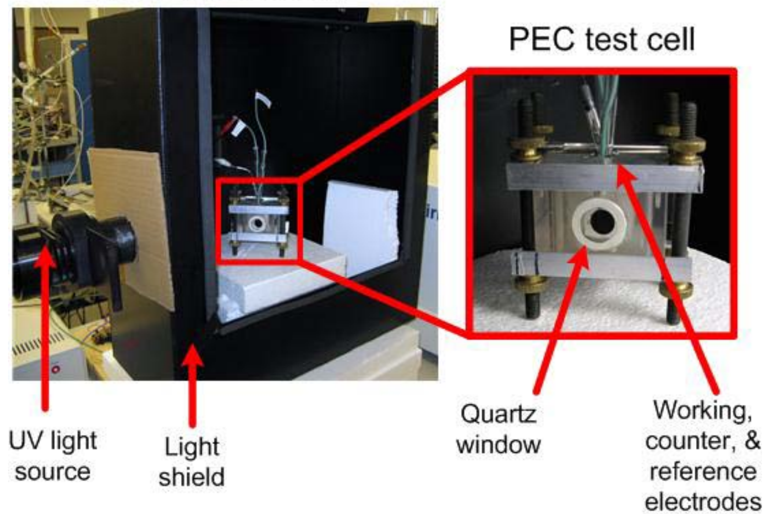
Technical Accomplishment

Phase I PEC Data

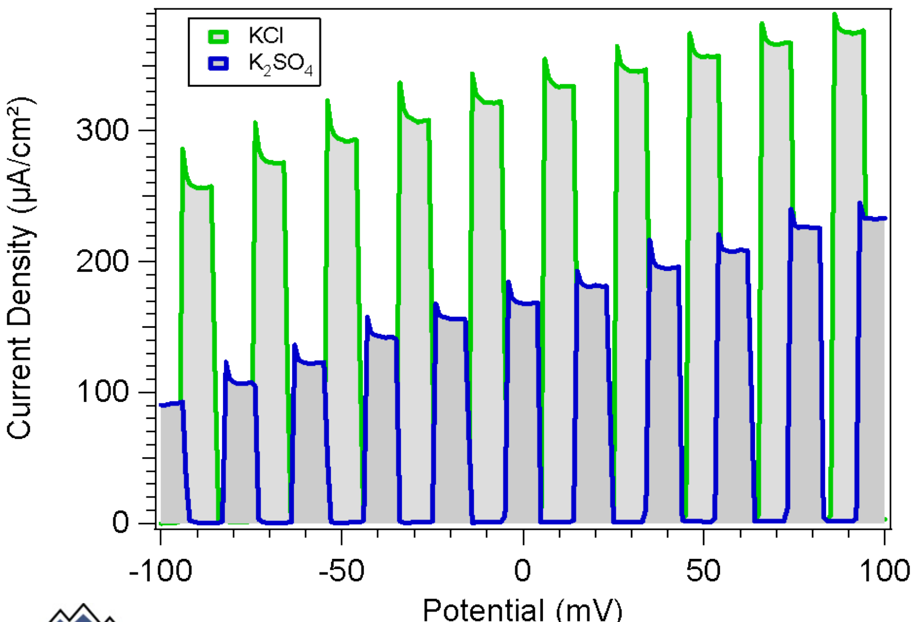
Test System

- 3-electrode setup
- Calibrated to 1 sun exposure
- 0.1 M K_2SO_4 test solution

PEC test system



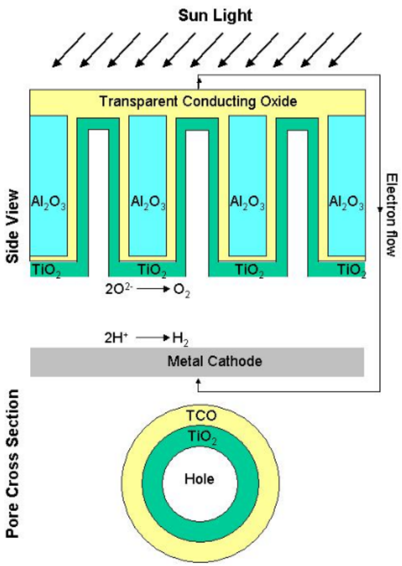
Typical Cyclic Voltammogram



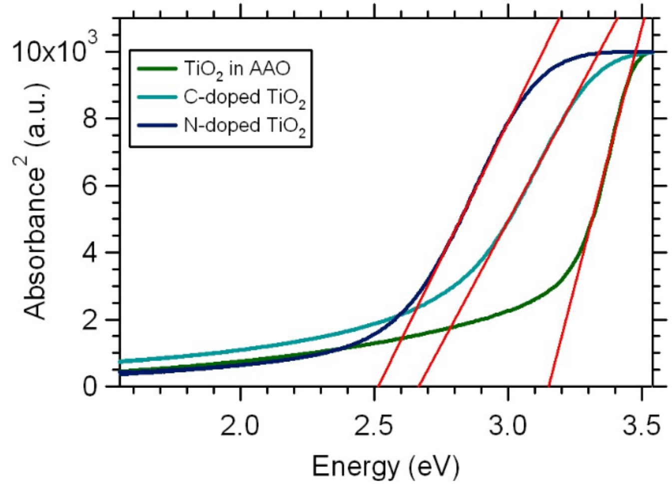
Highest current density obtained on undoped TiO_2 using test conditions listed was 400 μA/cm².

