Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Monolithically Integrated Thin-Film/Si Tandem Photoelectrodes

Author Name: Zetian Mi

Date: November 14, 2017

Venue: NREL's Energy Systems Integration Facility

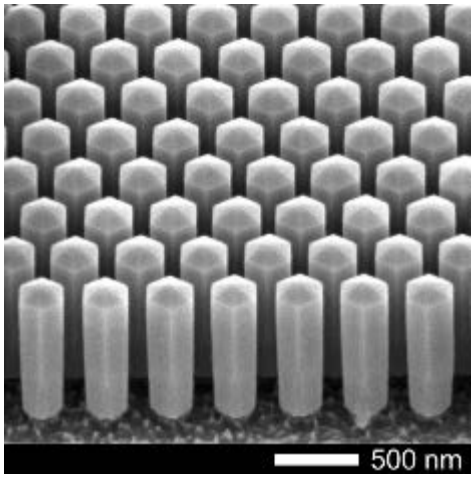
NREL
BERKELEY LAB
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

HydroGEN Kick-Off Meeting

MONOLITHICALLY INTEGRATED THIN-FILM/SILICON TANDEM PHOTOELECTRODES FOR HIGH EFFICIENCY AND STABLE PHOTOELECTROCHEMICAL WATER SPLITTING

Zetian Mi, University of Michigan, Ann Arbor
Thomas Hamann, Michigan State University
Dunwei Wang, Boston College
Yanfa Yan, University of Toledo

Award #	EE0008086
Year 1 Funding	$250,000

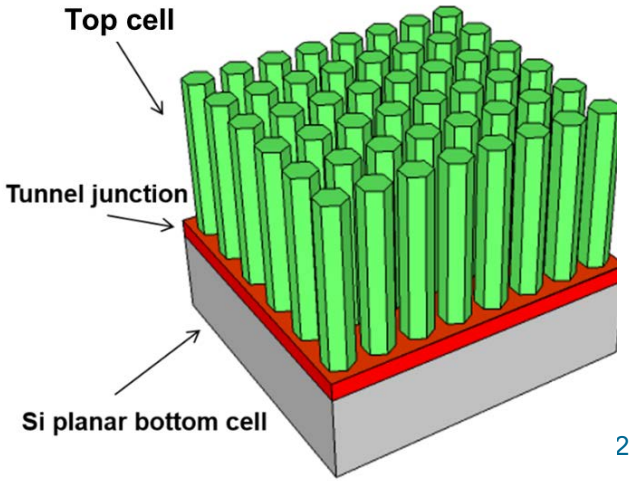


Project Vision

We propose to develop monolithically integrated thin-film/Si tandem photoelectrodes to achieve both high efficiency (>15%) and stable (>1,000 hrs) water splitting systems.

Project Impact

Success of the project will help meet the DOE 2020 target (20% solar-to-hydrogen efficiency and $5.70 per kg H_2) and pave the way for widespread commercialization of solar hydrogen production technologies.



Innovation and Objectives

Project history

The applicants have had complementary expertise in PEC water splitting:

- Ta_3N_5, BCTSSe, and InGaN top photoelectrodes with E_g ~1.7-2 eV.
- Low resistivity nanowire tunnel junction on Si wafer.
- Ultrathin N-rich GaN coating against photocorrosion and oxidation.

Proposed targets

Metric	State of the Art	Proposed
STH Efficiency / Stability	*16% 1.5 hrs*	*> 15% 1000 hrs*

