Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

All-Perovskite Tandem Photoelectrodes for Low-Cost Solar Hydrogen Fuel Production from Water Splitting

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The University of Toledo

Project ID: p218

DOE Project Award # DE-EE0010740
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DOE Hydrogen Program 2024 Annual Merit Review and Peer Evaluation Meeting

NREL Transforming ENERGY | BERKELEY LAB Bringing Science Solutions to the World | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory

Project Overview

Project Partners
PI, Yanfa Yan, University of Toledo
Co-PI, Zhaoning Song, University of Toledo

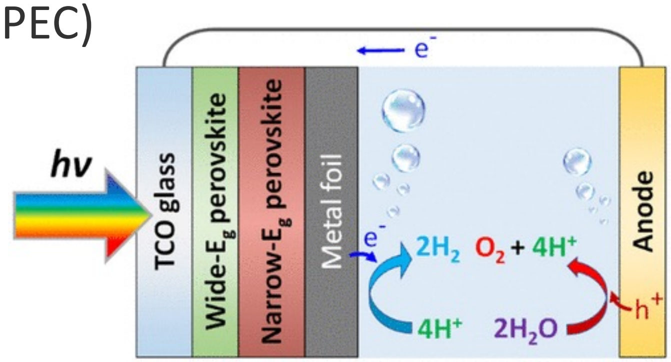
Award #	EE0010740
Start/End Date	10/01/2023 – 09/30/2026
Project Funding*	$1.0M

Project Vision

Design, fabricate, and test all-perovskite tandem photoelectrodes and panels to achieve low-cost, high solar-to-hydrogen efficiency as well as long-term stable, unassisted photoelectrochemical (PEC) water splitting systems.

Project Impact

Develop a low-cost, durable, and efficient PEC water-splitting system that meets the DOE cost targets of <$2/kg by 2026 and $1/kg by 2031 for clean hydrogen production.



Tandem photoelectrode

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

Approach – Summary

Project Motivation

- Paring two low-cost perovskite absorbers in a tandem photoelectrode to produce a PEC water-splitting system with up to 25% theoretical STH efficiency.
- Demonstrated 18% efficient tandem photoelectrodes in our last project.

Barriers

- Phase segregation in wide-Eg perovskites
- Sn2+ oxidation in narrow-Eg perovskites
- Scaling up production of tandem devices
- Photoelectrode panel assembling
- On-Sun PEC Testing

Key Impact

Metric	State of the Art	Expected Advance
STH eff.	*15 - 18%*	*>20%*
Stability	*100 - 500 h*	*> 1,000 h*
Area	0.1 - 1 cm^2	> 25 cm^2

Partnerships

HydroGEN EMN Nodes

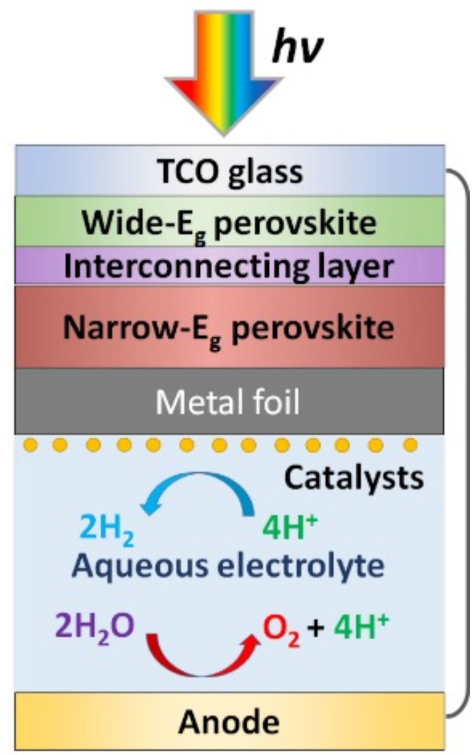
Todd Deutsch, NREL: PEC benchmarking

Kai Zhu, NREL: Experimentally investigate the instability of wide-/narrow-bandgap perovskites

Tadashi Ogitsu, LLNL: Theoretical understanding of the wide-/narrow-bandgap perovskites

Approach – Innovation

- **Wide-bandgap (1.7 - 1.8 eV) perovskite top absorbers**
  - Suppress halide segregation by reducing defect density
  - Use mixed 2D/3D and all-inorganic perovskites
- **Narrow-bandgap (1.2 - 1.5 eV) perovskite bottom absorbers**
  - Develop a single-crystal-synthesis route
  - Avoid catalytic interface erosion
- **Scaling-up production of tandem photoelectrode panels**
  - Leverage our perovskite module production capability
- **Understand material properties and intrinsic stability**
  - In collaboration with Kai Zhu at NREL (Experiment)
  - In collaboration with Tadashi Ogitsu at LLNL (Theory)
- **On-sun PCE testing**
  - In collaboration with Todd Deutsch at NREL

