Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Monolithically Integrated Thin-Film/Si Tandem Photoelectrodes

Zetian Mi

University of Michigan, Ann Arbor

Project ID # p163

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

Project Overview

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

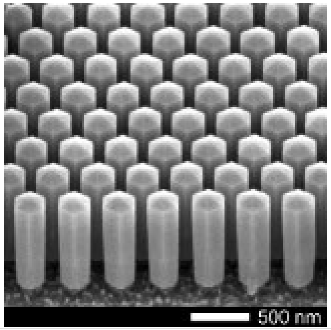
Zetian Mi, University of Michigan, Ann Arbor
Thomas Hamann, Michigan State University
Dunwei Wang, Boston College
Yanfa Yan, University of Toledo

Award #	EE0008086
Start/End Date	9/01/2017 – 02/28/2020
Year 1 Funding* Year 2 Funding*	$249,999 $373,530

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

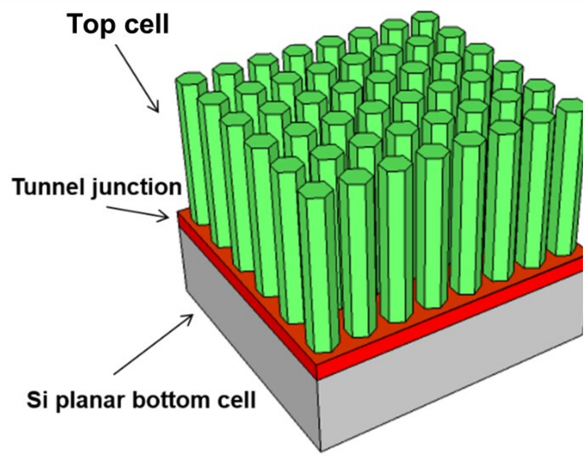
Project Vision

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.



Approach- Summary

Project motivation

We aim to tackle the challenges of achieving efficient, cost-effective PEC water splitting devices by developing tandem photoelectrodes, which consist of a bottom Si light absorber and a 1.7 eV top light absorber (InGaN). We have previously developed:

- ***InGaN top photoelectrodes with E_g ~1.8-2.0 eV.***
- ***Low resistivity nanowire tunnel junction, which will be used to fabricate top photoelectrode.***
- ***N-terminated GaN, which can protect against photocorrosion and oxidation.***

Barriers

- **Materials Durability – Bulk and Interface:** Identify intrinsically durable and efficient materials for PEC H_2 generation.
- **Integrated Device Configurations:** Develop efficient and stable integrated devices to meet the ultimate targets in PEC H_2 generation.
- **Synthesis and Manufacturing:** Scalable manufacturing of PEC materials and devices.

Key Impact

Metric	State of the Art	Expected Advance
Stability/ Efficiency	*~0.5 hr @ 16-19%*	*>1,000 hrs @15%*
Cost/ scalability	*~$150 for 4" GaAs wafers*	*~$100 for 12" Si wafers, i.e. ~10 times reduction in wafer cost*