Technical Accomplishment

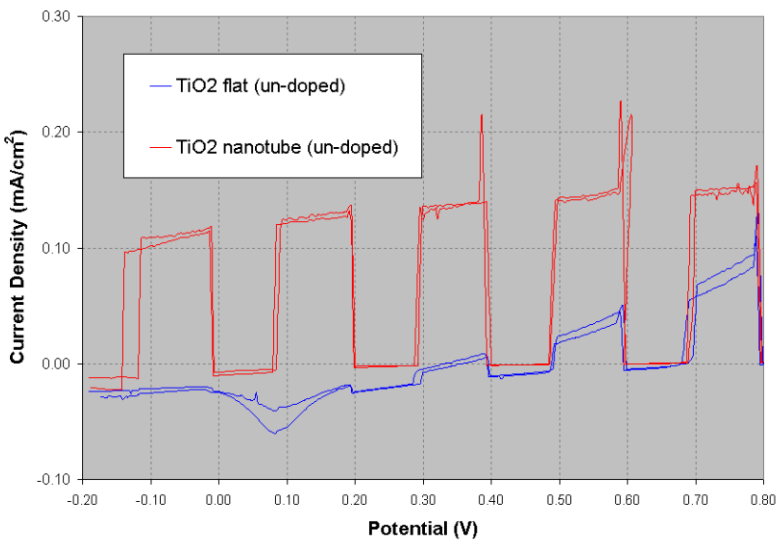
Phase I Results



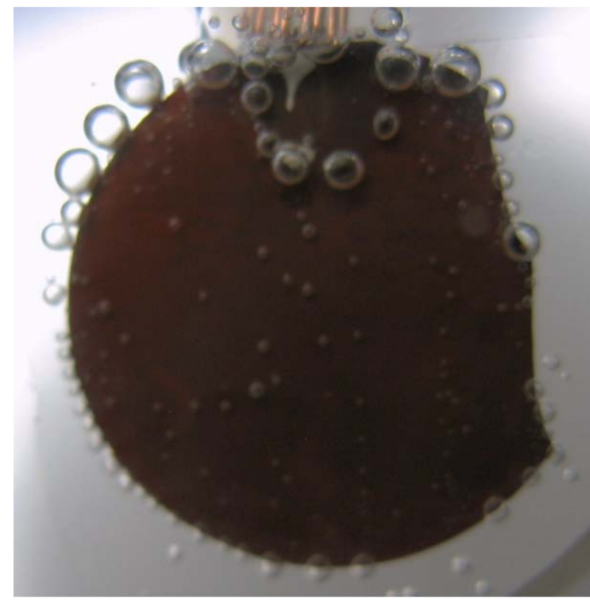
Able to reduce bandgap to 2.5 eV



Sample was active with zero applied potential!!!



Photoelectrolysis



We conclusively showed that nanostructuring increased the efficiency of photoelectrolysis

