Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices

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Co-PI: Martha Greenblatt
Presenter: Mr. Shinjae Hwang
Rutgers, the State University of New Jersey
4/30/2019

Project ID # p160

NREL BERKELEY LAB Sandia National Laboratories INL Idaho National Laboratory Lawrence Livermore National Laboratory SRNL

Project Overview

Partners

Rutgers PIs: E. Garfunkel & G. C. Dismukes, coPI: M. Greenblatt

NREL 4 Nodes (MOVPE, PEC, HTE & HOIPS): T. Deutsch, D. Friedman, M. Steiner, A. Zakutayev, K. Heinselman, K. Zhu, & J. Berry

Award #	EE0008083
Start/End Date	09/01/17 - 12/30/20
Yr 1 Funding*	
Yr 2 Funding*	

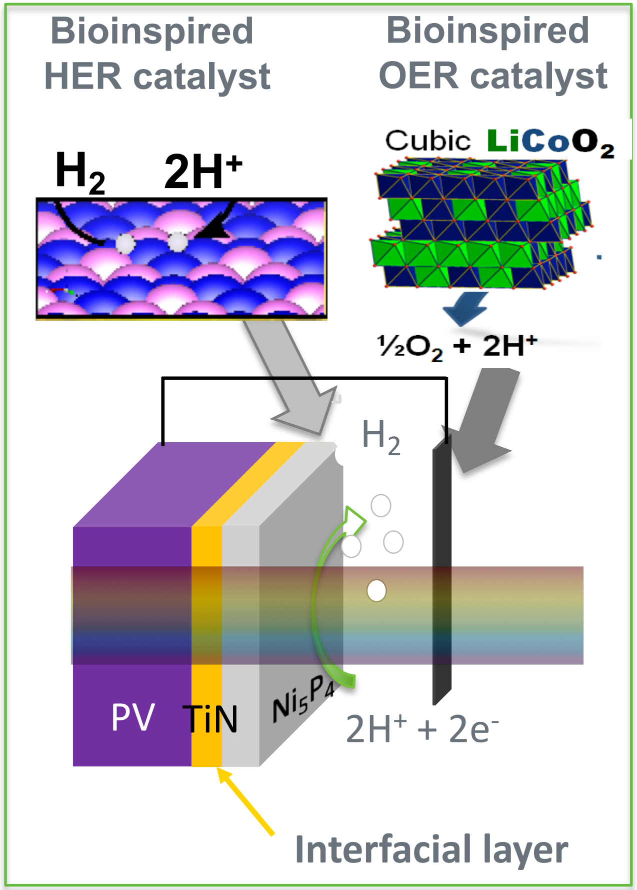
* this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)

Vision

Identify the best technical approaches to fabricate both High Performance (HP) & High Value (HV) PGM-free PECs:
-Use NREL-proprietary tandem III-V as HP photovoltaic
-Use NREL nitrides & Rutgers perovskite oxynitrides in tandem as HV PV
-Use Rutgers-proprietary electro-catalysts for O_2 and H_2 evolution

Impact

- Reveal performance limits of two limiting PV configurations (HP vs. HV) using RU PGM-free Cats.
- Identify & solve catalyst/PV interface problems.



Approach- Summary

Project Motivation

High-performance Photovoltaics: State of the art material is NREL HP III-V tandems (STH 16.7%) vs. multi-junction silicon (STH 9.5%).
High-value (HV) – emerging photoabsorbers: $SrNbO_2N$ and NREL-developed, $ZnSnN_2$, HOIPs all coupled with Si are potential efficient PV for water splitting and low-cost.
TiN vs. TiO_2 – Rutgers developed thin-film diffusion barrier and protection layer.
$LiCoO_2$ OER eCat – Rutgers developed for alkali w. performance superior over PGM-catalysts.
Ni_5P_4 HER eCat – Rutgers developed for acid & alkali w. performance on par with Pt.

Barriers

PGMs eCats with PGM-free eCats without compromising STH efficiency
➔ Develop optically thin-films of R.U. eCats performing on par with thin-film PGM eCats.
Reduce light losses in Cat/Absorber interface (literature:
5 nm MoS_2/MoO_x ~ 25% current loss)
➔ choose catalyst + diffusion barrier & optimize thicknesses
Photoabsorbers corrode in alkaline electrolyte
➔ Develop proper protection layer for alkaline RU eCats.

Key Impact – year 1

Metric	State of the Art	Expected Advance
HP – STH Efficiency	Non-PGM PEC STH ~10%	Yr1: Match or beat using non-PGM Rutgers-eCats.
HV - $BiVO_4$ benchmark	Yr1: J_{ph} = 1.5mA/cm^2 at E – 1.23 V vs. RHE Stable >90% for 1h, material-cost	Yr1: $ZnSnN_2$, Improve two or more metrics.

Partnerships - NREL

III-V Semiconductor Epi-Structure Device Design and Fab
MOPVE GaInP/GaAs growth & engineering capabilities
D. Friedman & M. Steiner

On Sun Characterization of Bulk and Interfaces
Solar testing and benchmarking capabilities
T. Deutsch, & J. Young

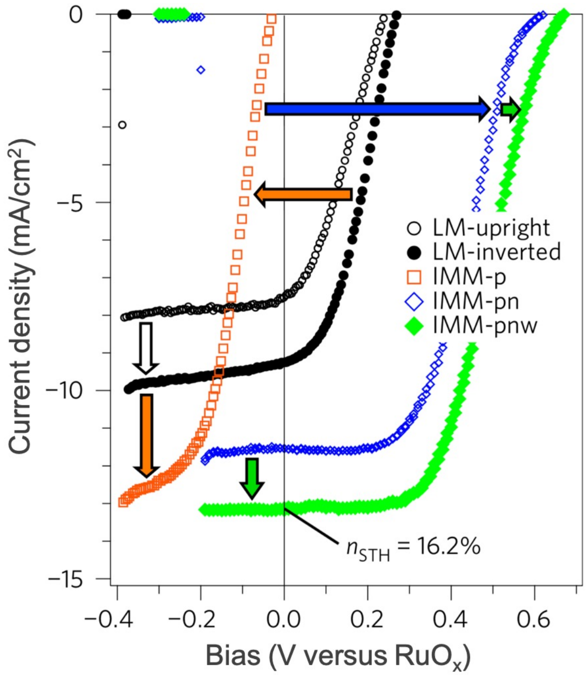
High-Throughput Thin-film Combinatorial Capabilities
Multi-source and reactive sputtering capabilities
A. Zakutayev & K. Heinselman

Hybrid Organic Inorganic Perovskites for Water Splitting
K. Zhu & J. Berry

Approach- Innovation – HP device

RUTGERS 250
1766-2016

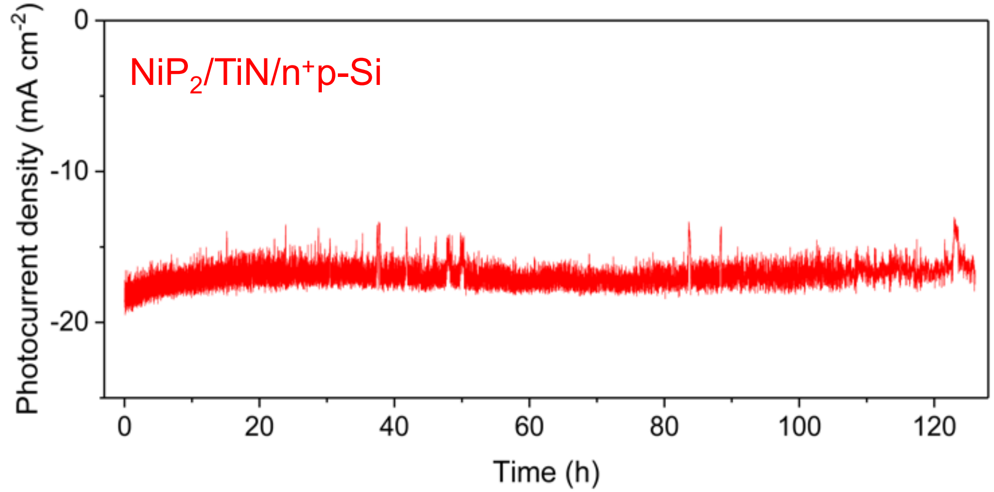
NREL III-V semiconductors



Inverted methamorphic structure III-V with PtRu catalyst, 16.2% STH, but unstable

Nature Energy **2017**, 2, 17028.

