
HydroGEN seedling: Best-in-Class Platinum Group Metal-Free Catalyst Integrated Tandem Junction Photoelectrochemical Water Splitting Devices

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Overall Objectives

- Demonstrate two photoelectrochemical (PEC) cell configurations: high-performance III-V semiconductors versus emerging low-cost semiconductors fabricated with high-efficiency non-precious metal catalysts for water splitting.
- Evaluate the performance of both PEC cell configurations and investigate the bottlenecks of device performance.
- Achieve benchmark metrics in solar-to-hydrogen (STH) efficiency and durability using both PEC devices.
- Compare the trade-offs between performance and cost for both configurations.

Fiscal Year (FY) 2019 Objectives

- Evaluate PEC performance of catalyst and protection layers on a buried junction n⁺p-GaInP₂/p⁺-GaAs half-cell device.
- Establish STH efficiency >10% using a non-platinum group metal (PGM) catalyst on n⁺p-GaInP₂/n⁺p-GaAs tandem cell.
- Synthesize and evaluate PEC properties of Sr_{2-x}Nb_xO₂N photoanode.

- Initiate a new High-Value device approach: Hybrid Organic-Inorganic Perovskites (HOIPs) and pn-Si in a tandem PEC device.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) Plan¹:

- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability.

Technical Targets

The goal of this project is to attain or exceed the DOE benchmark STH energy conversion efficiency. This is being investigated in two thrusts by developing two PEC devices for direct comparison; the first is a high-performance monolithic device based on state-of-the-art GaAs/GaInP₂ tandem solar cells developed at the National Renewable Energy Laboratory (NREL), and the second is a high-value device based on earth-abundant photoabsorber materials. Both these devices will be paired with electrocatalysts developed for this purpose at Rutgers by adapting them to thin films on the photoabsorbers. These catalysts are based on the hydrogen evolution reaction (HER) catalysts (Ni₃P₄), oxygen evolution reaction (OER) catalysts (LiCo₂O₄) previously developed at Rutgers for high-efficiency electrolyzers. Both devices employ tandem photoabsorbers using both a narrow and a wide bandgap material in series. The aim is to meet the following DOE technical targets as FCTO MYRDD Plan:

- Solar to hydrogen energy conversion ratio: 20% (by 2020)
- Cost of hydrogen production: <\$2/kg H₂

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Electrode Replacement Lifetime: 0.5 years.

FY 2019 Accomplishments

- Achieved non-PGM activity on par with PGM on n⁺p-GaInP₂ buried junction photocathode.
- Developed a non-PGM catalyst protection layer (Ni₅P₄/TiN) on GaInP₂/GaAs multi-junction structure that achieved >10% STH and longer lifetime.
- Using a photovoltaic (PV) device comprised of second-generation III-V semiconductors and quantum wells and non-PGM catalysts, achieved >12% STH.
- Synthesized Sr_{1-x}Nb_xO₂N photoabsorber on Si, characterized by X-ray fluorescence, X-ray diffraction, electron microscopy.
- PEC oxidation test performed on Sr_{1-x}Nb_xO₂N/Si photoanodes using barrier-free ferrocyanide redox couple and photocurrent density, which surpassed the benchmark (planar Ta₃N₅/Si) performance.
- Developed Hybrid Organic-Inorganic Perovskites with a bandgap in the range of 1.6–1.8 eV and tested their PV properties.

INTRODUCTION

Current PEC devices suffer from both poor stability and low efficiency. This project aims to address both these critical limitations by significantly increasing the STH conversion efficiency to above 10% while achieving long-term operation without corrosion.

APPROACH

The industry-accepted benchmark standard for PEC performance is conducted with PGM catalysts (RuO₂ and PtRu). Our approach differs by developing methods to interface two classes of photoabsorbers with the Rutgers-developed non-PGM catalysts and protection layers. Our approach to increasing the STH efficiencies up to 10% with >100 h durability has two thrusts:

Thrust 1: Using GaInP₂/GaAs dual-junction devices with bandgaps optimized to match the solar spectrum, these will provide sufficient photovoltages to drive the energetically uphill splitting water reaction (The NREL PV cell has a demonstrated maximal solar to electrical power efficiencies >16%. However, STH efficiencies still struggle to reach this value due to unfavorable catalytic kinetics).