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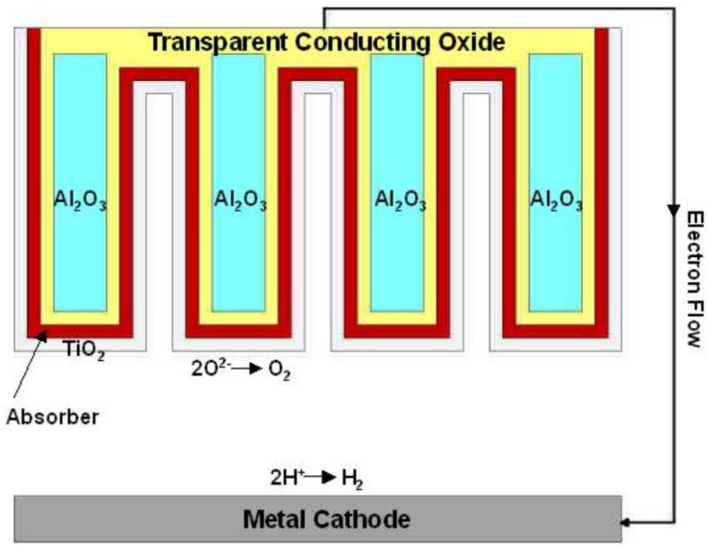
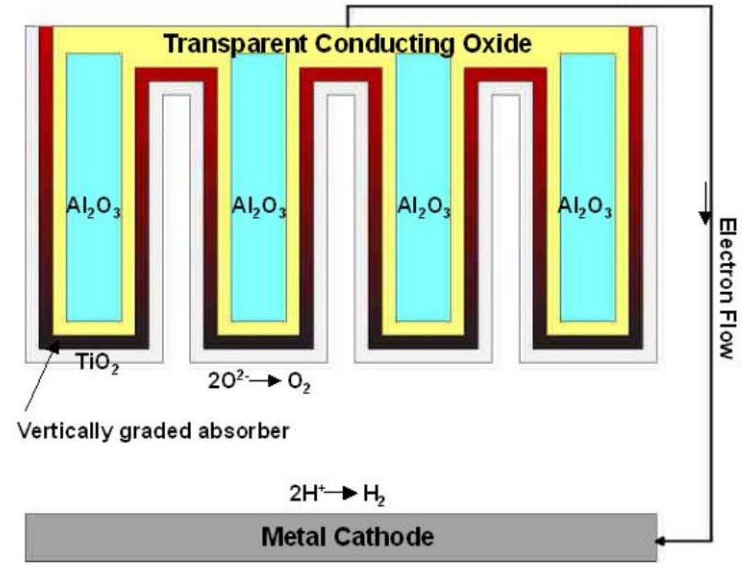
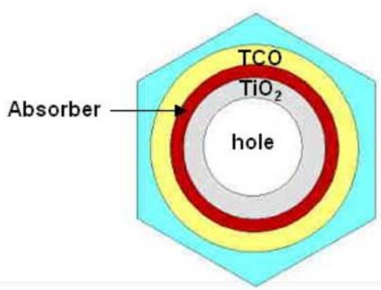
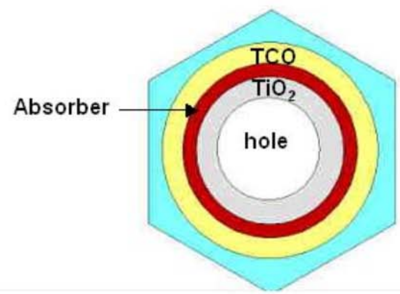
Phase II Approach: Nanorod Absorber Arrays for PEC Hydrogen









- Instead of modifying the TiO_2, we will add a separate absorber material to harness light
- This absorber can (in principle) be vertically graded in order to absorb a wider range of the the solar spectrum.

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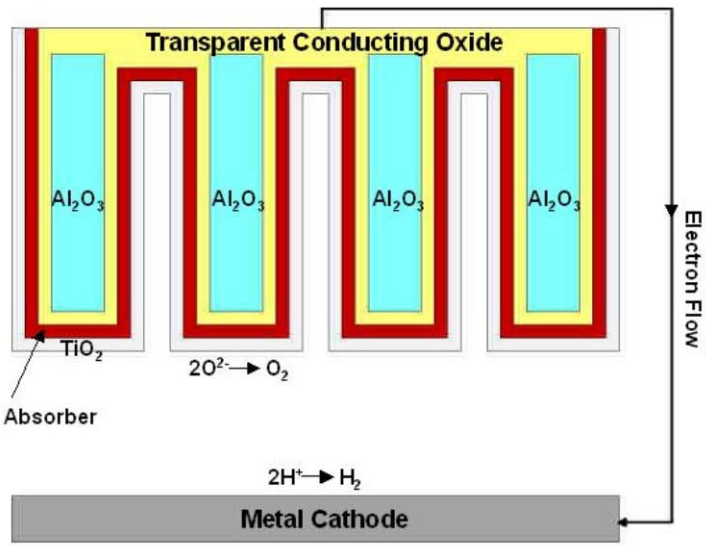
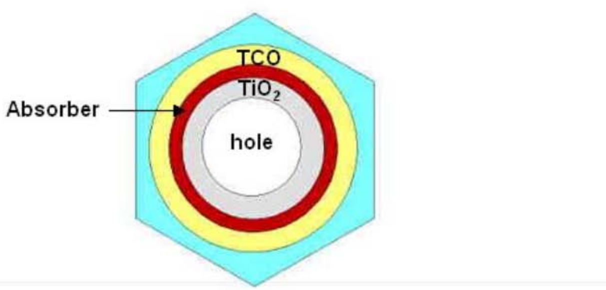
Phase II Approach Absorber Layer

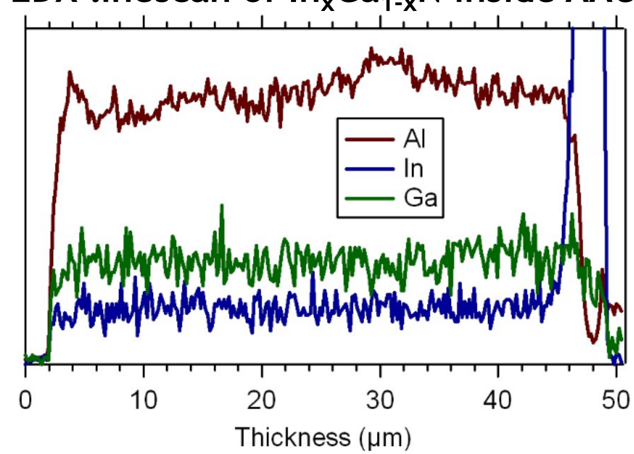
III-V Absorbers: InN, GaN, and $In_xGa_{1-x}N$





