SYNKERA TECHNOLOGIES, INC.
2021 Miller Drive, Suite B
Longmont, CO 80501
www.synkera.com

# Nanotube Array Photoelectrochemical Hydrogen Production

Rikard A. Wind

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

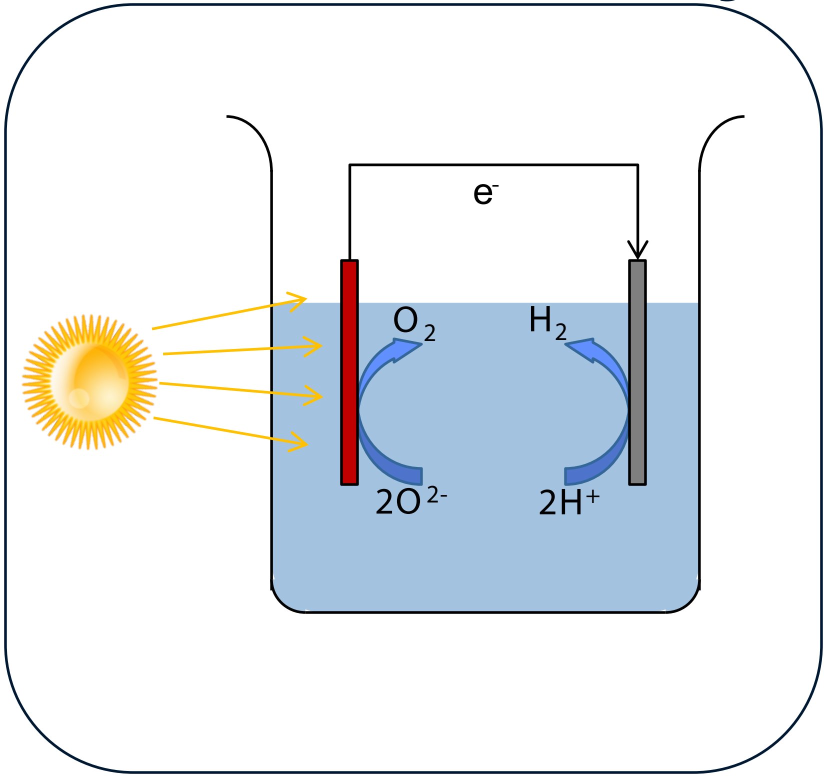
- Total: $750,000
  - DOE share: $750,000
  - Contractor share: $0
- FY09 Funding: $260,000
- FY10 Funding: $365,225

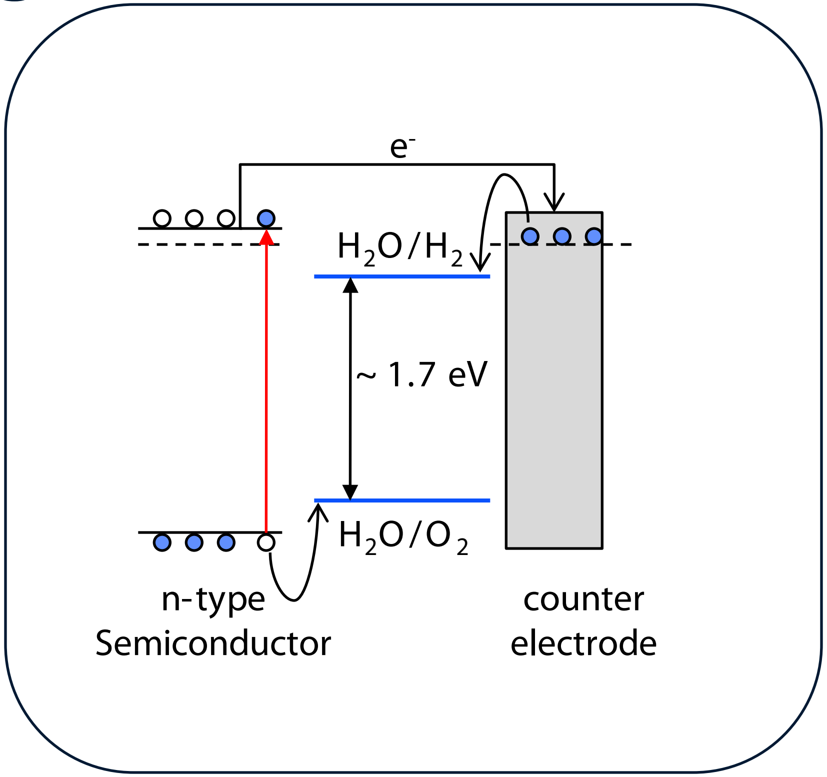
## Partners

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

SYNKERA TECHNOLOGIES, INC.

# 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.

# 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 |

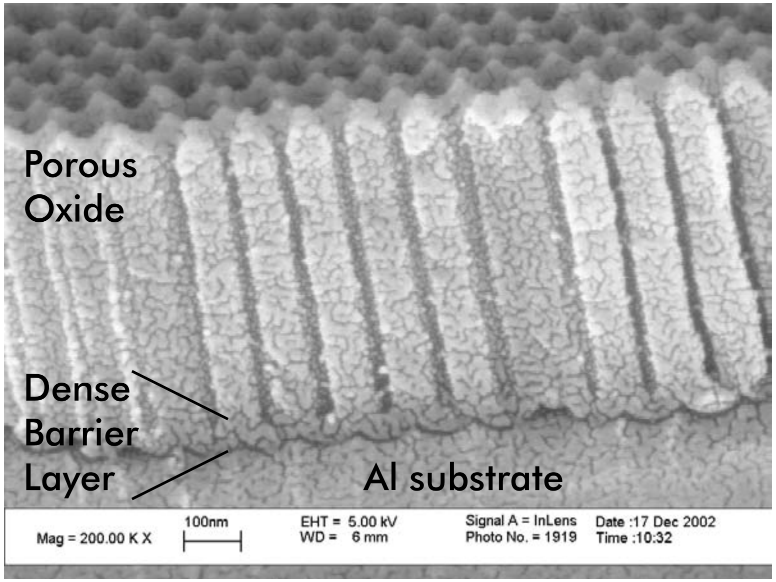
SYNKERA TECHNOLOGIES, INC.

