Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

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June 13, 2018

Project ID #164

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

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

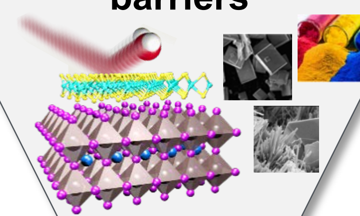
Project Vision

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

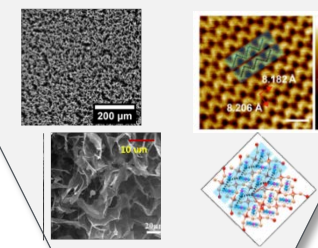
Project Impact

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

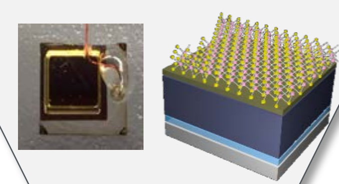
Perovskite solar cells with barriers



HER & OER catalysts



Integrated catalysts in PEC devices



PEC characterization of STH

** 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

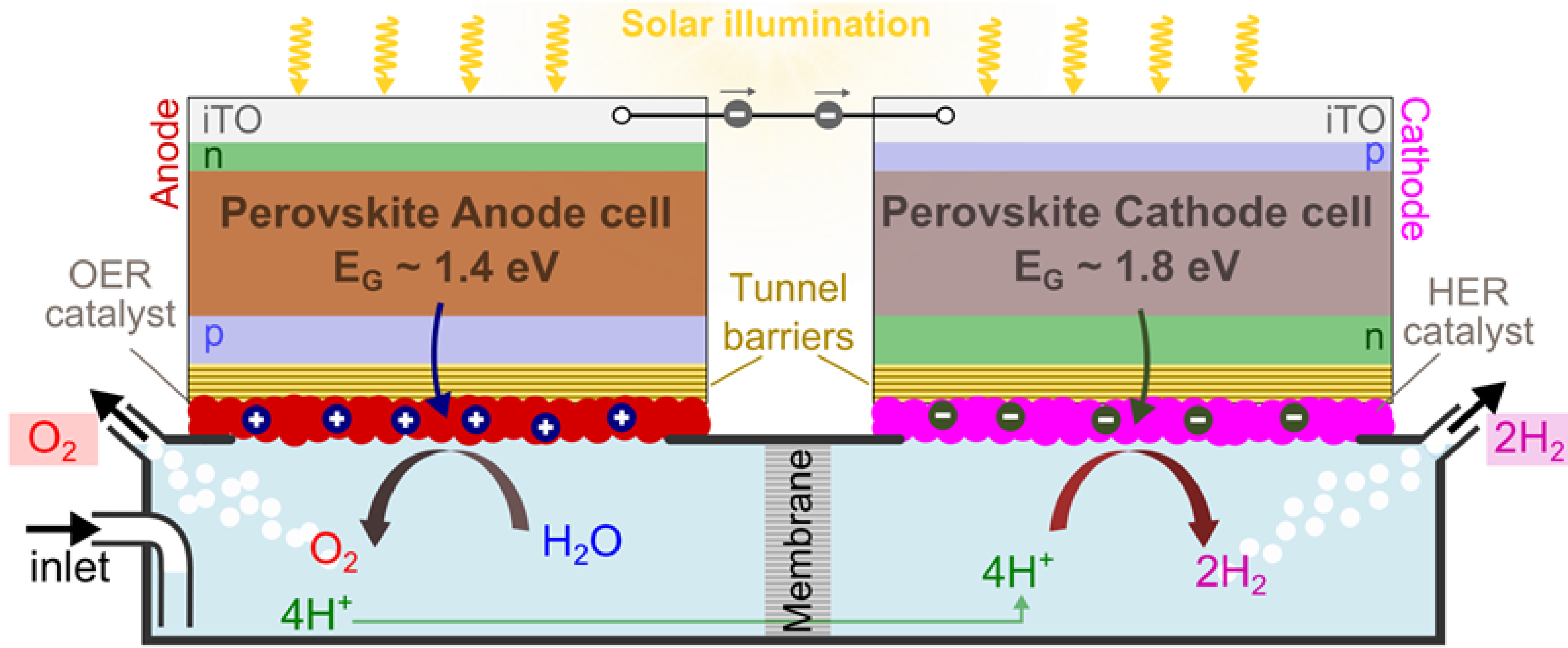
Key Impact

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

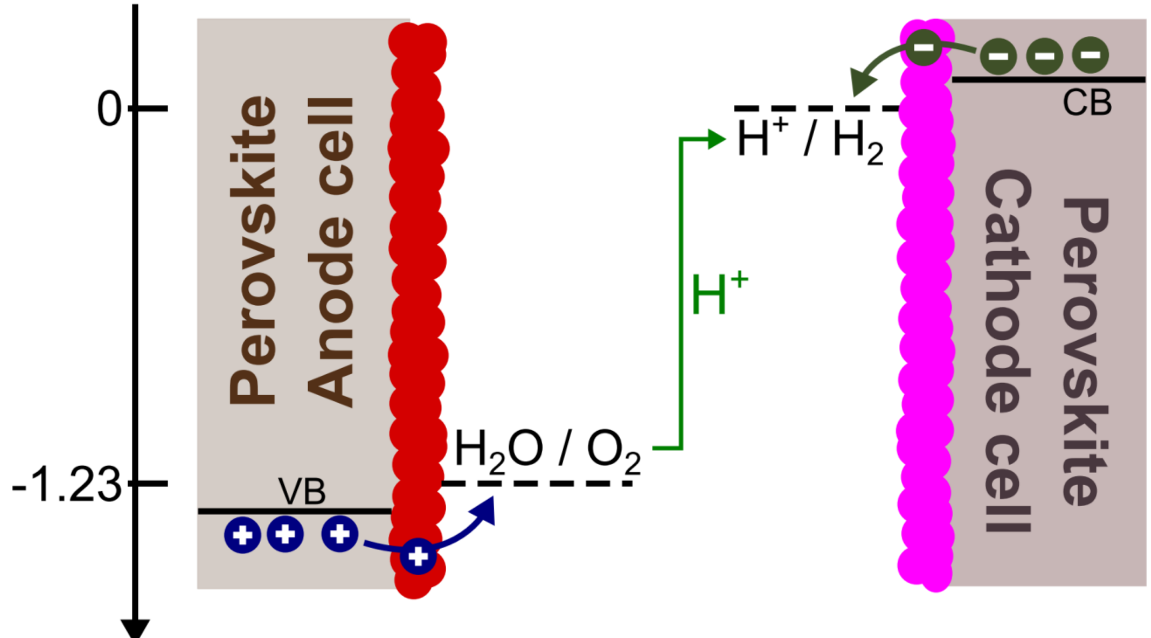
Approach- Innovation



V_{OC} > 2V for OER reaction

- **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



$$2H_2O + 4h\nu \rightarrow O_2 + 2H_2$$

- 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											**G3**	

In-time progress / partially achieved

Accomplished

Milestones

No	Milestones / Decision criteria
M9	• 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, yearr 1)** • PEC stability >1000 hrs (<10% voltage degradation) using perovskite + commercial catalysts **(GNG Phase 1, year. 1)**
• M18	• 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 yearr 2)**
• M33	• STH of 15% with 5000 hrs. stability. **(GNG year 3 - Final deliverable)**

