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Nanotube Array Photoelectrochemical Hydrogen Production

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Synkera Technologies Inc.

06/07/2010

Project ID # PD062

Overview

Timeline

Project start date: 08/15/08

Project end date: 08/15/10

Percent complete: 81%

Barriers

Photoelectrochemical Hydrogen Production

- AC. Device Configuration Designs

Budget

- Total: $750,000
  - DOE share: $750,000
  - Contractor share: $0
- FY09 Funding: $260,000
- FY10 Funding: $365,225

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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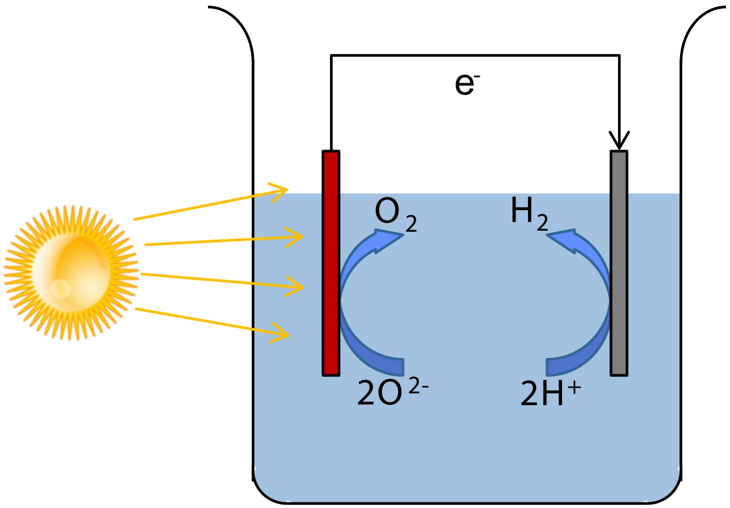
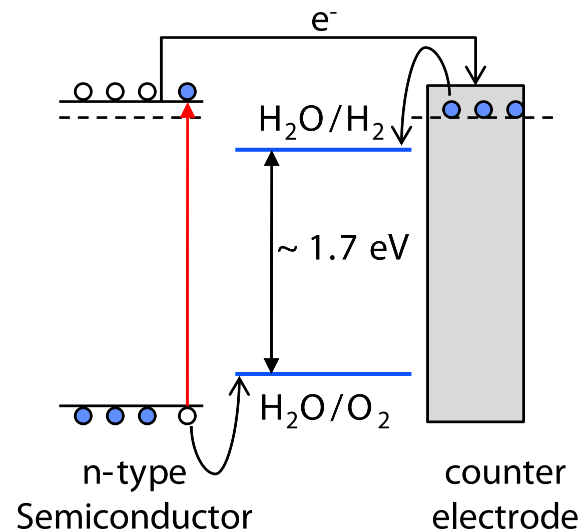
Relevance: Photoelectrochemical (PEC) Hydrogen





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: Key Milestones for Phase II Project

Key Milestone	% Completed
Complete and test upgrade of ALD reactor	100
Complete fabrication of architecture prototypes	100
Complete membranes for development of absorber materials.	100
Determine process for InGaN deposition	90
Complete fabrication of absorber prototypes	75
Prototype able to meet all DOE goals	50

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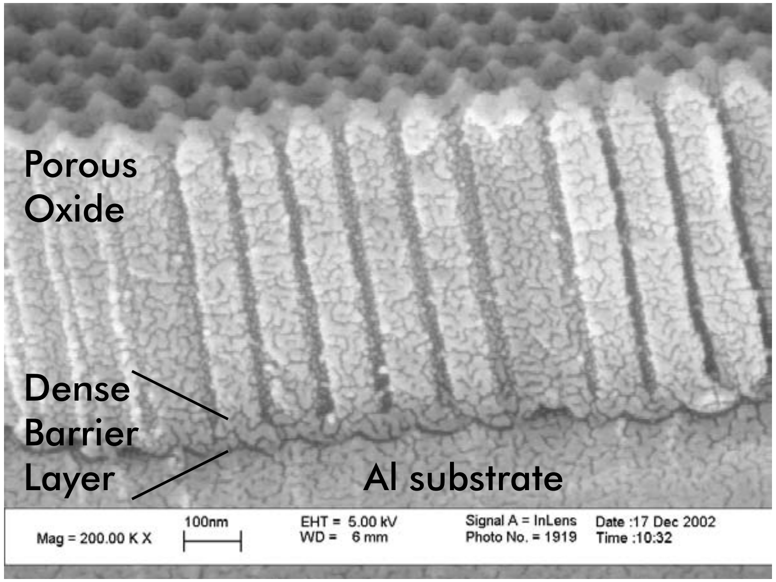
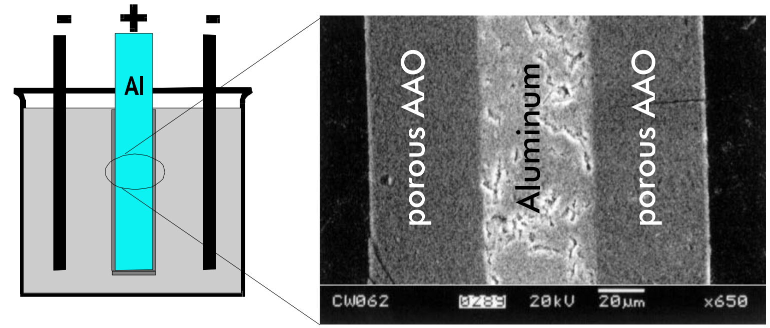
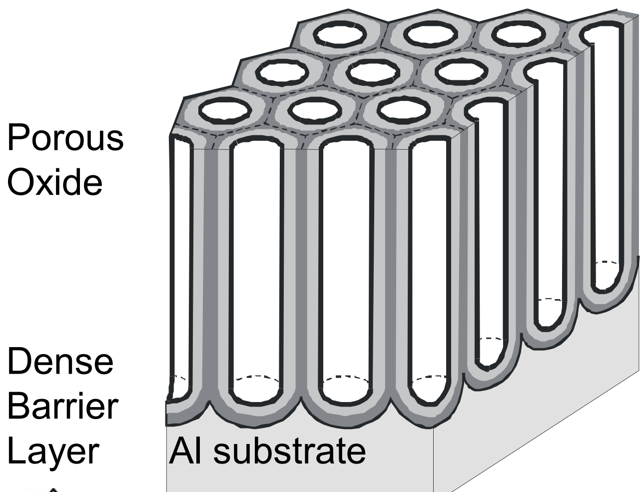
Approach: Anodic Aluminum Oxide as a Scaffold for PEC Materials