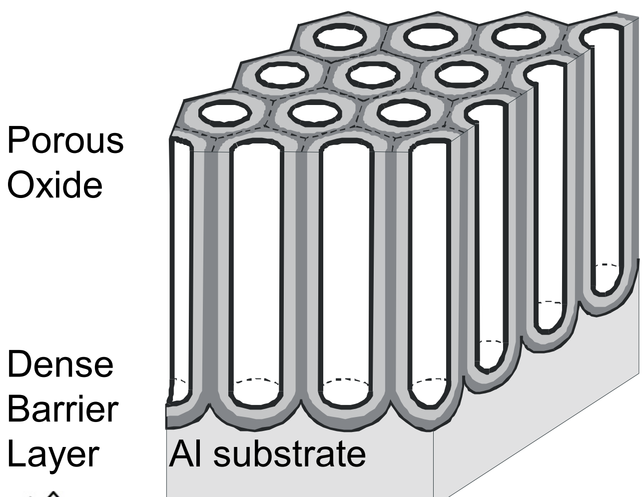
# Relevance: Key Milestones for Phase II Project

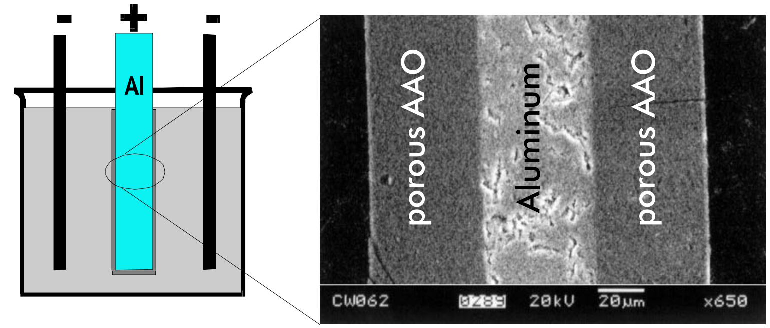
| Key Milestone | % Completed |
|---|---|
| Complete and test upgrade of ALD reactor | 100 |
| Complete fabrication of architecture prototypes | 100 |
| Complete membranes for development of absorber materials. | 100 |
| Determine process for InGaN deposition | 90 |
| Complete fabrication of absorber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

SYNKERA TECHNOLOGIES, INC.

# Approach: Anodic Aluminum Oxide as a Scaffold for PEC Materials



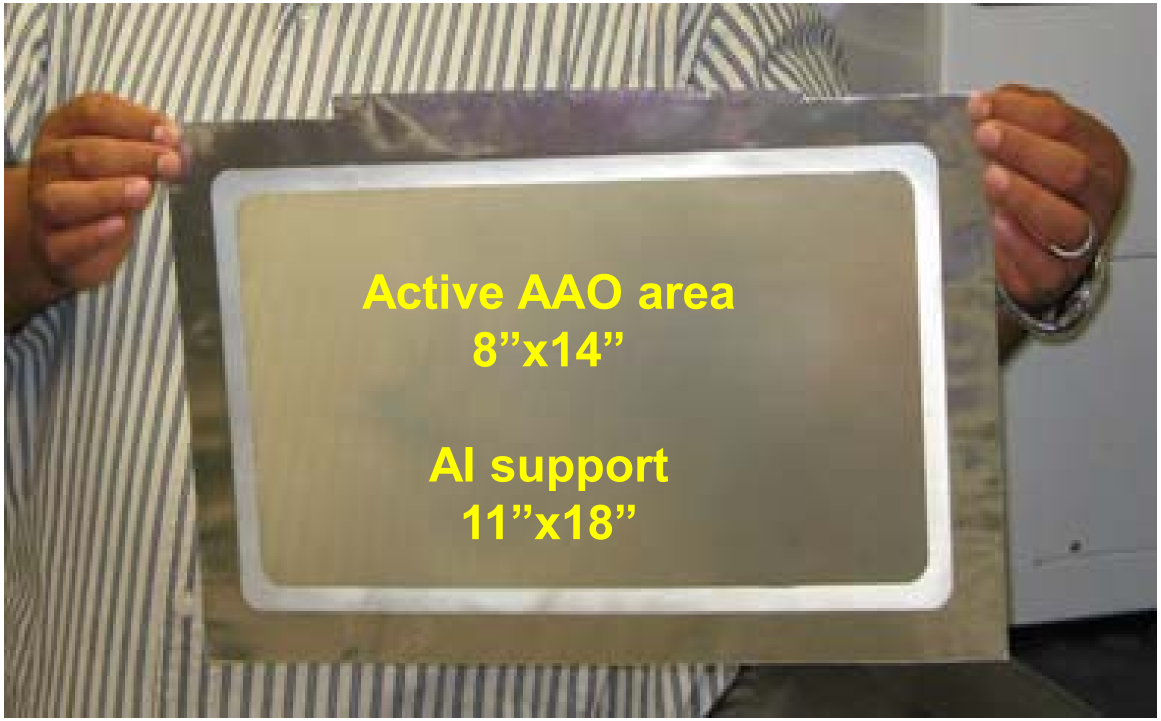




- High quality self-organized material with regular nanoporous lattice
- Uniform & aligned arrays of cylindrical nanopores
  - Pore diameter: 5 - 300 nm
  - Pore density: $10^{12}$ -$10^{8}$ cm$^{-2}$
  - Thickness: 0.1 - 300 µm
- Formed by anodic oxidation of Aluminum
- Scaleable, manufacturing-friendly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

SYNKERA TECHNOLOGIES, INC.