Partnerships

Co-PIs

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

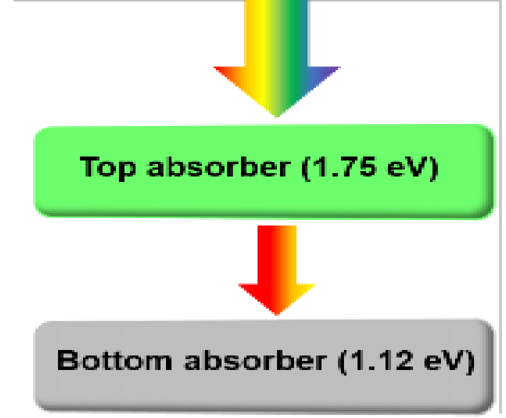
HydroGEN nodes

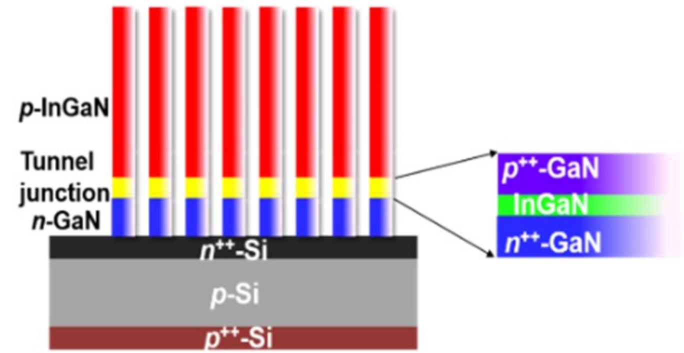
- **Glenn Teeter, NREL:** Surface analysis cluster tool, surface measurements
- **Francesca Toma, LBNL:** Photoelectrochemical AFM and STM
- **Tadashi Ogitsu, LLNL:** Ab initio modeling of electrochemical interfaces
- **Todd Deutsch, NREL:** Surface modifications and protection

Adv. Ener. Mater., 7, 1600952, 2017. *Adv. Mater.* 28, 8388, 2016. *Nano Lett.*, 15, 2721, 2016.

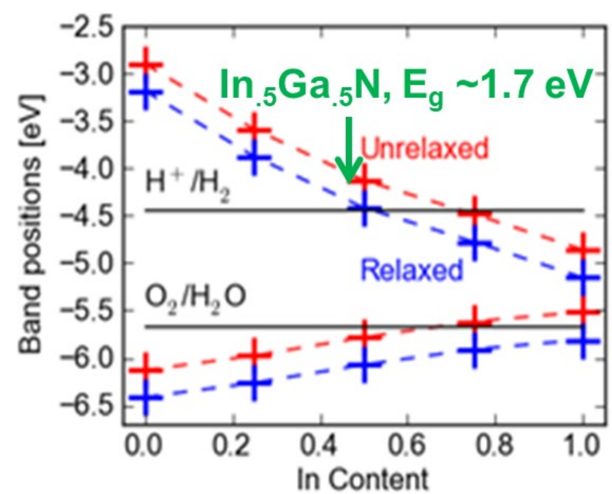
Approach- Innovation

- The use of Si as the bottom light absorber to reduce the cost of tandem water splitting devices.
- The use of recently developed low cost $In_{0.5}Ga_{0.5}N$ photoelectrodes as the top light absorber.
  - Direct bandgap ~1.7 eV.
  - Controlled n or p-type doping.
  - Straddle water splitting potentials.
- Si and GaN are the two most produced semiconductors in the world.
  - Scalable, low cost manufacturing.
- The use of GaN nanowire tunnel junction to fabricate top photoelectrodes on Si.
  - Low resistivity, and reduced voltage loss.
  - Reduced defect formation due to the efficient surface stress relaxation.