- 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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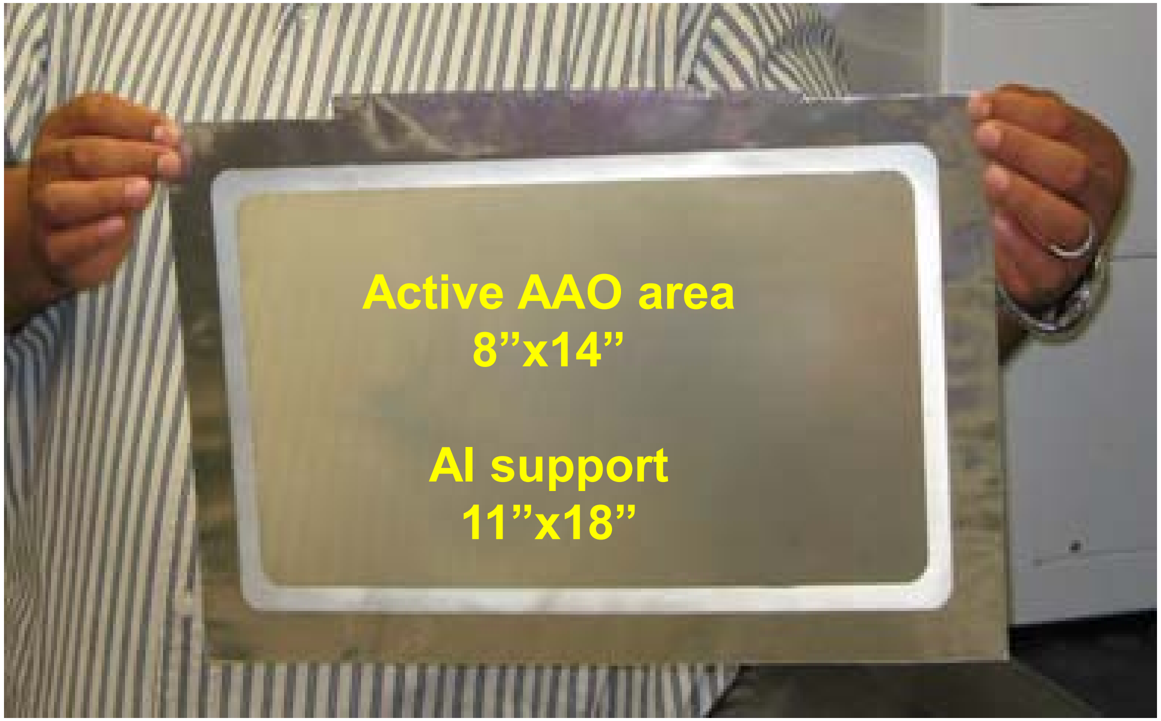
Approach: AAO a Scalable Material



World’s largest nanoporous AAO membrane produced at Synkera

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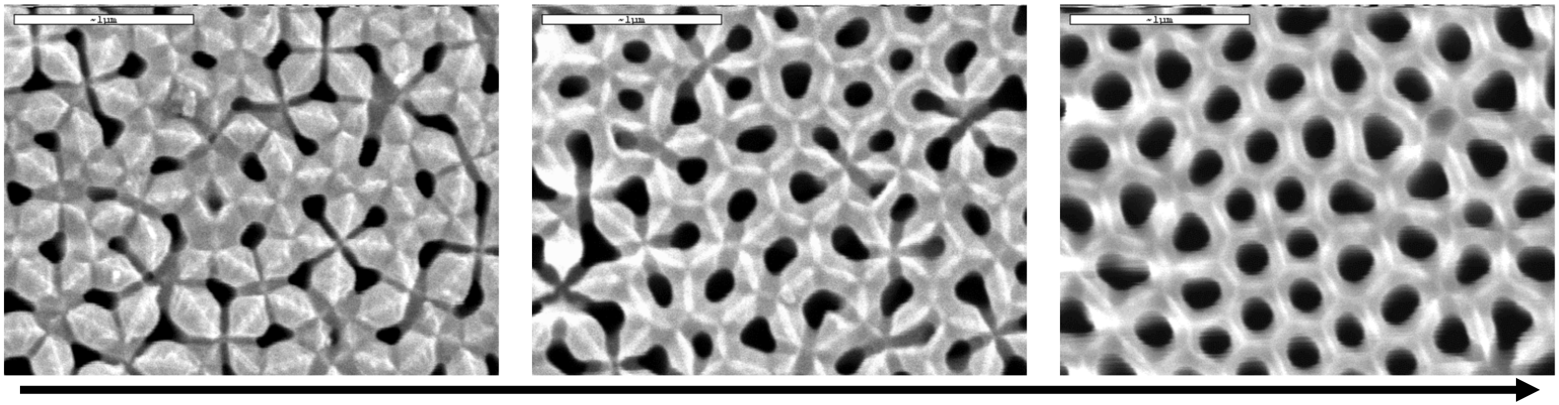
Technical Accomplishment