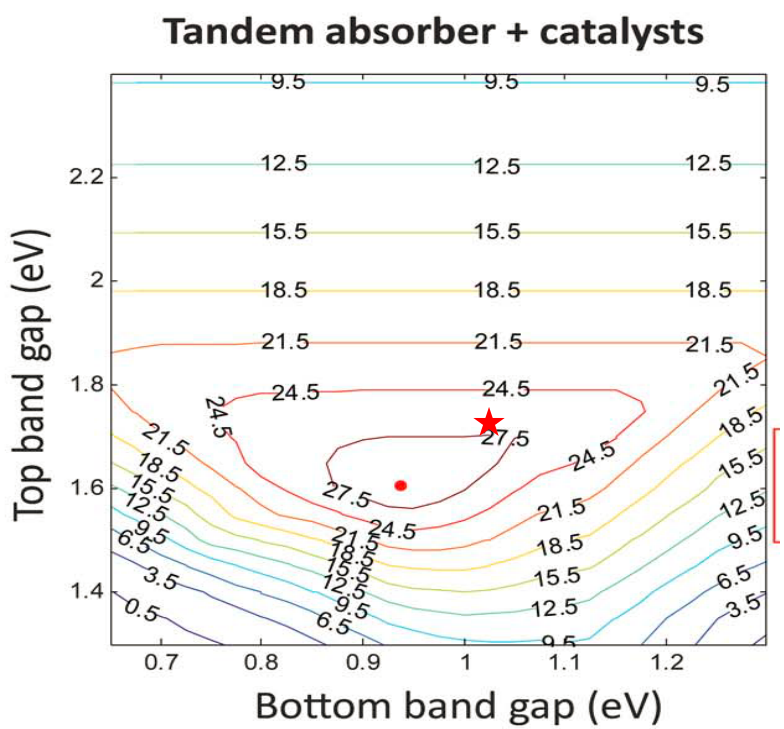
Barriers

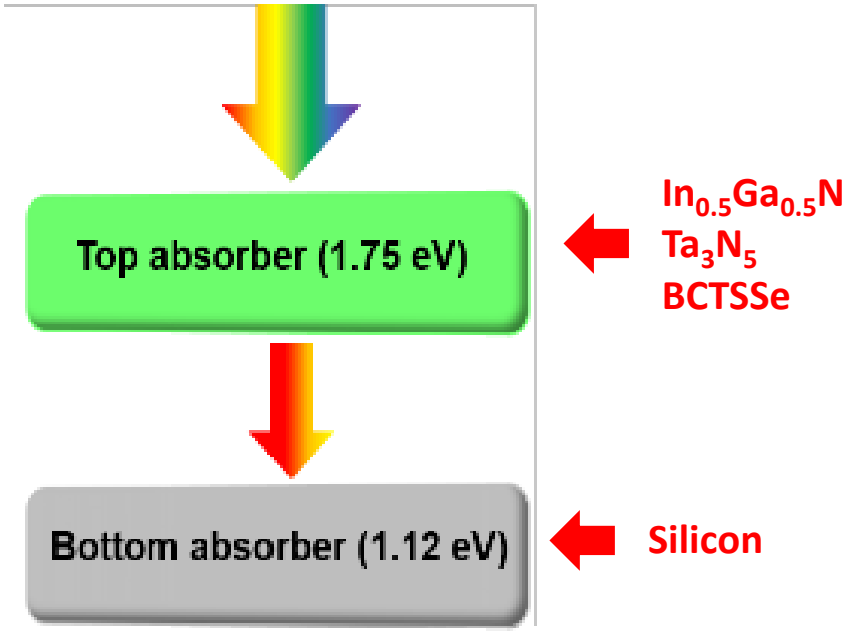
- Further improve the performance and stability of top photoelectrodes.
- Integration of the top photoelectrodes with the Si bottom light absorber through nanowire tunnel junction.

Partnerships

- **Thomas Hamann, Michigan State Univ.:** Ta_3N_5, PEC characterization
- **Dunwei Wang, Boston College:** Cocatalyst deposition, surface protection
- **Yanfa Yan, Univ. Toledo:** Sputtering deposition and PEC characterization of BCTSSe