Ongoing testing

Accomplished

In-time progress / partially achieved

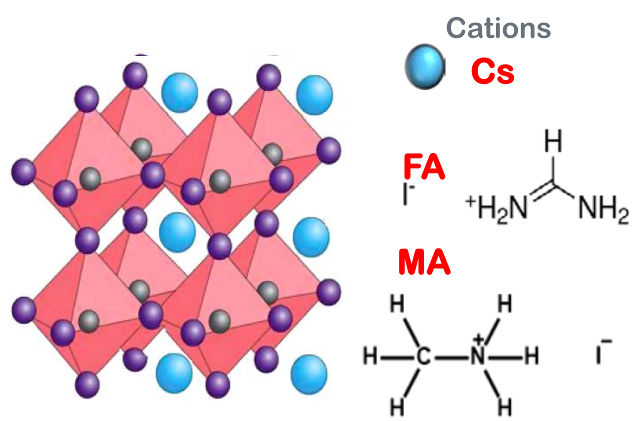
Accomplishments

- **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]
  - $Nb_{1.35}S_2$ HER catalyst with overpotential <150 mV and >>20 mA/cm^2 with stability 100 hrs [Milestone complete-BP2]
  - Ni-Fe@MW-rGO OER catalyst with overpotential <200 mV and 1 mA/cm^2 [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

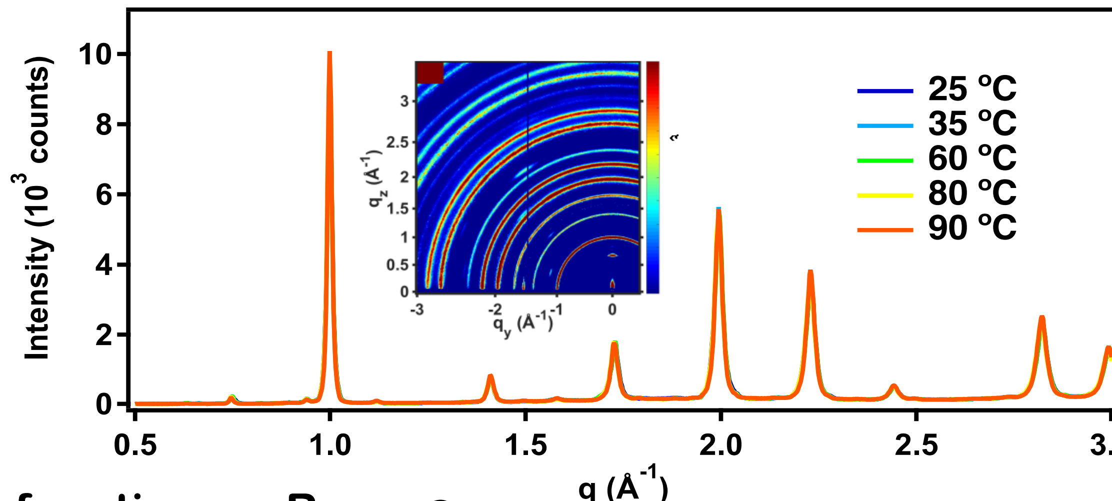
Innovation: Developed new chemistry for hybrid perovskites

Multiple cations to achieve cubic phase

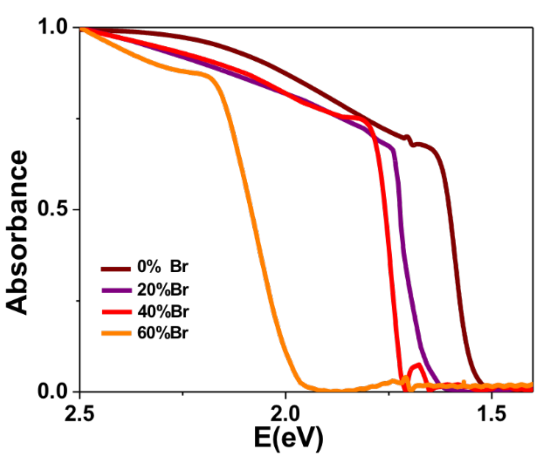


$FA_{0.75}MA_{0.2}Cs_{0.05}PbI_{3-x}Br_x$

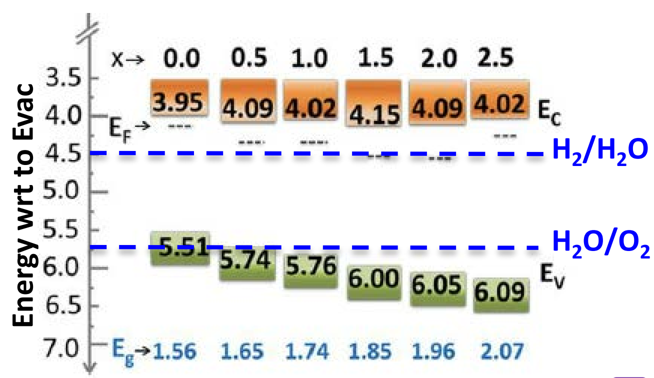
Stable after temperature cycling



Tunable band-gap



Work function vs. Br conc.



ials

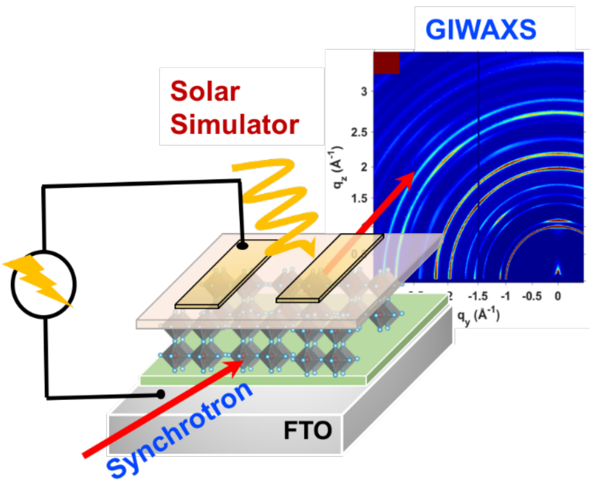
- Obtained stable cubic phase
- Red shifted band-gap E_g~1.55 eV for single junction cells
- Stable after temperature cycling