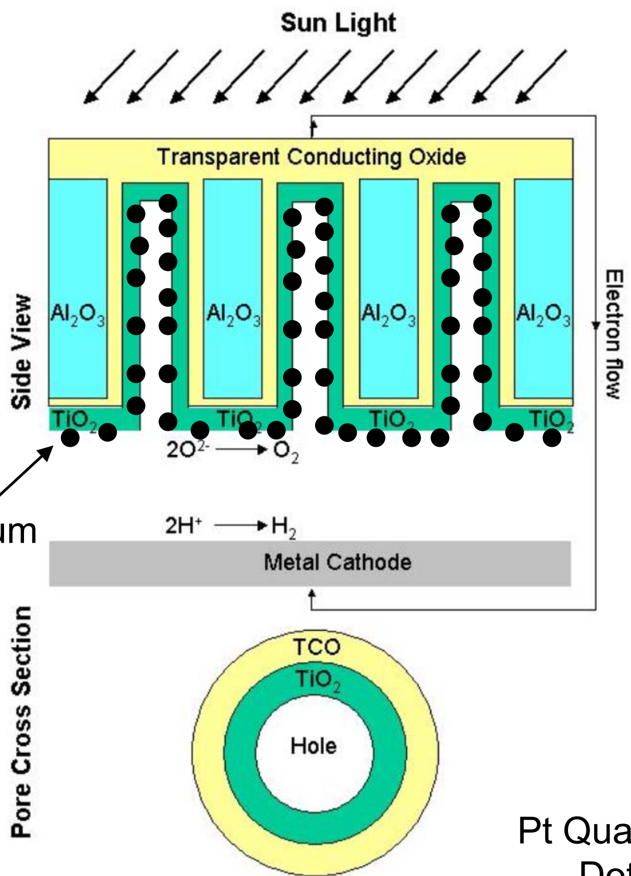
Left: InN **Right: GaN**

EDX linescan of $In_xGa_{1-x}N$ inside AAO



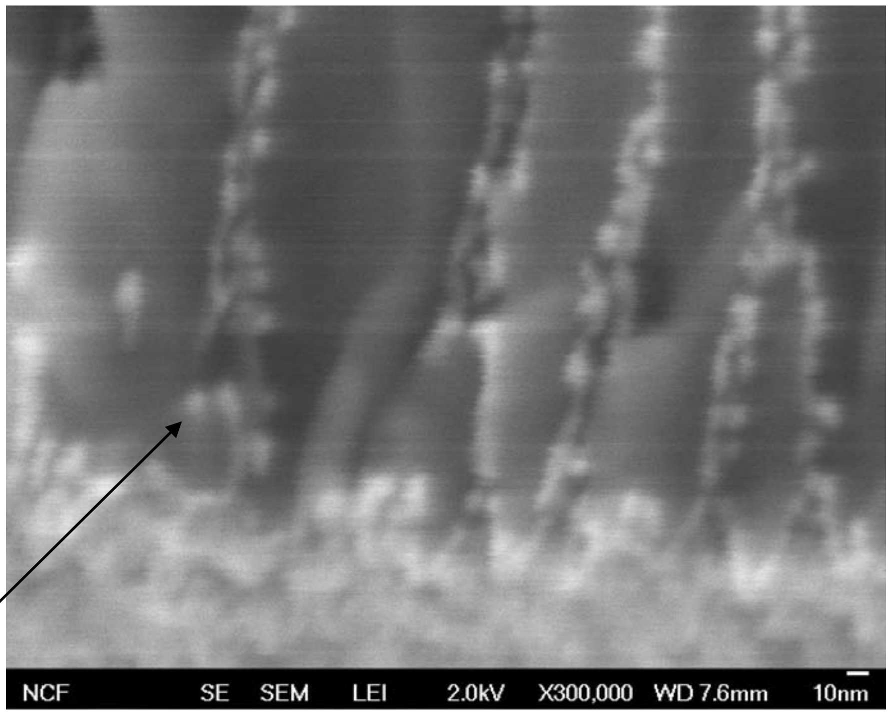
- TCO is the electron conductor
- Absorber material is used to harness light
- TiO_2 provides protective surface

Phase II Approach: Quantum Dot Absorber



Quantum Dots

SEM of Pt QD inside AAO



Pt Quantum Dots

- Instead of modifying the TiO_2 quantum dots are added to the surface to harness light
- Pt ALD chemistry has been developed

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Technical Accomplishment

Construction of Pilot Scale ALD Reactor

Synkera has begun construction of a pilot scale ALD reactor for coating large numbers of membranes.