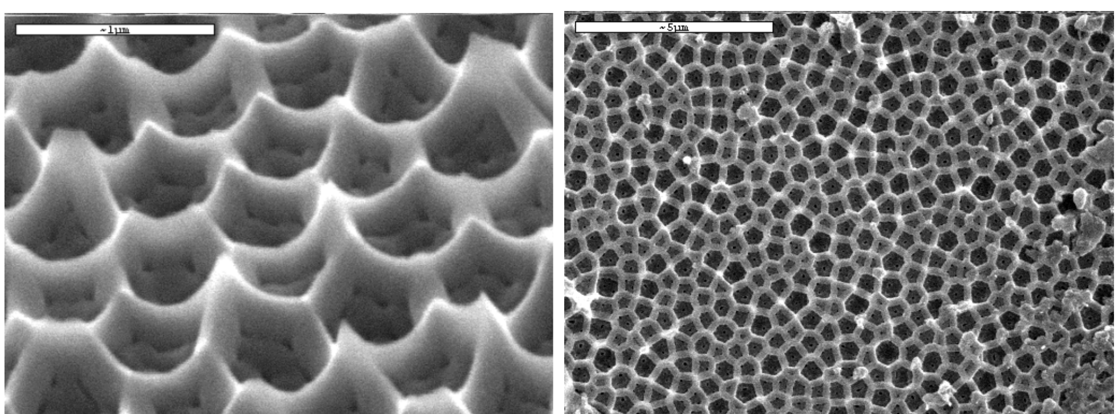
Engineered Nanotemplates for PEC

Synthesis of anodic aluminum oxide with large pore sizes.



Increasing Etch Time

Anodic aluminum oxide with minimally reflective surface.



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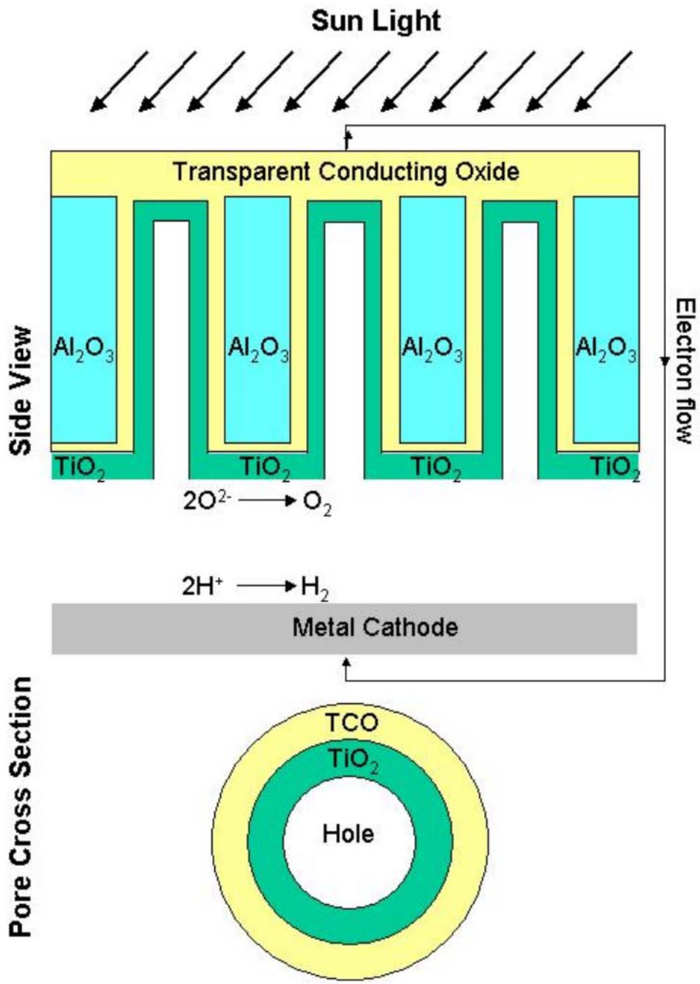
Approach: Nanorod Arrays for PEC Hydrogen (Phase I design)