Tsai et al Science 2018

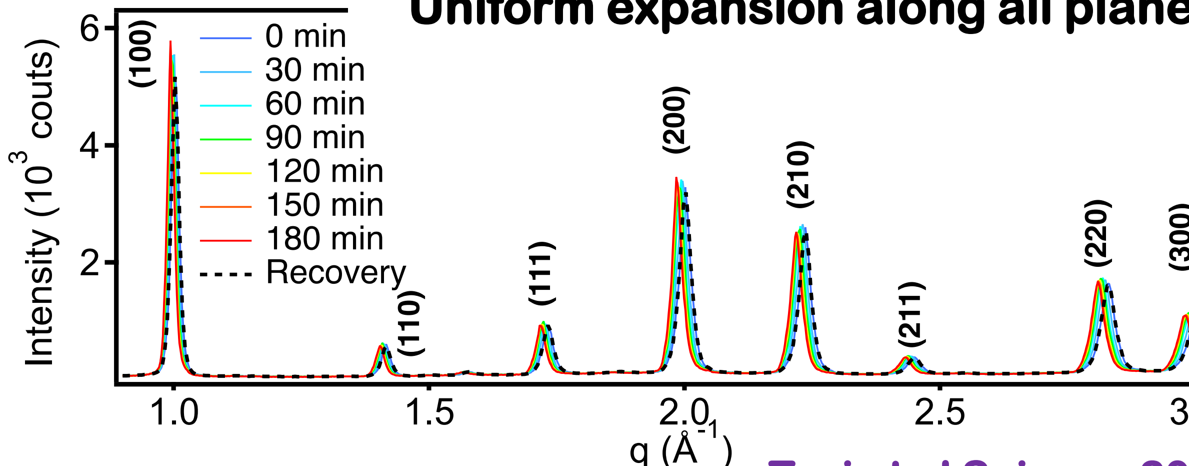
Accomplishments & progress

Discovery of new effect: Light-induced lattice expansion

In-situ GIWAXS studies

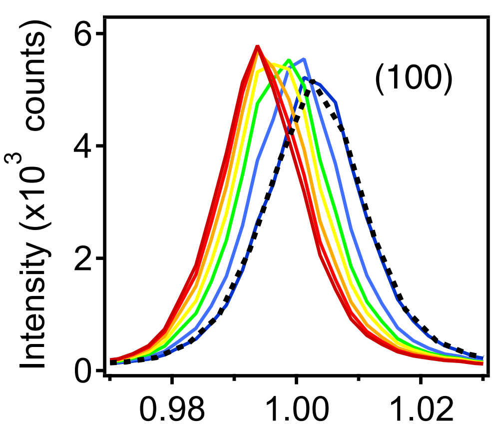


Uniform expansion along all planes

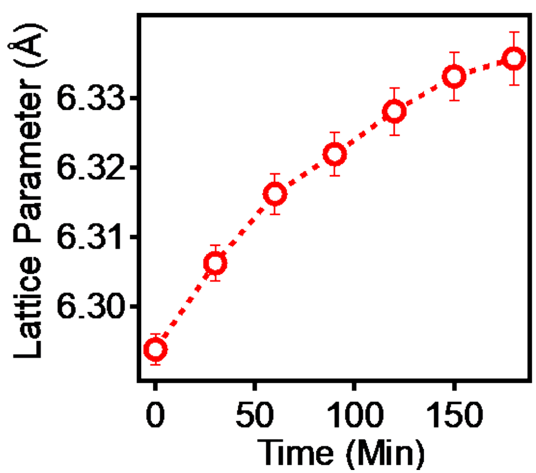


Tsai et al Science 2018

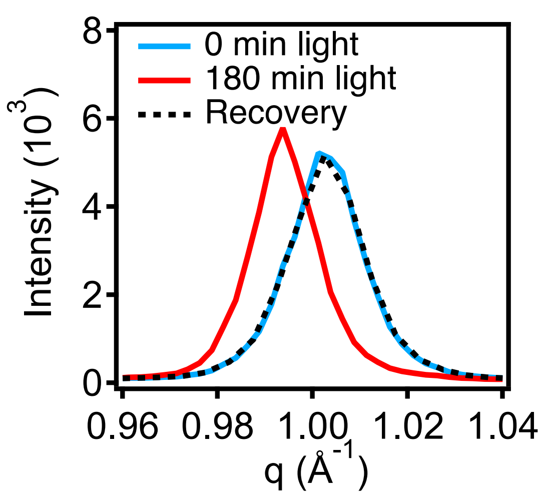
<100> plane



Lattice constant vs. illumination time



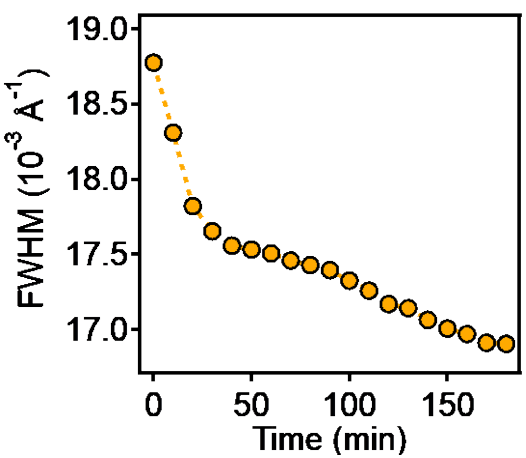
Reversible



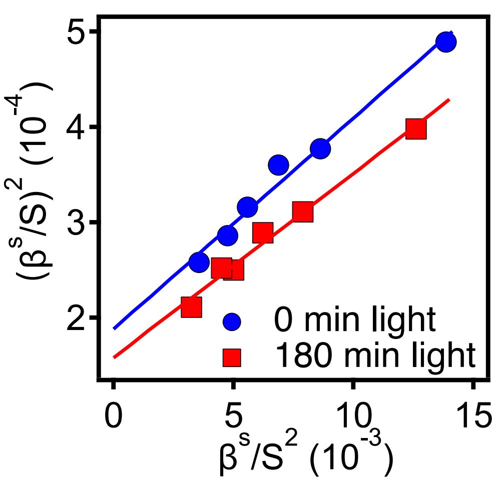
Accomplishments & progress

Light-induced lattice expansion cures interface/bulk defects

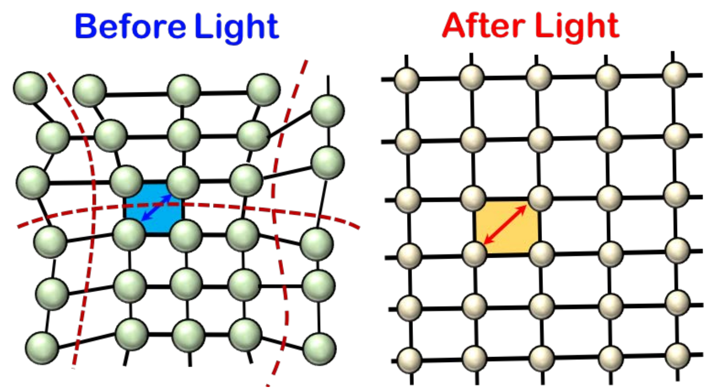
Enhanced crystallinity



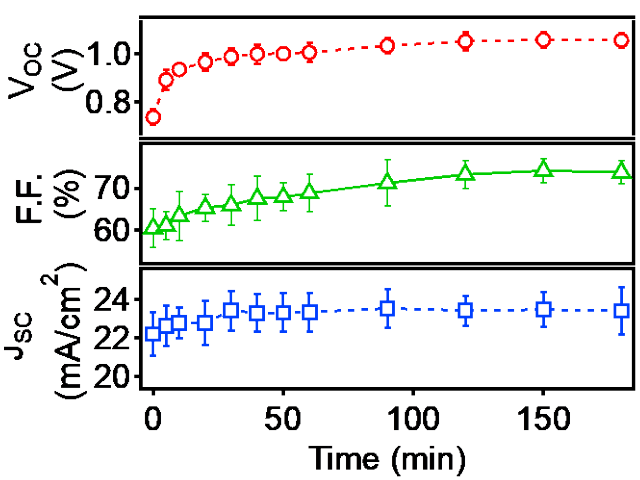
Halder–Wagner plot