Technology Innovation

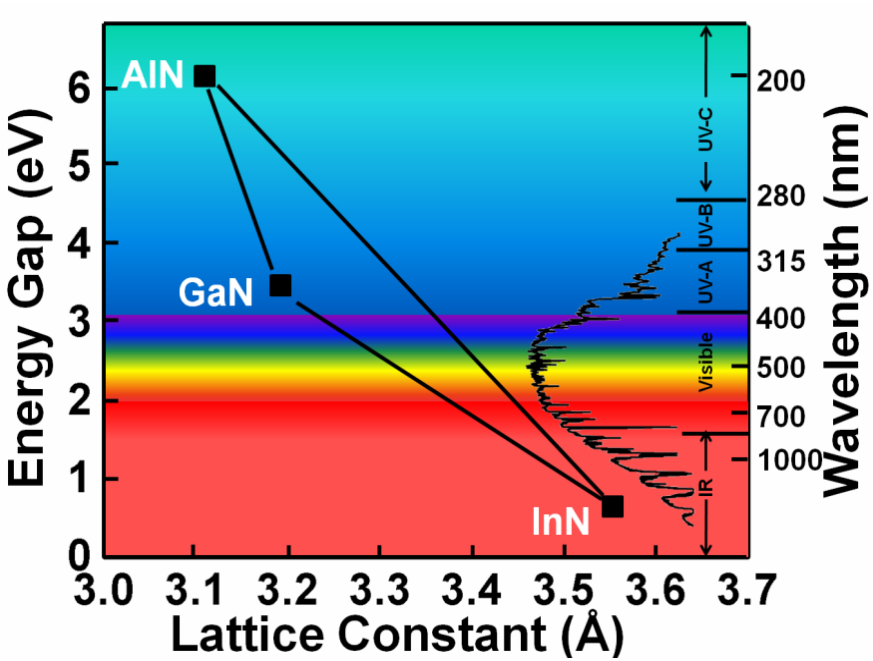


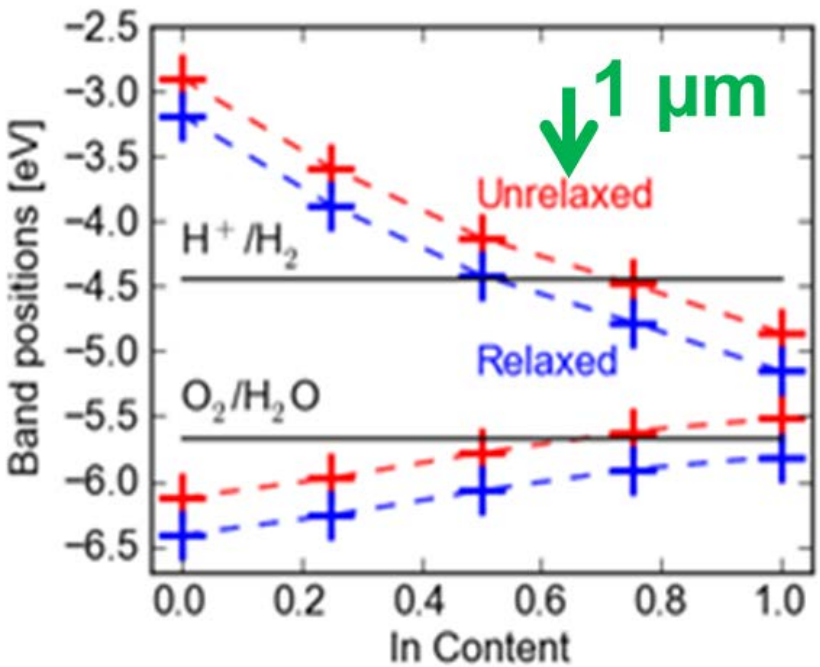


Hu, S. et al., Energy Environ. Sci., 6 (2013), 2984–2993.

- The use of Si substrate as the bottom light absorber to reduce the cost of PEC water splitting.
- The use of recently developed low cost Ta_3N_5, BCTSSe, and $In_{0.5}Ga_{0.5}N$ photoelectrodes as the top light absorber, which have a direct energy bandgap of 1.7-2.0 eV.

Technology Innovation



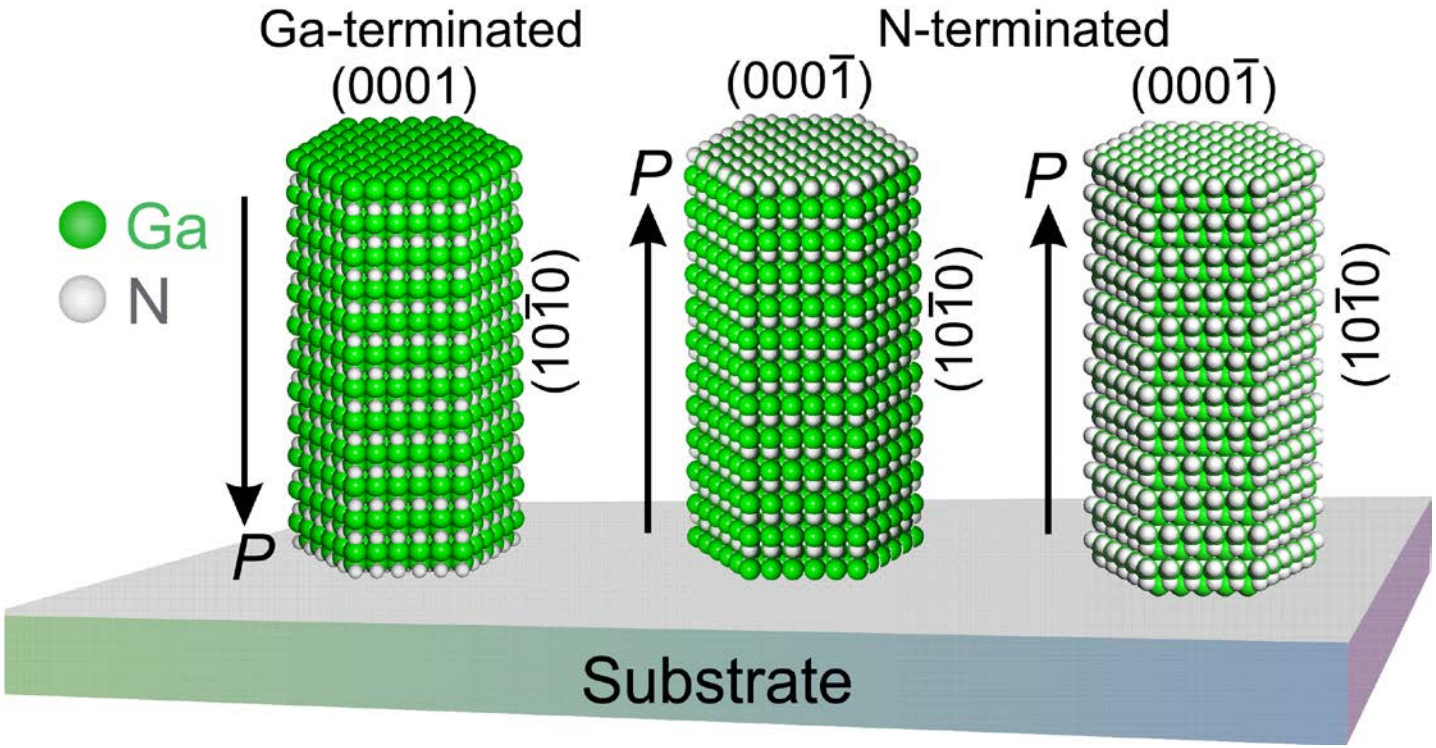


- III-nitrides are the only known semiconductors whose energy band edges can straddle water redox potentials under deep visible and near-IR light.