- 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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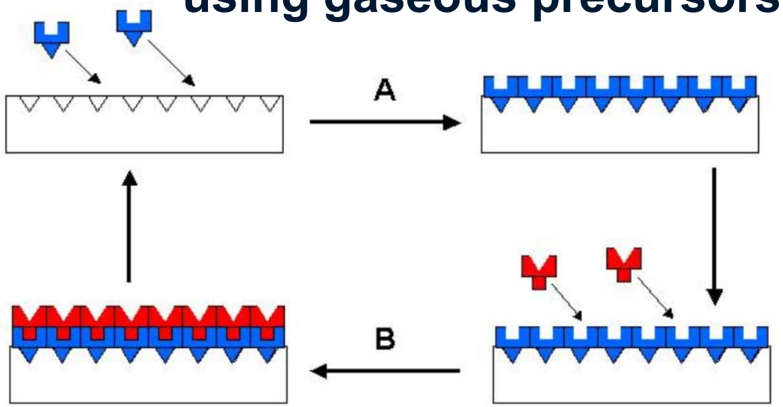
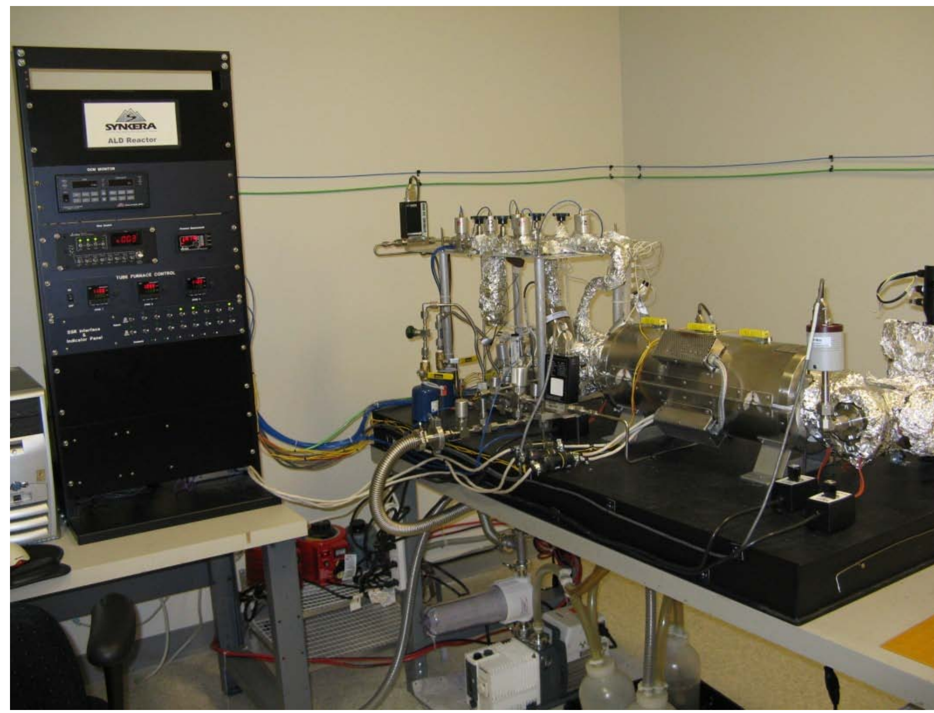
Approach: Fabrication by Atomic Layer Deposition

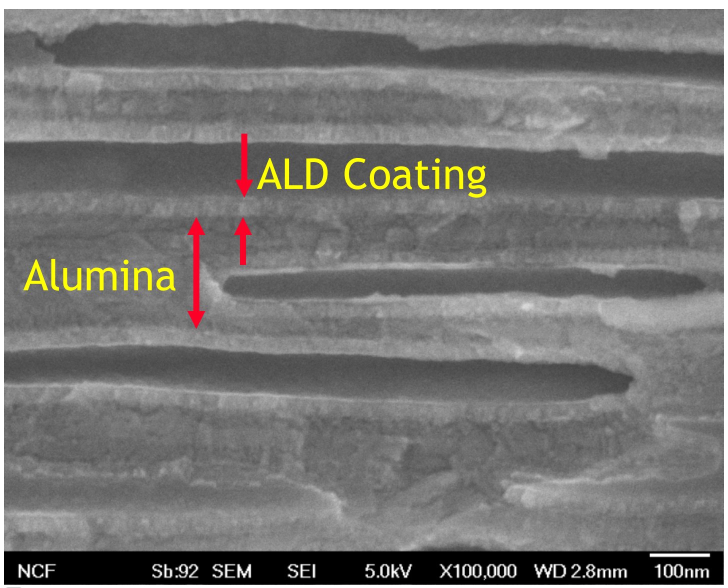
ALD consists of sequential self-limiting surface reactions using gaseous precursors applied in ABAB… fashion.



Synkera ALD Reactor



ALD inside AAO



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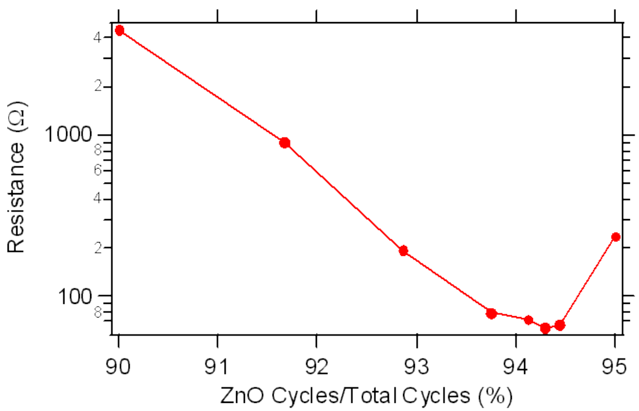
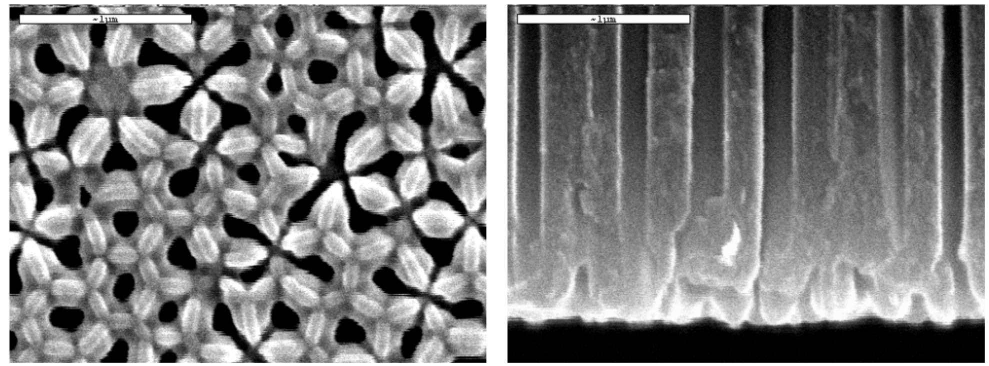
Transparent Conductor and TiO_2 by ALD