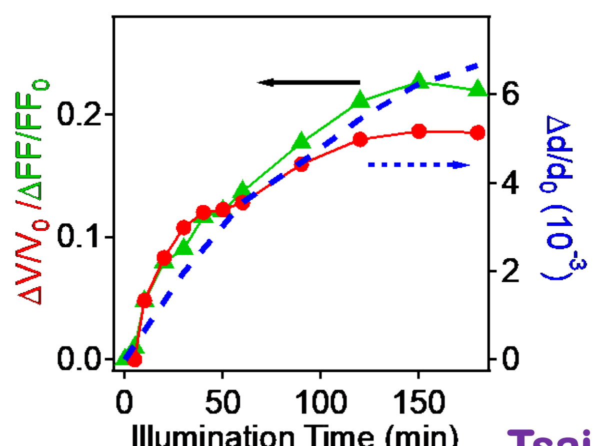


Decreased mosaicity & microstrain

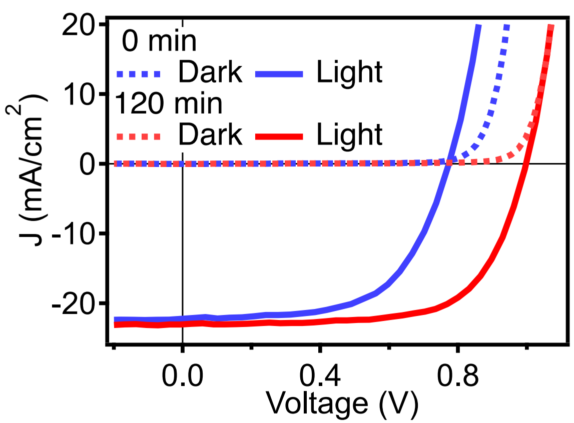


Solar cell parameters vs. lattice constant change





Efficiency >20.5%

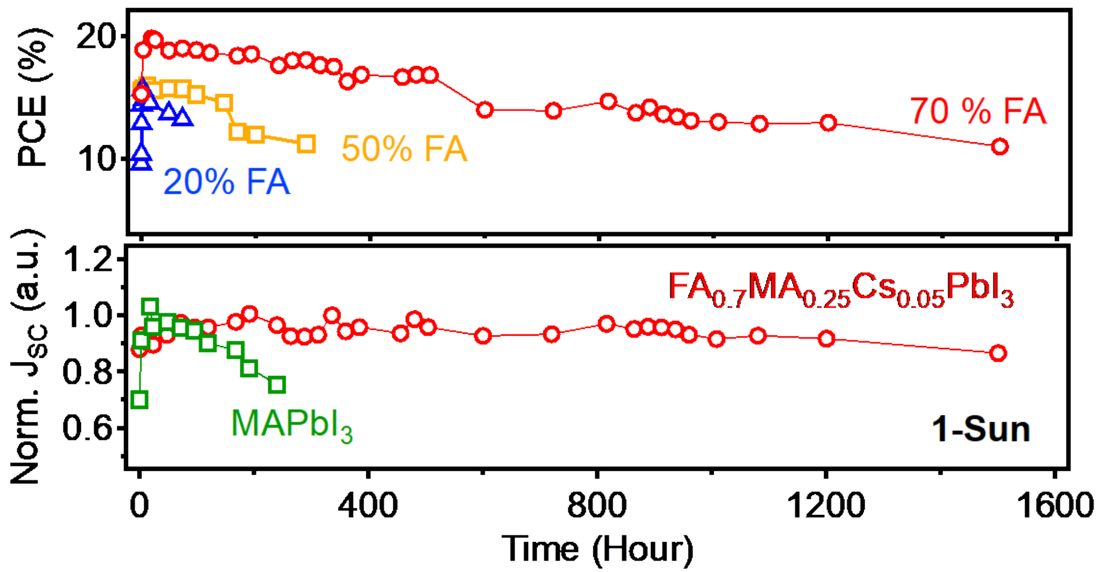


Tsai et al Science 2018

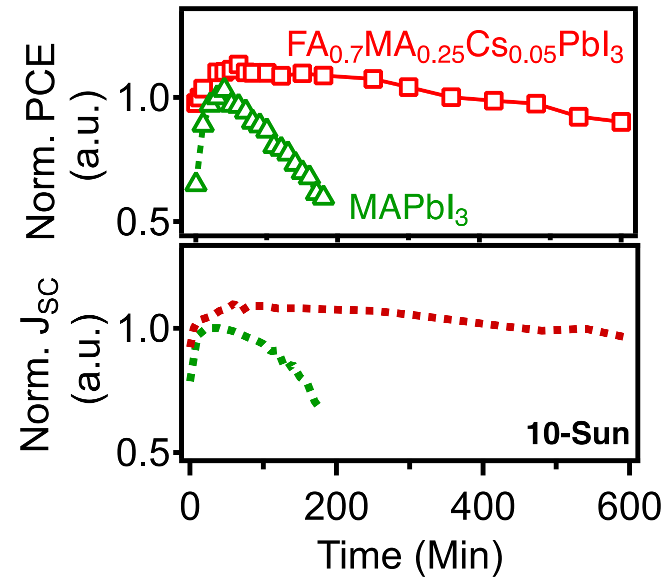
Accomplishments & progress

Excellent photostability under 1-Sun and 10-Sun

Long term photo-stability



Stability under 10-Suns



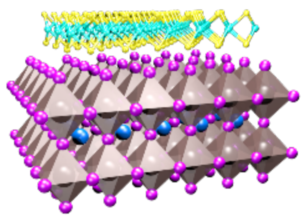
❖ **Long-term stability achieved under 1-Sun for >1500 hrs and also under 10-Sun illumination.**

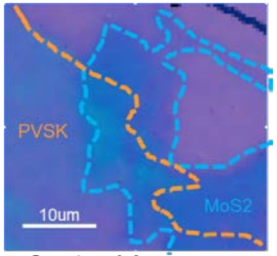
❖ **Stability comparable to 2D perovskite but efficiency >20.5% - Promising for PECs (Cathodes and Anodes)**