Rutgers thin-film catalyst and protection layer



Demonstrated high catalytic activity (high TOF among non-noble metal HER catalyst) and undiminished performance (>120 h) on a Si photocathode

J. Mat. Chem. A., **2019**, **7**, 2400-2411

Project Goal:

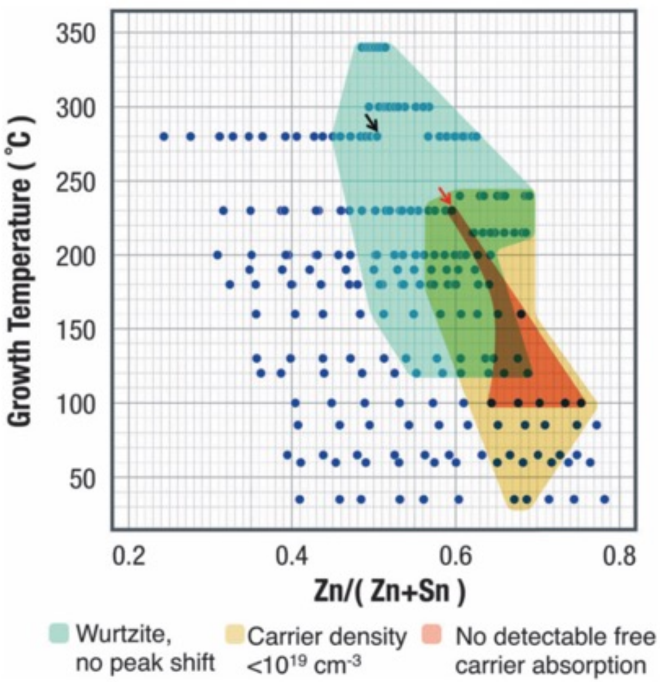
- 10% solar-to-hydrogen efficiency
- > 100 hours stability

BP1 scope: 1st GEN III-V tandem photocathode

- Integration of Ni_5P_4/TiN layer synthesis
- Initial test of half-cell stability
- Evaluate solar-to-hydrogen (STH) efficiency
- Achieve non-PGM activity on par with PGM

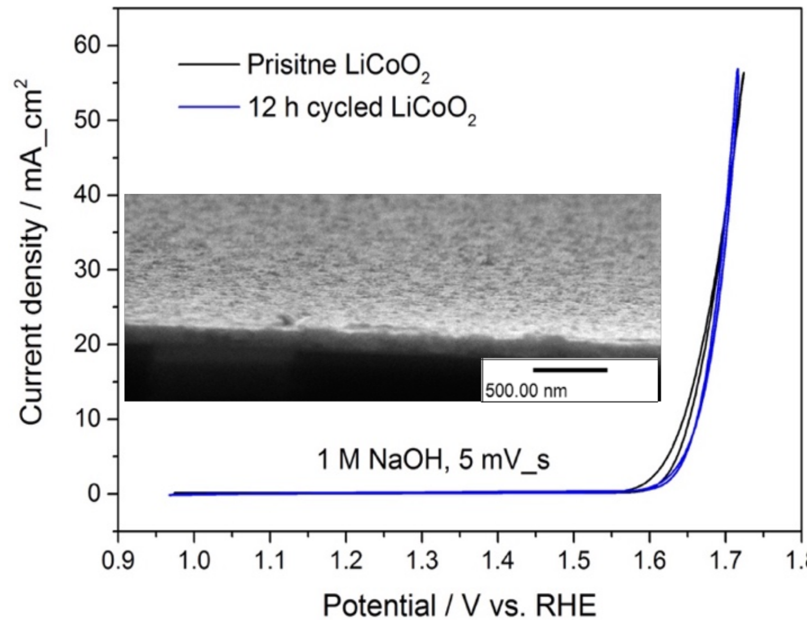
Approach - Innovation – HV device

NREL $ZnSnN_2$ semiconductor



J. Mater. Chem. C, 2015,3,11017-11028

Rutgers thin-film catalyst



S. Hwang, *et al.*, *ECS Trans.* 2016, *72*, 31–51.

Project Goal:

- Reduce PEC device costs enabling lower H_2 price
- ~ 10% STH

BP 1 scope: Evaluate $ZnSnN_2$

- Synthesis on TCO substrate
- Optimize carrier density through synthesis conditions
- Test $ZnSnN_2$ aqueous stability
- Characterize PV
- Evaluate cost metrics for $ZnSnN_2$

Relevance & Impact

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]					
Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Solar to Hydrogen (STH) Energy Conversion Ratio [e, f]	%	4 to 12%	15	20	25

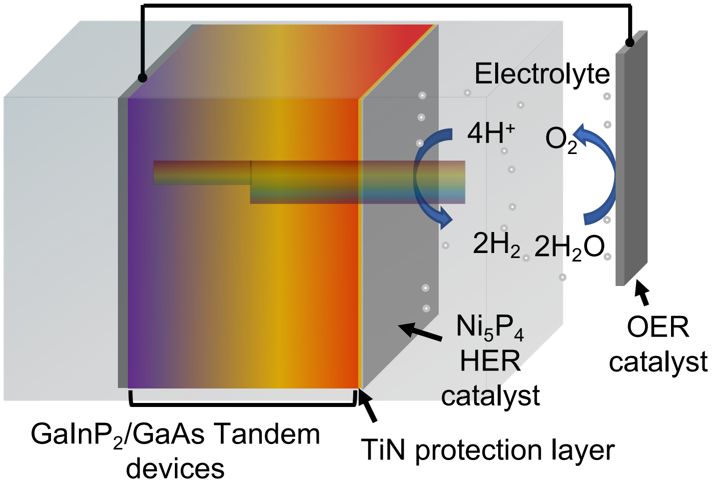
- This project focuses on two competing device designs that will be compared using techno-economic analysis to demonstrate the route to hydrogen production at <$2/kg

- **HydroGEN consortium**
  The HP device utilizes the EMN node expertise of the MOPVE, PEC, and on-sun nodes to produce a PEC device with high stability. High-stability and efficiency off-sets the photoabsorbers' costs

- The HV devices leverages the NREL high-throughput synthesis node to produce high quality $ZnSnN_2$ or $SrNbO_2N$ photoelectrodes. BP1 evaluated the TRL of $ZnSnN_2$ photocathodes. BP2 will evaluate the $SrNbO_2N$ vs HOIPs as low cost photoabsorbers. HOIPs, similar to III/V photoabsorbers, need both protection and catalyst layers for continued operation. $SrNbO_2N$ provides improved stability but must be interfaced with the RU-catalyst.