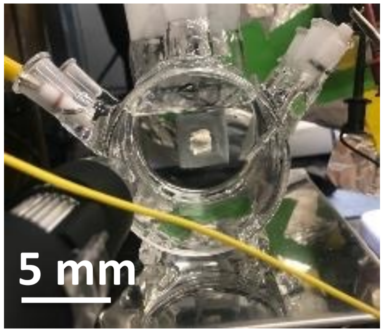


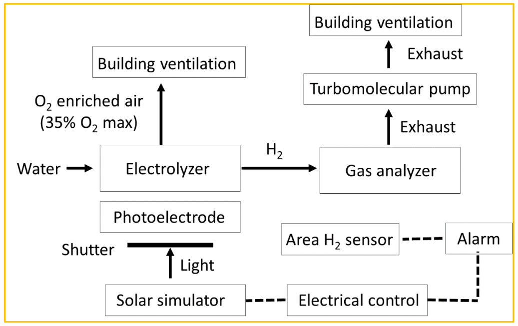
Goal: Demonstrate hydrogen production at a rate of 0.1 g/h for diurnal operation over two weeks

Approach – Safety Planning and Culture

- A safety plan was required for review by the HSP.
  - Comments and Recommendations from the HSP were greatly appreciated.
  - Followed the protocols of **safety planning for low-volume hydrogen projects**.
    - (No H_2 cylinder and supply; H_2 generation rate at **0.001 - 0.1 g/hr**; pressure at 1 atm; maintained ventilation at ~100 fpm; 10+ yr experience working with H_2; Emergency response plan)
  - More technical diagrams and detailed descriptions were added.
  - A revised safety plan and responses would be sent to the HSP for review.
- Prioritizing safety and analyzing hazards:
  - Project team members will take Lab Safety training and pass the exam.
  - Environmental Health and Radiation Safety (EHRS) will have weekly inspections of the lab. The project team will document and address safety vulnerabilities.
  - Hydrogen monitors to read hydrogen levels in the lab.
- Lessons learned and best safety practices:
  - Monthly meeting to review safety misconducts, near-misses, incidents, etc.

Electrolyzer





Gas analyzer

Potential Impact

- Design and fabricate all-perovskite tandem devices with comparable STH efficiency with state-of-the-art III-V tandem photoelectrodes but at 1/1000 of the cost.
- Team up with HydoGEN EMN nodes for materials synthesis, characterization, simulation, and PEC measurements.
  - Kai Zhu, NREL, materials synthesis and characterization
  - Tadashi Ogitsu, LLNL, theory and modeling
  - Todd Deutsch, NREL, PEC testing and benchmarking
- Contribute to the HydroGEN Benchmarking & Protocols to develop an understanding of emerging PEC materials (e.g., halide perovskites).
- Value propositions of the project
  - The success of the project can reduce the PEC hydrogen generation cost to <$1/kg.
  - Build a workforce for the future hydrogen industry.
  - Provide training and educational experience to underrepresented and underserved communities.
  - Support environmental/energy justice for regions heavily relying on fossil fuels.

Summary of Deliverables and Goals

- **Budget Period 1 (Q1-Q4):** Demonstrating all-perovskite tandem photoelectrode baseline.
  - Develop an all-perovskite tandem photoelectrode baseline for efficient PEC water splitting.
  - Focus on intrinsic and extrinsic stability issues of all-perovskite tandem photoelectrodes.

- **Deliverables:** Demonstrate efficient (>16% STH efficiency) and stable (retaining 90% efficiency after 300 hours) all-perovskite tandem photoelectrodes (Active area of 0.1 cm^2).

- **End of Project Goal:**
  - All-perovskite tandem photoelectrodes show an STH efficiency of >18% and retain 80% of their initial efficiency for more than 500 hours. (Active area of 25 cm^2).
  - PEC systems demonstrate hydrogen production at a rate of 0.1 g/h for diurnal operation over two weeks.