Conductive and Titania Coatings

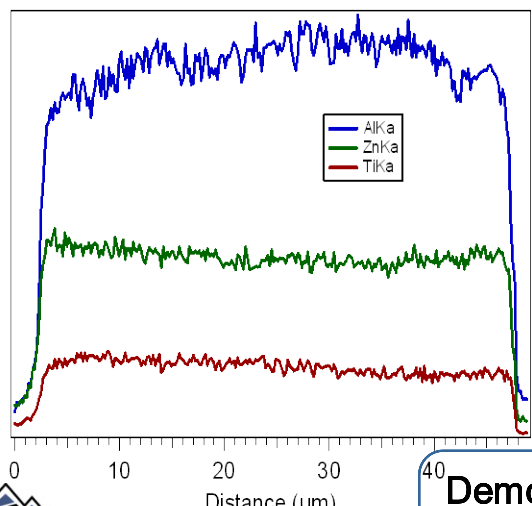
Resistance of nanotubes



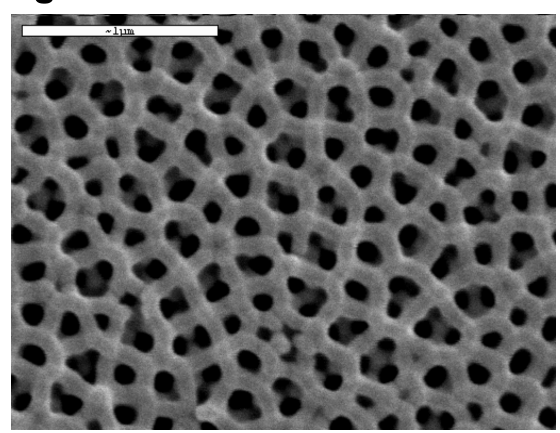
SEM images of AAO coated with conductive layer



EDX linescan of Materials inside AAO



SEM images of AAO coated with both materials



Demonstrated conformal coatings inside high-aspect ratio pores.

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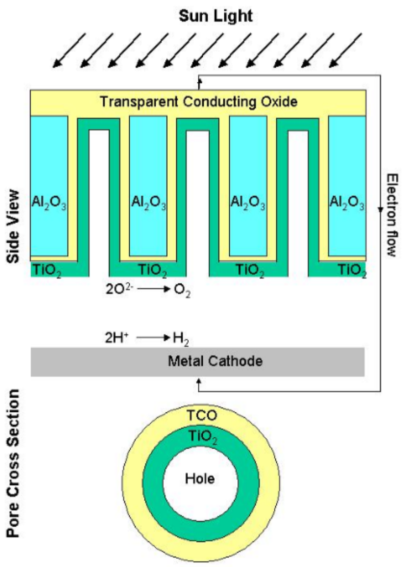
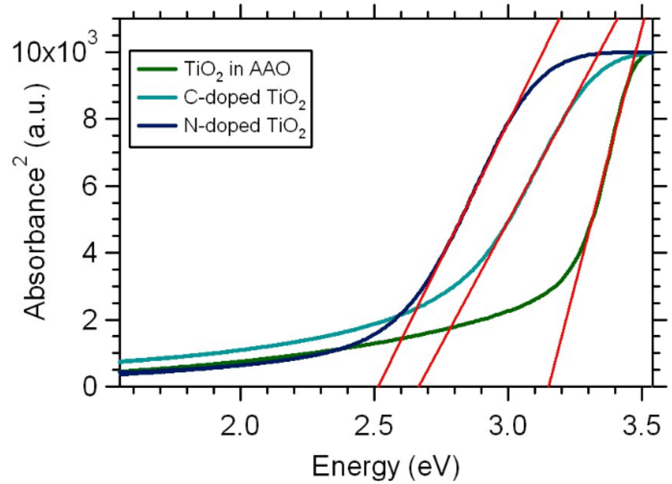
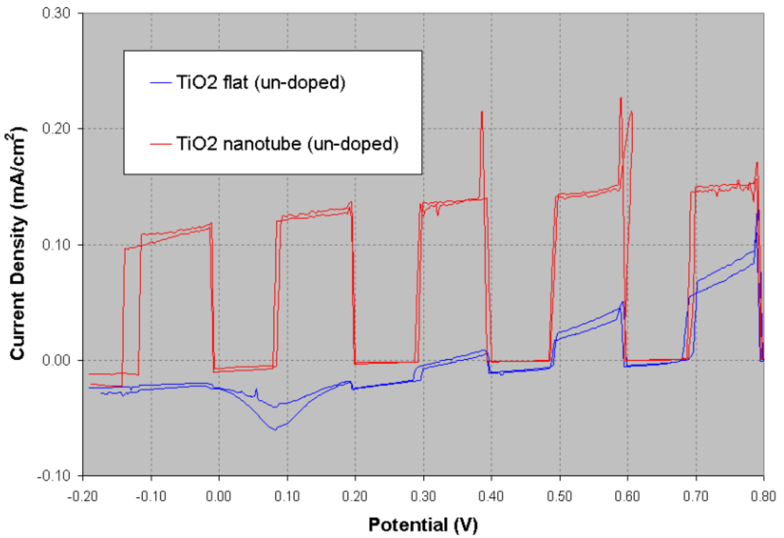
Phase I Results