Accomplishments:
High performance device (III-V PEC)

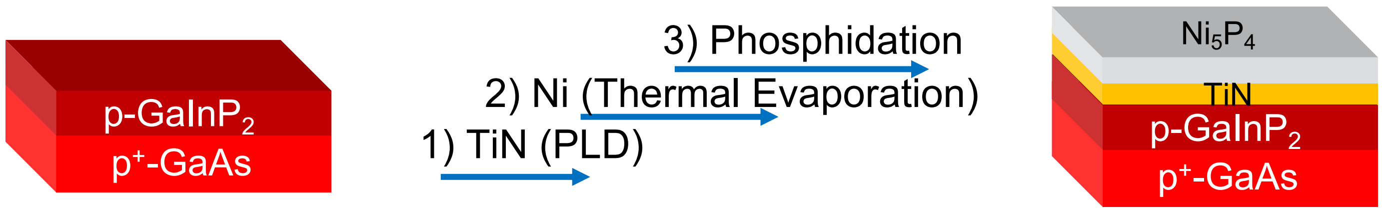
Ni_5P_4 (electrocatalyst) – TiN (protection layer) on III-V semiconductors



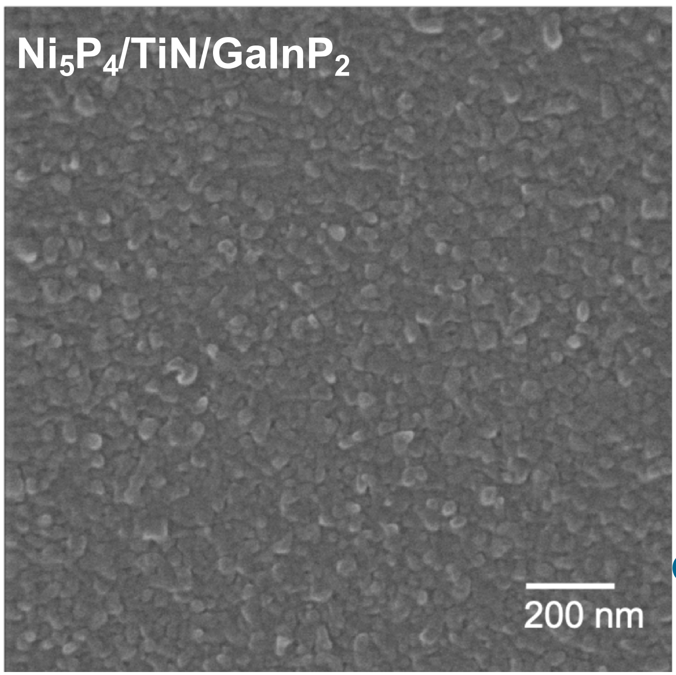
Year 1 Target (GNG)	Year 1 Result
Tandem device: STH> 10%	Tandem device: STH> 11.5%
J_{ph} (at 0 V vs. RHE) > 10mA/cm² (half-cell)	Match
>24 h durability (half-cell)	>120 h durability (half-cell)

1. **Successful integration of Ni_5P_4 HER catalyst with TiN protection layer on $GaInP_2$** (Task 2)
2. **Achieved 10 mA/cm² and over 120h durability by half-cell measurement with np-$GaInP_2$/p^+GaAs** (Go/No-Go decision point metric)
3. **Exceeded unassisted solar-driven water splitting target: STH ~ 11.5%** (Go/No-Go decision point metric)

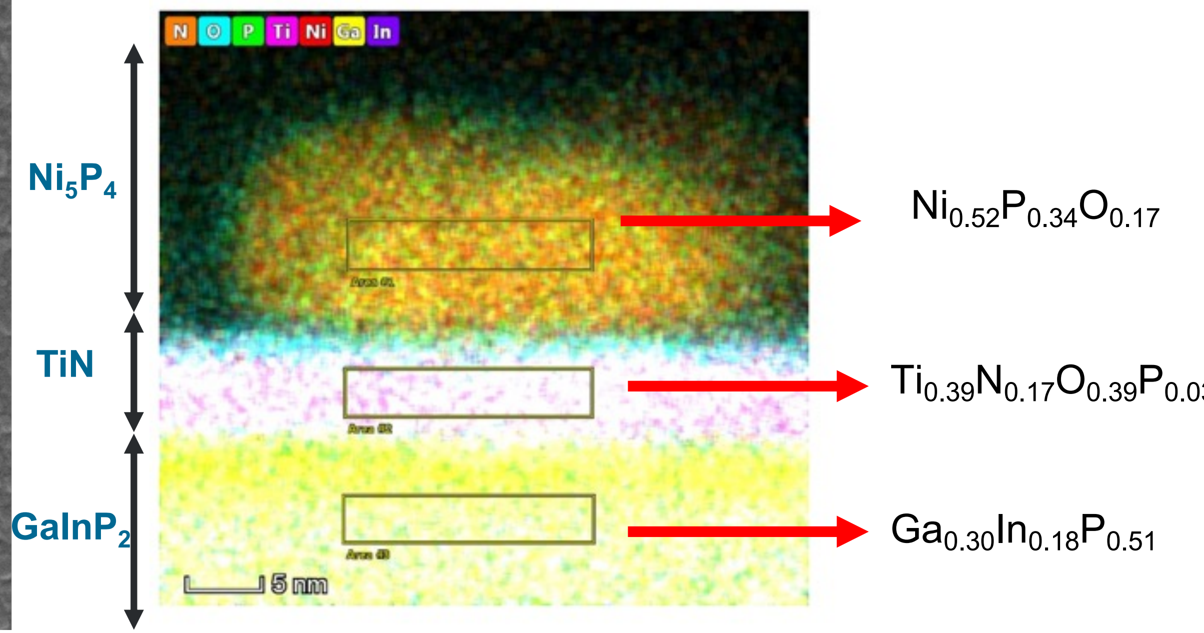
Accomplishments: Successful integration of $Ni_5P_4/TiN/GaInP_2$



Helium ion microscope (HIM) image



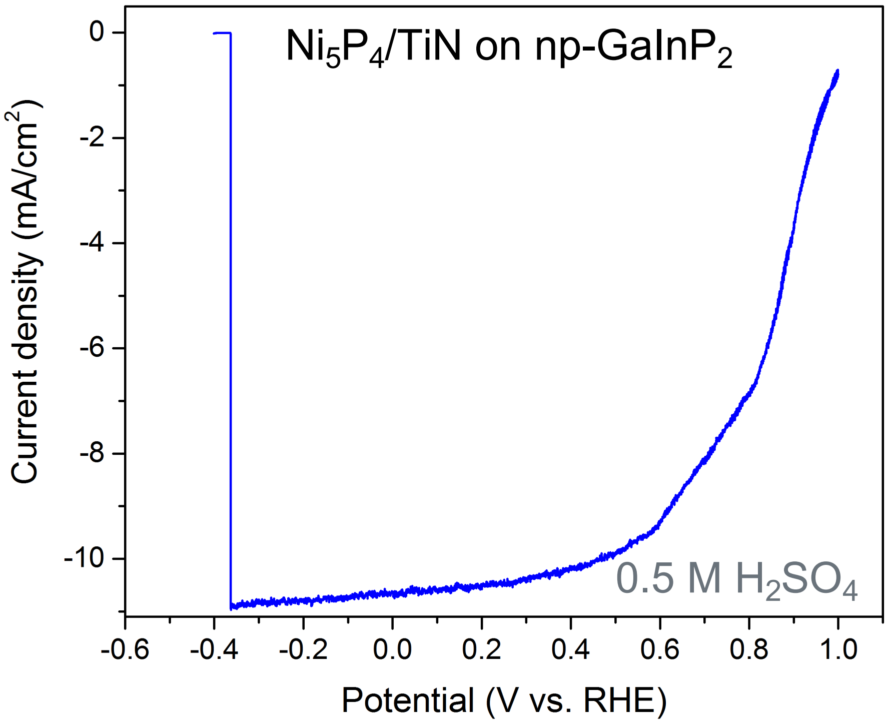
TEM/EDS mapping of $Ni_5P_4/TiN/GaInP_2$