Summary of Go/No-Go Milestones

Milestone Summary Table							
Task #	Task or Subtask Title	Milestone Type	Milestone Number	Milestone Description	Milestone Verification Process	Anticipated Quarter	Note
1.0	Optimize absorbers for efficient tandem photoelectrodes	Milestone	1.1	Achieve a J_{SC} of >16 mA/cm^2 in tandem cells with an active area of 0.1 cm^2.	More than 5 devices show the target J_{SC}. Measured at the University of Toledo/NREL.	1	Complete
2.0	Demonstrate tandem photoelectrode baseline	Milestone	2.1	Demonstrate an all-perovskite tandem photoelectrode baseline with an STH efficiency > 15% (Active area of 0.1 cm^2).	More than 5 devices show the target efficiency. Measured at the University of Toledo/NREL.	2	Complete
3.0	Improve tandem photoelectrode stability	Milestone	3.1	Tandem photoelectrodes retain >90% of their initial STH efficiency after continuous operation for more than 100 hours. (Active area of 0.1 cm^2)	More than 5 devices show the target efficiency and stability. Measured at the University of Toledo/NREL.	3	In progress
4.0	Improve tandem photoelectrode efficiency	Milestone	4.1	Improve tandem photoelectrode STH efficiency to > 16% and stability of 300 hours of operation. (Active area of 0.1 cm^2)	More than 5 devices show the target efficiency and stability. Measured at the University of Toledo/NREL.	4	In progress
5.0	DEIA	Milestone	5.1	Recruit at least one female graduate student or one female postdoc will be hired to work on Tasks 1-4.	Report to DOE	4	Complete
GNG	Go/No-Go Decision Point			Tandem photoelectrodes deliver an STH efficiency of > 16% and retain more than 90% of their initial efficiency for more than 300 hours of operation under 1 sun operation. (Active area of 0.1 cm^2)	More than 5 devices show the target efficiency and stability. Measured at the University of Toledo/NREL. Report sent to DOE for verification.	4	In progress

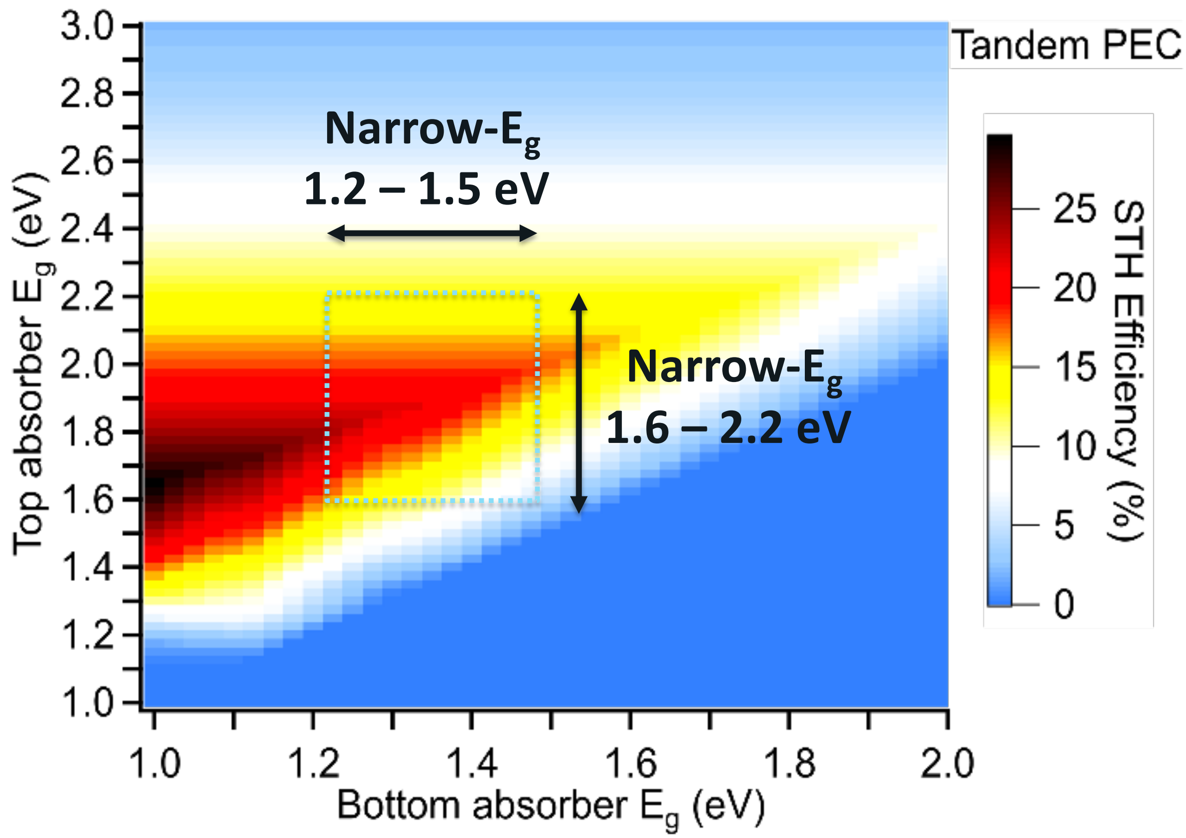
Summary of Accomplishments

Budget Period 1 Q1-Q2 (10/23 - 3/24)

- Performed device simulations on all-perovskite tandem photoelectrodes.
- Developed a better understanding of the buried interface degradation in Sn-Pb perovskite subcells and a mitigation strategy to improve their stability.
- Demonstrated all-perovskite tandem cells with a J_{SC} = 16 mA/cm^2. (**Milestone 1.1**)
- Demonstrate an all-perovskite tandem photoelectrode baseline with an STH efficiency > 15%. (**Milestone 2.1**)