J. Mater. Chem. A, 4, 2801, 2016.
Appl. Phys. Lett. 96, 021908 2010.

Technology Innovation

- N-terminated surface protecting against corrosion and oxidation



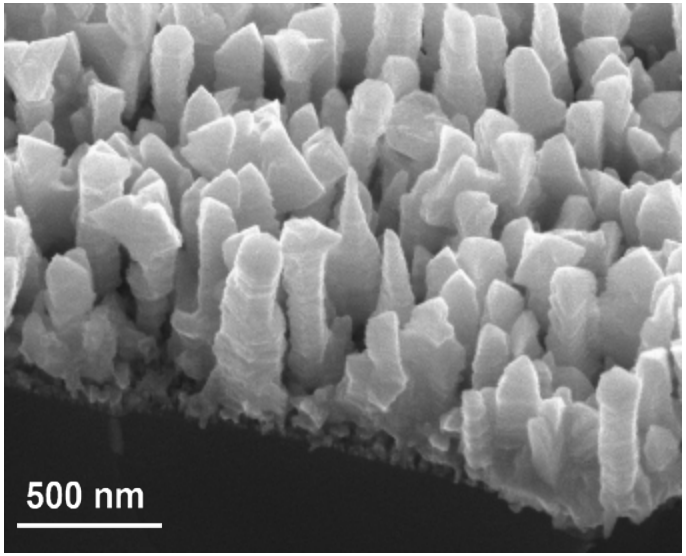
Ga polarity

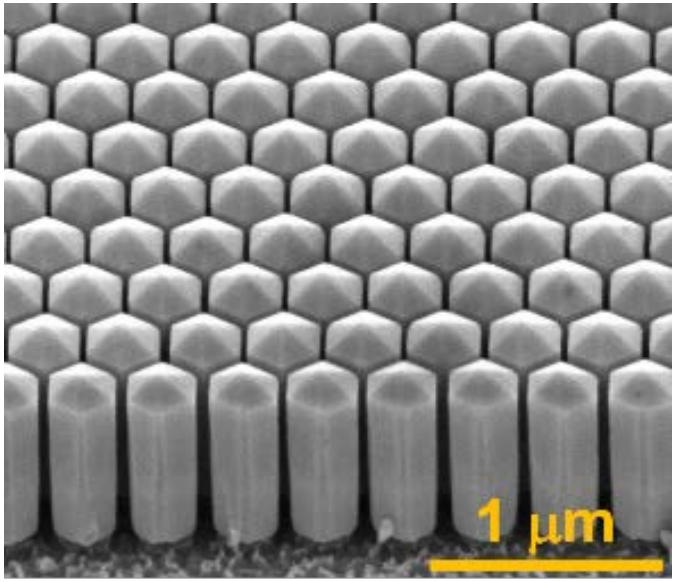
- Unstable
- Difficult to extract holes

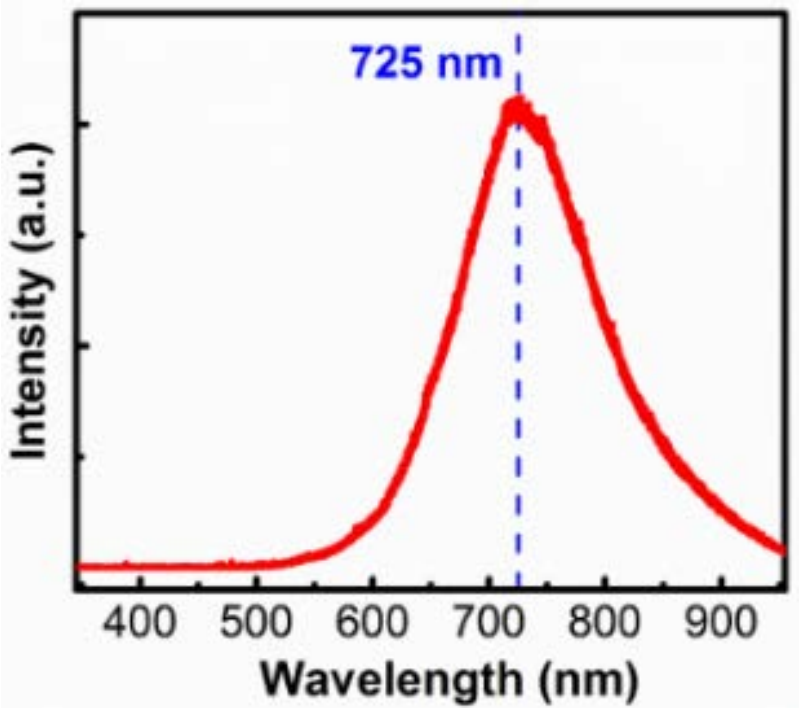
N polarity

- Stable
- Efficient hole extraction