Thrust 2: The GaInP₂/GaAs photoabsorbers have dominated the state-of-the-art PEC devices due to their high efficiency. In contrast, high-value (scalable) photoabsorbers have not seen photon to hydrogen activities near these values. Therefore, there is a significant need to develop new photoabsorbers (or improve the performance of existing candidates) to address the scalability of PEC hydrogen production. Here we aim to develop novel photoabsorbers based on earth-abundant materials utilizing the recently developed record-breaking PV materials (HOIPs) and by improving the performance of a known durable oxynitride (SrNbO₂N). Both these materials have a wide bandgap and may be paired with narrow bandgap Si photoabsorber in a tandem configuration to achieve greater solar spectral coverage.

RESULTS

In Thrust 1, we started by developing methods for protecting the corrosion-prone photoabsorbers, GaInP₂ and GaAs, using a TiN layer between it and the top catalytic layer. Protection is needed both during the fabrication of the catalyst layer and during PEC operation in corrosive electrolytes. It has to be compatible with the synthesis of the nickel phosphide compound (Ni₅P₄) as a catalyst. To gain insights into the processing of these layers, we first developed methods using a single junction device (FY 2018), demonstrating that this strategy indeed can increase device lifetimes from a <6 hours to >80 hours. Further increasing complexity, the next step is to introduce a buried junction in the GaInP₂ photoabsorber.

Achieved benchmark activity and extended durability on n⁺p-GaInP₂ buried junction photocathode

After carefully cleaning and etching the as-received n⁺p-GaInP₂ interface (using procedures described in FY 2018), thin-film layers of Ni₅P₄/TiN (catalyst and protection) were fabricated on a buried junction n⁺p-GaInP₂ photocathode using the previously reported optimized synthesis conditions. The PEC performance of such

devices was measured at Rutgers and verified by the NREL PEC benchmark node and compared to the PtRu-based benchmark device. Figure 1(A) shows the current versus voltage curve (J-V curve) of the benchmark PtRu device (using a catalyst/absorber junction, no protection layer) compared to the device employing the Ni₅P₄/TiN catalyst and protection layers, both devices made from the same photoabsorber. The results show the J-V performance with thin film Ni₅P₄/TiN layers is on par with the PtRu benchmark catalyst. Figure 1(B) shows the incident photon-to-current efficiency (IPCE) measurement also indicates comparable performance (10 mA/cm²) of the benchmark and Ni₅P₄/TiN catalyst and protection layers modified device. This indicates that the catalyst and protection layers do not hamper the performance compared to the noble metal benchmark.

