



Efficient Solar Water Splitting with 5,000 Hours Stability Using Earth-abundant Catalysts and Durable Layered 2D Perovskites

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Los Alamos National Laboratory
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Project ID #164

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Project Overview

Aditya Mohite, LANL
Manish Chhowalla, Rutgers University
Gautam Gupta, Univ. of Louisville
EMN Partners: LBNL and NREL

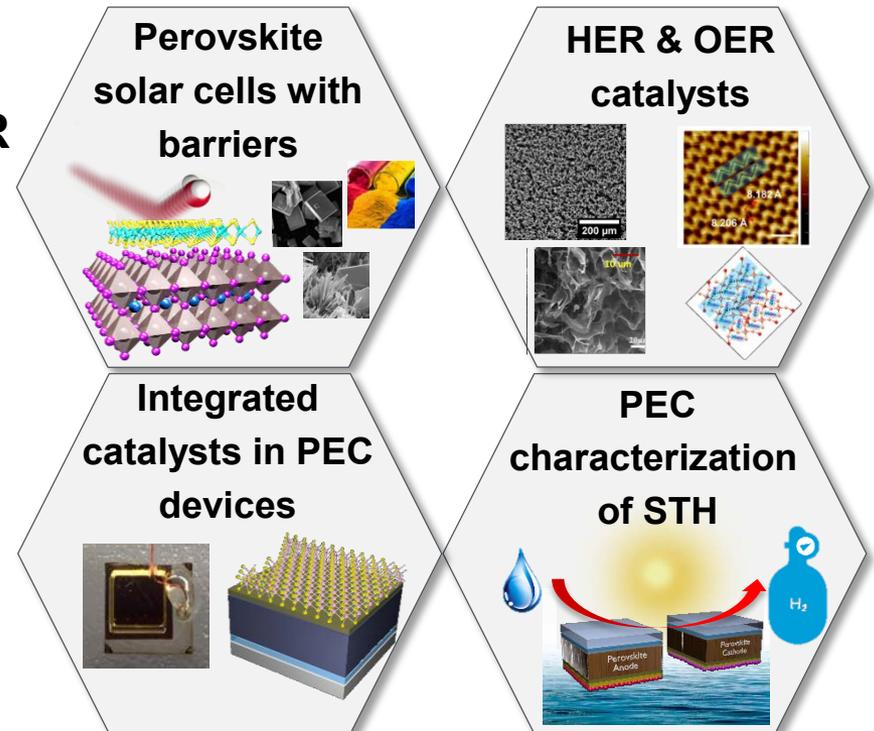
Start Date	10/01/2017
Yr 1 End Date	10/01/2018
Project End Date	TBD
Total DOE Share	\$994,305
Total Cost Share	\$116,804
Year 1 DOE Funding*	\$250,000

Project Vision

Combine high-efficiency low-cost perovskite solar cells with HER and OER catalysts made from earth abundant materials to achieve STH of $>15\%$ efficiency with 5000 hours stability

Project Impact

Develop a first of its kind durable and efficient water splitting system for H_2 production using low-cost abundant materials



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



Approach- Summary

Project Motivation

- ❖ Pioneering breakthroughs on high-efficiency perovskite solar cells (Science 2015, Nature 2016, Science 2017, Science 2018)
- ❖ Seminal work on using low-cost, earth abundant materials for HER & OER catalysts (Nature Mat. 2014, Nature Mat. 2016, Nature Comm. 2016, Science 2017)
- ❖ Combine these to develop a disruptive low-cost PEC platform that would be a paradigm shift from state-of-the-art

Barriers

- AE Materials efficiency – Bulk & interface
- AF Materials durability – Bulk & interface
- AI Auxiliary materials
- AJ Synthesis & manufacturing
- AG Integrated device configurations

Key Impact

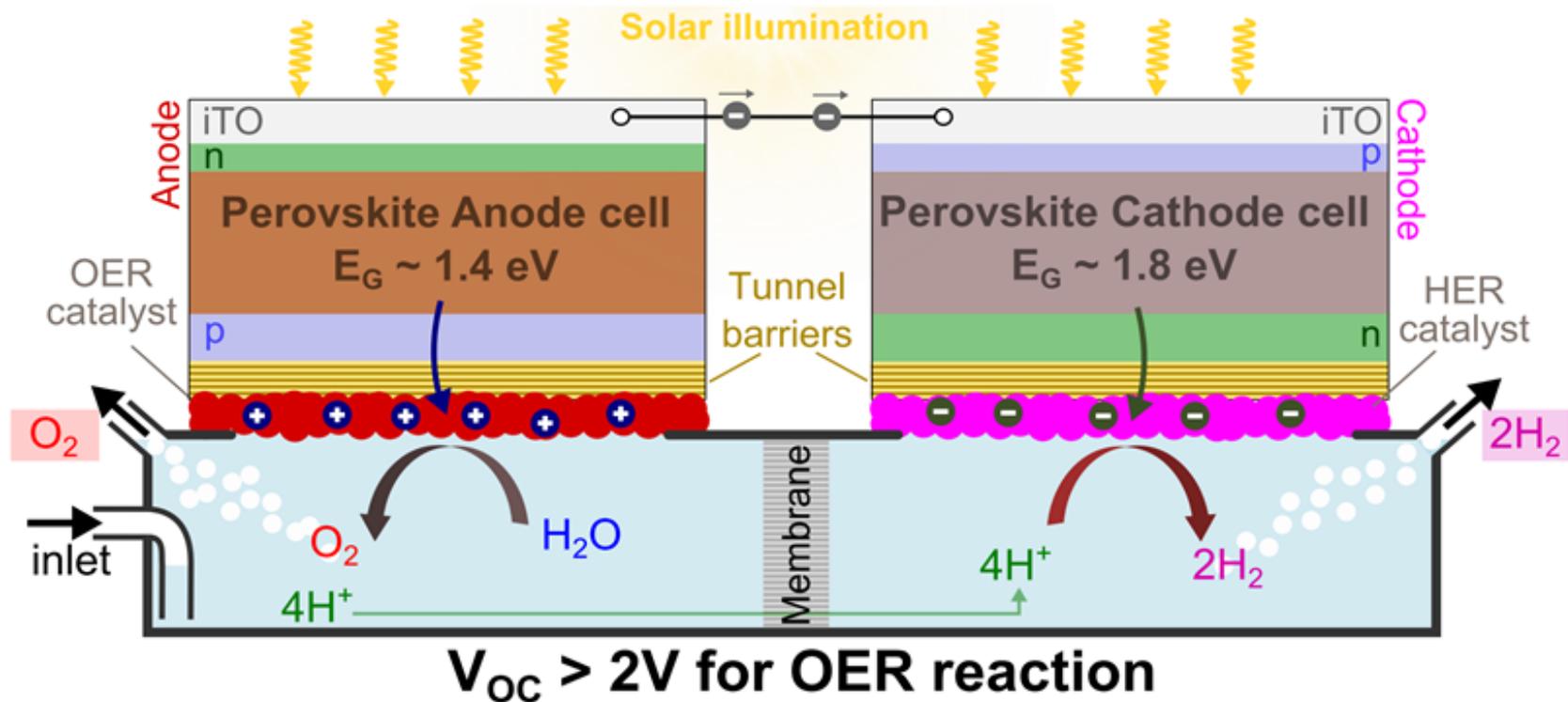
Metric	State of the Art	Expected Advance
STH Efficiency	12-15% on III-V based PECs	5-10% on perovskite based PEC
STABILITY	80 hours (III-V based PEC) (No report for perovskite PEC)	>100 hours Perovskite-based PEC
COST	>\$2/kg	<\$2/kg

Partnerships

- ❖ Rutgers University – Manish Chhowalla
- ❖ Univ. of Louisville – Gautam Gupta
 - HER and OER catalysts on carbon platforms and their stability
- ❖ LBNL EMN Node – Nemanja Danilovic, Francesca Toma & Adam Weber
 - PEC testing and interface
 - Degradation characterization
 - Benchmarking PEC performance
- ❖ NREL EMN Node – Genevieve Saur
 - Techno economic analysis