# Approach: AAO a Scalable Material



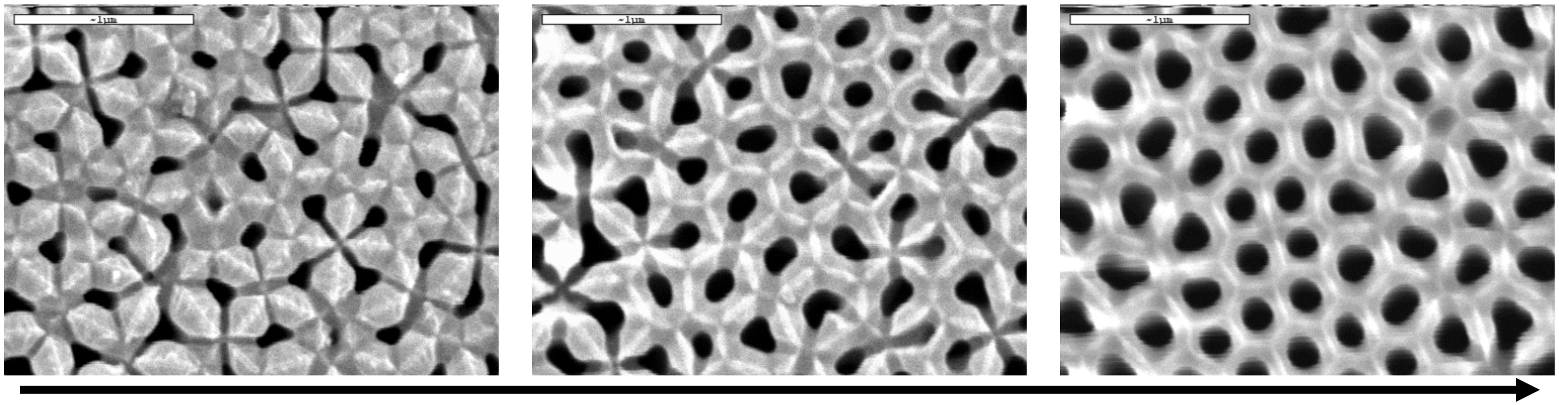

**World’s largest nanoporous AAO membrane produced at Synkera**

SYNKERA TECHNOLOGIES, INC.

Technical Accomplishment

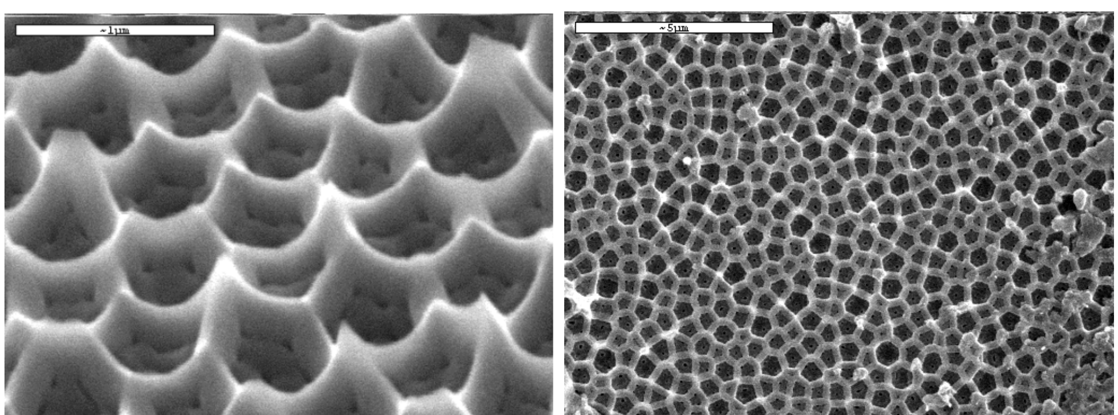
# Engineered Nanotemplates for PEC

## Synthesis of anodic aluminum oxide with large pore sizes.



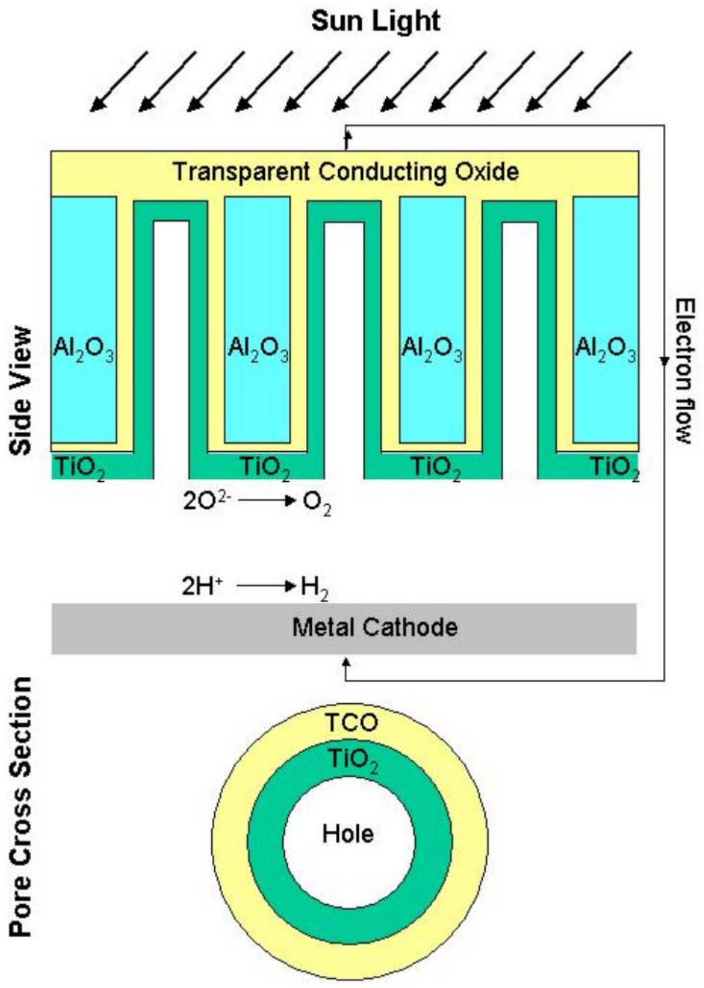
Increasing Etch Time

## Anodic aluminum oxide with minimally reflective surface.



SYNKERA
TECHNOLOGIES, INC.