Current Synkera ALD Reactor

- 3” ID with 7” long reaction zone
- Coats 20 samples at a time
- 7 precursors
- Designed for research

Pilot Scale ALD Reactor

- 6” ID with 18” long reaction zone
- Coats 200 samples at a time
- 12 precursors
- Designed for pilot scale manufacturing
- Accommodates large area PEC samples
- Expected completion date: 5/1/11

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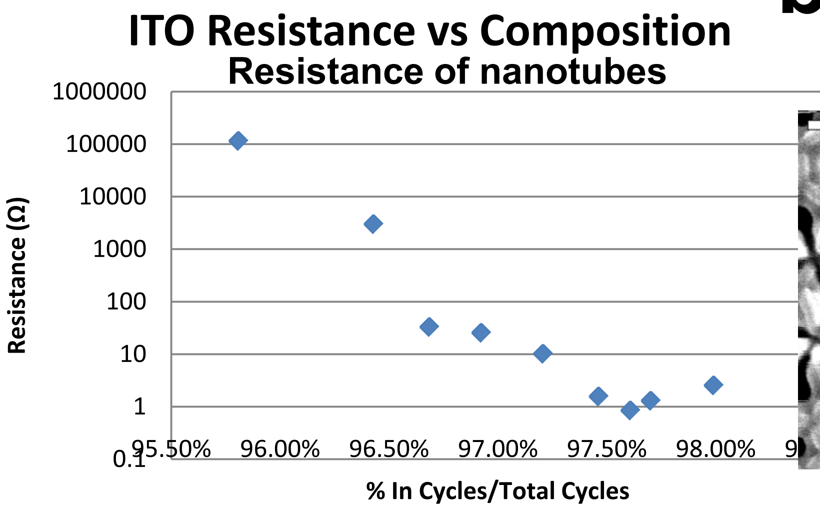
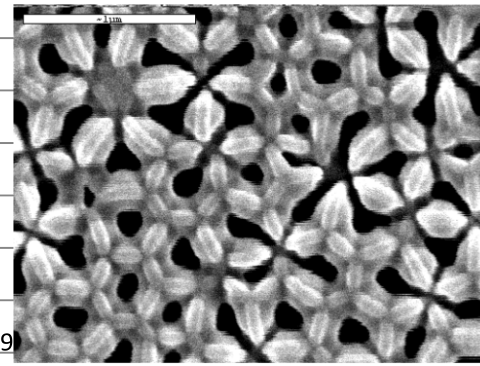
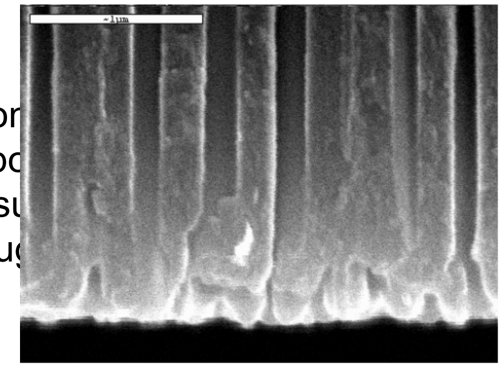
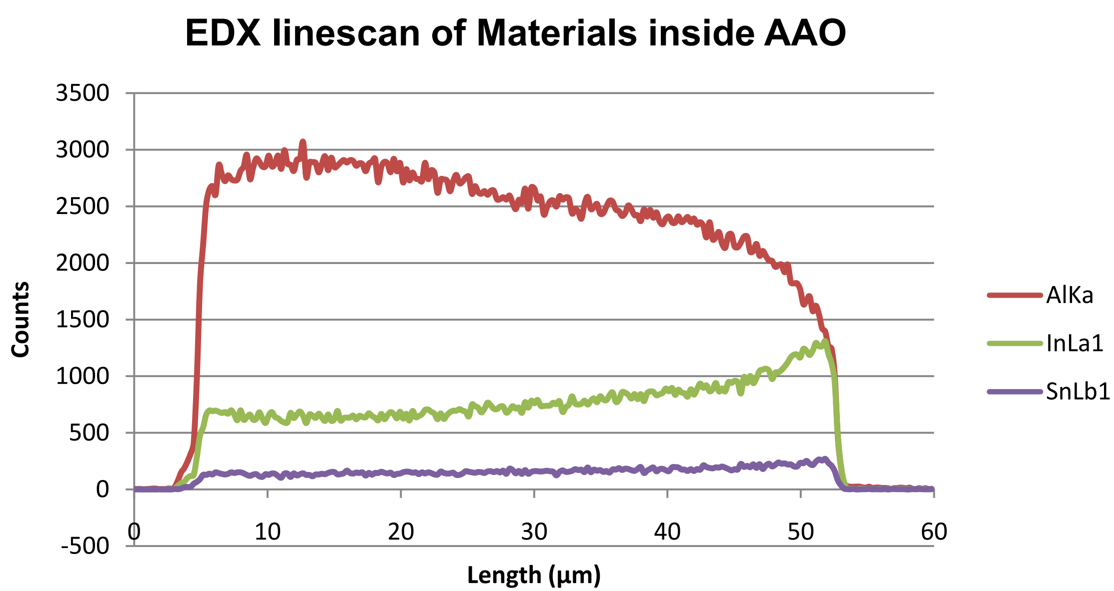
Technical Accomplishment