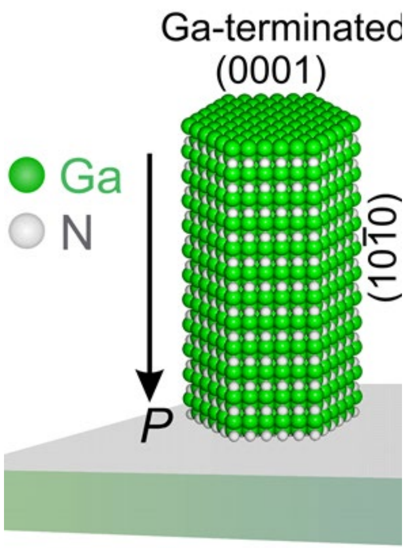
Integrated photocathode

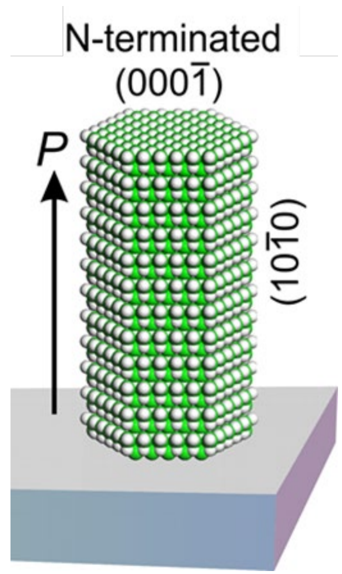


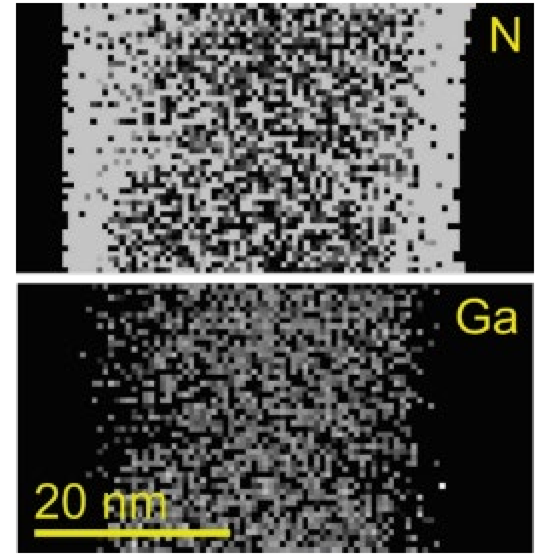
Appl. Phys. Lett. 96, 021908 2010.

Approach- Innovation

➤ **Surface protection by N-terminated GaN surfaces**



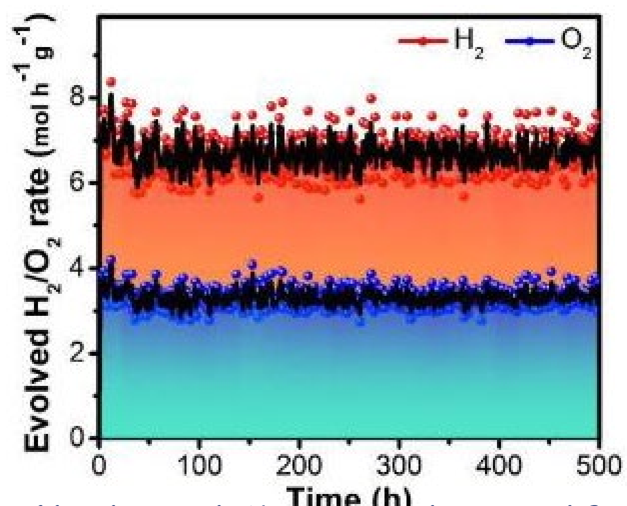




STEM studies reveal N-rich surfaces for MBE grown GaN nanowires.

Conventional GaN grown by CVD has Ga polarity.

GaN nanostructures grown by MBE have N-termination.



No degradation was observed for 500 hours of photocatalytic water splitting reaction without surface protection.

➤ **Unstable in water splitting.**

➤ **Stable in water splitting**

Adv. Mater. 28 (38), 8388-8397, 2016. *ACS Energy Lett.* 3, 2230, 2018

Approach - Innovation

Budget Period 1 Go/No Go Milestones and Highlights

- Demonstrated top photoelectrodes with bandgap ~1.7-2.0 eV on Si that can deliver J_{ph} >10 mA/cm^2 and open circuit potential (OCP) >0.7 V.
- Proof-of-concept demonstration of a double-junction photoelectrode on Si.