Technology Innovation



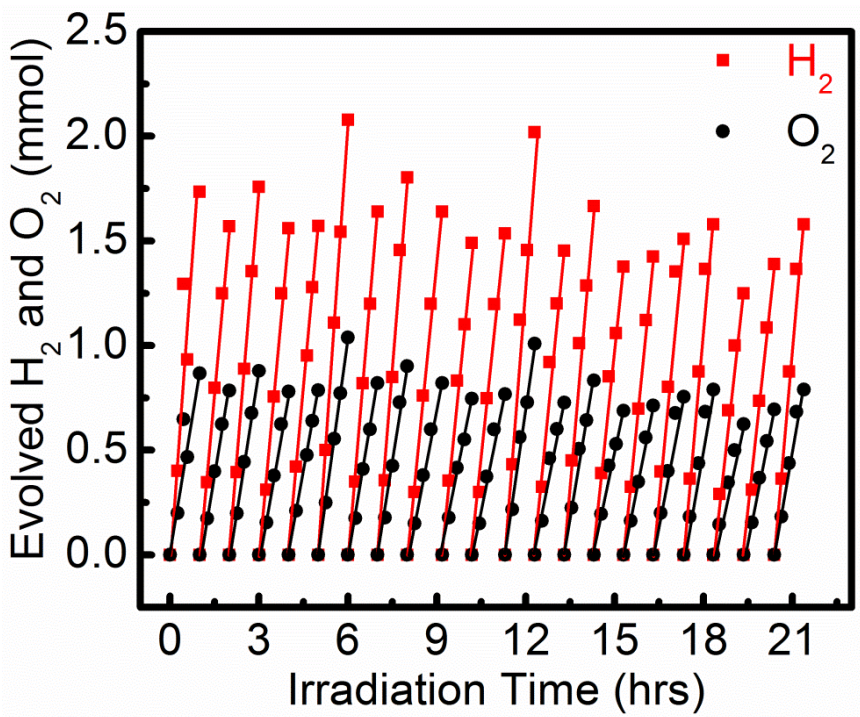




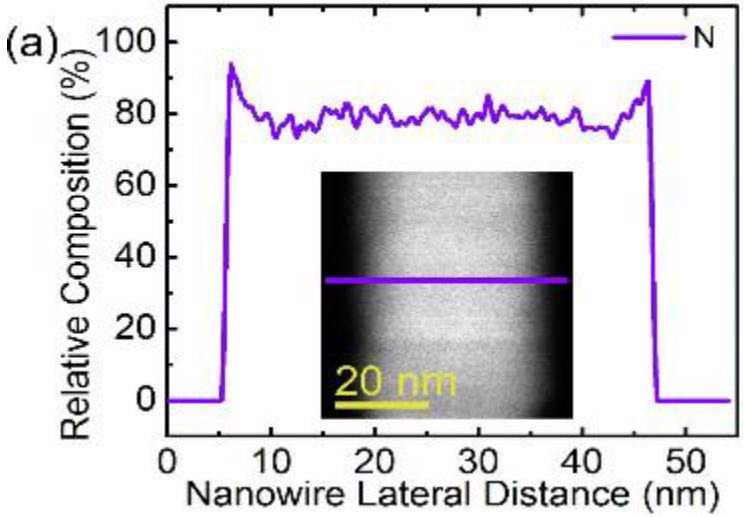
- InGaN nanowires with various sizes and surface morphology can be grown, with energy bandgap tuned from the visible to the infrared.

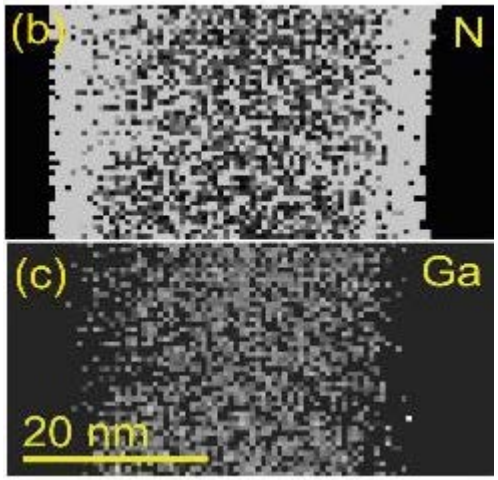
Advanced Energy Materials, vol. 7, 1600952, 2017.
Advanced Functional materials, vol. 27, 1702364, 2017.