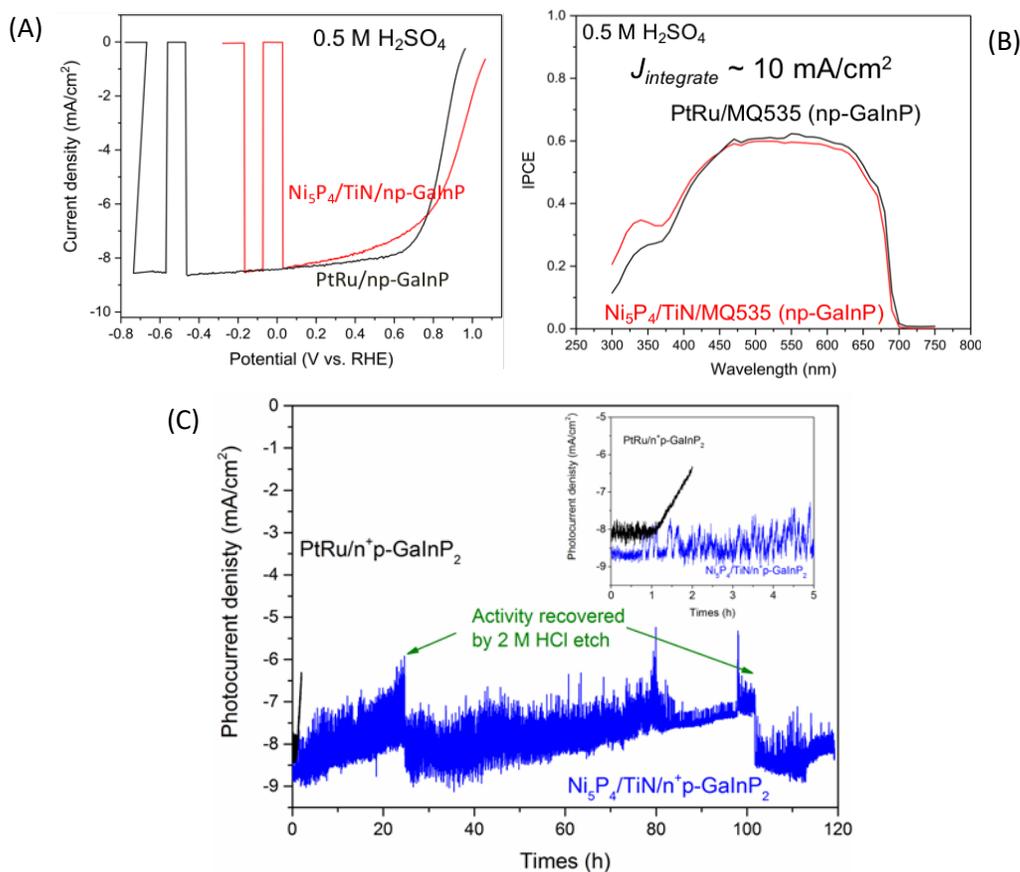


Figure 1 J-V curves (A) and IPCE measurement (B) of Ni₅P₄/TiN and PtRu benchmark on buried junction photocathode tested at NREL (C) Chronoamperogram of Ni₅P₄/TiN/np-GaInP₂ at +0.25 V vs. RHE and PtRu benchmark at +0.78 V vs. RHE in 0.5 M H₂SO₄. Inset shows initial stability of two devices.

Figure 1(C) shows the significantly improved stability of the Ni₅P₄/TiN modified np-GaInP₂ photocathode in 0.5 M H₂SO₄ compared to that of the benchmark device. The benchmark device immediately starts undergoing degradation with ~25% loss of activity within 6 hours. In contrast, the modified device showed no failure over at least 120 h, the duration of the test. It was noted that during the 120 h test, a slight decrease of photocurrent was observed over time, which we determined was due to Cu deposition on the catalyst caused by corrosion of the connection wire during the tests (confirmed by XPS). This surface contamination was easily removed by dipping in 2 M HCl for 2s intermittently, fully recovering the original activity (green arrows in Figure 1(C)). This treatment demonstrates not only the parasitic origin of the photocurrent loss from Cu deposition but also the robust nature of the catalyst and protection layers to washing in HCl.

Based on the positive results from the single junction device, we applied the catalyst and protection layers to the complete (dual-junction) tandem device. In early FY2 019, we achieved 11.5% STH using this Ni₅P₄/TiN on GaInP₂/GaAs tandem junction device.

To push the STH conversion efficiency even further, a higher photocurrent is required while retaining similar photovoltage. One way to achieve this is to use a III-V inverted metamorphic multi-junction (IMM) structure, which holds the STH record (using noble metals)[1]. However, IMM structures are mechanically unstable and are not compatible with higher processing temperatures ($>150^{\circ}\text{C}$). Because such conditions are required for the synthesis of the Ni_5P_4 catalyst, we instead used the second generation $\text{GaInP}_2/\text{GaAs}$ multi-junction system, which is built on a mechanically and thermally stable lattice-matched (LM) upright structure. This structure was further adapted to introduce quantum wells (QWs) into the bottom GaAs junction to adjust the bandgap resulting in an increase in both light absorption and overall efficiency. The second-generation photoabsorber was grown by the NREL metal-organic vapor phase epitaxial (MOVPE) node on a custom-built, atmospheric pressure MOVPE reactor, the same as the previous first-generation $\text{GaInP}_2/\text{GaAs}$ multi-junction photoabsorber. After growth, the semiconductor structure was processed into individual devices to measure the PV properties.

In Figure 2(A), the J-V curves for the first- and second-generation devices show that introducing the QWs increases the photocurrent slightly, but results in a small loss in the V_{oc} . This is due to the decrease in the bandgap of the bottom cell caused by the QW (see Figure 2(B)). Figure 2(B) also shows that the top GaInP_2 cell limits the current in both devices. The Rutgers team has fitted this device with the previously described Ni_5P_4 catalyst layer combined with a modified protection layer that incorporates a top anti-reflective coating (ARC) made of TiO_2 , together with the TiN protection layer described previously. The J-V performance in Figure 2(C) shows a saturation current density (J_{sat}) and unbiased current density ($J_{unbiased}$) of -11.7 mA/cm^2 and -10.4 mA/cm^2 , respectively. The latter is equivalent to an STH of 12.8%. This is a significant improvement over the previously reported 11.5% STH for the first generation device. In FY 2019-2020, our effort will be on further increasing the efficiency by current matching the bottom and top junctions in combination with an antireflective coating.