Accomplishments

Tandem PEC photoelectrode modeling



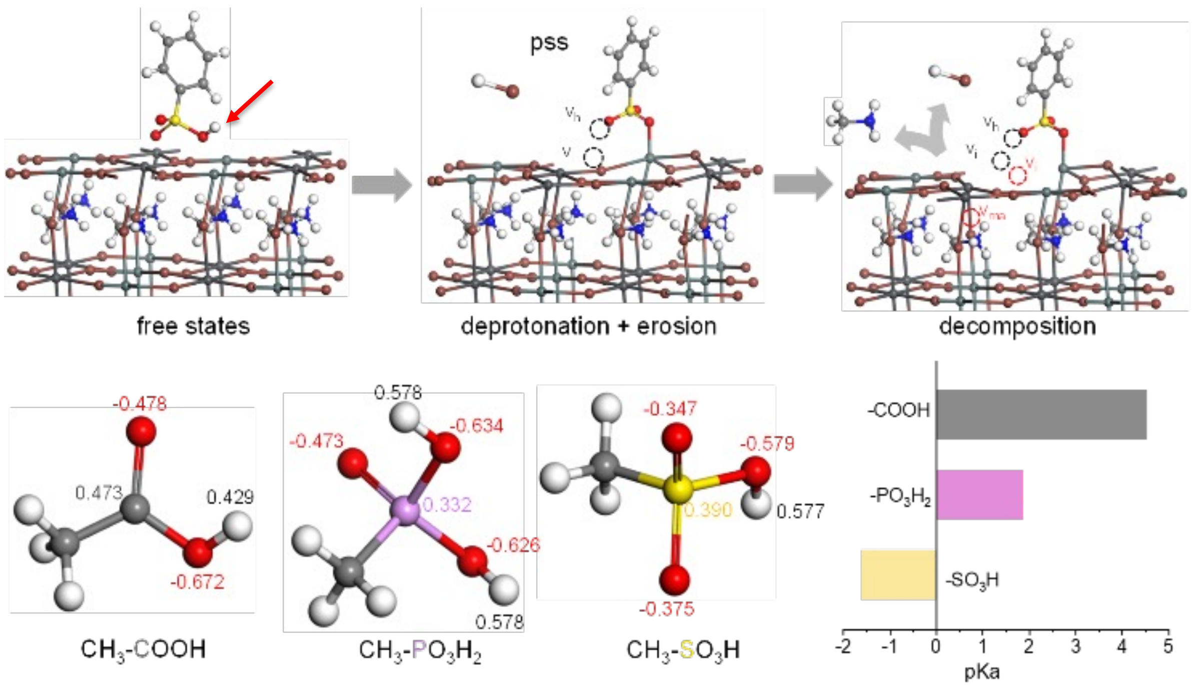
- All-perovskite tandem photoelectrodes promise theoretical STH efficiencies of more than 22%.
- Both top and bottom absorber layers are processed using low-cost, low-temperature solution-based techniques.
- Capable of achieving <$1/kg hydrogen cost.

Song et al. ACS Energy Lett. 8, 2611 (2023).

Accomplishments

Understanding interface degradation in Sn-Pb perovskite subcells

DFT calculations of the perovskite/HTL interface degradation



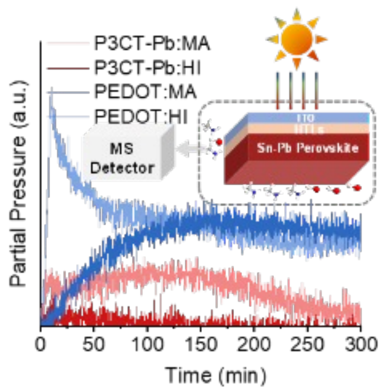
- Deprotonation from the hole-transport layer (HTL) is the root cause of interface degradation in Sn-Pb perovskite subcells.
- Rational selection of HTL with a low acid dissociation constant (pK_a) is the key to stabilizing the interface.
- The carboxylic acid (-COOH) group is more suitable for the HTL of Sn-Pb perovskites

Sheng et al. (2024), under review.