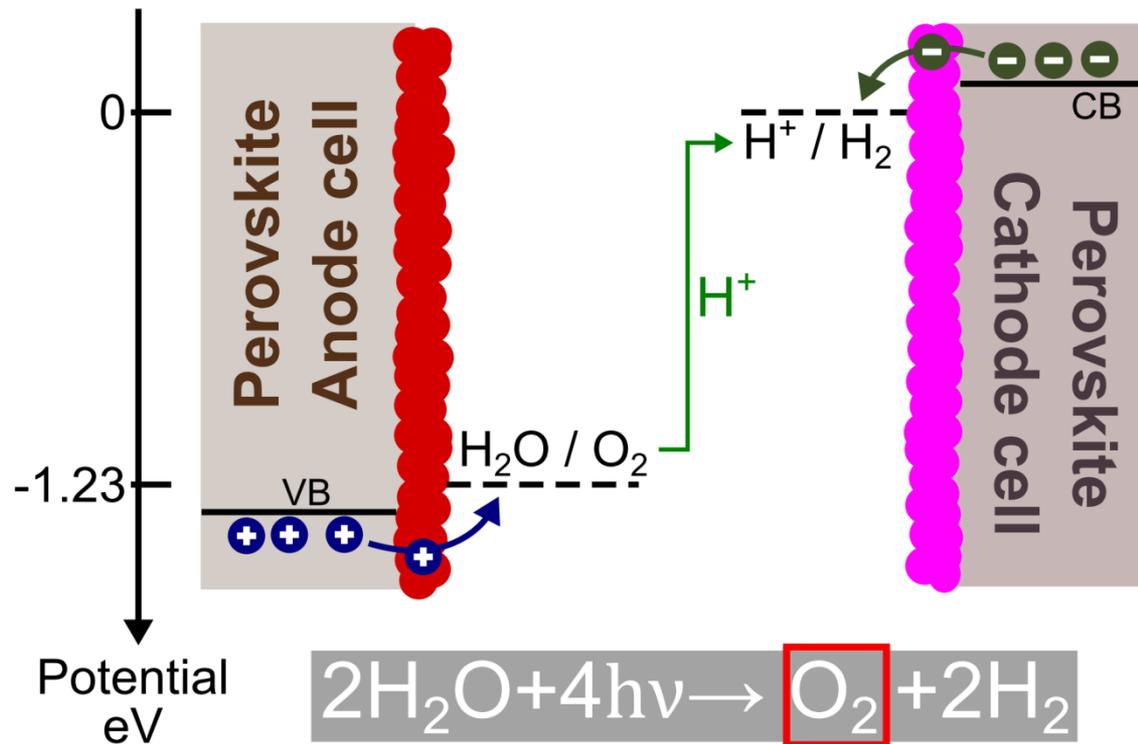
Approach- Innovation



- ❖ **Innovative PEC device design** for optimal collection of sunlight using tandem perovskite solar cells in series.
- ❖ **Design of tunnel barriers** for >20% perovskite solar cells with 1000 hrs stability in operation (<10% V_{OC} degradation).



Approach- Innovation



- ❖ Synthesis of perovskite materials with optimal optical and electronic properties for water splitting: bandgap tunability, energy level alignment, work functions, transport properties
- ❖ HER and OER catalysts made from earth abundant materials (precious metal free).



Relevance - objectives

Long term goals

Demonstrate a disruptive PEC technology with >5000 hours of operation by interfacing stable hybrid perovskites with HER and OER catalysts with 12% STH efficiency to produce hydrogen for <\$2/kg

Specific to year 1

- ❖ Demonstrate band-gap tunability from 1.5 to 2.0 eV with the appropriate band alignments
- ❖ Demonstrate photocathode and photoanodes using hybrid perovskites with standard catalysts (with EMN Node LBNL)
- ❖ Demonstrate first of its kind photocathode and photoanode with 1000 hours of stability

Relevance to DOE Hydrogen & Fuel Cell Program

AE Materials efficiency – Develop hybrid perovskite based semiconductors with a tunable band-gap from 1.5 eV to 2 eV with desired band alignment for HER and OER

AF Materials durability – Develop perovskite photoabsorbers and catalysts that are intrinsically durable under operating conditions thus extending lifetime

AI Auxiliary materials – Develop barrier strategies using layered materials for protecting the hybrid perovskites from degradation in aqueous media

AJ Synthesis & manufacturing – Develop strategies that allow for large-scale production of materials such a solution processing based approaches, blading, slot die, production of catalysts in milli secs

AG Integrated device configurations – Develop strategies for integration of perovskite photocell with HER and OER catalysts with multiple barriers and optimal light absorption



Tasks

No	Task/ Subtask	Duration (m)	2017				2018				2019						
			1	2	3	4	1	2	3	4	1	2	3	4			
T1	2D perovskite PVs with barriers	18	M1.1 M1.2→M1.3 M1.4														
S1	Selection of materials from first Principle	6	↓	↑													
S2	Fabrication of 2D perovskite PV cell with >15% efficiency	12	↓			G1											
S3	Deposition of moisture resistant barriers on PVs	9				↓	↑										
S4	Technology tests of durability and humidity	9				↓	↑										
T2	HER and OER Catalysts	18	M2.1 M2.2 M2.3														
S1	Synthesis of HER Catalysts on carbon supports	18	↓	↑													
S2	Synthesis of OER catalysts nanosheets	18	↓	↑	↓	↑	G2										
S3	Electrochemical and Spectroscopy	18	↓	↑	↓	↑											
T3	Integrated catalysts in PEC devices	9	M3														
	HER and OER catalysts integrated in perovskites photocells	9															
T4	PEC characterization of STH	15	M4														
	PECs optimized for efficiency and durability	15															



In-time progress /
partially achieved



Accomplished



Milestones

No	Milestones / Decision criteria
M9	<ul style="list-style-type: none">• Perovskite solar cells with > 15% efficiency for one band-gap material.• Band-gap tunability from 1.5 to 2.0 eV → discrete perovskite samples with band gaps of 1.5 (+/- 0.3), 1.75 (+/- 0.3) and 2.0 (+/- 0.3) eV (GNG Phase 1, year 1)• PEC stability >1000 hrs (<10% voltage degradation) using perovskite + commercial catalysts (GNG Phase 1, year. 1)
• M18	<ul style="list-style-type: none">• HER and OER catalysts with overpotential of 150 mV & 200 mV at J of 20 mA/cm² (GNG year 2)• Demonstration of a barrier layer with 5000 hrs. stability of PV. (GNG year 2)
• M33	<ul style="list-style-type: none">• STH of 15% with 5000 hrs. stability. (GNG year 3 - Final deliverable)

Ongoing testing



Accomplished



In-time progress /
partially achieved



Accomplishments

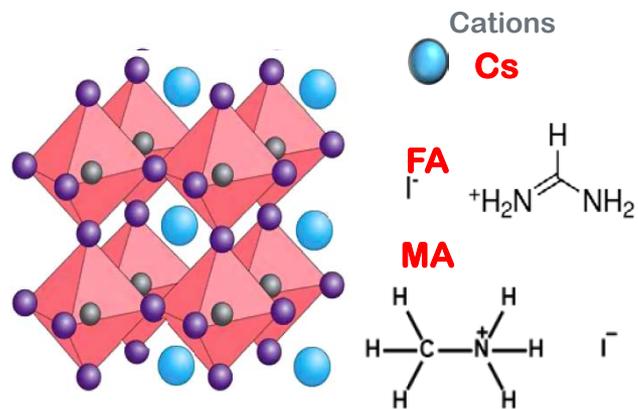
- **Most important technical accomplishments and results**
 - Discovery of a new mechanism to stabilize perovskite thin films ([Science 2018](#)) → stable (>1500 hrs) perovskite solar cells with >20% efficiency [**Milestone complete – BP1**]
 - Perovskite with tunable bandgap (1.5 – 2 eV) and optimized band alignment [**Milestone complete- BP1**]
 - Integration of perovskite cathode cell in PEC devices and stability tests ongoing [**50% complete – Due Oct 2018 – BP1**]
 - Nb_{1.35}S₂ HER catalyst with overpotential <150 mV and >>20 mA/cm² with stability 100 hrs [**Milestone complete-BP2**]
 - Ni-Fe@MW-rGO OER catalyst with overpotential <200 mV and 1 mA/cm² [**90% complete- Due June 2019 - BP2**]
- **Projected outcomes expected before end year 1**
 - Testing of perovskite solar cells with barrier layers
 - Integration of solar cells in PEC devices with commercial catalysts → test for 1000 hrs. stability [only milestone left for this period]