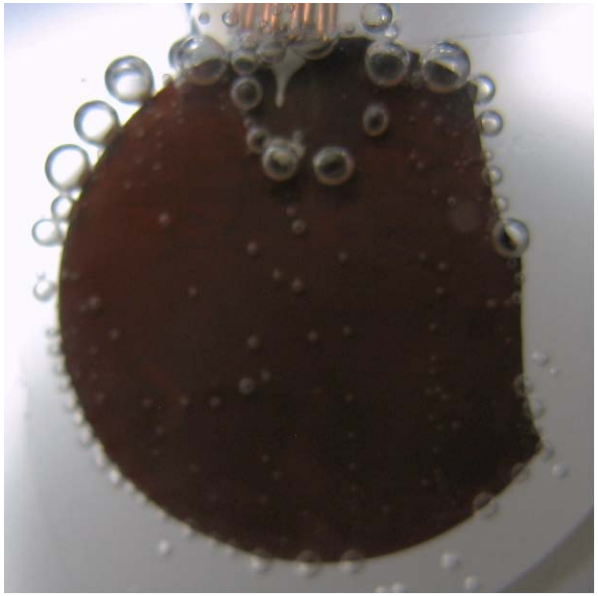
Able to reduce bandgap to 2.5 eV



Sample was active with zero applied potential!!!



Photoelectrolysis



We conclusively showed that nanostructuring increased the efficiency of photoelectrolysis

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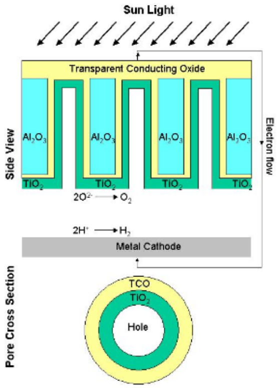
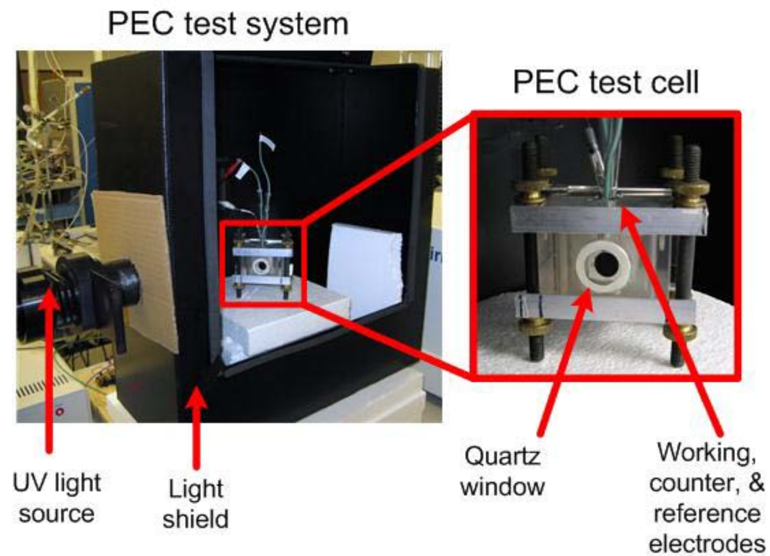