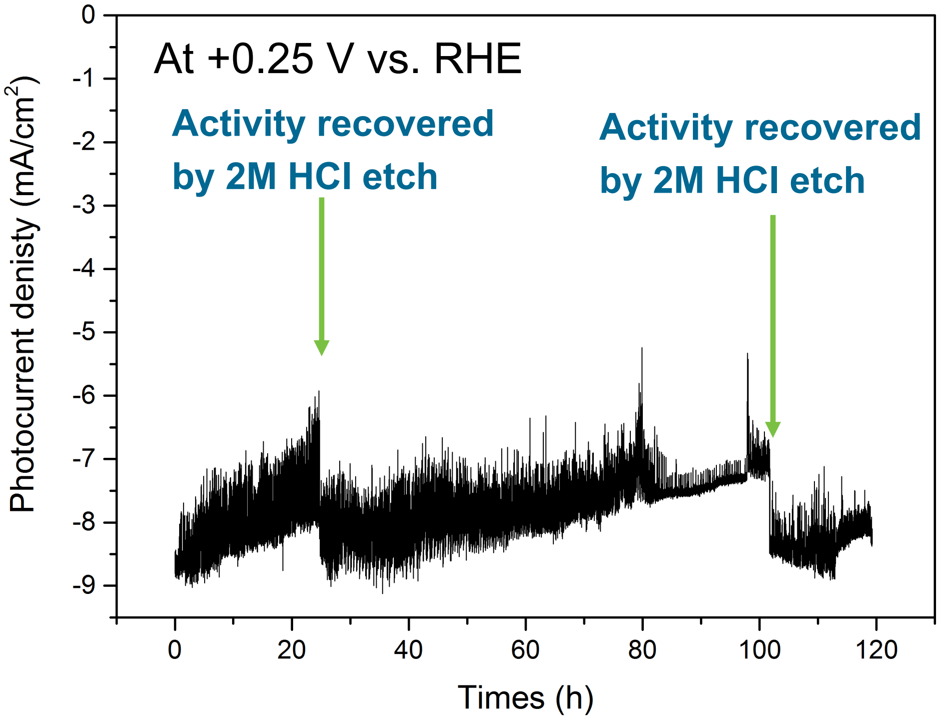
- HIM image shows dense polycrystalline catalyst coverage
- TEM/EDS mapping confirms catalyst and protection layer without atomic diffusion of In and Ga

Accomplishments: Performance of Ni_5P_4/TiN/np-$GaInP_2$

J-V Performance

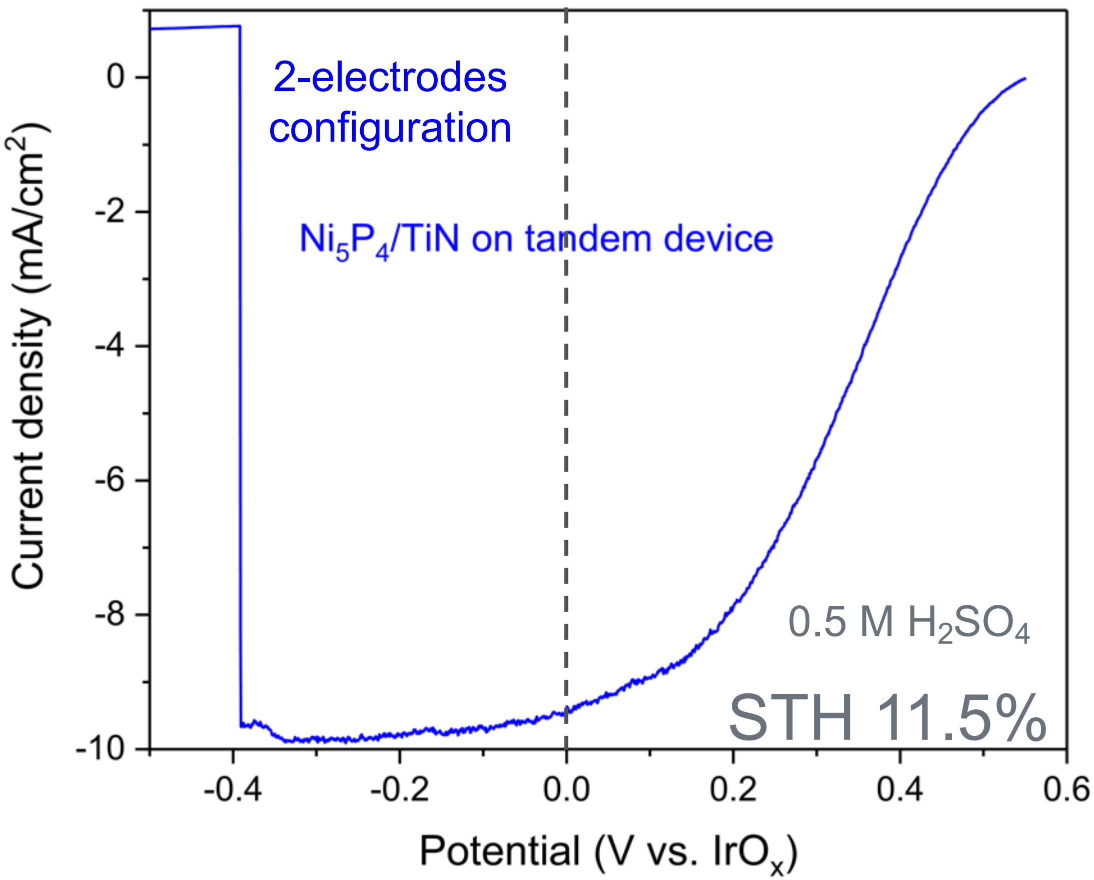


Durability test



- J-V curve shows ~10 mA/cm^2 current density which has been confirmed by IPCE measurement (NREL PEC node)
- Durability test demonstrates 120 h stability of Ni_5P_4/TiN/np-$GaInP_2$ (buried junction)
- Surface Cu-contamination during the measurement decreases photocurrent
- Contamination traced to epoxy failure (slow leaching of Cu-contact through epoxy)

Accomplishments: Unassisted Solar-Driven Water Splitting



- Using the published Faradaic efficiency of 100%* yields solar-to-hydrogen (STH) conversion efficiency of 11.5%
- **Exceed Go/No-go Decision Point Thrust 1 Criteria: STH> 10%**

*Laursen, A. B., *et al. Energy Environ. Sci.* **2015**, *8*, 1027–1034.

Accomplishments: Increasing STH from 11.5% towards >13%

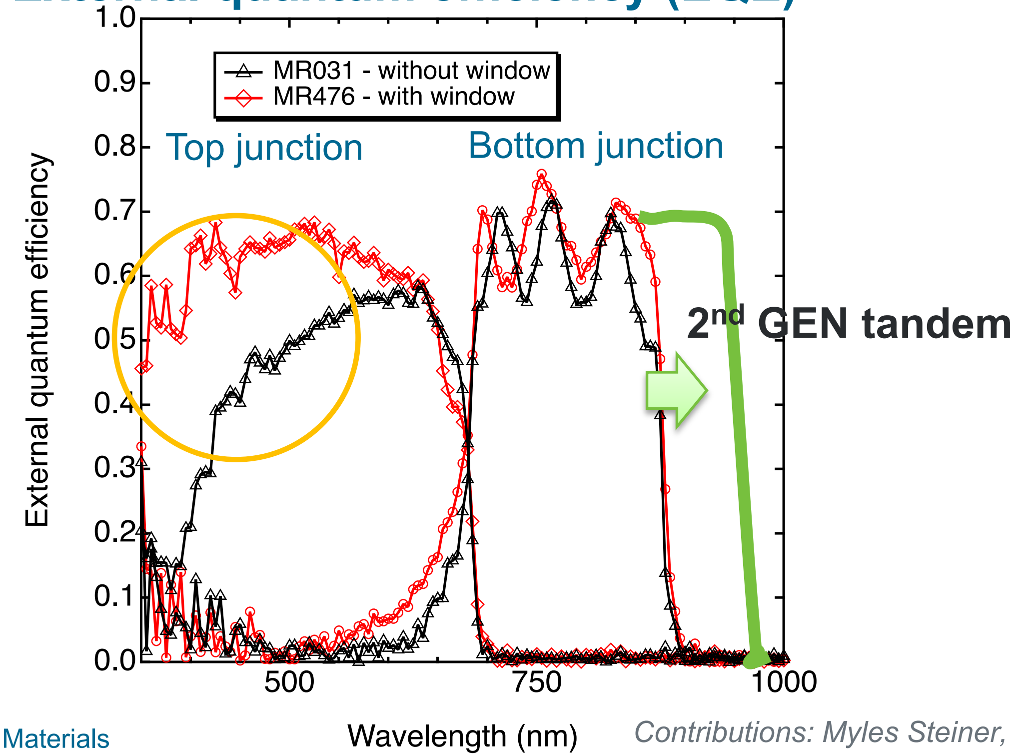
Top junction:

- AlInP increases EQE at low wavelengths by decreasing recombination
- TiN interlayer provide improved protection of the acid soluble AlInP window layer

Bottom junction:

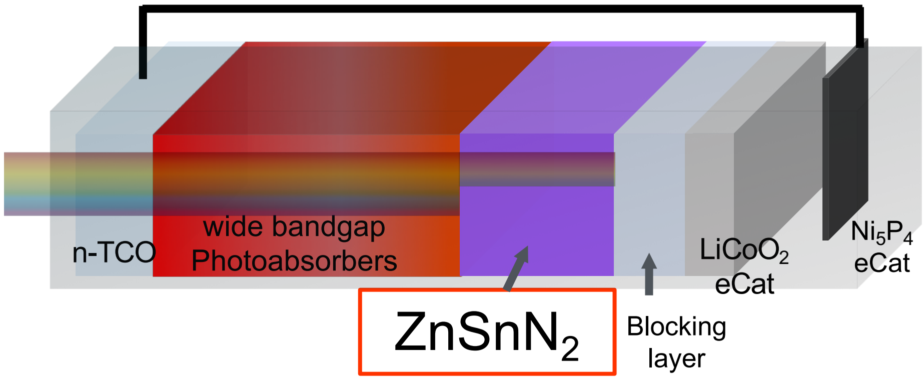
- 2nd GEN tandem with quantum well can capture more light above 900 nm

NREL MOPVE node: External quantum efficiency (EQE)



Contributions: Myles Steiner, NREL MOVPE node

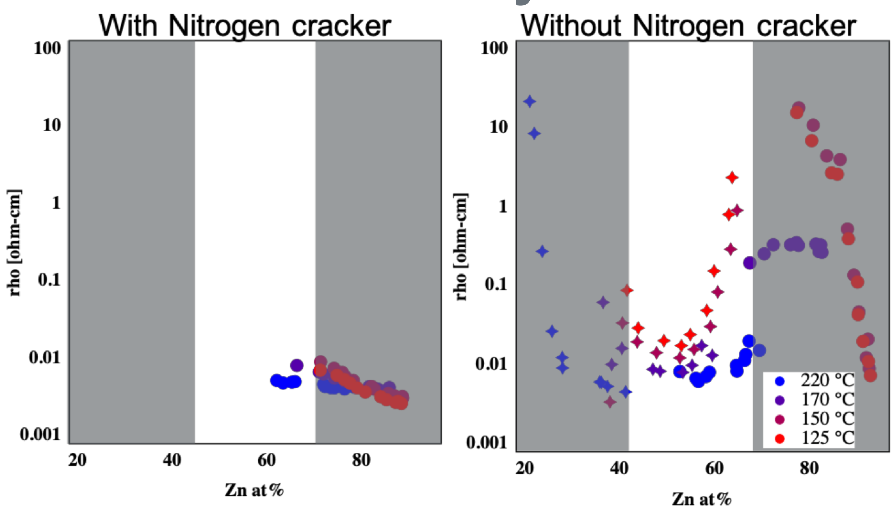
Accomplishments:
HV device – $ZnSnN_2$ photoanode (HTE node)



Go/no-Go decision point:

- Photocurrent densities of > 1.5mA/cm² (at 1.23 V vs. RHE) ?
- Stability 90% for 1 h ?
- Improved costs metrics over the $BiVO_4$ benchmark ✓

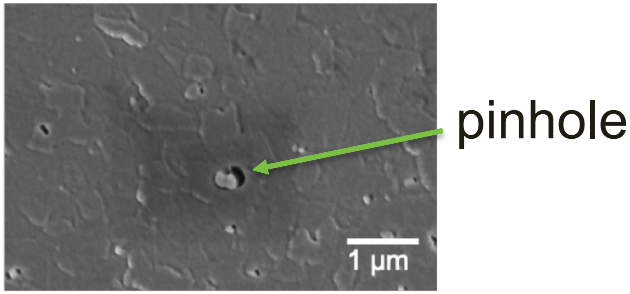
Carrier density control



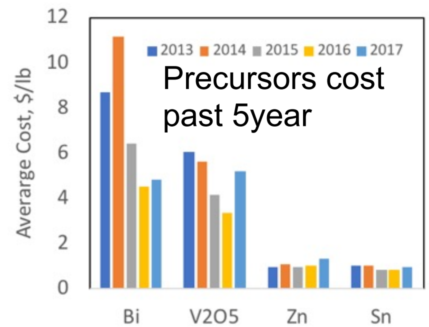
Carrier density was improved, but no PV properties observed

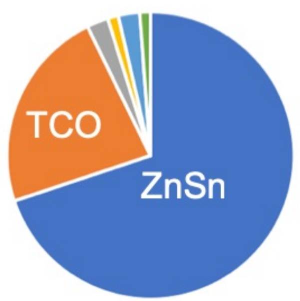
Due to the lack of PV performance of $ZnSnN_2$, we will not be pursued in BP2.

Protection layer

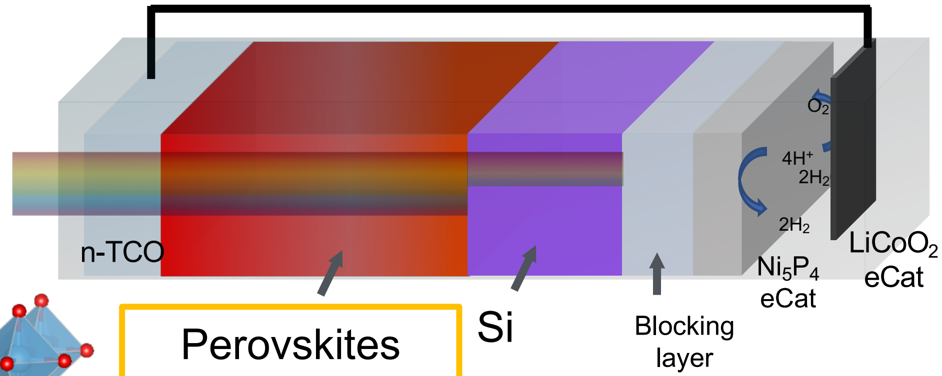


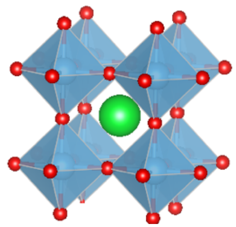
Precursors/All material costs





Accomplishments: Perovskites photoabsorbers (new approach)





Perovskites wide bandgap photoabsorbers

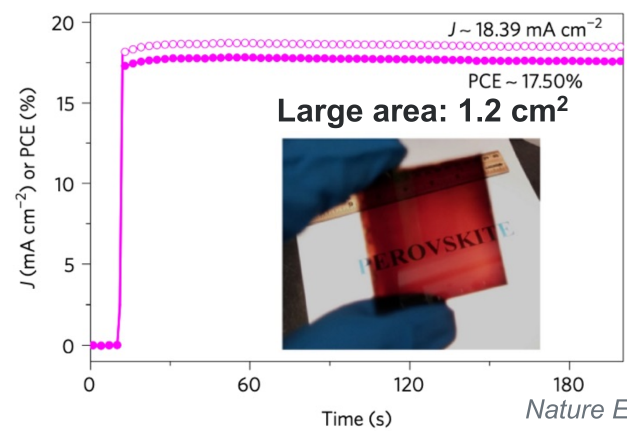
HTE node:

- **Experimentally measured band structure of $SrNbO_2N$ (Rutgers, DOE/NSF-CBET)**
- **Oxynitrides show superior stability over nitrides and sulfides**
- **Low temperature synthesis method applied**