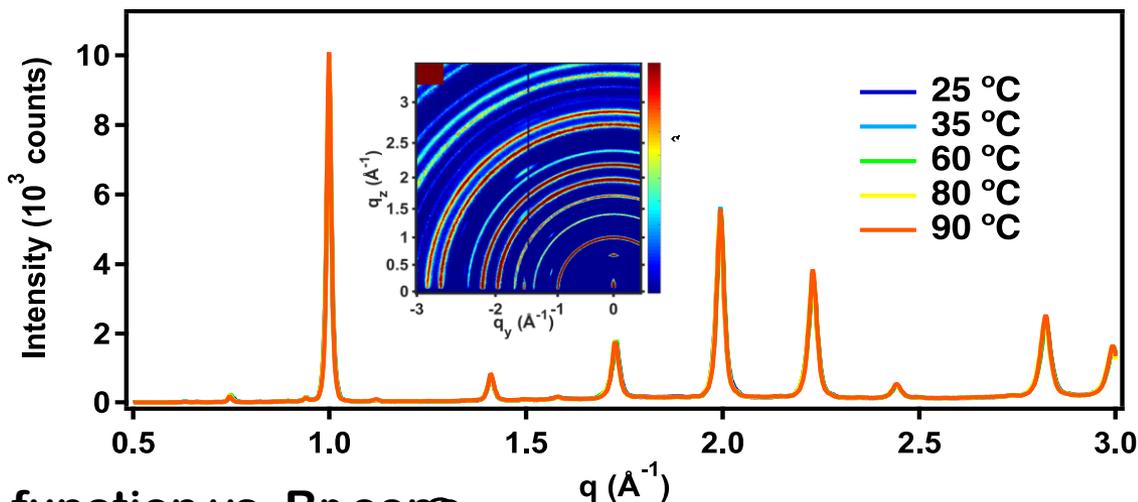
Accomplishments & progress

Innovation: Developed new chemistry for hybrid perovskites

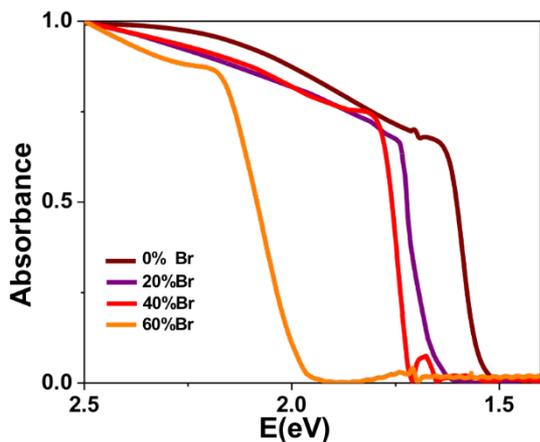
Multiple cations to achieve cubic phase



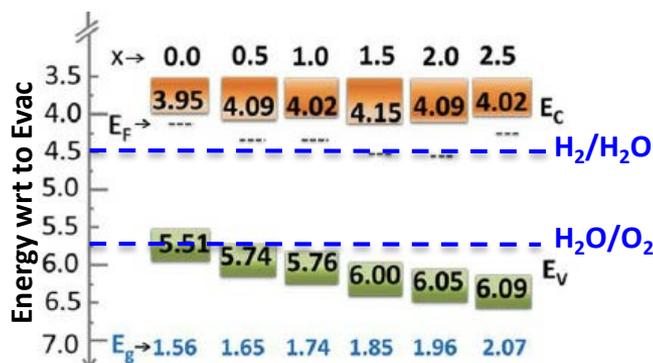
Stable after temperature cycling



Tunable band-gap



Work function vs. Br conc.



- ❖ Obtained stable cubic phase
- ❖ Red shifted band-gap $E_g \sim 1.55$ eV for single junction cells
- ❖ Stable after temperature cycling