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

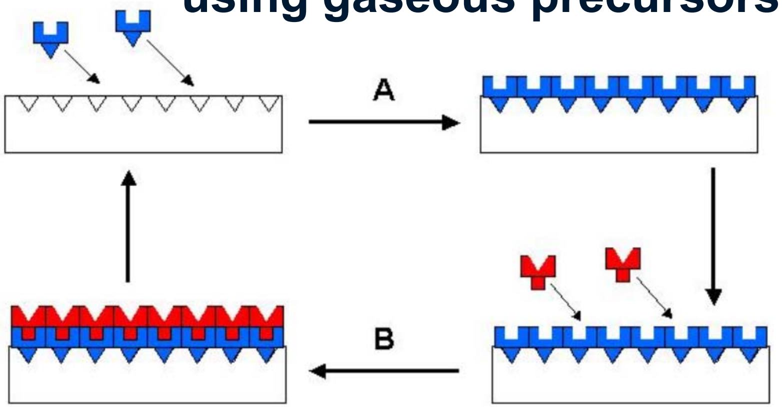



- Based on AAO nanotemplate
- Short distance to conductors allows for efficient electron-hole separation
- Small pore size will reduce gas bubble formation
- $TiO_2$ is doped to reduce the band gap, but conductivity through TCO is unaffected
- Fabricated using atomic layer deposition (ALD)

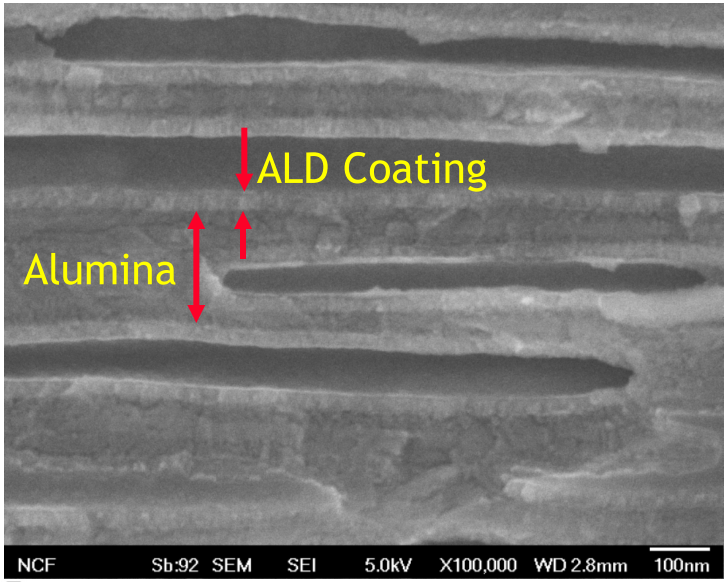
SYNKERA TECHNOLOGIES, INC.

# Approach: Fabrication by Atomic Layer Deposition

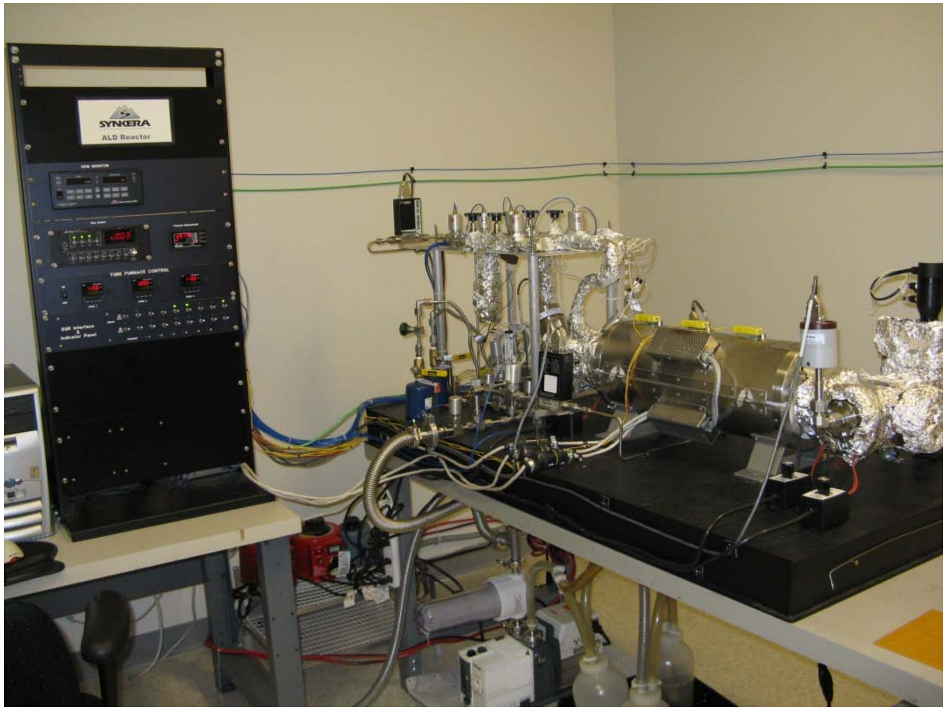
**ALD consists of sequential self-limiting surface reactions using gaseous precursors applied in ABAB… fashion.**




**ALD inside AAO**




**Synkera ALD Reactor**

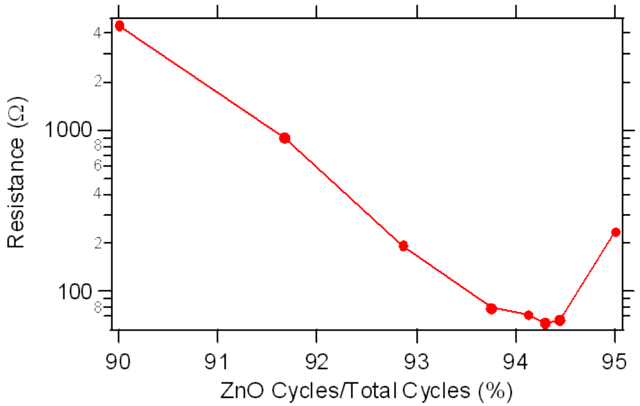



SYNKERA TECHNOLOGIES, INC.