Accomplishments & progress

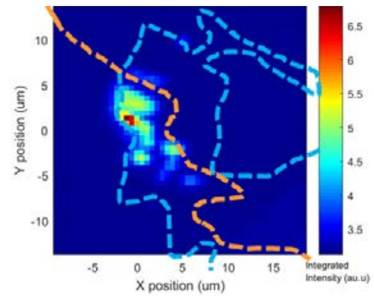
Innovation: Strategies for barriers on perovskite solar cells (ALD, layered materials, Oxides)

❖ Protection of perovskite using layered materials



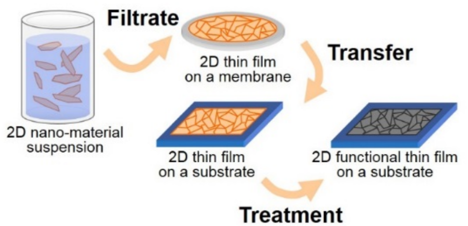


Optical Image

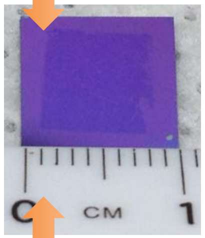


Photoluminescence image shows **no degradation of the perovskite under 2-layers of MoS_2**

❖ Example of strategy development in progress



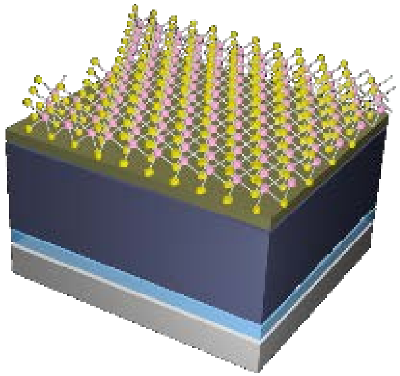
Chemical vapor deposition (Vacuum processing)



Large area graphene

Vacuum filtration (Solution processing)

Dry transfer process

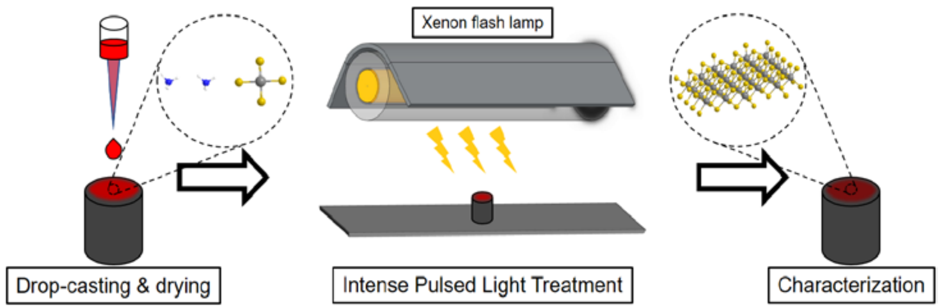


Protected solar cells (in testing)

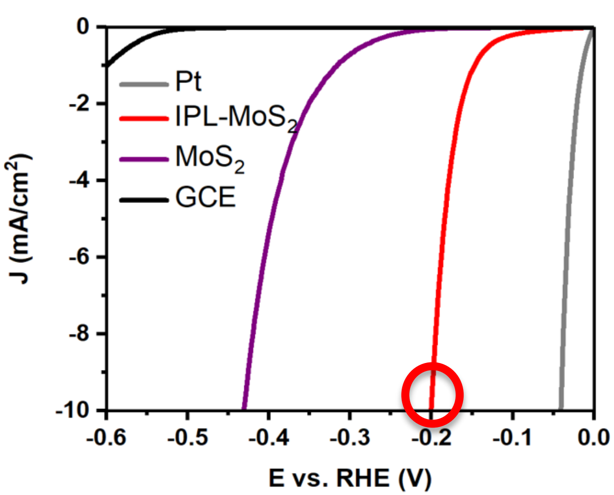
Accomplishments & progress

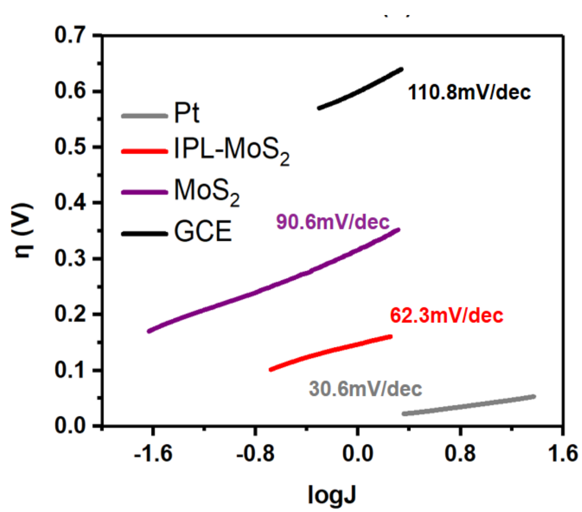
HER Catalysts

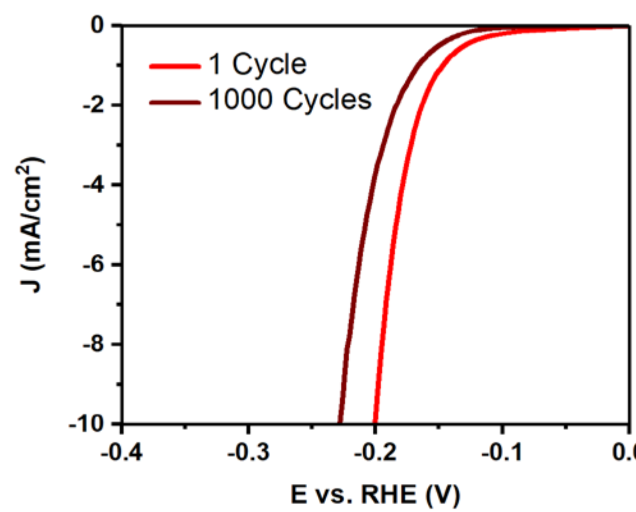
Innovation: Novel method to mass produce MoS2 based HER catalysts obtain in milliseconds



Key Advantage: IPL technique established for hybrid perovskite and here we demonstrate the technique to develop MoS_2 based catalysts.