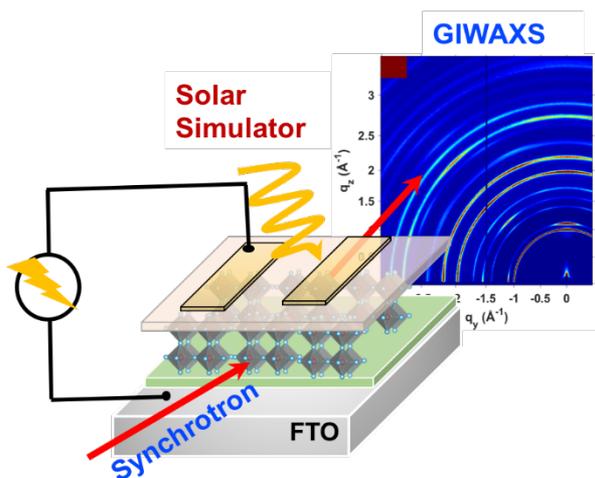
Tsai et al Science 2018



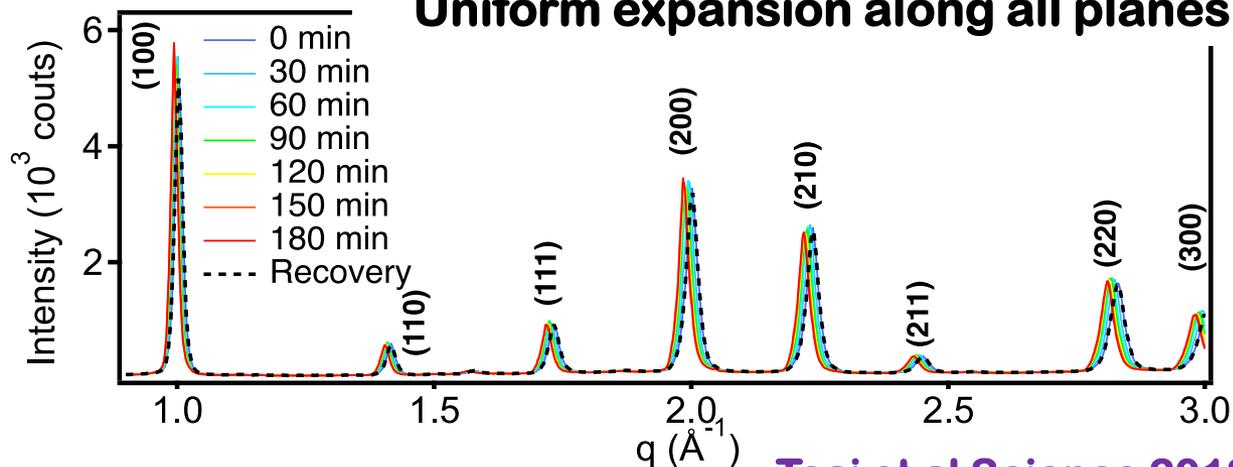
Accomplishments & progress

Discovery of new effect: Light-induced lattice expansion

In-situ GIWAXS studies



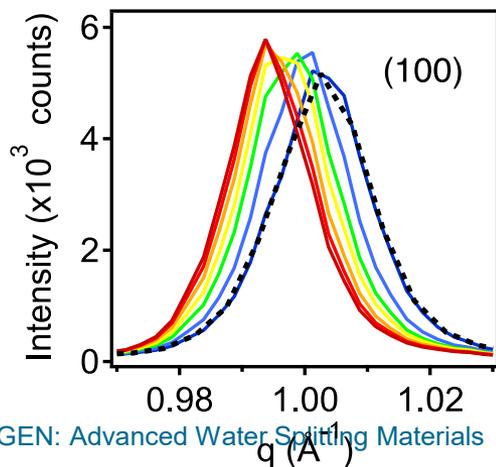
Uniform expansion along all planes



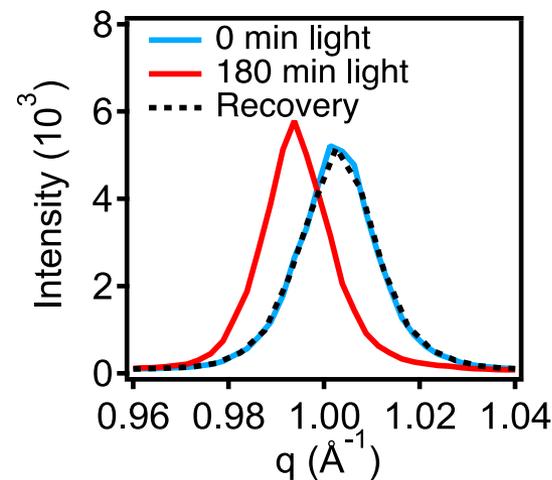
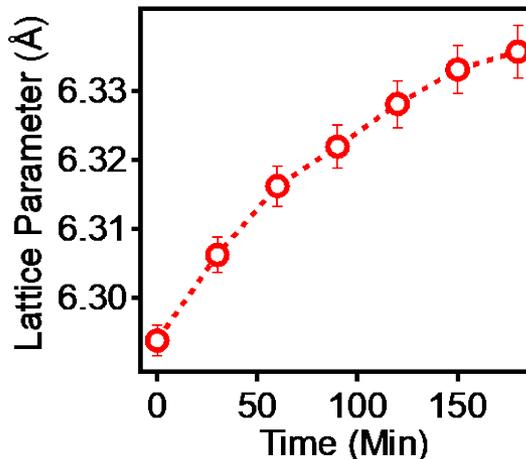
Tsai et al Science 2018

Reversible

<100> plane



Lattice constant vs. illumination time

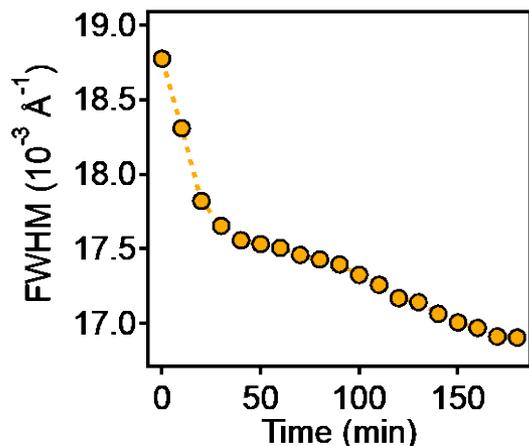




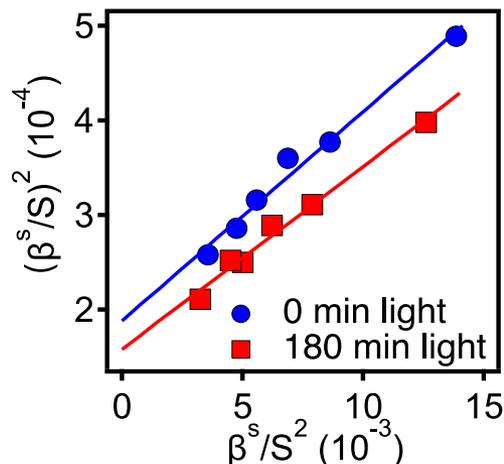
Accomplishments & progress

Light-induced lattice expansion cures interface/bulk defects

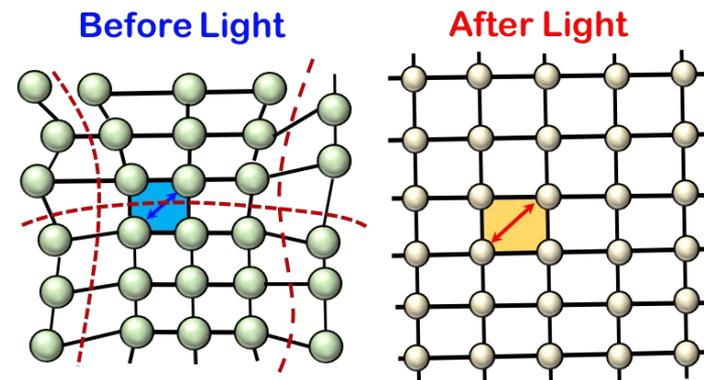
Enhanced crystallinity



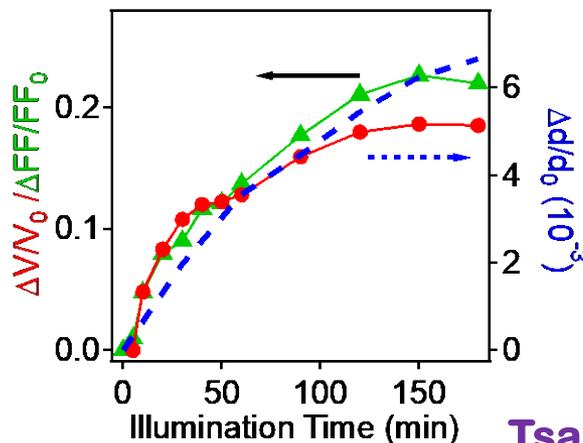
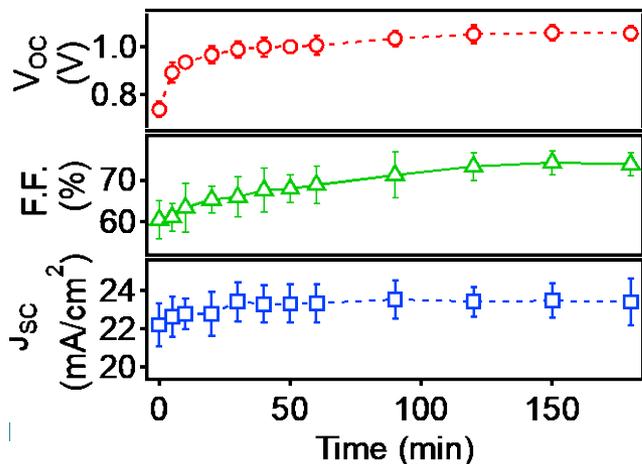
Halder-Wagner plot