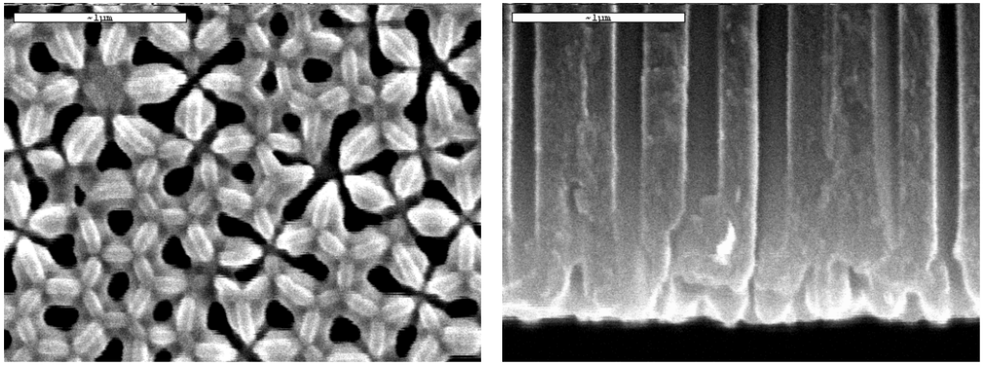
# Transparent Conductor and $TiO_2$ by ALD

## Conductive and Titania Coatings

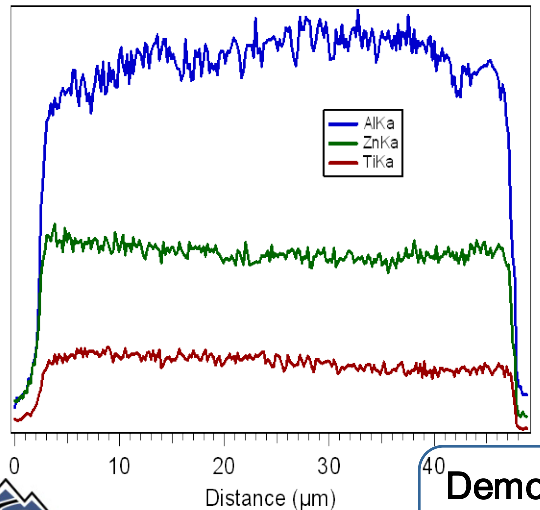
### Resistance of nanotubes



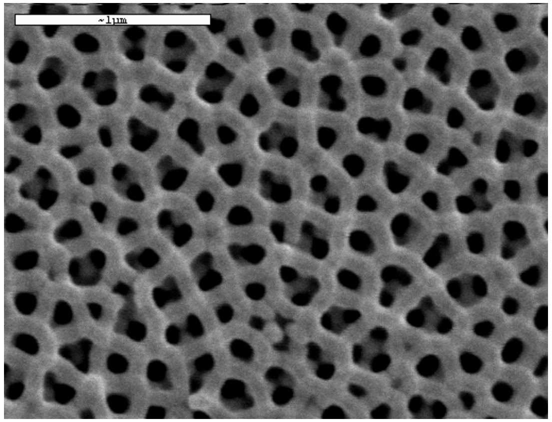

### SEM images of AAO coated with conductive layer



### EDX linescan of Materials inside AAO




### SEM images of AAO coated with both materials

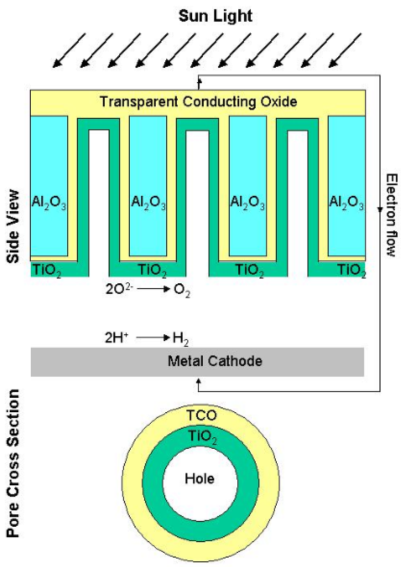


Demonstrated conformal coatings inside high-aspect ratio pores.

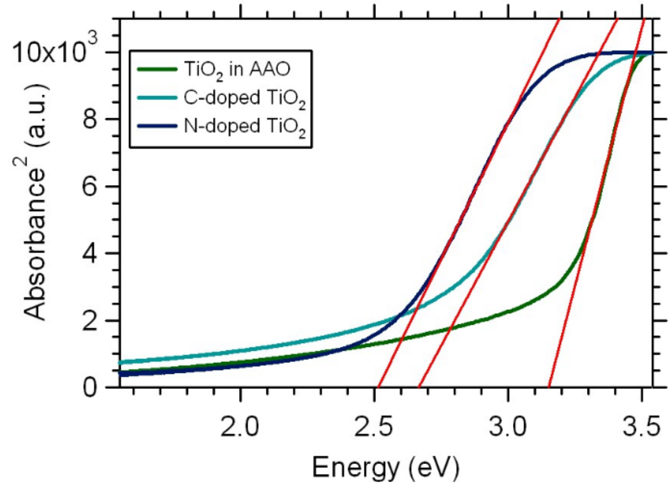
SYNKERA TECHNOLOGIES, INC.