Indium Tin Oxide Transparent Conductor by ALD









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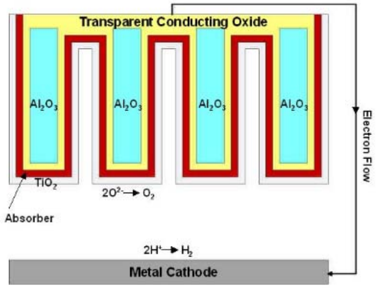
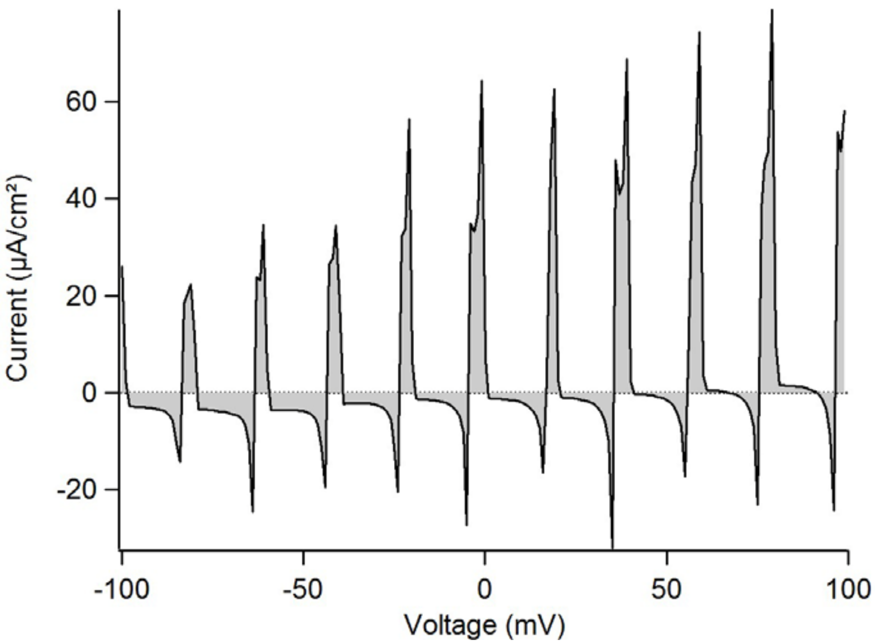
Technical Accomplishment

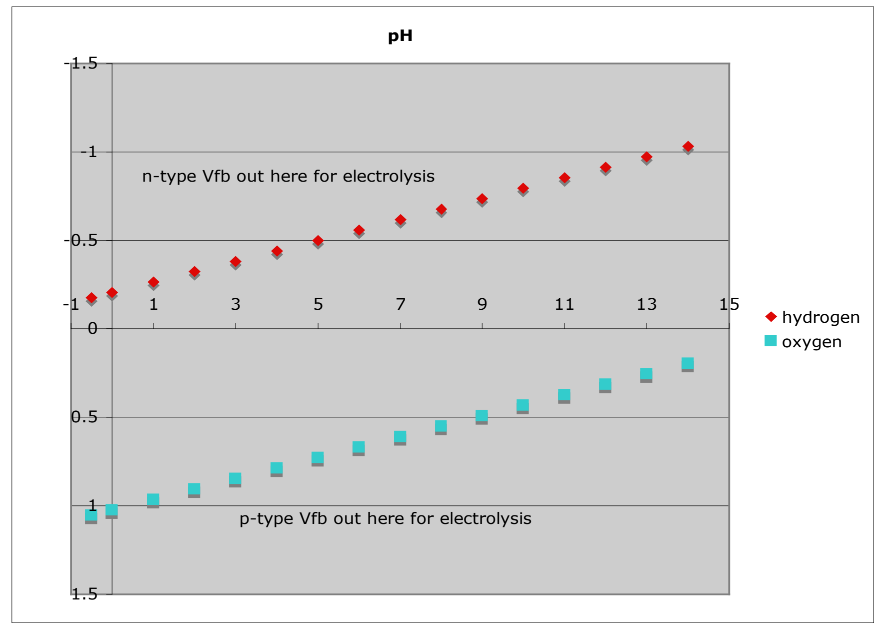
GaN as Absorber



Chopped light I-V for the GaN/TiO_2 electrodes



Flatband (V_{fb}) potentials necessary for unbiased photoelectrolysis vs. pH for GaN



Conduction bandedge of GaN is insufficient to drive photoelectrolysis of water. Similar results with InN.