Hwang et al. In preparation

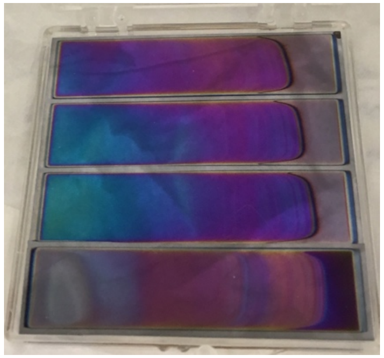
Hybrid Organic Inorganic Perovskites (HOIPs) node:

- **World leading group for Hybrid Organic-Inorganic Hybrid perovskites solar cell.**
- **V_{oc} ~ 1.1 V, J_{sc}, ~21 mA/cm^2**



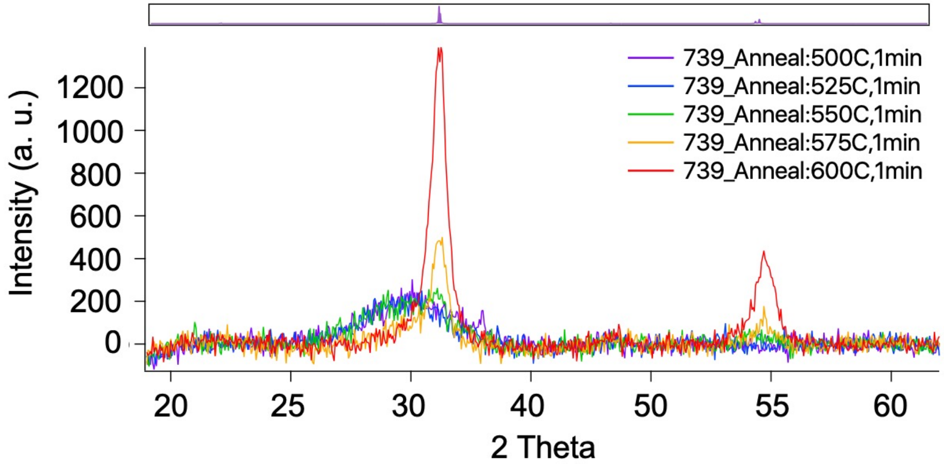
Nature Energy **2,** 17038 (2017)

Accomplishments:
Low temperature synthesis of $SrNbO_2N$

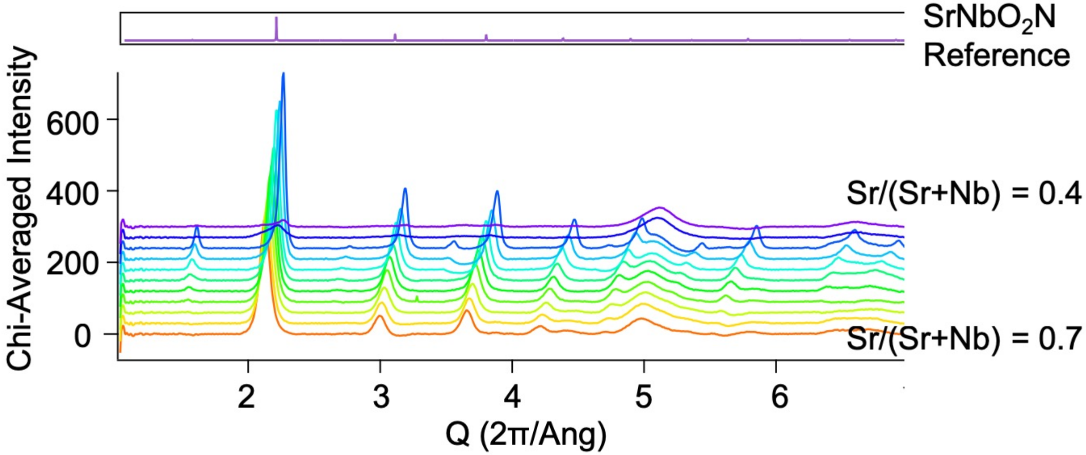


$Sr_xNb_{2-x}O_2N$ (0.8<x<1.4) film on Si substrate

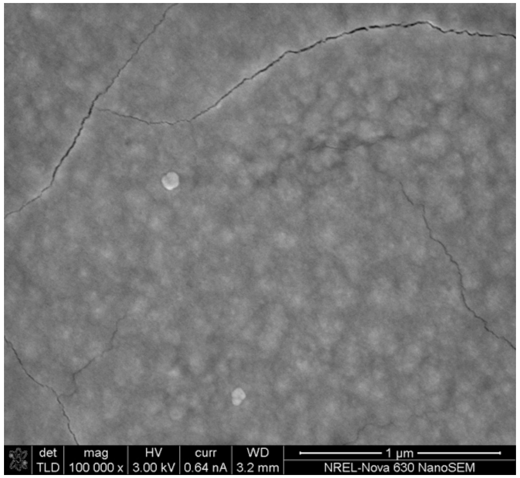
RF-sputtered film with Sr to Nb gradient from left to right.
Rows 1-3 as deposited
Row 4 annealed: 575℃ for 2 min



RTA: Crystallinity starting at around 550℃



SLAC Data: Maintaining perovskite structure w/ lattice shifts across a wide range of Sr/Nb ratios



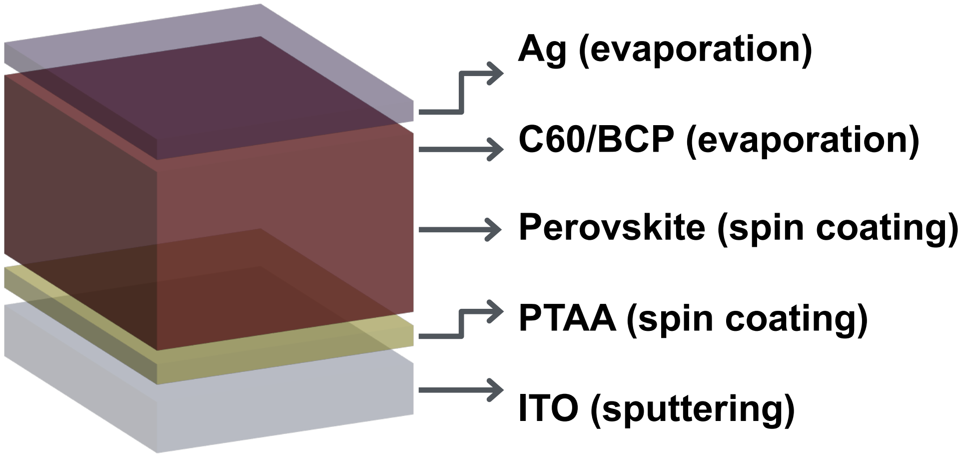
Sr/(Sr+Nb) = 0.5, 575 ℃, 2 min dwell: Problematic cracking observed

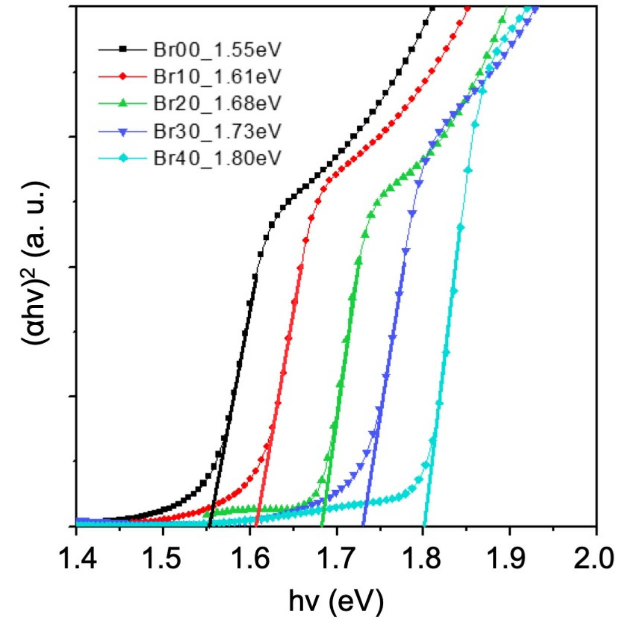
Contributions: Karen Heinselman and Andriy Zakutayev, NREL HTE node