Technical Accomplishment

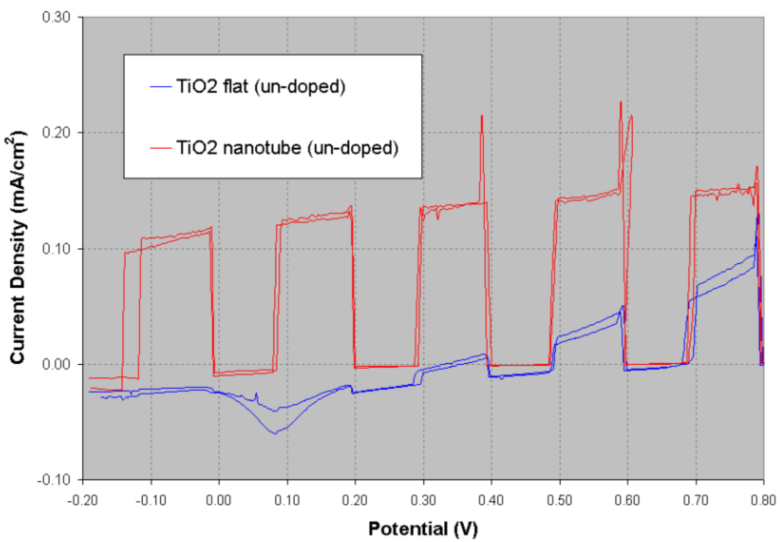
# Phase I Results



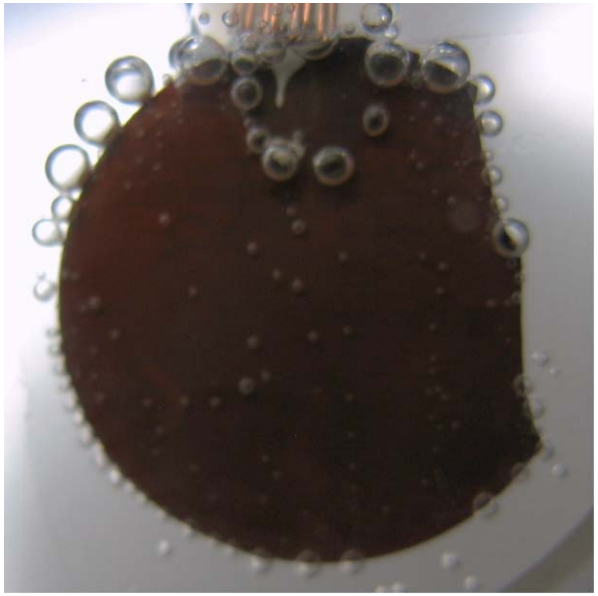

Able to reduce bandgap to 2.5 eV




Sample was active with zero applied potential!!!




Photoelectrolysis

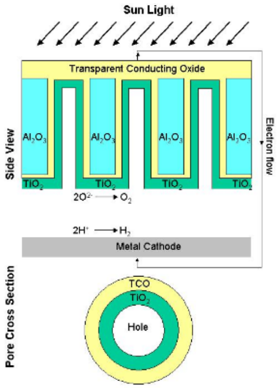


**We conclusively showed that nanostructuring increased the efficiency of photoelectrolysis**

SYNKERA TECHNOLOGIES, INC.