Technology Innovation



STEM reveals N-rich m-plane surfaces from MBE grown GaN Nanowires.

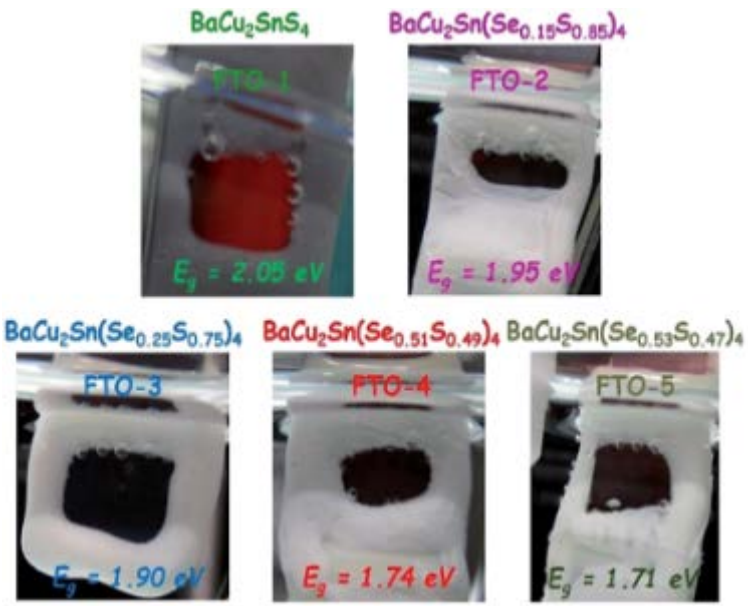


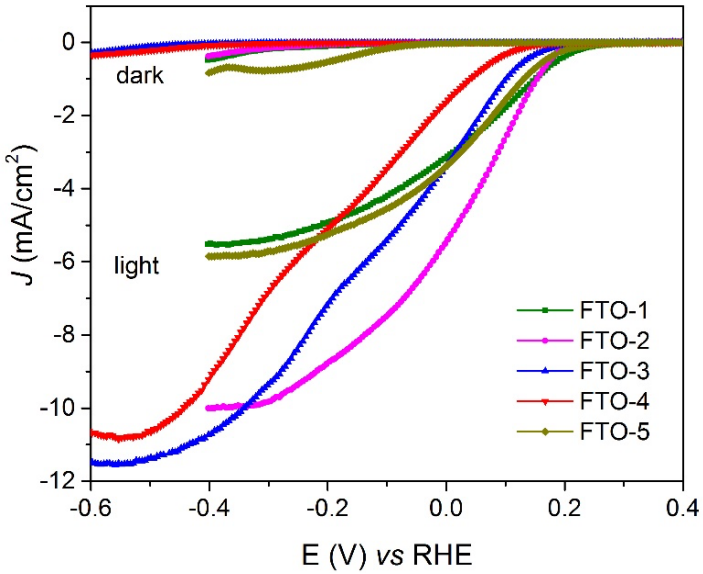


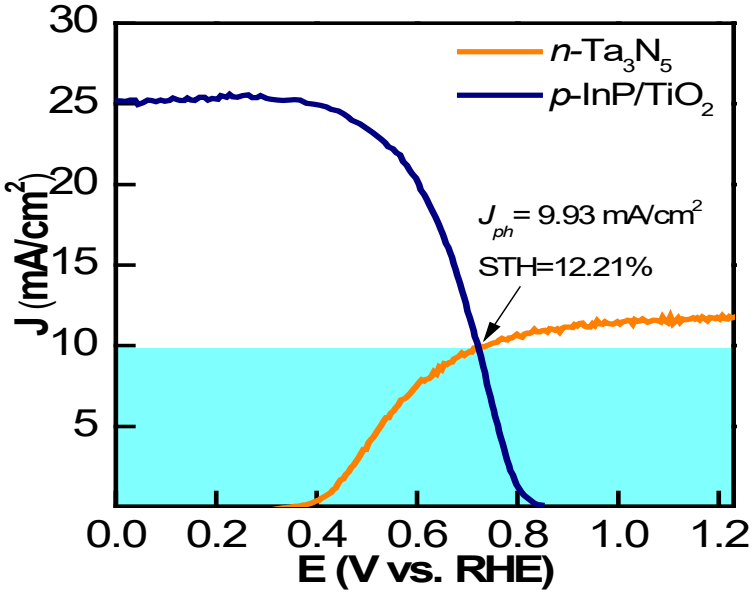
The N-terminated surfaces of InGaN nanowires protect against photocorrosion and oxidation, leading to long-term stable operation in overall water splitting.