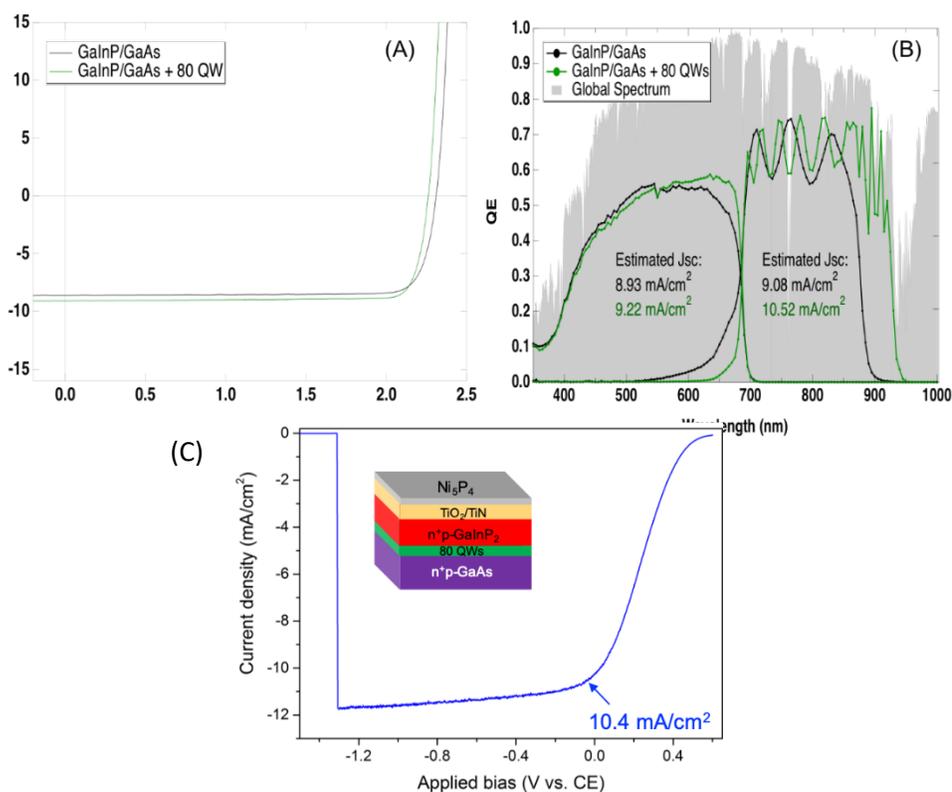


Figure 2 (A) Solid-state J-V curves of $\text{GaInP}_2/\text{GaAs}$ (1st GEN, black) and GaInP/GaAs (second generation), green) under 1 sun illumination (B) quantum efficiency of first and second generation devices with global spectrum (gray). (C) J-V curve of the second generation tandem device with catalyst (Ni_5P_4), diffusion protection (TiN), and ARC layers (TiO_2). Inset shows device structure.

Successful fabrication of $\text{Sr}_{1-x}\text{Nb}_x\text{O}_2\text{N}$ on Si and its PEC activity

Previous work by the Rutgers team has shown that the conventional high-temperature synthesis of SrNbO_2N photoabsorbers is incompatible with fabrication on silicon photoabsorbers. This prevents the development of an integrated dual junction tandem device on Si. The high reaction temperature (900°C) of conventional thermochemical processing to make SrNbO_2N results in the formation of undesired Nb^{4+} states (that serve as trap sites) as well as diffusion of Sr and Si to form a strontium-silicate phase. Significantly lowering the synthesis temperature is believed to be the necessary development to allow this dual junction to be produced.