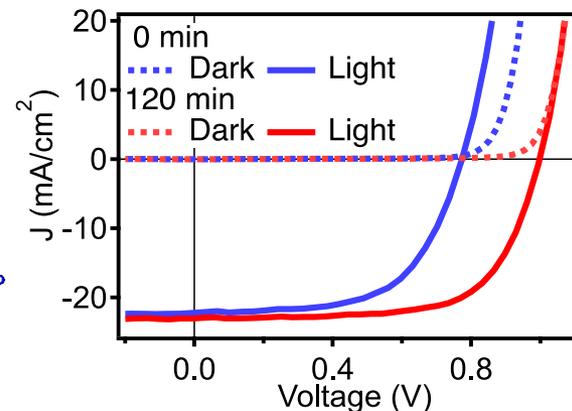
Decreased mosaicity & microstrain



Solar cell parameters vs. lattice constant change



Efficiency >20.5%

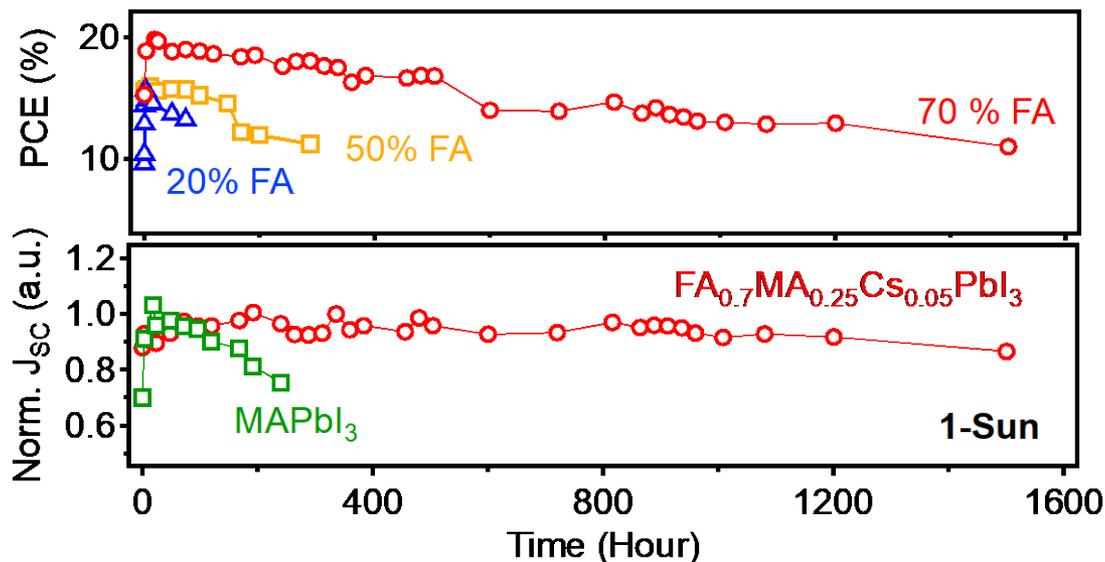




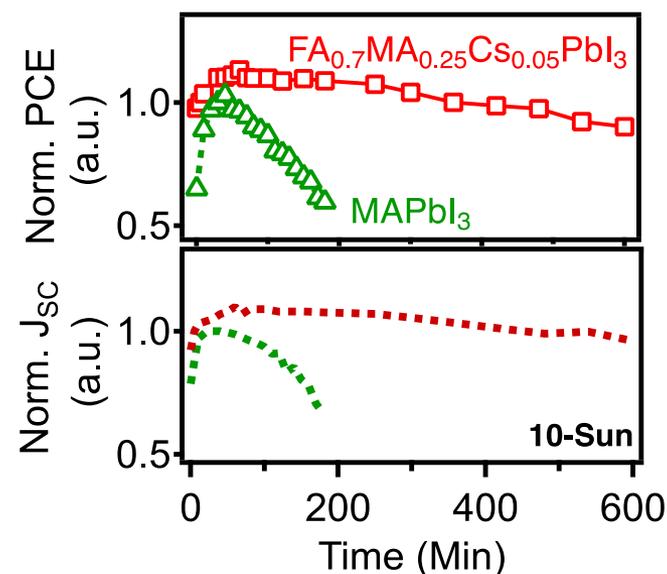
Accomplishments & progress

Excellent photostability under 1-Sun and 10-Sun

Long term photo-stability



Stability under 10-Suns



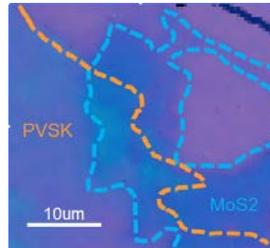
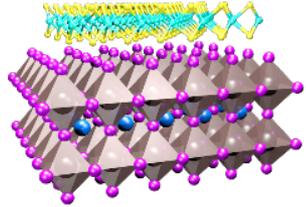
- ❖ Long-term stability achieved under 1-Sun for >1500 hrs and also under 10-Sun illumination.
- ❖ Stability comparable to 2D perovskite but efficiency >20.5% - Promising for PECs (Cathodes and Anodes)



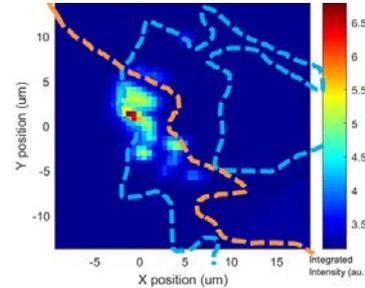
Accomplishments & progress

Innovation: Strategies for barriers on perovskite solar cells (ALD, layered materials, Oxides)

❖ Protection of perovskite using layered materials

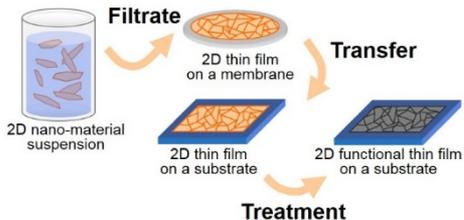


Optical Image



Photoluminescence image shows **no degradation of the perovskite under 2-layers of MoS₂**

❖ Example of strategy development in progress

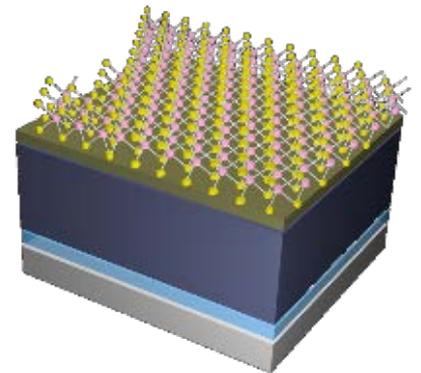


Chemical vapor deposition
(Vacuum processing)

Large area
graphene

Vacuum filtration
(Solution processing)

Dry transfer
process



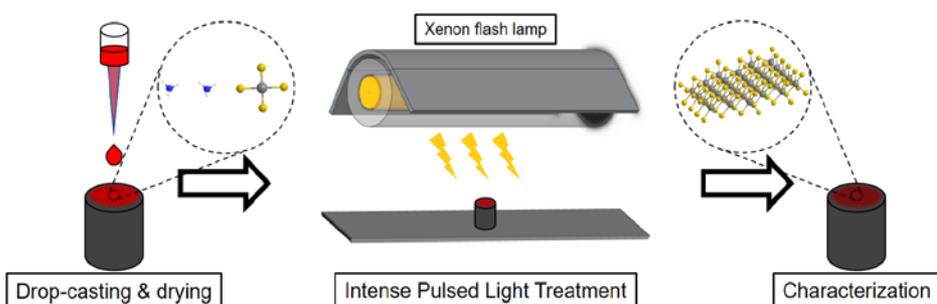
Protected solar cells
(in testing)



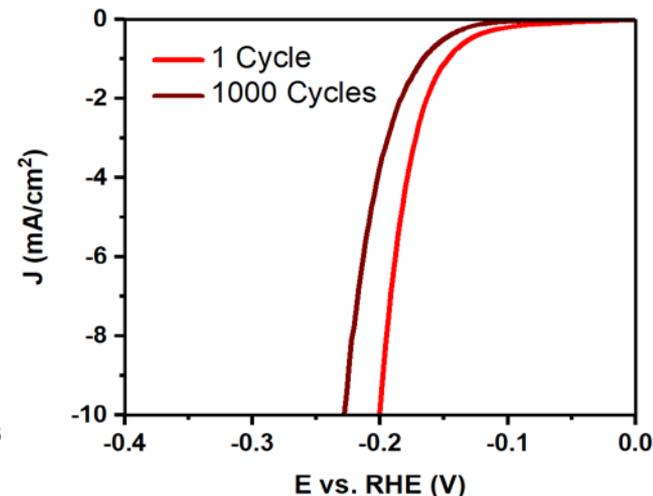
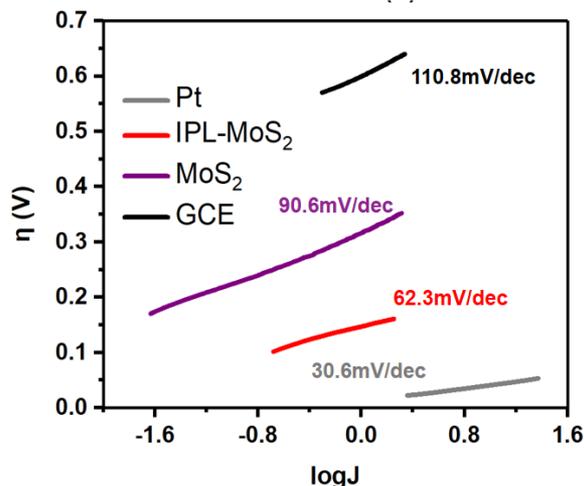
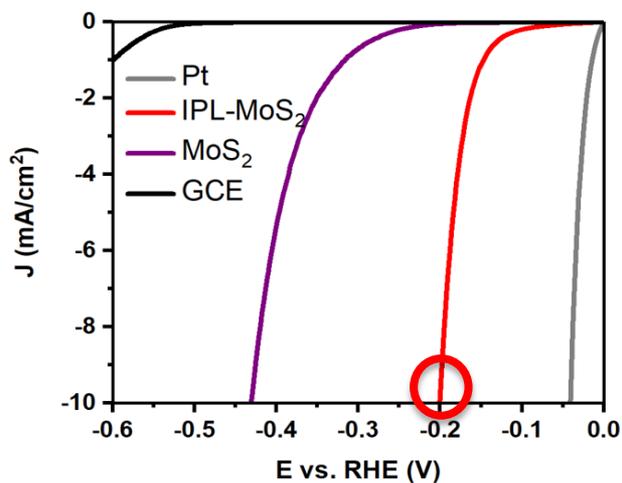
Accomplishments & progress

HER Catalysts

Innovation: Novel method to mass produce MoS₂ based HER catalysts obtain in milliseconds



Key Advantage: IPL technique established for hybrid perovskite and here we demonstrate the technique to develop MoS₂ based catalysts.