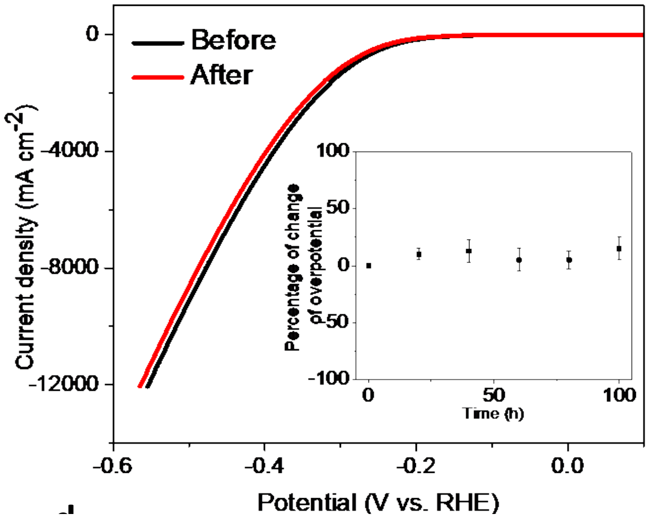


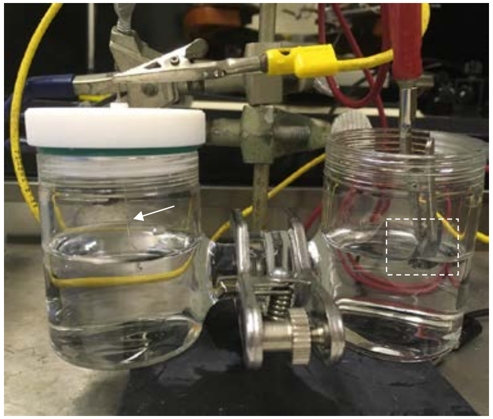
Gautam Gutpa research group - UofL

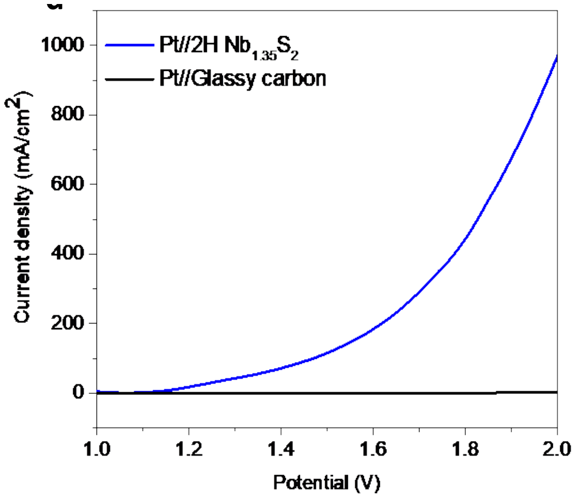
Accomplishments & progress

HER Catalysts

Innovation: **Developed new $Nb_{1.35}S_2$ catalysts with very high current density – demonstrated electrolyzer**







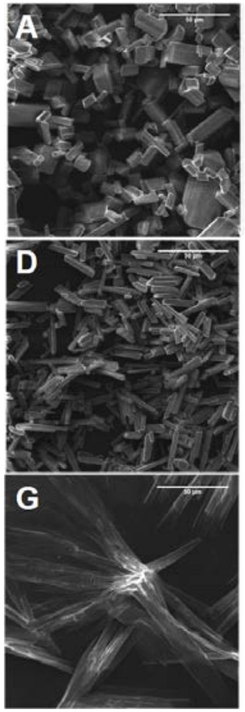
- ❖ $Nb_{1.35}S_2$ catalysts demonstrated good stability
- ❖ Incorporated $Nb_{1.35}S_2$ catalyst in an electrolyzer

Chhowalla research group - Rutgers

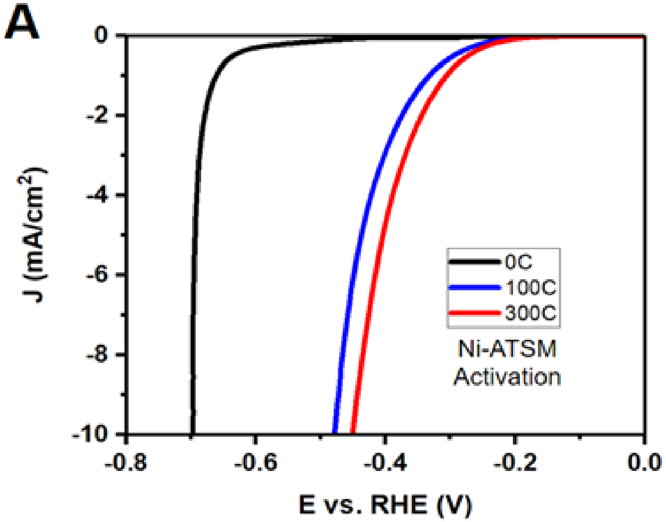
Accomplishments & progress

HER Catalysts

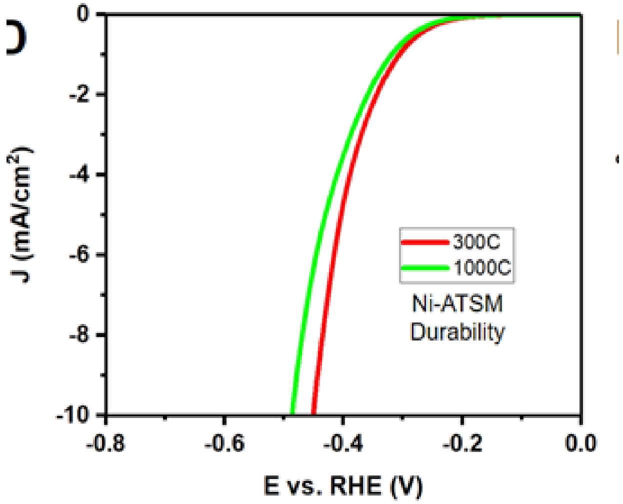
Innovation: **Nickel based molecular catalysts – excellent durability & solvent compatibility with perovskites**