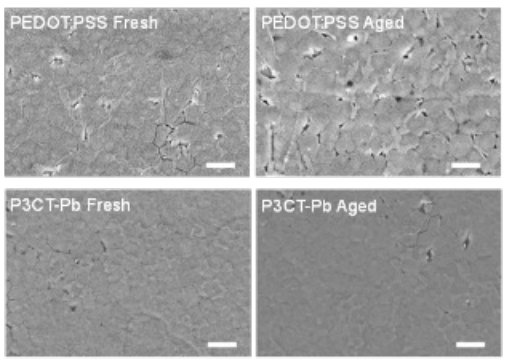
Accomplishments

Understanding interface degradation in Sn-Pb perovskite subcells

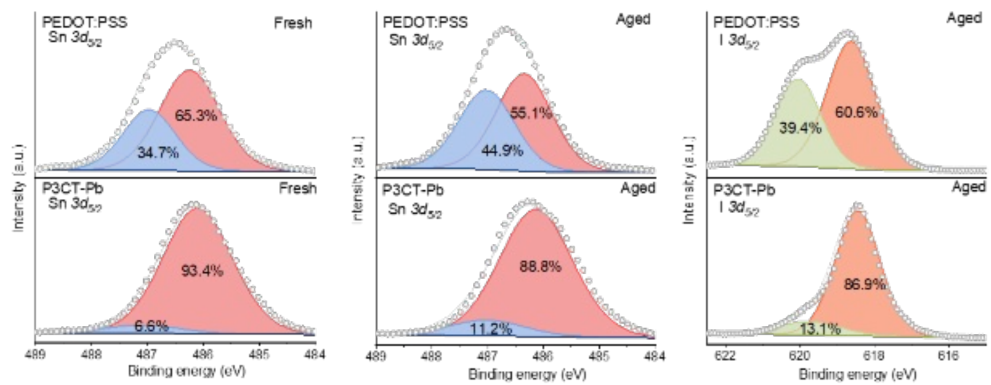
Mass spectroscopy



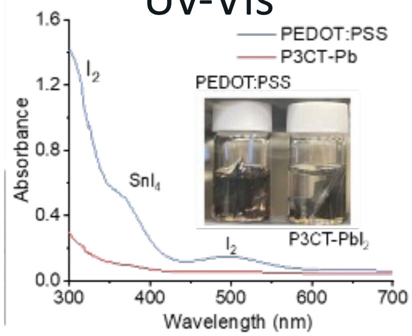
SEM



XPS analysis



Uv-Vis



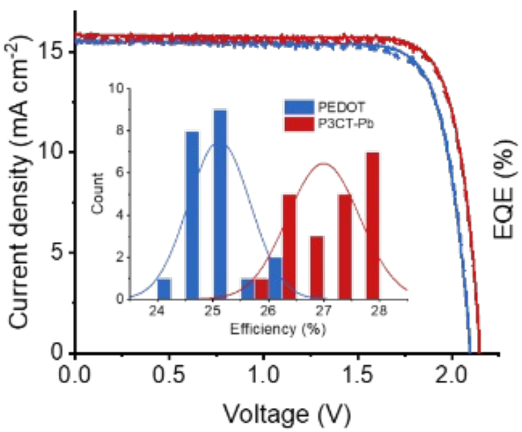
- The acidic PEDOT: PSS HTL causes severe photodegradation of the buried interface of Sn-Pb perovskites.
  - Voids/cracks formation, I_2 and methylamine gases release, Sn^{2+} oxidation
- The designed near-neutral P3CT-Pb HTL mitigates the buried interface degradation issues.

Sheng et al. (2024), under review.