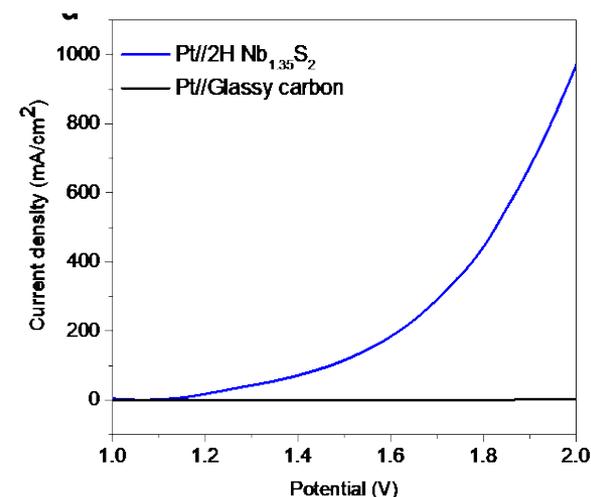
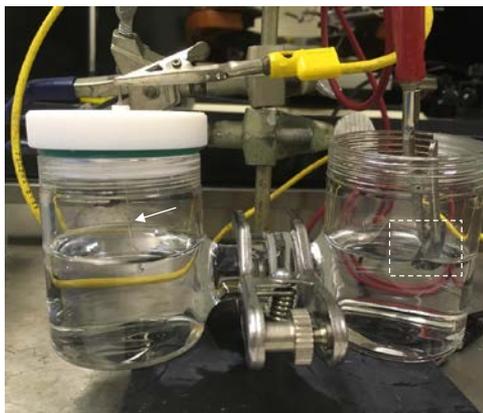
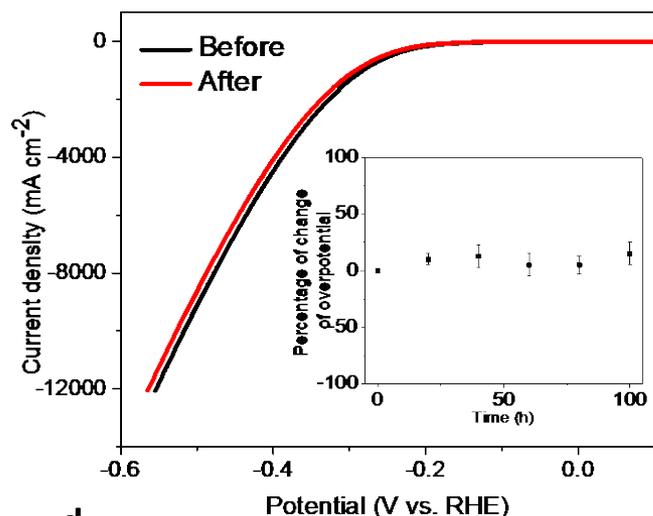




Accomplishments & progress

HER Catalysts

Innovation: Developed new $\text{Nb}_{1.35}\text{S}_2$ catalysts with very high current density – demonstrated electrolyzer



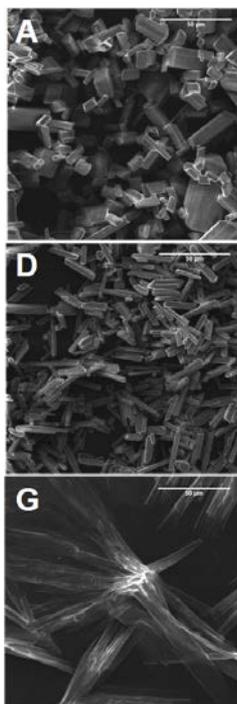
- ❖ $\text{Nb}_{1.35}\text{S}_2$ catalysts demonstrated good stability
- ❖ Incorporated $\text{Nb}_{1.35}\text{S}_2$ catalyst in an electrolyzer



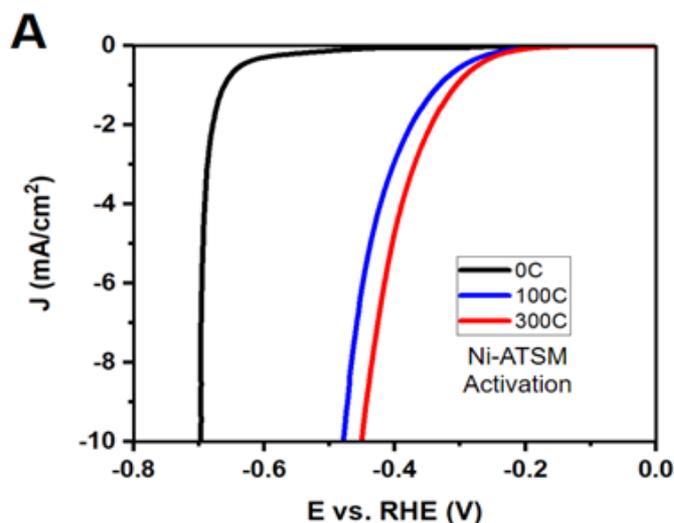
Accomplishments & progress

HER Catalysts

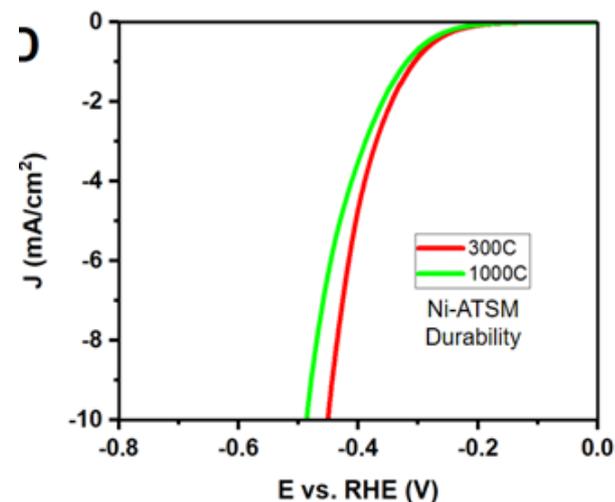
Innovation: Nickel based molecular catalysts – excellent durability & solvent compatibility with perovskites