Catalyst Activation



Durability



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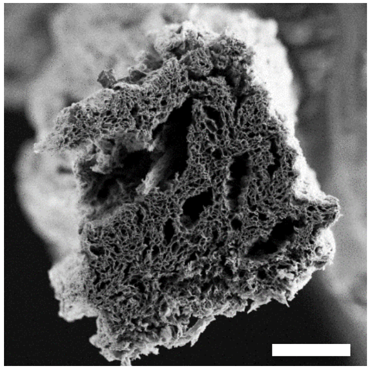
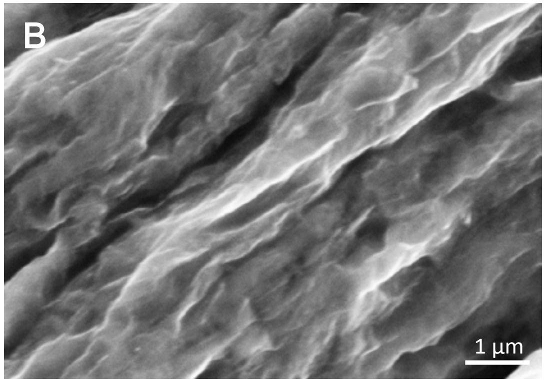
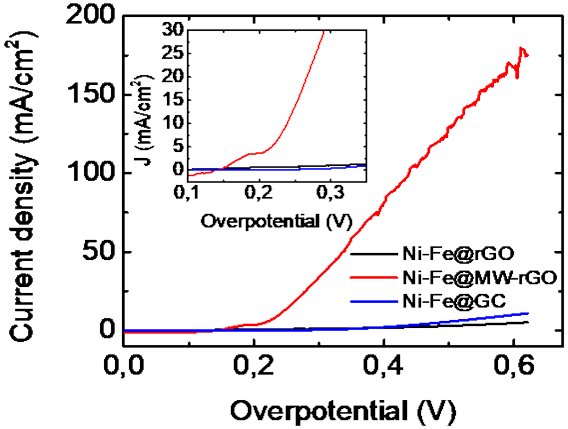
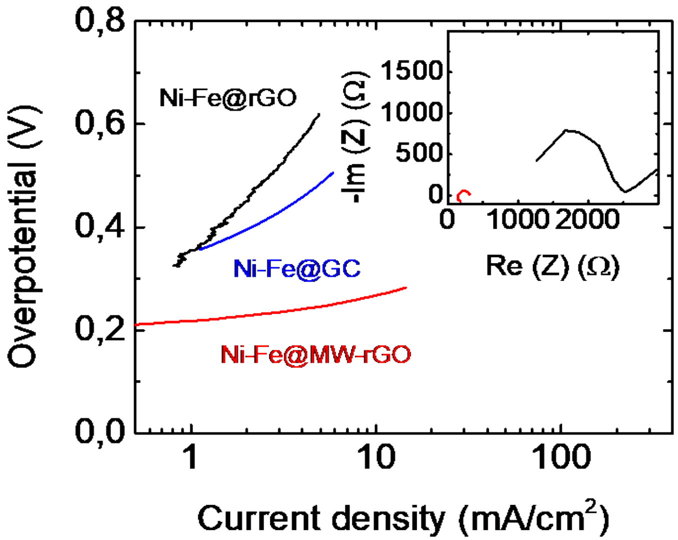
OER Catalysts

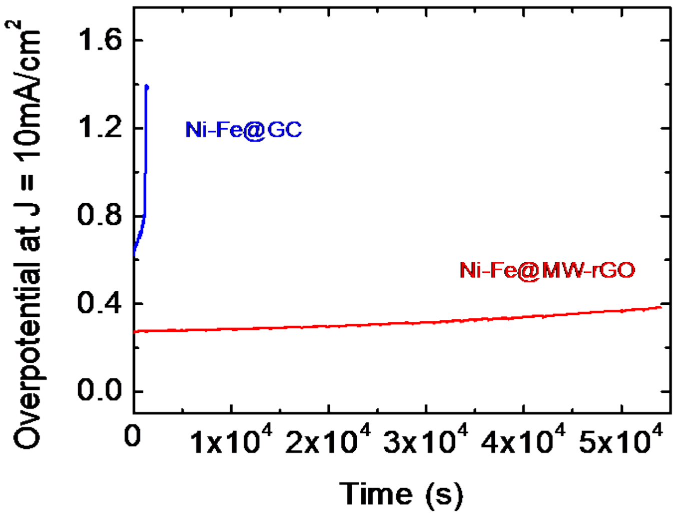
Innovation: Developed Ni-Fe catalysts with an overpotential of 200 mV on rGO supports







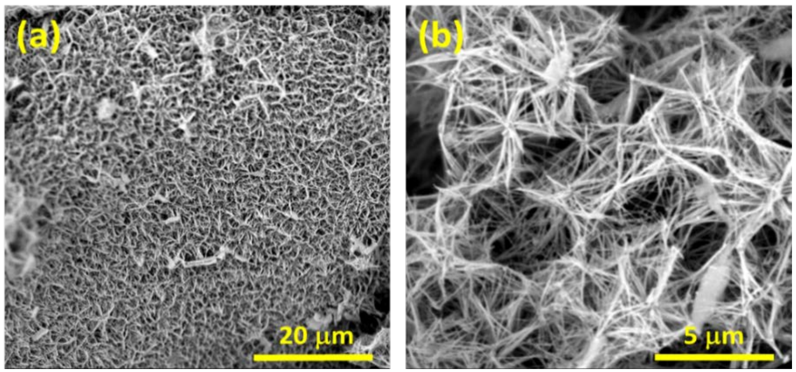


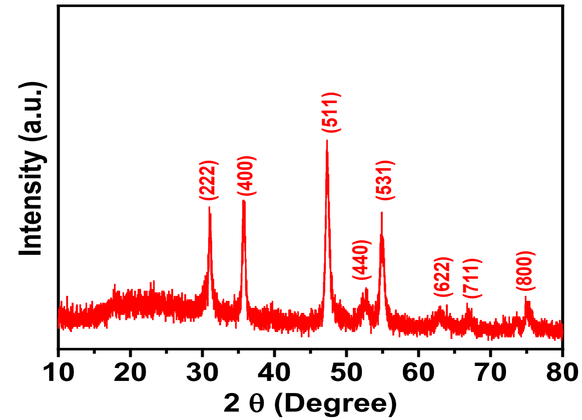


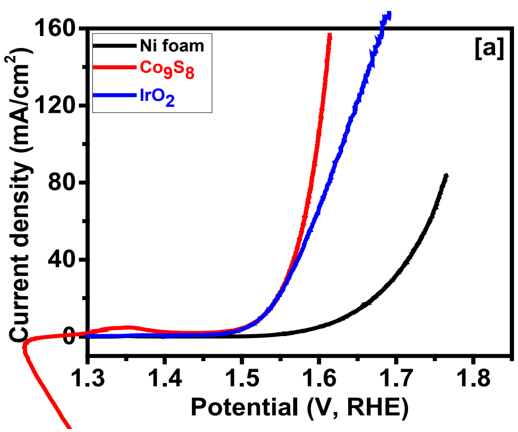
Accomplishments & progress

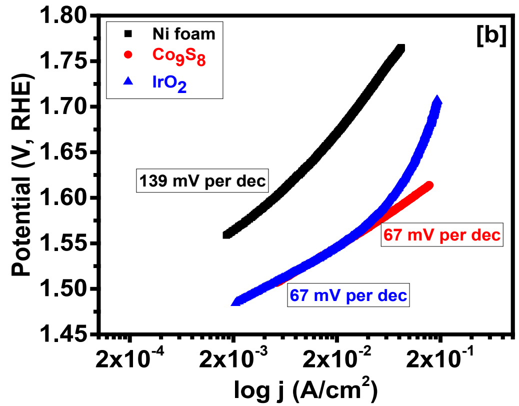
OER Catalysts

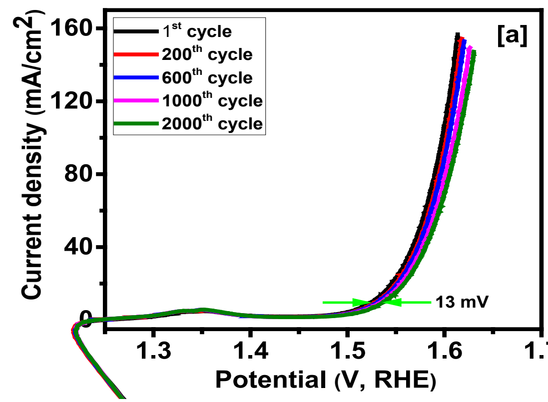
Innovation: Highly efficient and durable electro-catalysts based CoS nanowires