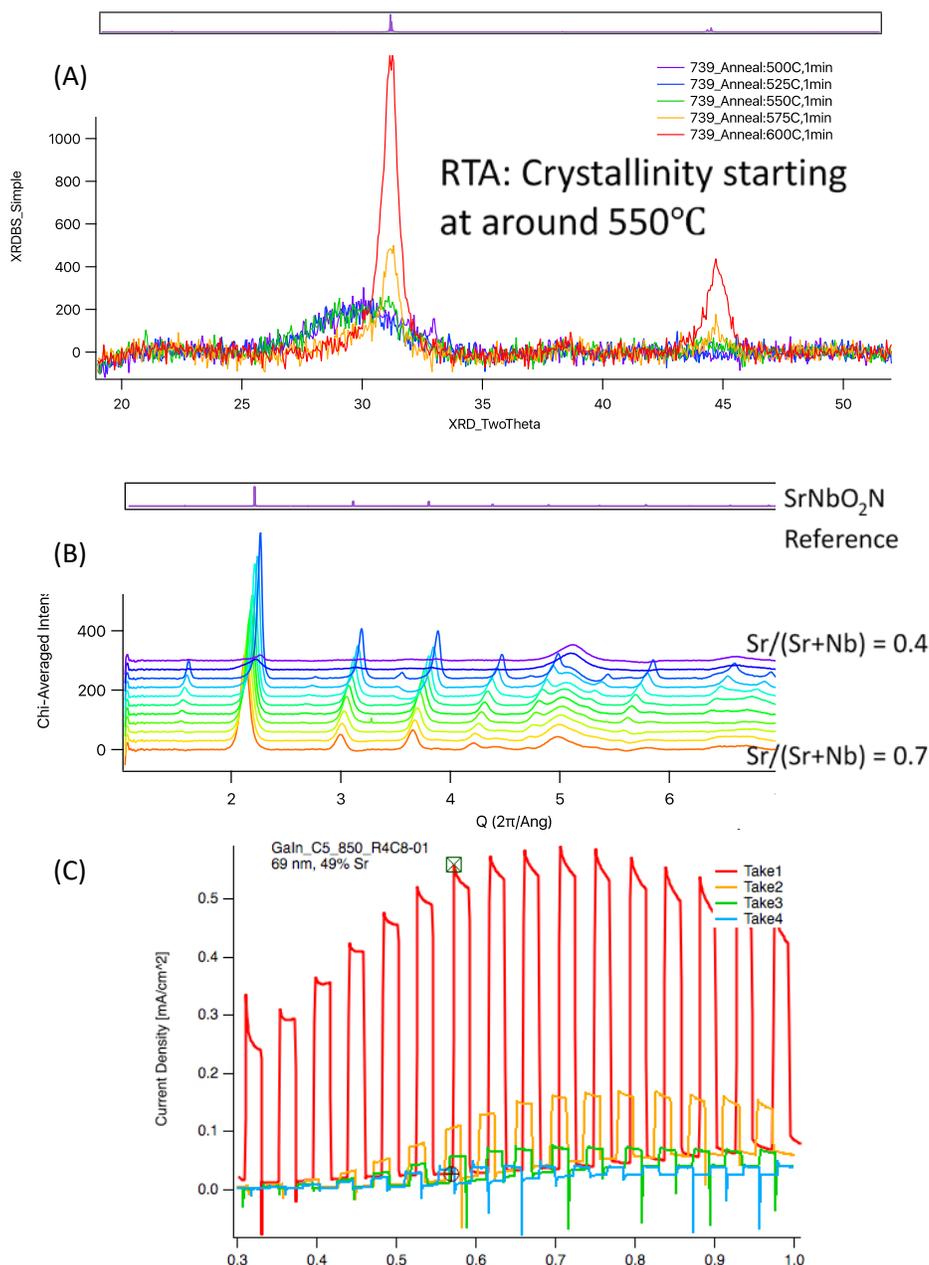


Figure 3 (A) XRD pattern of SrNbO_2N samples rapid annealed at various temperatures from 500–600°C with 1 min hold. (B) Diffraction pattern of SrNbO_2N with varying Sr-concentration. (C) Current density [mA/cm^2] vs. Working electrode voltage [V] vs. the Ag/AgCl (3 M NaCl) reference (in 0.4 M KCl supporting electrolyte). Chopped light voltammetry to show the highest photocurrent of $0.53 \text{ mA}/\text{cm}^2$ @ 1.23 V vs. RHE (0.57 V vs Ag/AgCl).