Technical Accomplishment

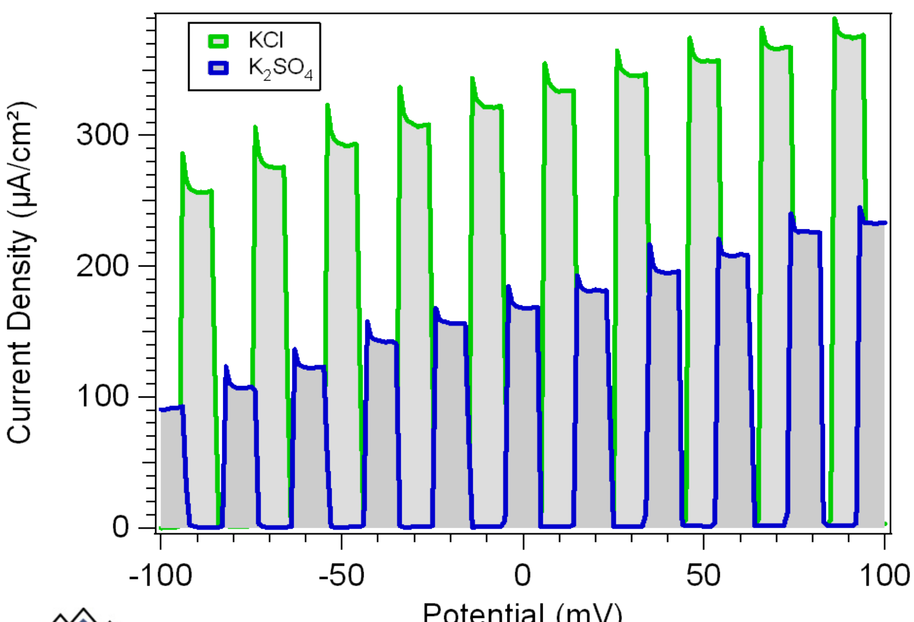
Phase II PEC Data

Test System

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



Typical Cyclic Voltammogram



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

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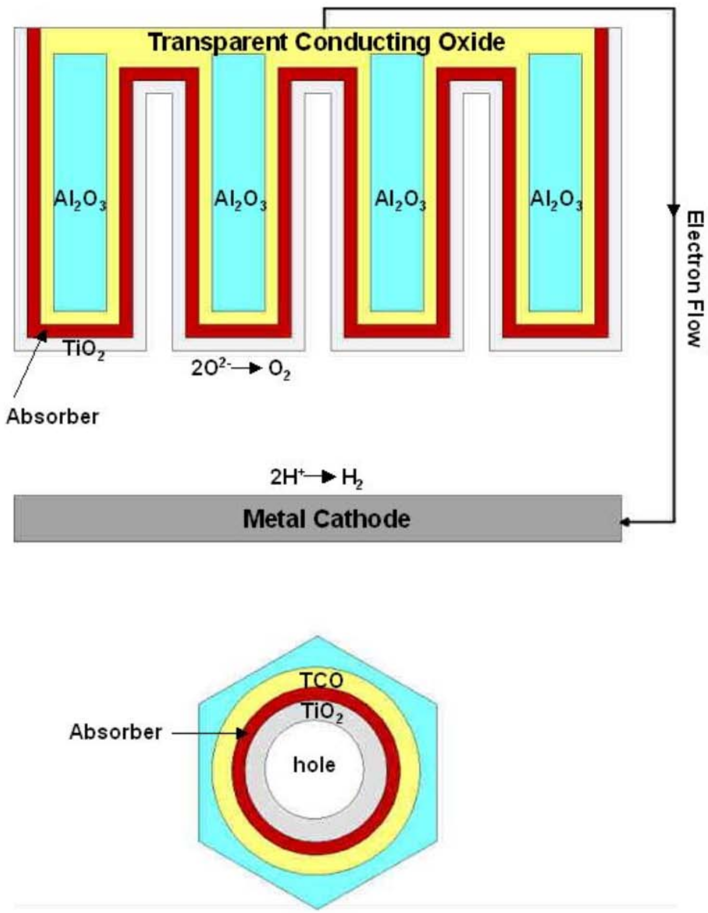
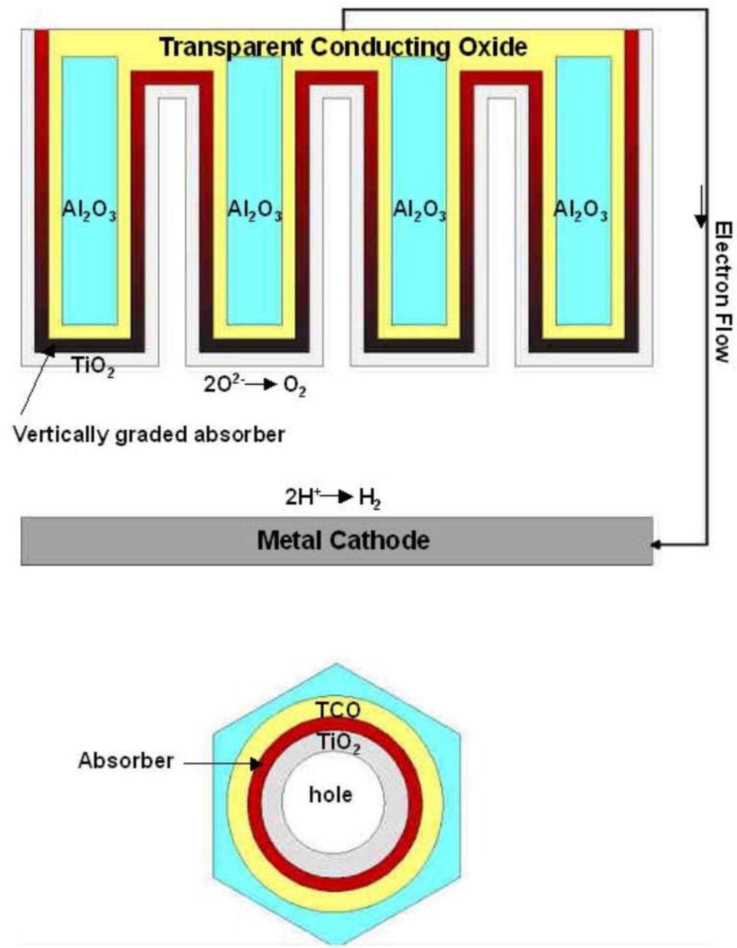
Phase II Approach: Nanorod Absorber Arrays for PEC Hydrogen





- 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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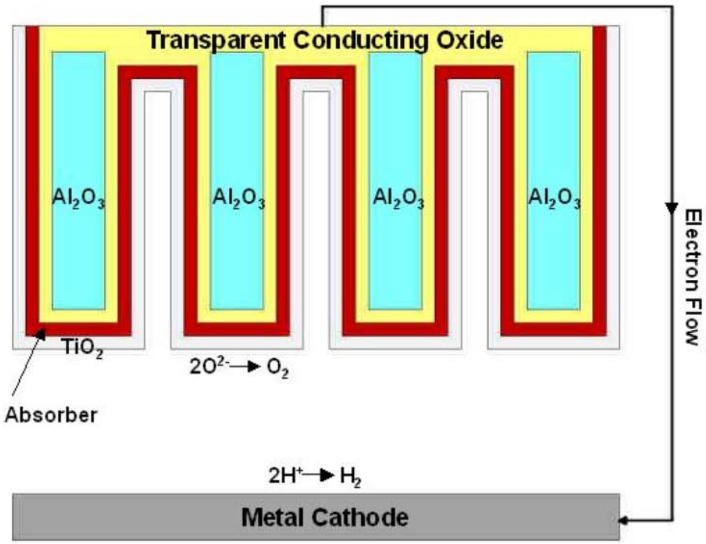
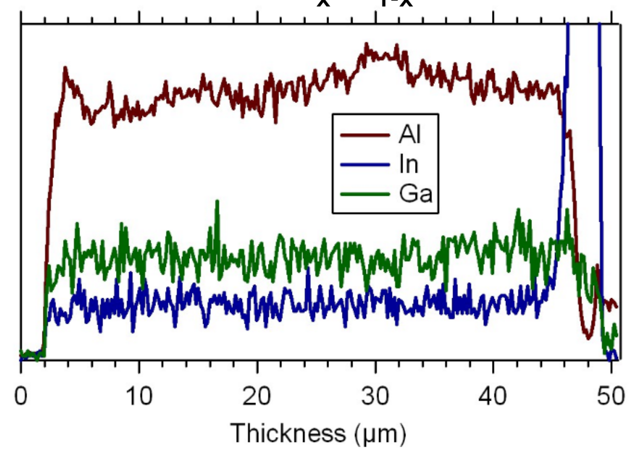
Phase II Approach Absorber Layer