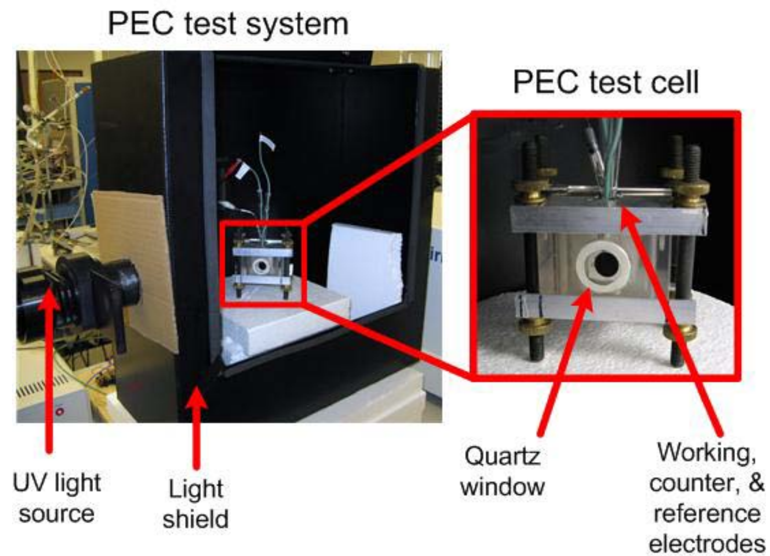
#### Technical Accomplishment

# Phase II PEC Data

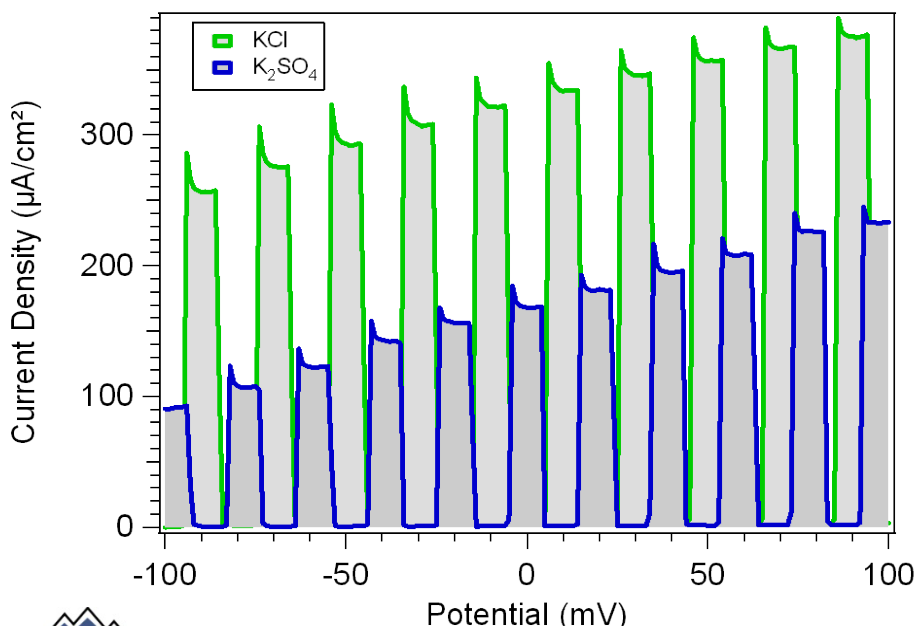



## Test System

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



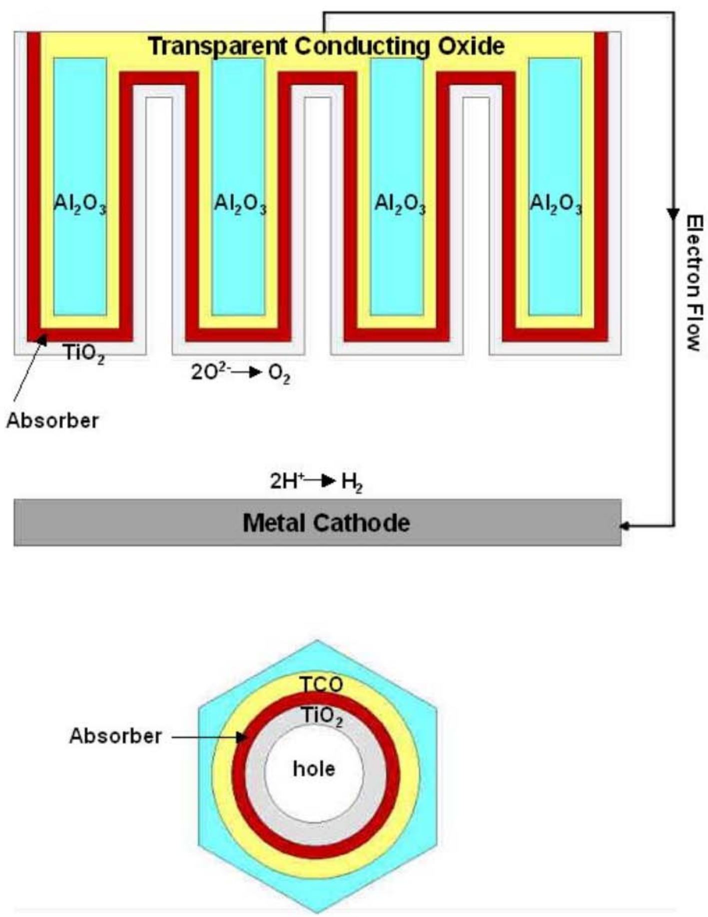

Typical Cyclic Voltammogram

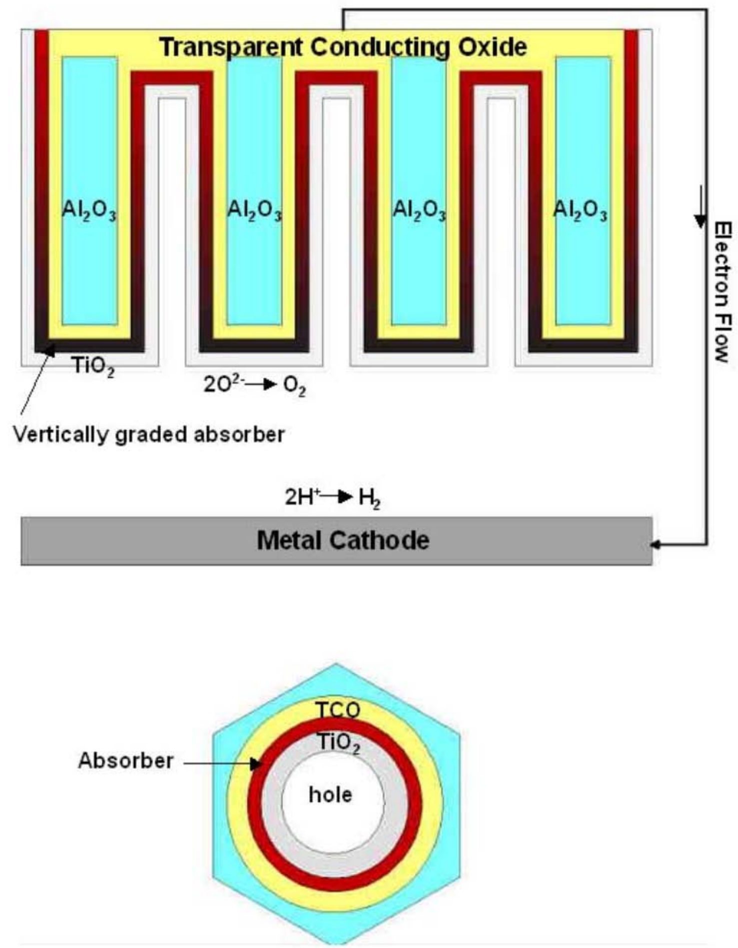



**Highest current density obtained on undoped $TiO_2$ using test conditions listed was 400 μA/cm².**

SYNKERA TECHNOLOGIES, INC.

# Phase II Approach: Nanorod Absorber Arrays for PEC Hydrogen

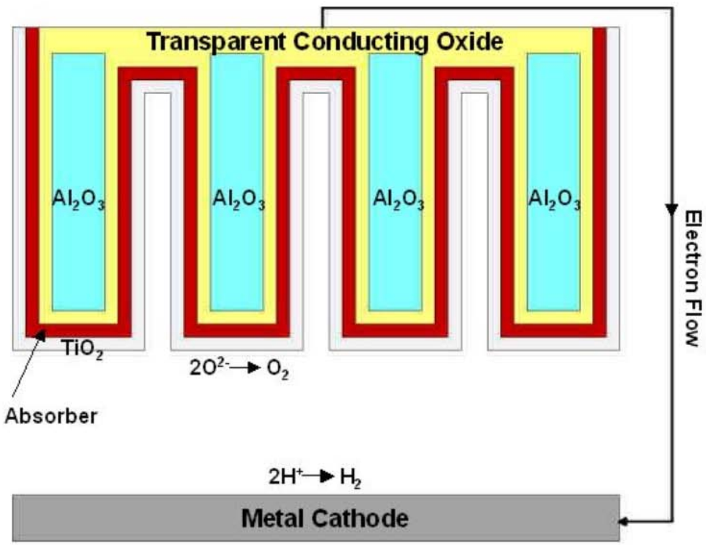


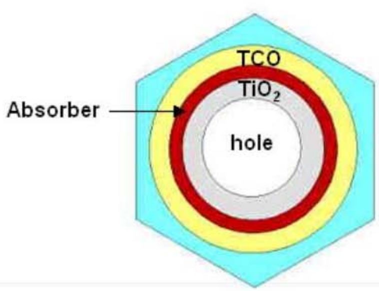




- Instead of modifying the $TiO_2$, we will add a separate absorber material to harness light
- This absorber can (in principle) be vertically graded in order to absorb a wider range of the the solar spectrum.