Hence, the Rutgers and NREL high-temperature electrolysis (HTE) node team devised a strategy to lower the synthesis temperature by using reactive sputtering. The NREL HTE node fabricated $\text{Sr}_{1-x}\text{Nb}_x\text{O}_2\text{N}$ thin-film on Si by co-sputtering of Nb and Sr targets in a mixed O_2/N_2 plasma to directly achieve the initial oxynitride material. The sputtering procedure was modified to create a gradient composition by varying the Sr/Nb ratio. To achieve the high crystallinity of the stoichiometric compound (low lattice defect concentration) required for photoabsorber applications, further processing by thermal annealing is needed. The thin film was processed by rapid annealing at 500–600°C for a very short time (1–2 min). Figure 3(A) shows the XRD pattern of the deposited film with various annealing temperatures from 500–600°C. At temperatures above 550°C, the SrNbO_2N perovskite crystallinity appears. The two observed diffraction lines are in good agreement with the phase pure SrNbO_2N phase. The diffraction data of the Sr/Nb composition gradient ($\text{Sr}_{1-x}\text{Nb}_x\text{O}_2\text{N}$) thin film, following annealing at 575°C for 2 min (recorded at SLAC), is shown in Figure 3(B). This demonstrates the distinct crystalline features from $\text{Sr}_{1-x}\text{Nb}_x\text{O}_2\text{N}$ comprising the thin film and that the lattice constants shift systematically across a wide range of Sr/Nb ratios, as expected.

These films were cut and fabricated into electrodes for electrochemical measurements. We tested performance using a reversible redox couple: 0.1 M ferrocyanide/1 mM ferricyanide, which is barrier-free and prevents limitations from kinetic overpotential as occurs using water/oxygen. Figure 3(C) shows the J-V curve under chopped AM1.5 G illumination. The highest photocurrent at 1.23 V vs. RHE was 0.53 mA/cm² obtained using ~70 nm annealed thin film and composition ~49% Sr/(Sr+Nb). The result shows a factor of two improvements in photocurrent density compared to a planar Ta_3N_5 thin film on Si photoanode literature benchmark [2].

Synthesis and benchmarking of HOIPs thin films

HOIPs have shown great promise as low-cost, high activity photoabsorbers. The improvement in power-current-efficiency (PCE) from its early discovery to now has increased more rapidly than any other photoabsorber. The disadvantage of HOIPs is its instability even in a moist atmosphere, let alone in water. Hence, these materials need to be rigorously protected from the environment. Typical HOIP bandgaps for the general perovskite composition $(\text{CsMAFA})\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ can be seen in Figure 6 (left); from this, the bandgap is tunable by adjusting the composition, in this case, I/Br ratio. Since a bandgap around 1.7–1.8 eV is ideal for matching with Si, an I/Br ratio around 40% is near-optimal. Figure 4 (right) shows an excellent PCE at bandgaps below 1.7 eV (~19%), which decreases between 1.73–1.80 eV. Our initial focus is, therefore, on improving the PCE for high bandgap HOIPs materials. Furthermore, the ordering of the electron extraction layers with respect to the light path, i.e., extracting electrons in the light direction or against it (n-i-p versus p-i-n), causes changes in PCE. The electron or hole migration length and transparency of hole versus electron extraction layers are some of the factors determining the change in performance with the direction of the light.

Studying both structures is needed to determine which configuration is more efficient in a tandem device with Si bottom cells, which may not be the same as in a single absorber mode. At the same time, using Si as either anode or cathode will mean that different protection layer strategies need to be employed. The typical J-V curves and the corresponding PCEs for both n-i-p and p-i-n structures are shown in Table 1 for the single junction device (without Si substrates). From Table 1, it is seen that the p-i-n and n-i-p devices with a 1.61 eV bandgap show similar cell performance. Whereas when the bandgap increases to 1.68 eV and 1.8 eV, the p-i-n device shows relatively higher performance.

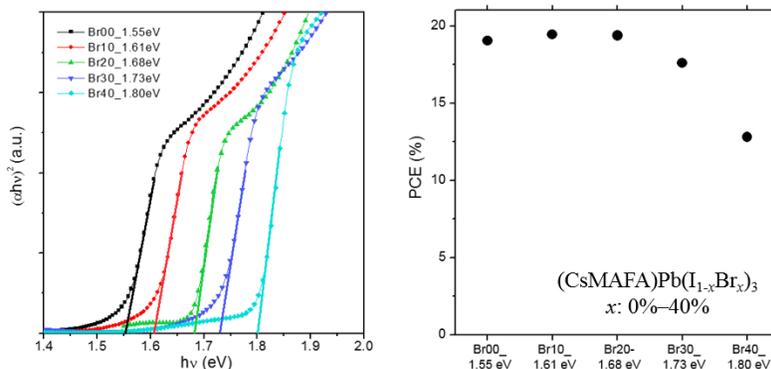


Figure 4. Impact of perovskite composition tuning on bandgap and device performance.