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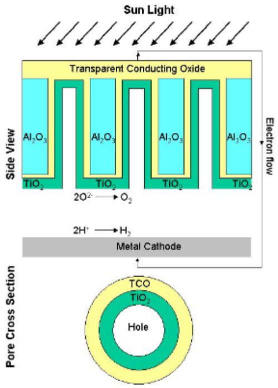
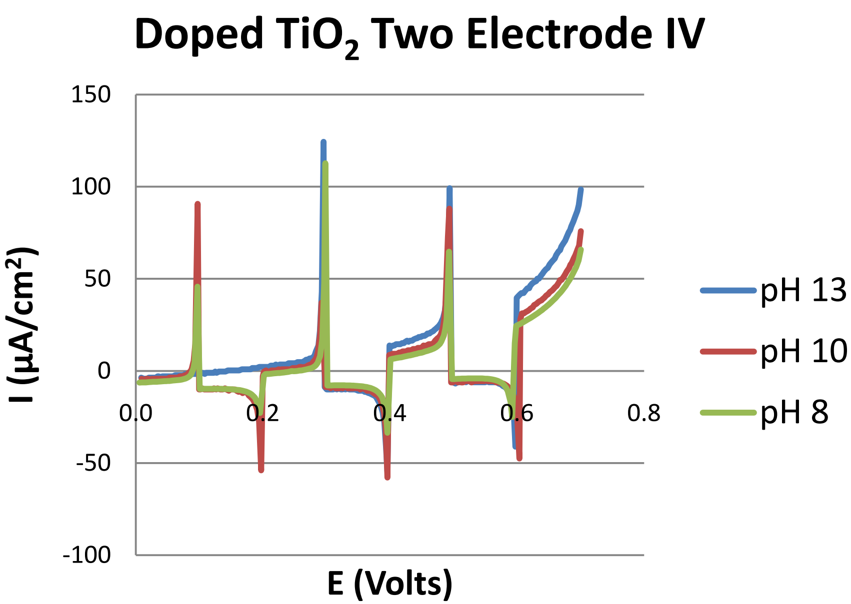
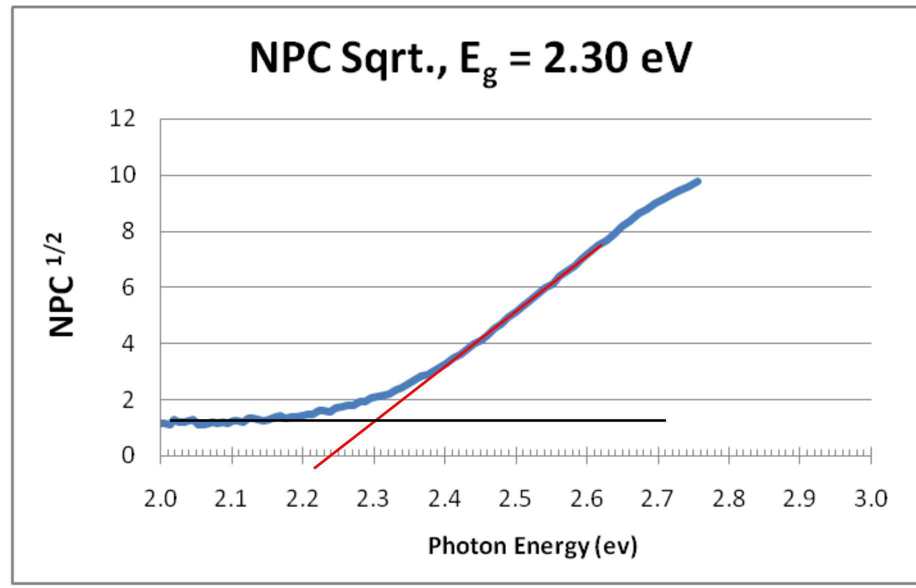
Technical Accomplishment

Doped TiO_2 as Absorber







- Photocurrent transients observed for chopped light IV
- Did not demonstrate Faradaic photocurrent necessary to achieve radiant to chemical energy conversion
- Indirect bandgap of 2.3 eV measured for doped TiO_2.