Catalyst Activation



Durability



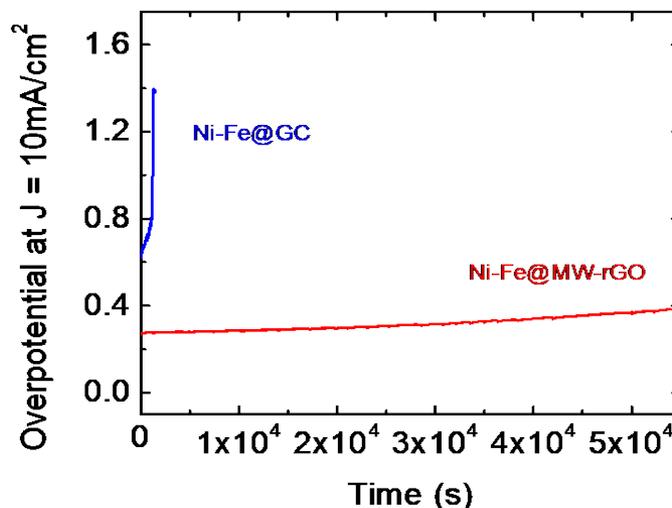
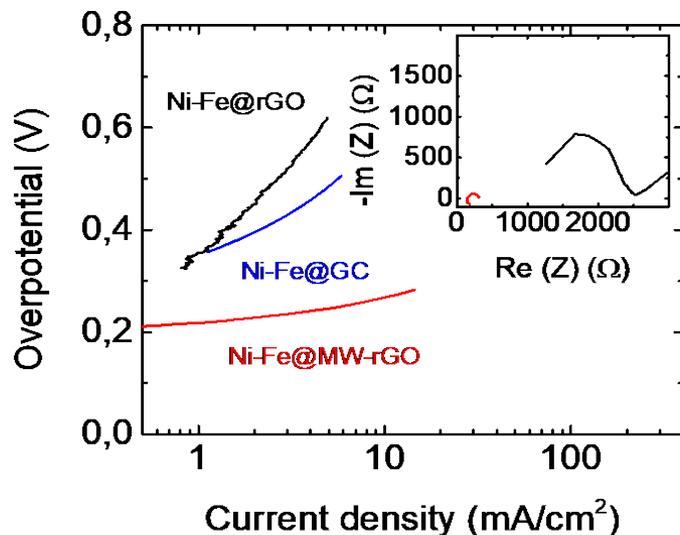
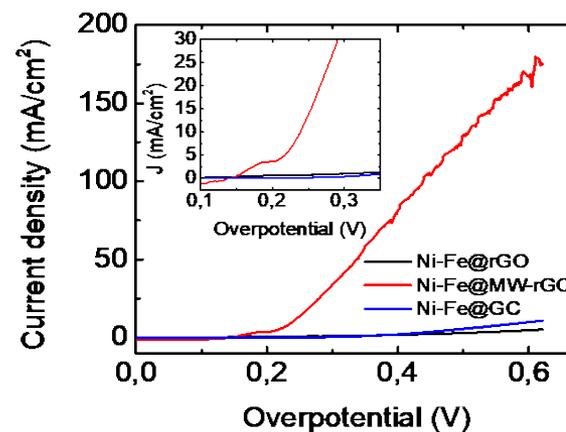
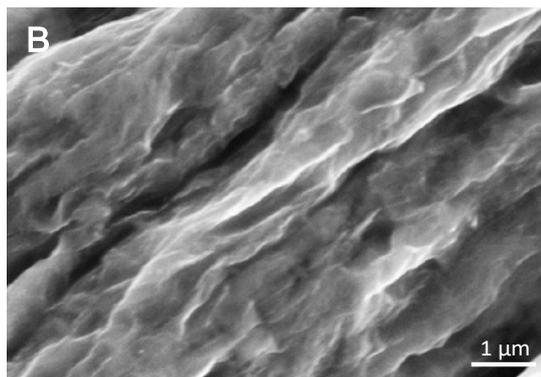
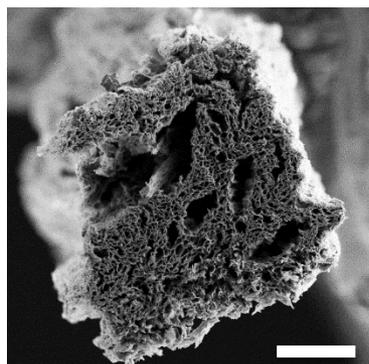
Gautam Gutpa research group - UofL



Accomplishments & progress

OER Catalysts

Innovation: Developed Ni-Fe catalysts with an overpotential of 200 mV on rGO supports

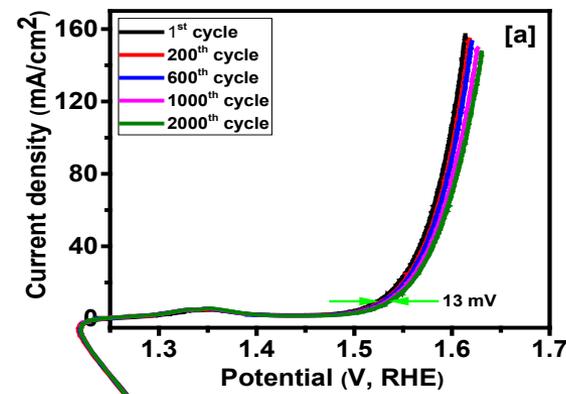
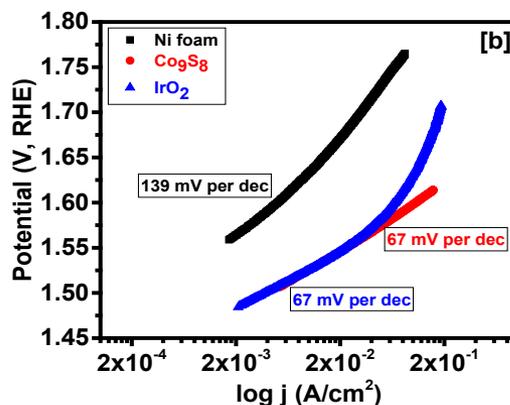
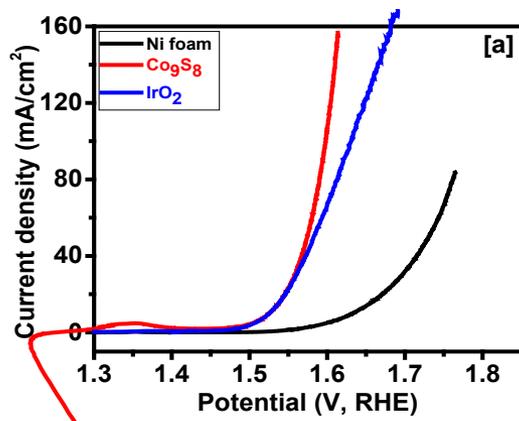
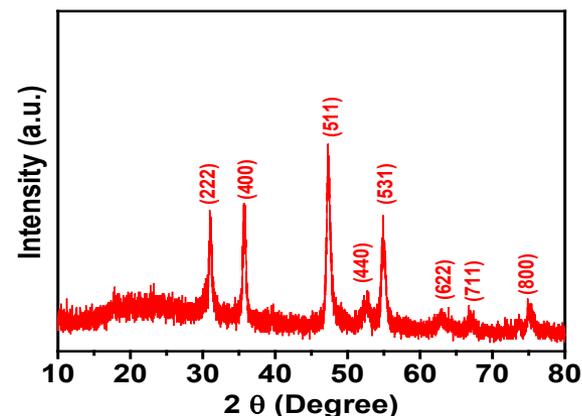
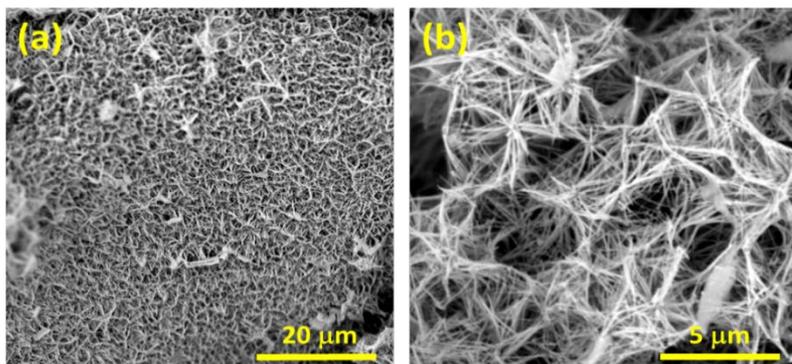




Accomplishments & progress

OER Catalysts

Innovation: **Highly efficient and durable electro-catalysts based CoS nanowires**