Key Advantages: **Good performance and excellent cycleability in alkaline media**

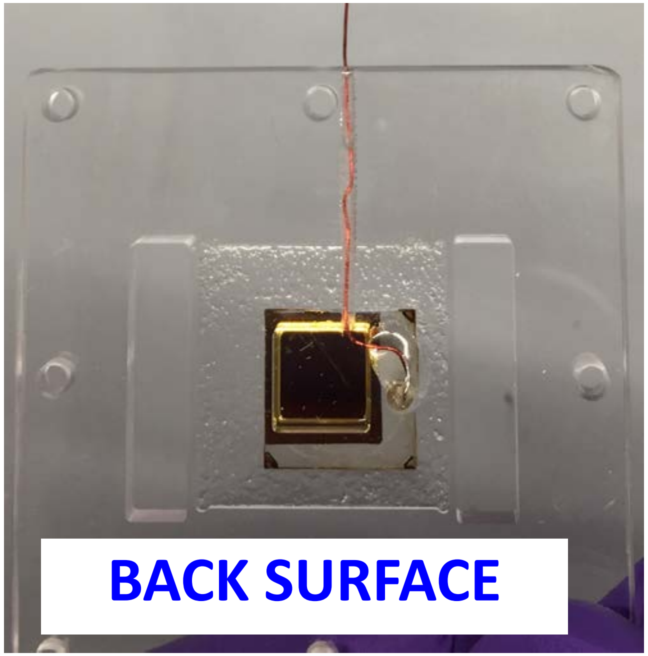
H

Gautam Gutpa research group - UofL

Accomplishments & progress

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

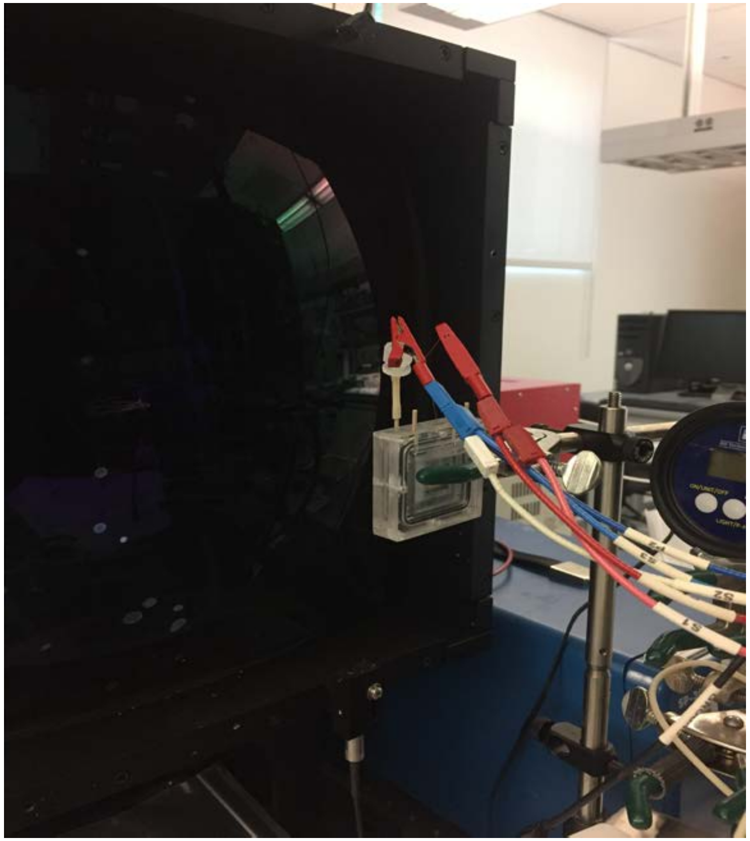
- Cell sits on an epoxied ledge
- Prevents exposure to solution
- Front contact (Au) exposed to solution through opening
- Wire is Ag epoxied to ITO (or FTO) through a hole in the plate,
- Backfilled with clear epoxy

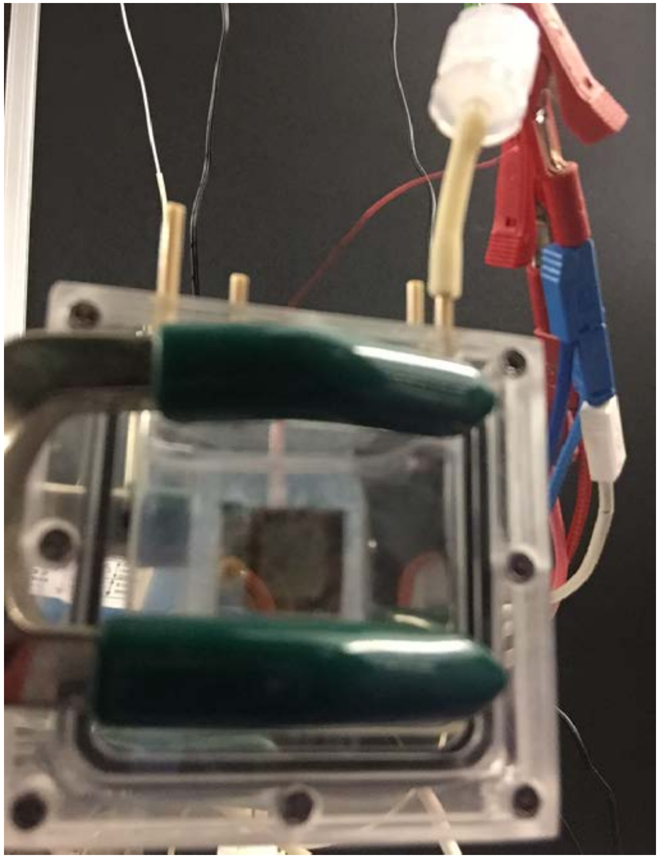


Accomplishments & progress

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. Planed 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, MoS_2, NbS_2) on hybrid perovskites
- Perform photocathode and photoanode measurements on perovskite/Pt and perovskite/Ir based catalysts
- Integrate earth abundant catalysts such as MoS_2 (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**
  - Discovery of a new mechanism to stabilize perovskite thin films (Science 2018) → stable (>1500 hrs) perovskite solar cells with >20% efficiency [Milestone complete]
  - 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]
  - $Nb_{1.35}S_2$ HER catalyst with overpotential <150 mV and >>20 mA/cm^2 with stability 100 hrs [Milestone complete]
  - Ni-Fe@MW-rGO OER catalyst with overpotential <200 mV and 1 mA/cm^2 [90% complete]
- **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]