Nature Commun., vol. 5, 3825, 2014.
Nature Commun., vol. 6, 6797, 2015.
Adv. Mater. vol. 28, 8388, 2016

Technology Innovation

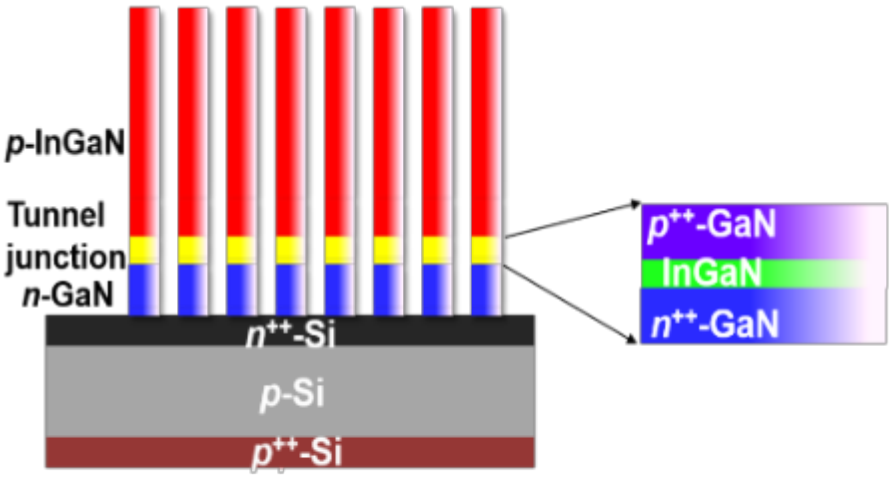




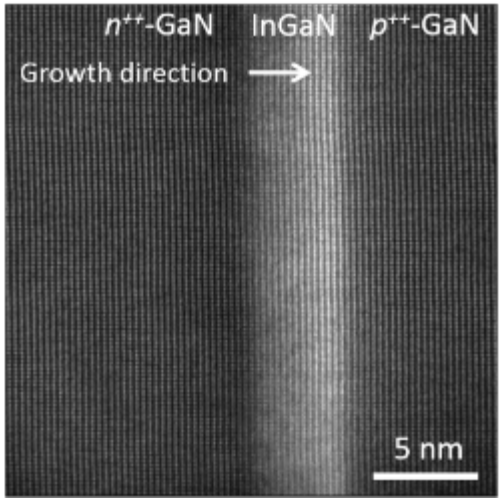


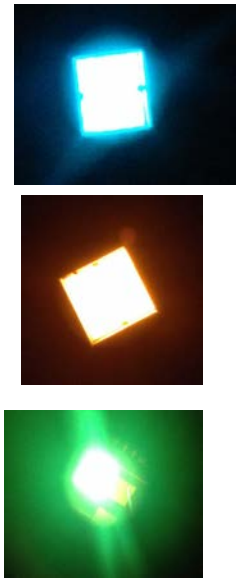
- We will also develop both BCTSSe and Ta_3N_5 thin films as efficient photocathodes and photoanodes for PEC water splitting.

Technology Innovation



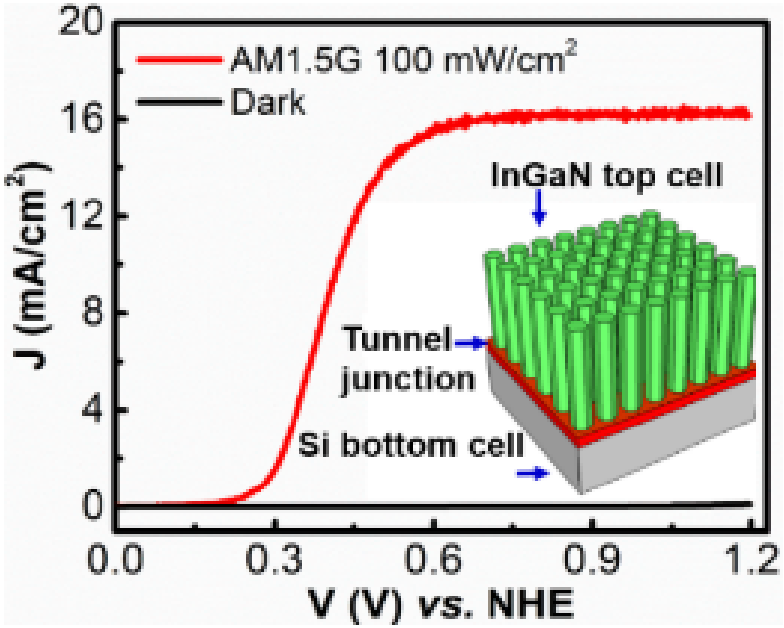
Integrated photocathode





- Nanowire tunnel junction will be used to connect to the the top light absorber (Ta_3N_5, BCTSSe, or InGaN) with the Si bottom junction.
- The use of nanowire tunnel junction can further reduce the formation of defects and dislocations in the top light absorber.