Accomplishments:
HOIPs device fabrication and tunable bandgap

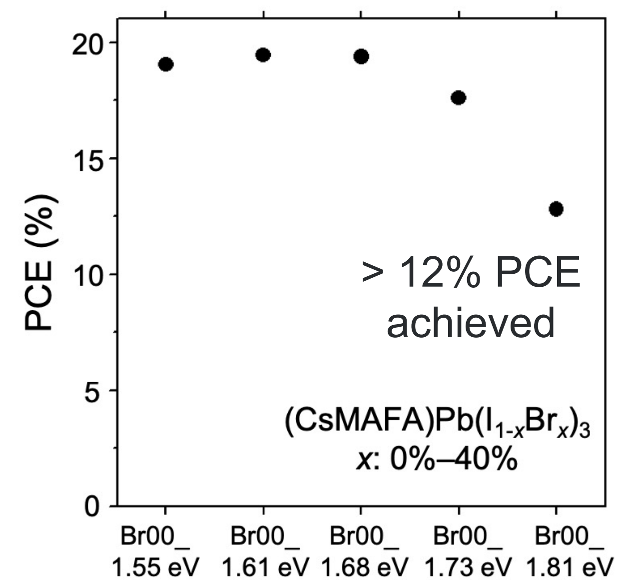
RUTGERS 1766-2016 250

Standard p-i-n device structure





- Variation of bandgap and p-i-n device performance with tuning Br content
- Further work on n-i-p device structure to increase pairing options with Si
- Further work to improve device performance with bandgap near 1.75 – 1.8 eV



Contributions: Kai Zhu, NREL HOIPs node

Project outcomes

Milestones	Planned	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Status
#1	BP1-Q1	Determine which substrate has the best performance/cost while optimizing the loading of the $LiCoO_2$ catalyst	E vs OER < 500mV, stable for 24h, loadings ≥ RDE pellets, Electrochemical test in flooded cells, Rutgers	complete
#2	BP1-Q2	Device test under illumination showing: V_{OC} > 1.85 V, J_{SC} > 10 mA/cm^2, and η_{eff} > 25%	Photoeletrochemical benchmarking, NREL	complete
Go/No-Go Criteria for Thrust 1	BP1-Q4	Evaluation of high performance PEC device with renewable catalysts	STH> 10%, stability > 24h, and/or J_{ph} (at 0 V vs. RHE) > 10mA/cm^2, Photoelectrochemical benchmarking, Rutgers and NREL	complete
#3	BP1-Q3	Fabricate and report optimized $ZnSnN_2$ device	Optimize reflector - max reflectivity, Balancing the highest possible carrier mobility with closeness to 1.1eV bandgap, Rutgers	complete
Go/No-go Criteria for Thrust 2	BP1-Q4	$LiCoO_2$/$ZnSnN_2$ photoanode fabricated and benchmarked against $BiVO_4$	Must outcompete on (at least 2 out of 3): J_{ph} (1.5mA/cm^2 at 1.23 V vs. RHE), stability >90% after 1h, and material cost, Rutgers, NREL	*Incomplete

***This class of material was not yielding sufficiently positive results for us to continue so a decision was made with NREL node partners to explore perovskites.**

Collaboration: Effectiveness
Multiple interactions with HydroGEN nodes

NREL: III-V semiconductor & semiconductor characterization nodes

NREL: High throughput experimental thin-film node

NREL: Hybrid Organic-Inorganic Perovskites node

Date	Meetings w/	Presenter	Outcomes
7/17/18	NREL	Rutgers NREL	Characterization of $ZnSnN_2$ and optimization of $ZnSnN_2$ fabrication **(Task 9, Milestone 3)**
7/17/18- 7/18/18	NREL NREL	N/A	Site visit: S. Hwang visited the NREL site and exchanged samples, test setup knowledge, and aligned sample prep. procedures. **(Task 1, 2, and 4)**
8/16/18	NREL	Rutgers NREL	A decision for $ZnSnN_2$ and BP2 plan for $SrNbO_2N$
8/27/18	NREL	Rutgers	BP2 plan for HP device **(Task 5-9, BP2 Go/No-Go)**
9/13/18	NREL	Rutgers NREL	Initiate collaboration for HV 2 device **(Task 13, Milestone 8)**
10/24/18- 10/25/18	HydroGEN	N/A	HydroGEN Workshop at ASU
2/1/19	NREL	Rutgers	Device structure of HOIPs half-cell and full cell **(Task 15,16, 17, and Milestone 11)**
Nov 2018 - Mar 2019 (15 times)	NREL	Rutgers NREL	One-on-one weekly update (S. Hwang – J. Young) **(Task 5,6, and Milestone 5)**

Collaboration: HydroGEN consortium

Data sharing and interaction with 2B benchmark team:

Verified data uploaded to HydroGEN site and Datahub. Quarterly reports with input from both RU and nodes shared in HydroGEN site and Datahub, and EMN nodes. This has allowed the continued sharing of progress, samples needed, problems encountered, and verification of experimental test procedures. The continuous sharing of results have been critical to rapid progress on this project. Contributions were made for the 2B benchmark team LTE, and PEC benchmark survey. Sharing the data to the water splitting R&D community is realized through publication as well as open access to the verified raw data in the datahub after the project period. Data shared in publications will be opened for sharing at the time of publication.

HydroGEN community interaction: (Since 2018 AMR)

Post-award	Means of communication	Node/point of Contact(s)
	Telecon	Todd Deutsch NREL
	In-person NREL visit	Todd Deutsch, Andriy Zakutayev NREL
	Telecon for progress report	Andriy Zakutayev NREL
	In-person (ASU AWSM workshop)	HydroGEN community
	Telecon for weekly progress meeting	James Young NREL

Proposed Future Work for BP2

High-performance device

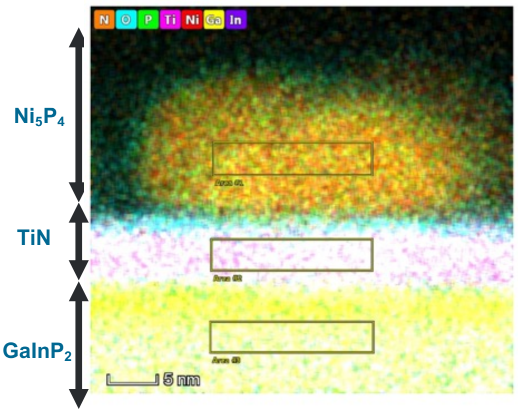
- 1st GEN upright tandem photoabsorber stability (no bias) – Task 5
- Develop next generation III-V lattice matched tandem devices to improve efficiency – Task 6, 8
- Verify the efficiency by on-sun testing – Task 7

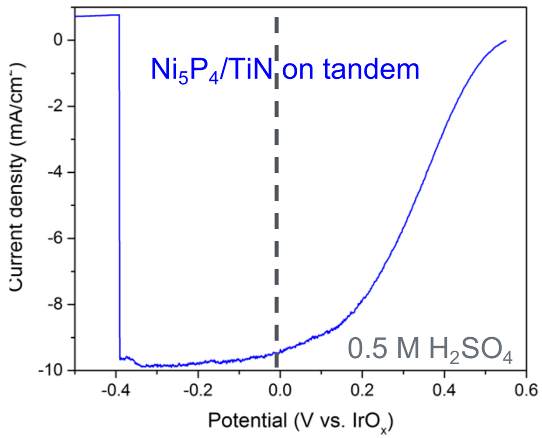
High-value (low-cost) device

- Develop p-$SrNbO_2N$ photocathode fabrication via sputtering at the NREL HTE node - Task 12
- Demonstrate half-cell with alternative wide bandgap anodes (Hybrid-Organic Inorganic Perovskites) collaboration with NREL HOIPs node - Task 13, 15