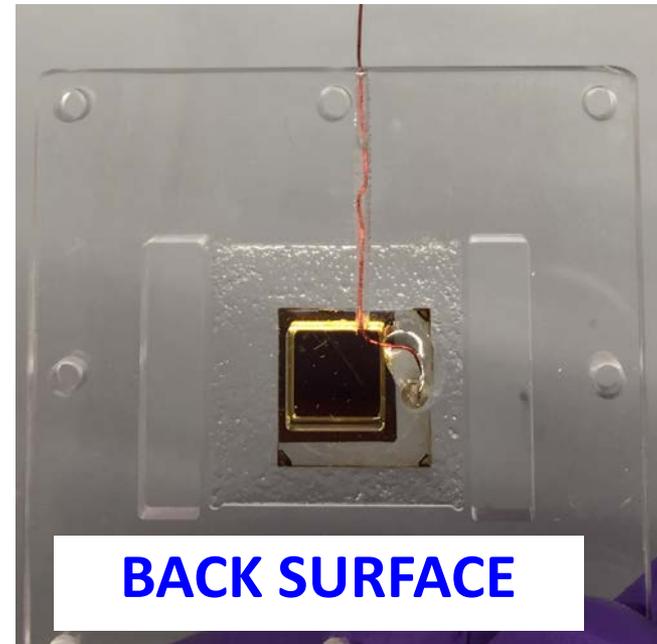
Key Advantages: Good performance and excellent cycleability in alkaline media



Accomplishments & progress

Innovation: Integration & testing strategy for perovskite/catalyst first of its kind PEC performed at LBNL

- ▶ Cell sits on an epoxied ledge
- ▶ Prevents exposure to solution
- ▶ Front contact (Au) exposed to solution through opening
- ▶ Wire is Ag epoxied to ITO (or FTO) through a hole in the plate,
- ▶ Backfilled with clear epoxy

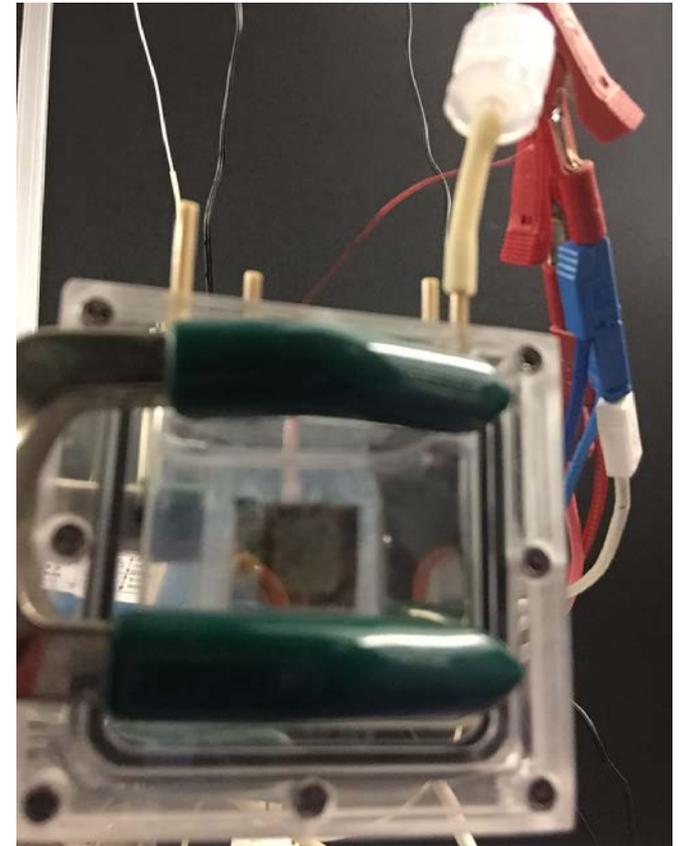
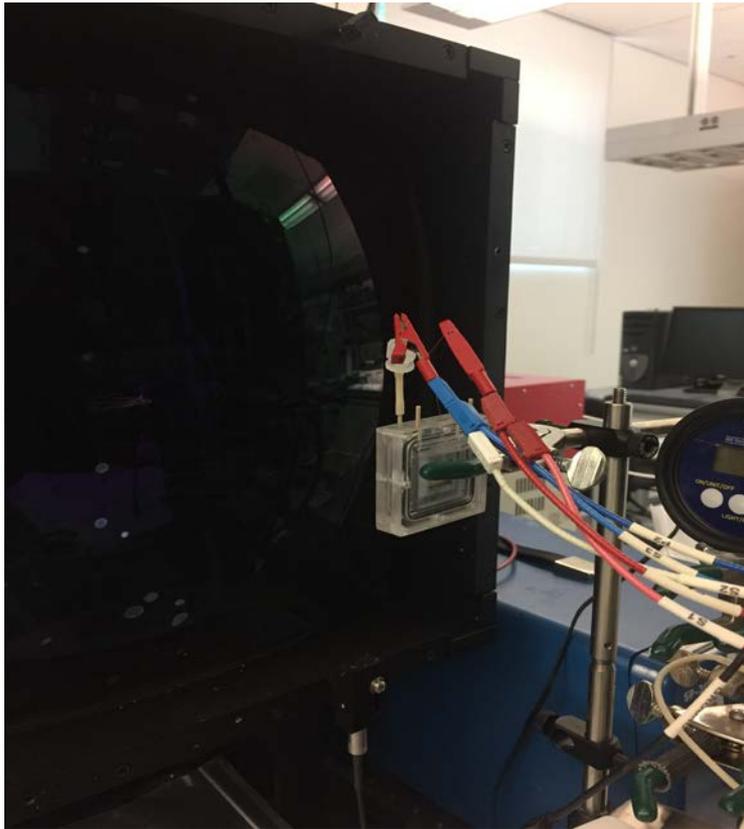




Accomplishments & progress

Full cell with Ir counter in 0.1M KOH

- Ir counter in 0.1M KOH
- Both faces exposed to the solution





Collaboration: Effectiveness

Effective interactions with EMN nodes, Data Hub & ECS working group

❖ **LBNL: PEC measurements and benchmarking**

Dr. Nemanja Danilovic & Dr. Francesca Toma

1. Site-visit (2-full days) to establish detailed protocols for hybrid perovskite PEC measurements
2. Established device design and interface layers for photocathode & anode
3. Design of complete PEC cell and validated design by loading perovskite/Pt photocathodes
4. Three batches of perovskite solar cells exchanged with different barrier layers

❖ **LBNL: Understanding degradation mechanisms in PECs through in-situ characterization techniques – Dr. Francesca Toma**

1. Planned work to perform in-situ degradation studies before and after PEC testing using in-situ scanning probe techniques such as conducting AFM
2. Planned work on measuring in-situ charge transfer using dynamic optical probes

❖ **LBNL: Multiscale modeling of PECs – Dr. Adam Weber**

1. Discussions to understand interfacial degradation processes using modeling

Impact on project: Critical for development of first of its kind perovskite-based PEC platform for testing, characterization and benchmarking performance and stability.

❖ **NREL: Techno economic analysis of perovskite based PEC system – Dr. Genevieve Saur**

Working to develop a rough techno-economic evaluation of the perovskite-based PEC

❖ **Benchmarking PECs: Participating in ECS working group for standardizing PECs**

❖ **Data Hub: Uploaded data on perovskite solar cells with >20% efficiency and stability**



Proposed Future Work

- ❖ **Test and develop interface barrier strategies (layered 2D materials e. g. rGO, MoS₂, NbS₂) on hybrid perovskites**
- ❖ **Perform photocathode and photoanode measurements on perovskite/Pt and perovskite/Ir based catalysts**
- ❖ **Integrate earth abundant catalysts such as MoS₂ (HER) and Li-Fe LDH, metal oxides on perovskite solar cells to create perovskite-PECs**
- ❖ **Understand charge transport and degradation mechanisms by using in-situ optical techniques**
- ❖ **Characterize STH efficiency and stability of perovskite based PEC with earth abundant HER and OER catalysts**



Project Summary

- **Most important technical accomplishments and results**
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 - Perovskite with tunable bandgap (1.5 – 2 eV) and optimized band alignment [**Milestone complete**]
 - Integration of perovskite cathode cell in PEC devices and stability tests ongoing [**50% complete**]
 - Nb_{1.35}S₂ HER catalyst with overpotential <150 mV and >>20 mA/cm² with stability 100 hrs [**Milestone complete**]
 - Ni-Fe@MW-rGO OER catalyst with overpotential <200 mV and 1 mA/cm² [**90% complete**]
- **Projected outcomes expected before end year 1**
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 - Integration of solar cells in PEC devices with commercial catalysts → test for 1000 hrs. stability [only milestone left for this period]