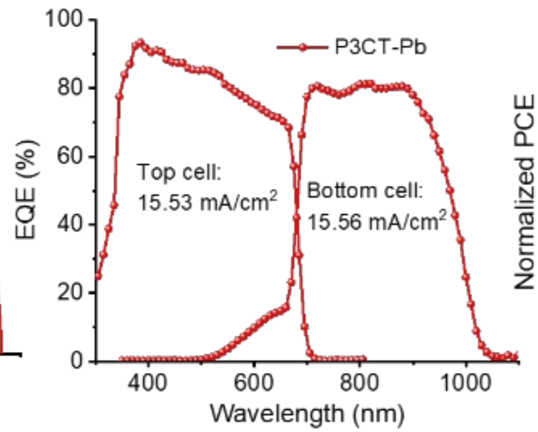
Accomplishments

Improved stability of all-perovskite tandem cells

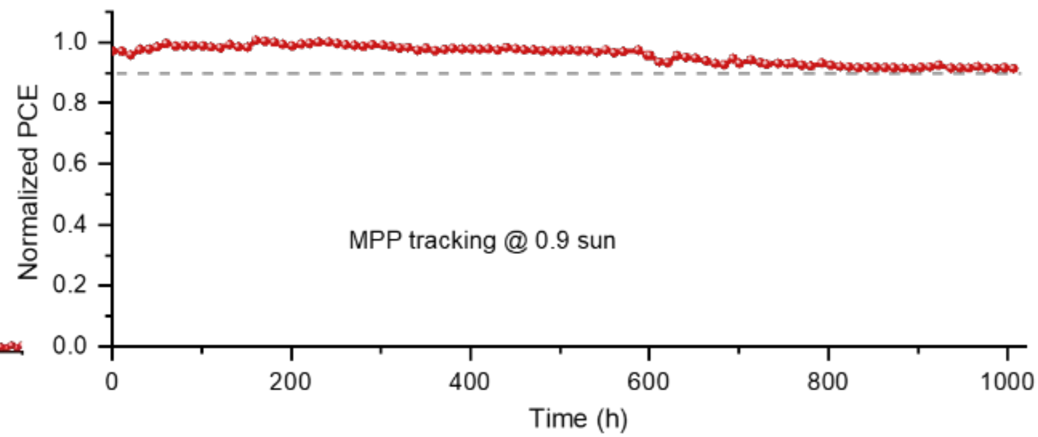
J-V



EQE



Long-term stability



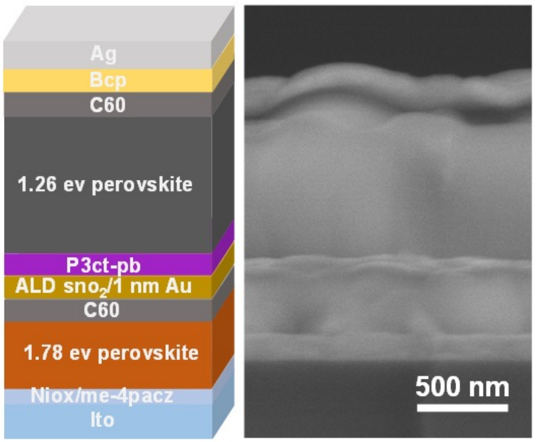
- The P3CT-Pb HTL enhances the efficiency and stability of all-perovskite tandem solar cells.

Sheng et al. (2024), under review.