Project Summary

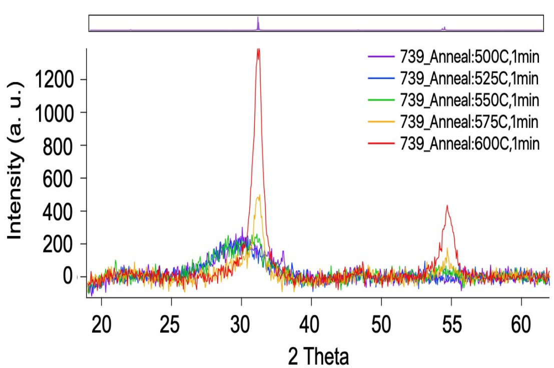
HP devices

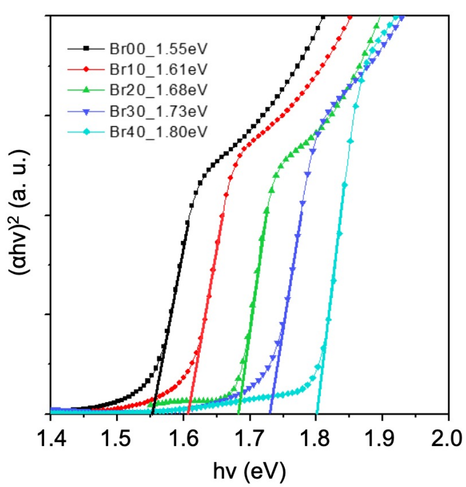




- Successful fabrication of Ni_5P_4/TiN thin-film on $GaInP_2$
- Achieve STH ~ 11.5%, and half-cell stability > 120 h

HV devices





- Evaluate the $ZnSnN_2$ – PV properties, material cost, and stability
- Successful fabrication of crystalline $SrNbO_2N$ at relatively low temperature
- A new approach for HV device – HOIPs for wide bandgap photoabsorber

Thank you for your attention

1766-2016
RUTGERS
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iAMDN
Institute for Advanced Materials, Devices, and Nanotechnology

RUTGERS
Energy Institute

Eric Garfunkel

Charles Dismukes

Martha Greenblatt

Anders Laursen

Shinjae Hwang

Technical Back-Up Slides

HV photoanode, $ZnSnN_2$

Protection layer development – protecting pin-holes:

Summary: NREL HTE node supplied samples to Rutgers for analysis and further modification. $ZnSnN_2$ showed rapid dissolution in base <30min. Protection layer development has been undertaken.

Figure 1(a) SEM of 10 nm TiO_2 grown directly on $ZnSnN_2$ by ALD. Figure 1(b) image showing a 10nm $TiO_2/ZnSnN_2$ in 1M NaOH.

Figure 1 (a)

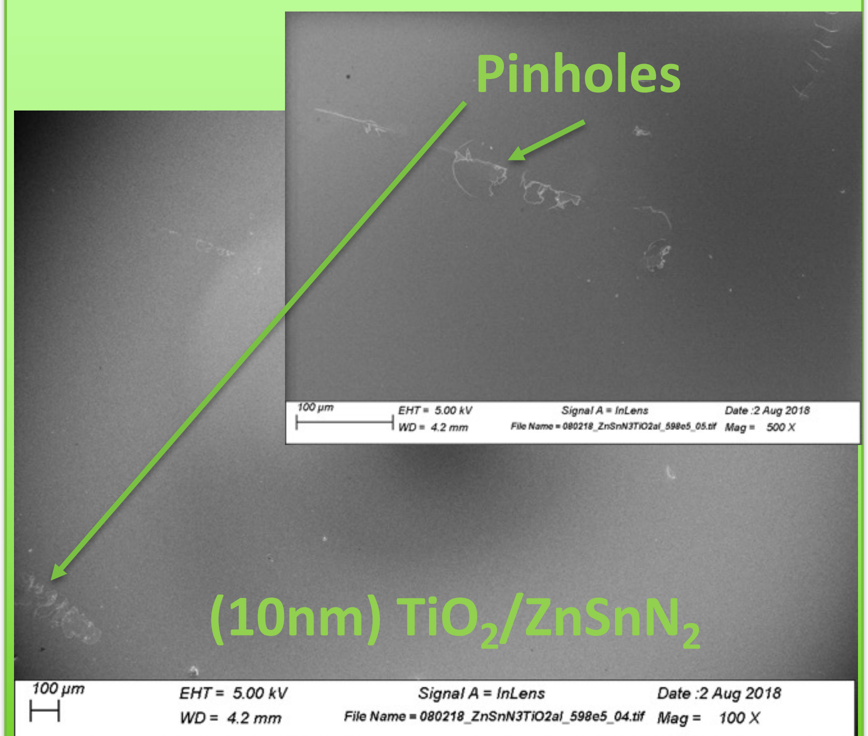
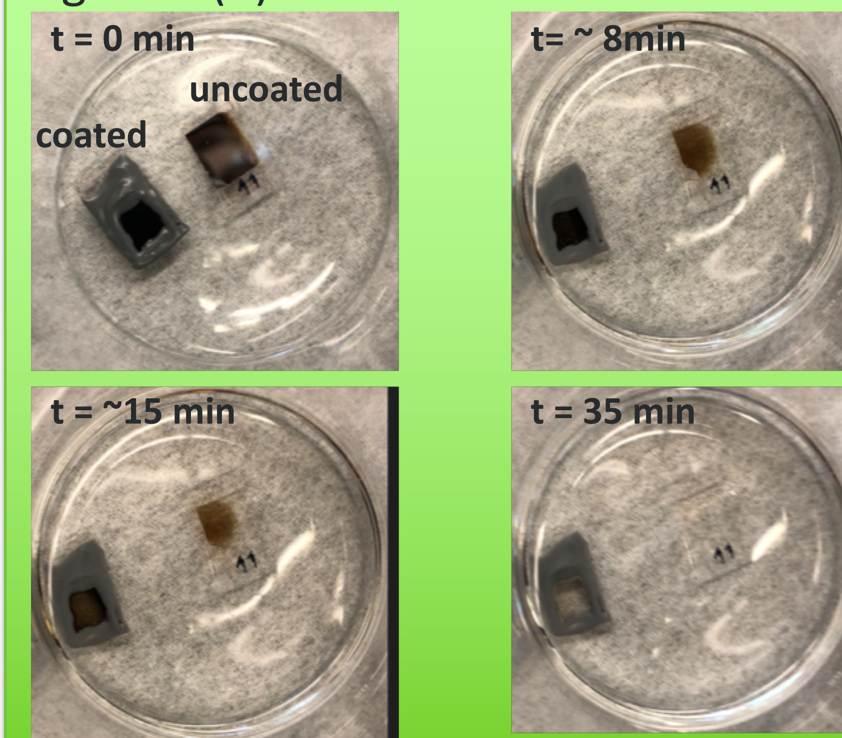


Figure 1 (b)



Publications & Presentations

Publications:

- S. Hwang, S. H. Porter, A. B. Laursen, H. Yang, M. Li, V. Manichev, K. U. D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel and G. C. Dismukes, “Creating stable interfaces between reactive materials: Titanium nitride protects photoabsorber-catalyst interface in water-splitting photocathodes”, *J. Mater. Chem. A*, 2019, **7**, 2400-2411

Presentations:

- G. C. Dismukes “Bioinspired heterogeneous electrocatalysts for CO2 reduction and
- water splitting: Energy-efficient C-C coupling rivaling enzymes” October 2018

    Leiden University, Institute of Chemistry, Leiden, the Netherlands

    Danish Technical University, Institute of Physics, Copenhagen, DK

    Aarhus University, iNano, Aarhus, DK

- E. Garfunkel “Photoelectrochemical water splitting to form hydrogen”, 2018 Telluride Semiconductor Surface Chemistry Meeting, Telluride CO