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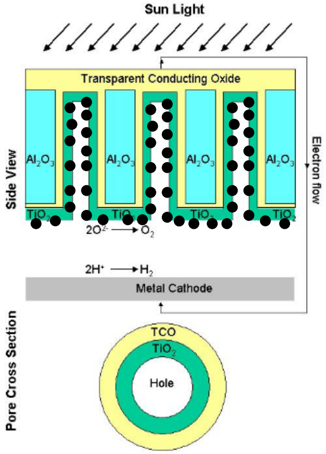
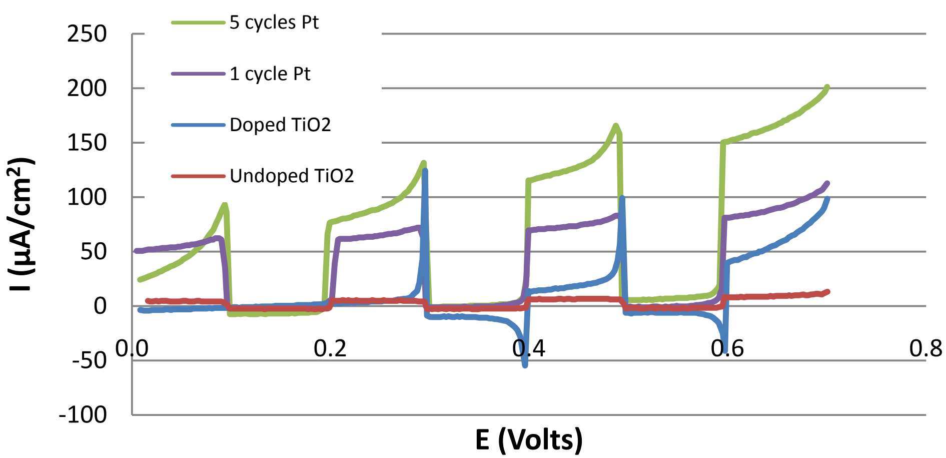
Technical Accomplishment

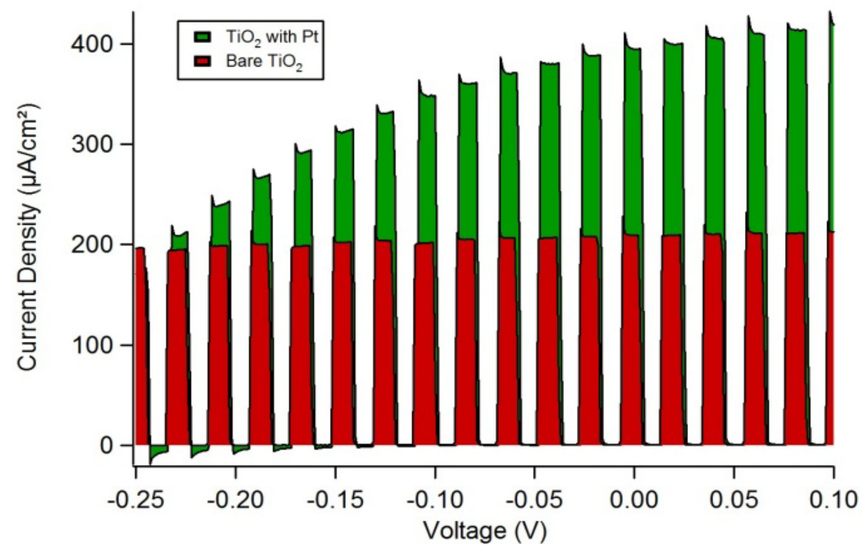
TiO_2 with Pt QD as Absorber



Two Electrode IV pH 13



Three Electrode IV vs Ag/AgCl (pH 13)



- Pt coated TiO_2 shows larger photocurrent than bare or doped TiO_2
- For 1 cycle of Pt ALD:
  - direct bandgap = 2.0 eV
  - indirect bandgap = 1.7 eV
- For 5 cycles of Pt ALD:
  - direct bandgap = 1.9 eV
  - indirect bandgap = 1.6 eV
- Pt coated electrodes show response to visible light!

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Collaborations

Partners

• National Renewable Energy Laboratory (Federal): Investigation of PEC efficiency and position of bandedges

• University of Colorado (Academic): High resolution SEM images of ALD coated samples

Commercialization

• HyGenera LLC was founded as a spin-off from Synkera for a variety of hydrogen related technologies, including PEC.

• Interested parties: Protonex Technology Corp., ITN Energy, McGuffy Energy Group, and CTI Petroleum, among others.

• Completed Technology Niche Assessment with Foresight Science & Technology to identify markets for spin-off applications.

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Proposed Future Work

- Manufacture samples with ITO as the TCO
- Further investigate Pt ALD of quantum dots to improve photocurrent
- Measure long-term stability of nanostructured films
- Scale up size of PEC samples to large areas using the new ALD reactor

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Summary Slide

Relevance: to develop hybrid photoelectrochemical devices that meet or exceed the 2018 performance targets.

Approach: Develop hybrid nanostructured devices where electron conduction, light absorption, and PEC reaction take place in separate materials.

Technical Accomplishments: Demonstrated visible light response using Pt quantum dots.

Collaborations: Synkera founded Hygenera LLC, a spinoff company designed to work with a variety of hydrogen related technologies.

Proposed Future Research: Examine in further detail effect of Pt quantum dots on PEC materials.

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