Table 1. PCE for different bandgaps with two n-i-p and p-i-n structures

Structure	Bandgap (eV)	PCE (%)
n-i-p	1.61	17.6
	1.68	11.4
	1.8	8.7
p-i-n	1.61	19.1
	1.68	17.5
	1.8	12.6

During FY 2020, we will further investigate this issue and integrate the HOIPs with the Si substrate using this knowledge. It is expected, based on the previous optimization of HOIPs photoabsorbers, that tuning the solvent mixtures and processing conditions (annealing time and temperature) can increase the PCE for the high-bandgap materials and will be critical for the integration into a tandem device. This development will be undertaken by the NREL HOIPs node.

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions derived from the work in FY 2019 are:

- $\text{Ni}_5\text{P}_4/\text{TiN}$ layer on buried junction $n^+p\text{-GaInP}_2/p^+\text{-GaAs}$ has demonstrated the comparable catalytic activity with benchmark samples with stable performance over 120 h.
- Fabrication of $\text{Ni}_5\text{P}_4/\text{TiN}$ layers on 1st and 2nd GEN tandem device demonstrated high STH (>12%) which is expected to increase further with optimization of semiconductor and anti-reflective coating thickness.
- Both $\text{Sr}_{1-x}\text{NbO}_2\text{N}$ thin-film and HOIPs demonstrated promising results for low-cost PEC devices and are expected to advance to a tandem device with a Si junction.

Future efforts:

- Thrust #1
 - Increase STH efficiency and stability of $\text{Ni}_5\text{P}_4/\text{TiN}$ coated on 1st and 2nd GEN $\text{GaInP}_2/\text{GaAs}$ tandem device.
 - Test full device under on-sun conditions and high flux.
- Thrust#2

- Develop a half-cell photoelectrode using hybrid-organic/inorganic perovskite photoabsorber interface with catalyst+protection layers.
- Assemble a photoanode comprised of OER/SrNbO₂N photoabsorber.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. S. Hwang, J. L. Young, R. Mow, A. B. Laursen, M. Li, H. Yang, P. E. Batson, M. Greenblatt, M. A. Steiner, D. Friedman, T. G. Deutsch, E. Garfunkel, and G. C. Dismukes. “Highly Efficient and Durable III-V Semiconductor-Catalyst Photocathodes Via a Transparent Protection Layer,” (Submitted 2019).
2. S. Hwang, S.H. Porter, V. Manichev, M. Li, V. Amarasinghe, E. Taghaddos, A. Safari, M. Greenblatt, E. Garfunkel, and G. C. Dismukes. “SrNbO₂N Thin-Film as a Photoanode for Solar-Driven Water Oxidation,” (Submitted 2019).
3. 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 (5) 2400-2411

Presentations:

1. S. Hwang, A. B. Laursen, G. Charles Dismukes, and E. Garfunkel. “Best-in-Class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices” 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting in Crystal City, VA, April 2019.
2. G. C. Dismukes, E. Garfunkel, M. Greenblatt, A. B. Laursen, and S. Hwang: “Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices,” U.S. DRIVE Hydrogen Production Tech Team, teleconference, February 2019.
3. G. C. Dismukes “Bioinspired Heterogeneous Electrocatalysts for CO₂ Reduction and Water Splitting: Energy-Efficient C-C Coupling Rivaling Enzymes,” Leiden University, Institute of Chemistry, Leiden, the Netherlands, Danish Technical University, Institute of Physics, Copenhagen, DK, Aarhus University, iNano, Aarhus, DK, October 2018.
4. E. Garfunkel “Photoelectrochemical Water Splitting to Form Hydrogen,” Semiconductor Surface Chemistry Meeting, Telluride, CO, August 2018.

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2. I. Narkeviciute, P. Chakthranont, A. J. M. Mackus, C. Hahn, B. A. Pinaud, S. F. Bent and T. F. Jaramillo, *Nano Lett.* 16 (2016): 7565–7572.