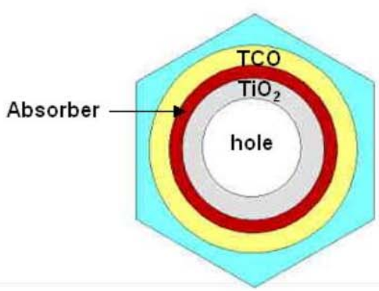
III-V Absorbers: InN, GaN, and $In_xGa_{1-x}N$



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

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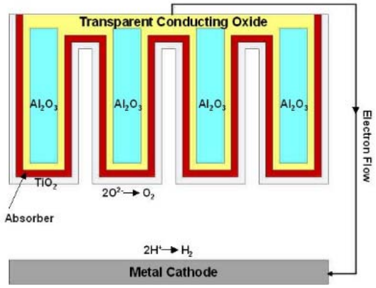
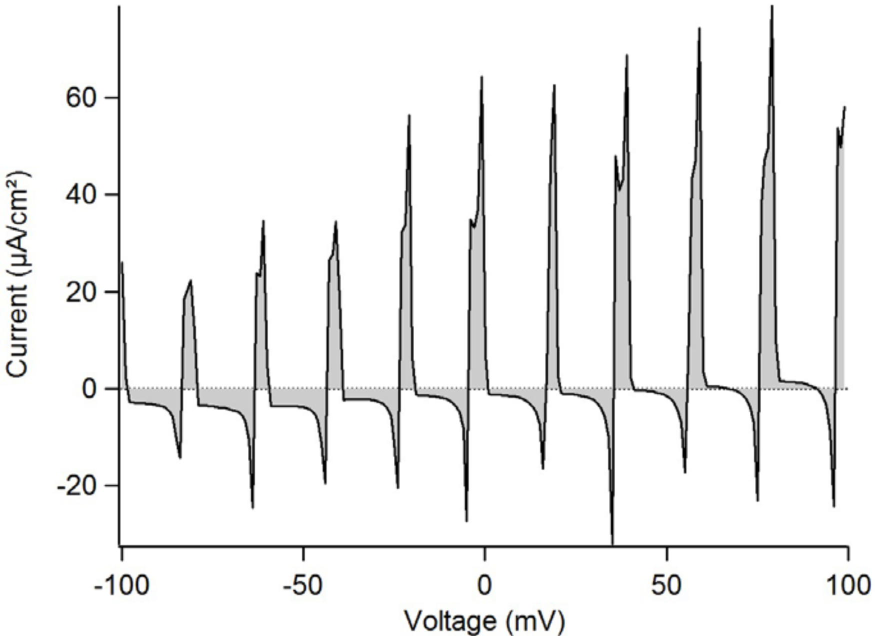


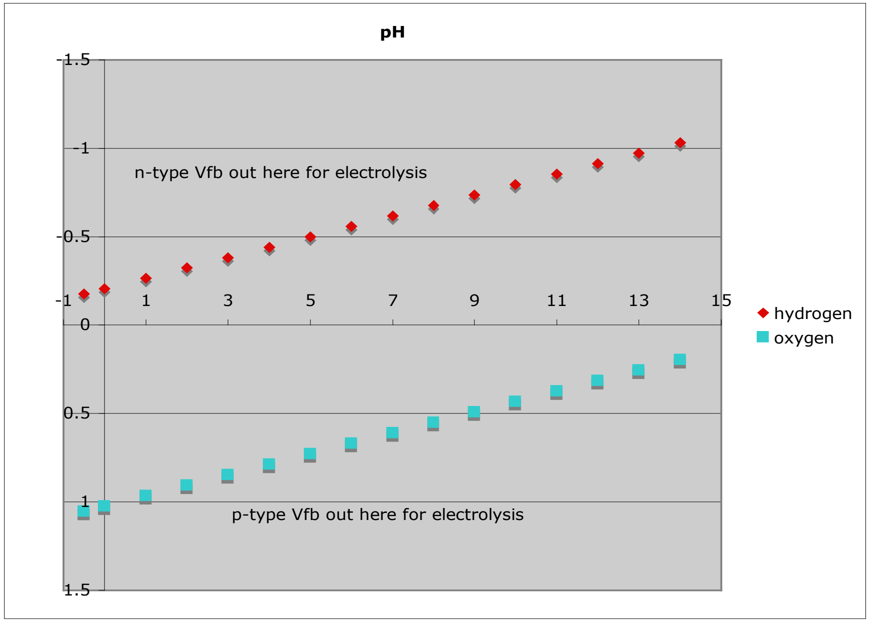
Technical Accomplishment

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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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

- Investigate WO_3 as a PEC material
- Revisit N-doping of TiO_2 as a means to push bandgap down to 2 eV
- Measure long-term stability of nanostructured films
- Investigate other absorber materials

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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 photoelectrolysis without any external bias. Demonstrated integration of all materials into a device.

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

Proposed Future Research: Examine other absorber and PEC materials and revisit doping of TiO_2 as means of meeting DOE targets.

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