SYNKERA TECHNOLOGIES, INC.

# Phase II Approach Absorber Layer



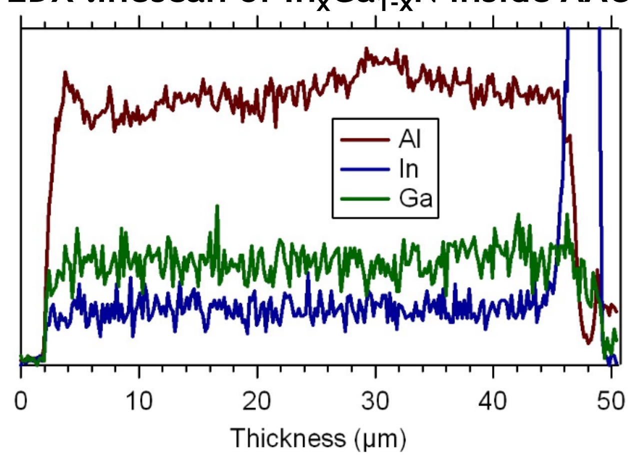




- TCO is the electron conductor
- Absorber material is used to harness light
- $TiO_2$ provides protective surface

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

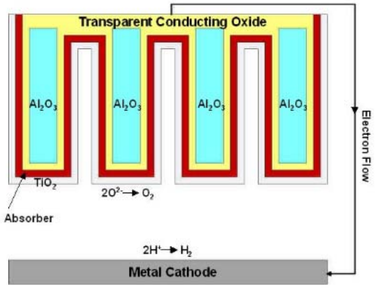
Left: InN Right: GaN


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

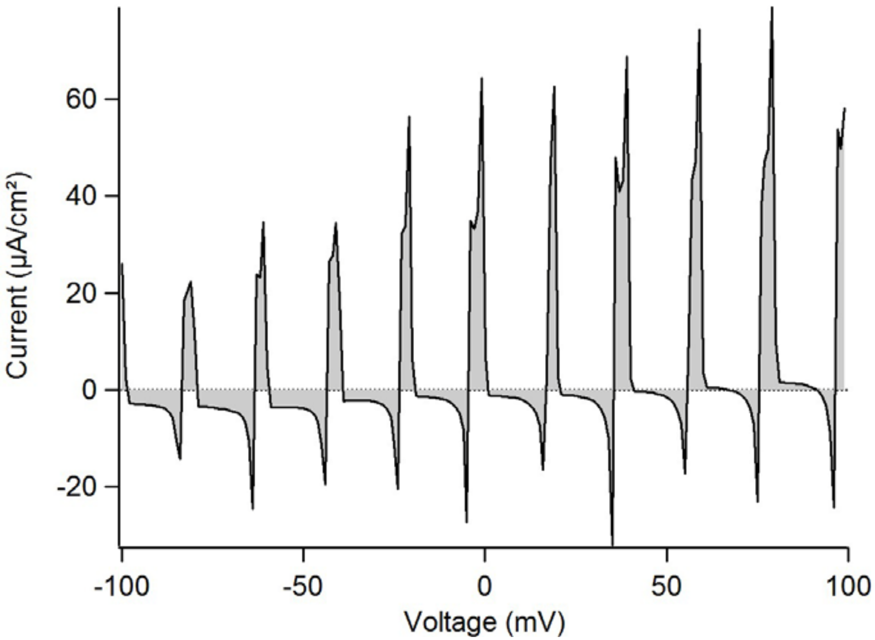


### Technical Accomplishment

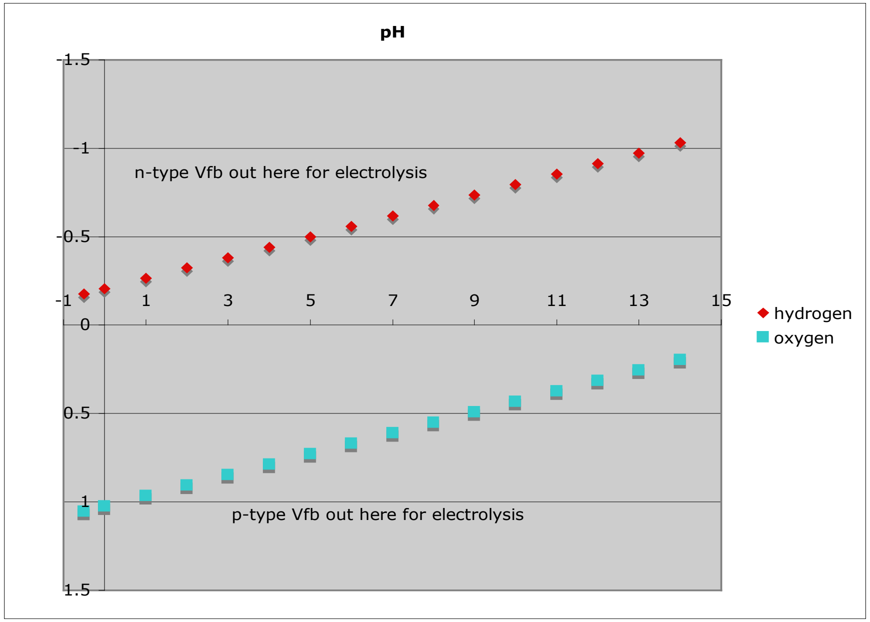
# GaN as Absorber




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.

SYNKERA TECHNOLOGIES, INC.

# 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.

# 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

SYNKERA TECHNOLOGIES, INC.

# 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.


**Rikard Wind**

**720-494-8401x111**

**rwind@synkera.com**


SYNKERA TECHNOLOGIES, INC.