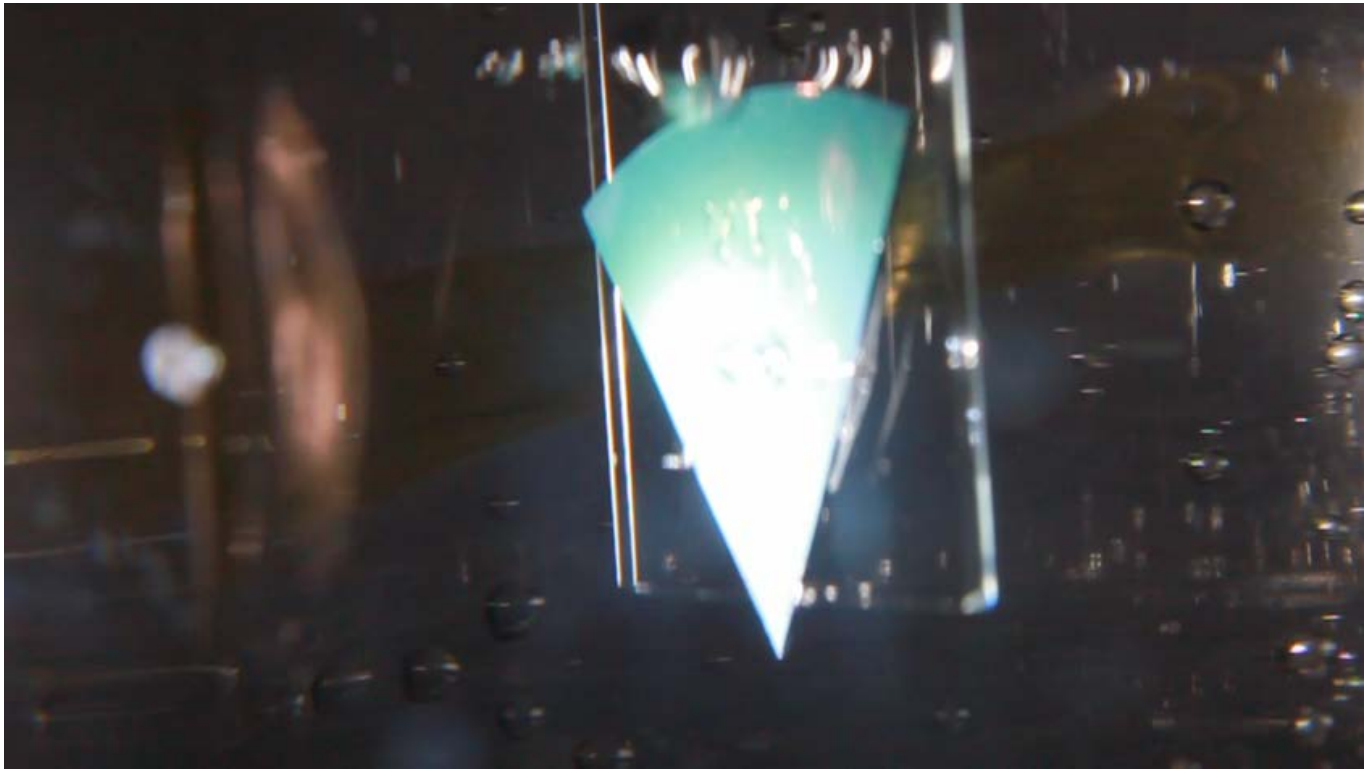
Advanced Energy Materials, vol. 7, 1600952, 2017.
Nano Letters, vol. 15, 2721, 2016.

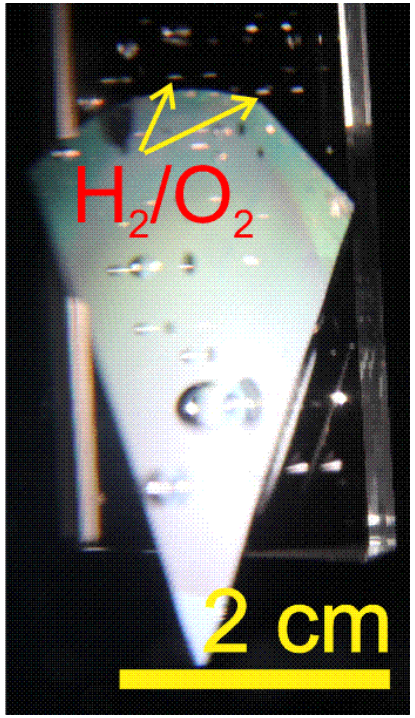


Effective Leveraging of the EMN Resource Nodes




- **Glenn Teeter, NREL:**
  Surface analysis cluster tool, surface measurements
- **Francesca Toma, LBNL:**
  Photoelectrochemical AFM and STM
- **Todd Deutsch, NREL:**
  Surface modifications and protection
- **Tadashi Ogitsu, LLNL:**
  Ab initio modeling of electrochemical interfaces





Thank you!

***Kibria et al. Nature Commun.*, vol. 6, 6797, 2015.**