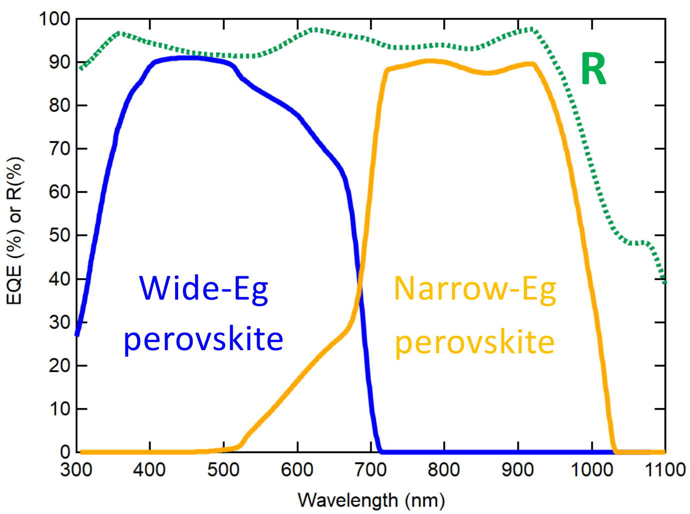
Accomplishments

Optical design of all-perovskite tandem cells

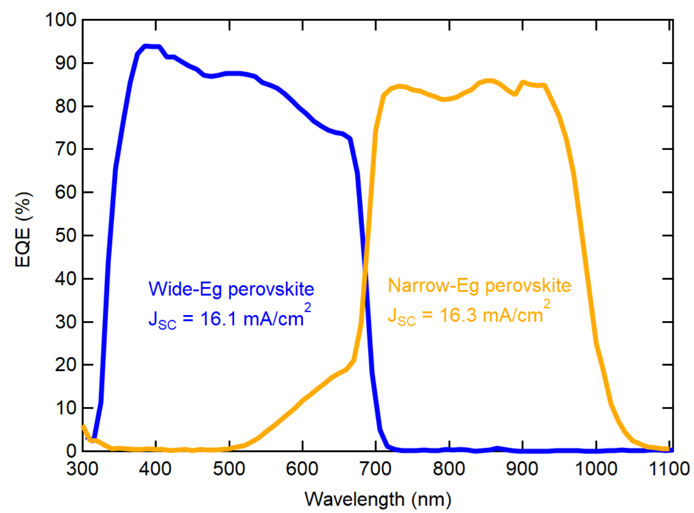
Tandem structure



Optical simulation



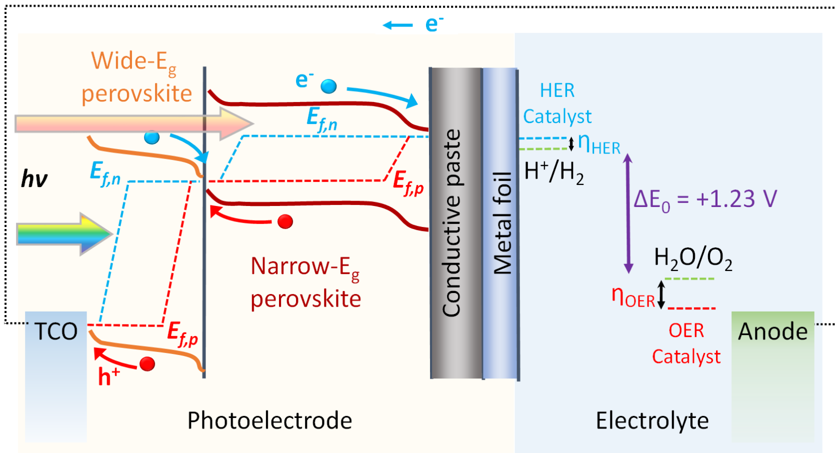
Experimental results

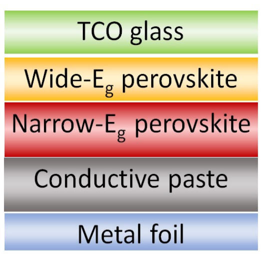


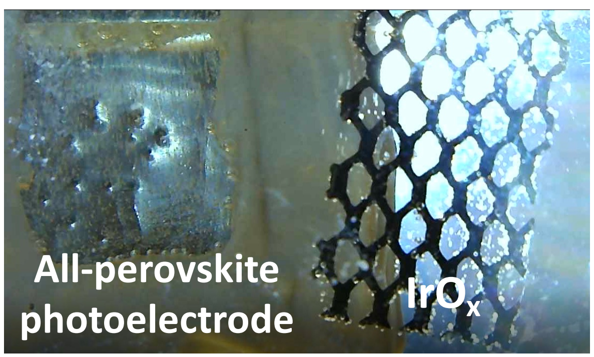
- Guided by optical simulation, we designed the tandem structure to enhance the J_{SC} of all-perovskite tandem cells to > 16 mA/cm^2.

Accomplishments

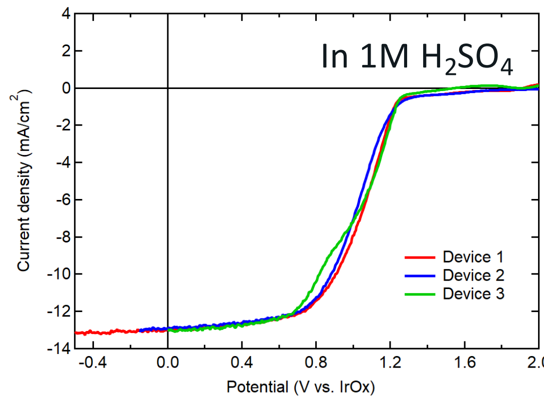
Established baseline for all-perovskite tandem photoelectrodes



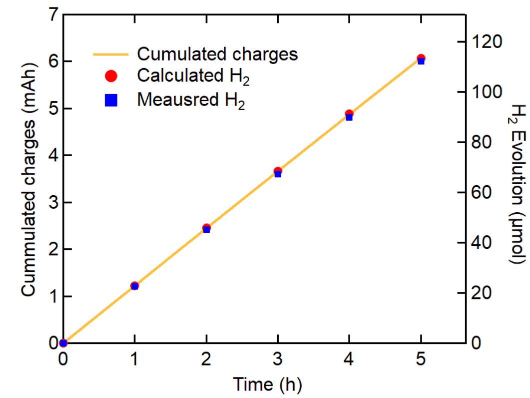




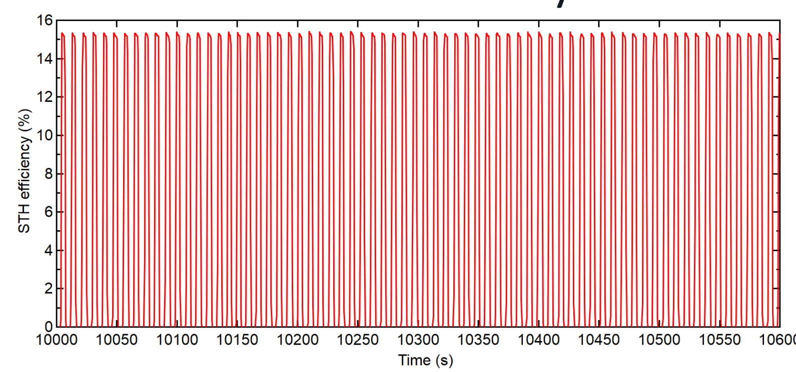
LSV scans



Cumulated H_2



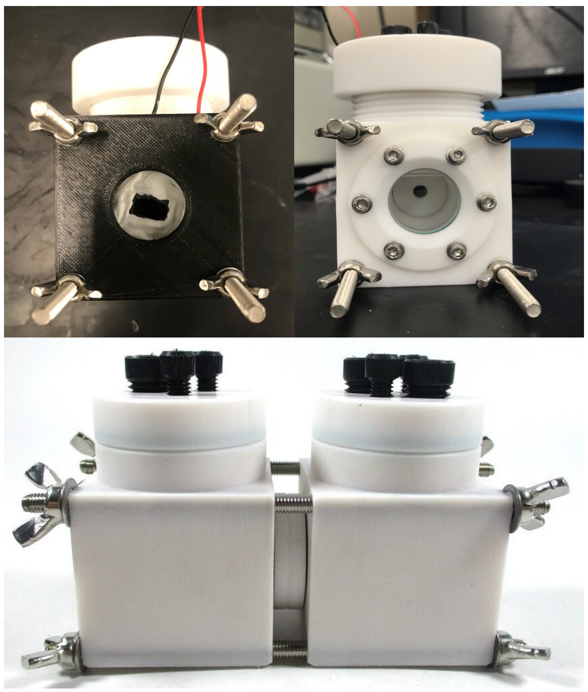
STH efficiency



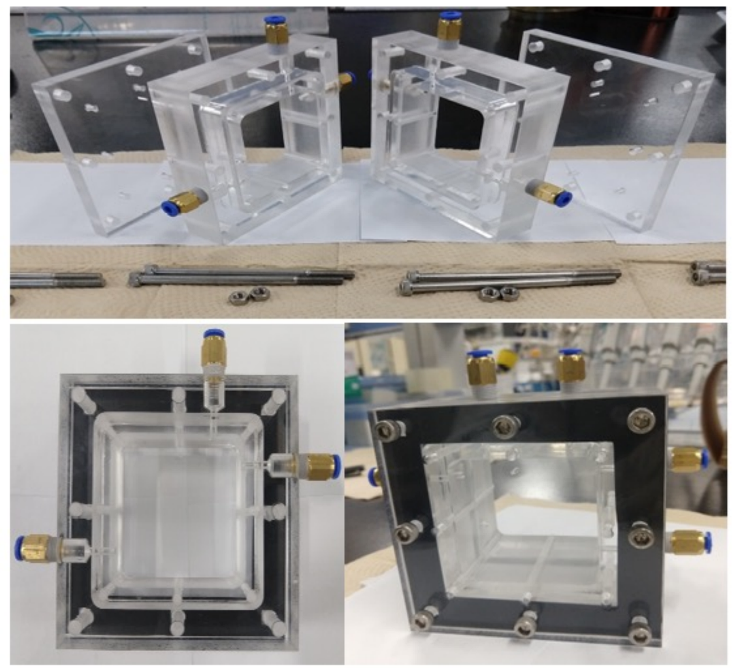
Accomplishments

Next Step: Design photoelectrode panel reactors

Front and rear views of the prototype reactor



Photoelectrode panel reactor



D. Hansora et al., Nat Energy (2024).
https://doi.org/10.1038/s41560-023-01438-x

Collaboration Effectiveness

- **Collaboration with HydroGEN Consortium**
  - **Kai Zhu (NREL):** Experimentally assess the perovskite stability, characterize degradation, and develop mitigation strategies.
  - **Tadashi Ogitsu (LLNL):** Theoretical understanding of the origin of perovskite instability and degradation.
  - **Todd Deutsch (NREL):** Benchmark measurement of efficiency and stability of perovskite photoelectrodes for water splitting.
- **Interactions with the Broader HydroGEN community**
  - Participate in the annual advanced water splitting benchmarking meeting and exchange ideas on protocols.
  - Disseminate research results at conferences.

DEIA/Community Benefits Plans and Activities

- Diversity, Equity, Inclusion, and Accessibility (DEIA)
  - **DEIA goal:** Recruit at least one female graduate student or one female postdoc to work on the hydrogen project.
  - **Accomplishments:** In this budget period, we hired one female graduate student and two female postdoc researchers to work on the project.
  - Advancing hydrogen technology education and workforce development for underrepresented groups.
  - Ordered materials/supplies from minority business enterprises (MBEs).
    - Kurt J. Lesker Company (a woman-owned and operated company) is our long-term industrial collaborator, providing materials/supplies and deposition technique supports.
  - Actively searching for collaborations with minority-serving institutions (MSIs)
  - **Challenges encountered:** difficult to identify MSIs and MBEs. A database would greatly help the collaborations and implementation of DEIA and CBP plans.

Proposed Future Work

- **Plans for FY 2024:**
  - Continued investigation on enhancing the stability of perovskite subcells and tandem photoelectrode.
  - Demonstrated >300 hours of continuous operation of tandem photoelectrodes with STH efficiency > 16%.

- **Plans for FY 2025:**
  - Demonstrate scaling-up tandem photoelectrode with areas > 1 cm^2.
  - Design and build panel reactors to validate the performance of 1-cm^2 all-perovskite tandem photoelectrodes.

Project Summary

Objective: Develop all-perovskite tandem photoelectrode panels (25 cm^2) for low-cost (<$1/kg) PEC water splitting.

Approach: Develop efficient and stable wide- and narrow-bandgap perovskite absorbers for all-perovskite tandem photoelectrodes

Accomplishments:

- Investigated and Improved the stability of Sn-Pb perovskite subcells.
- Enhanced J_{SC} of all-perovskite tandem cells to 16 mA/cm^2.
- Demonstrated all-perovskite tandem photoelectrode baseline with an STH efficiency of >15%.

Collaboration: Close collaboration with EMN nodes at NREL and LLNL and broad hydrogen community.