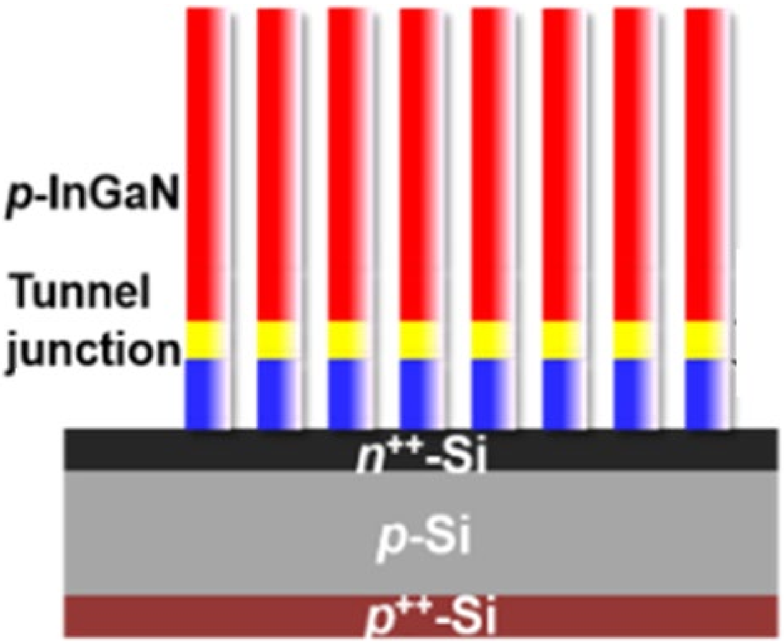
Budget Period 2 Scope of Work

- Design and demonstrate InGaN/Si double-junction photoelectrode with STH >10%, and further perform detailed spectroscopic and kinetic studies.
- Study the stability of InGaN and Si photoelectrodes, and achieve stable operation >500 hrs for the constituting single junction devices and >50 hrs for double-junction devices in two-electrode unassisted water splitting.

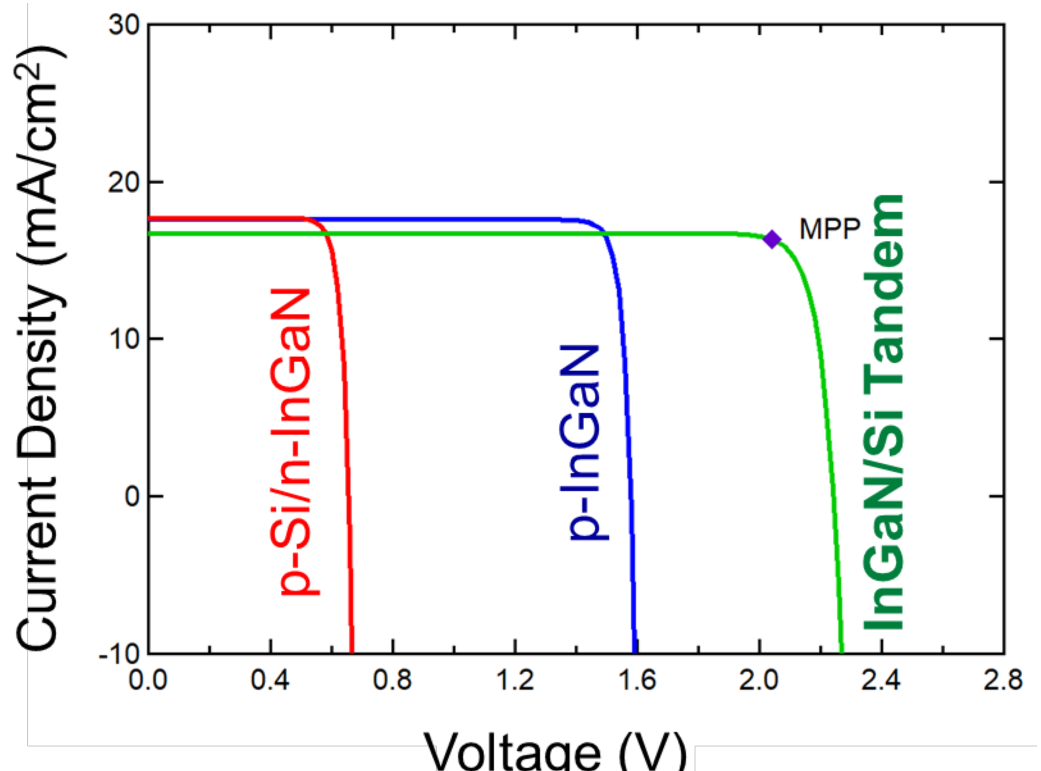
Importance toward project success and overall technology progress

- The realization of unassisted solar water splitting >10% STH efficiency will be the highest value reported for a non III-V PEC device, which paves the way for the low cost manufacturing of high efficiency PEC devices.
- The realization of stable operation >50 hrs in two-electrode, unassisted water splitting, compared to previously best reported <1 hr for high efficiency PEC devices, will help address the stability bottleneck.

Accomplishments: *Design of Si-based tandem photoelectrodes*



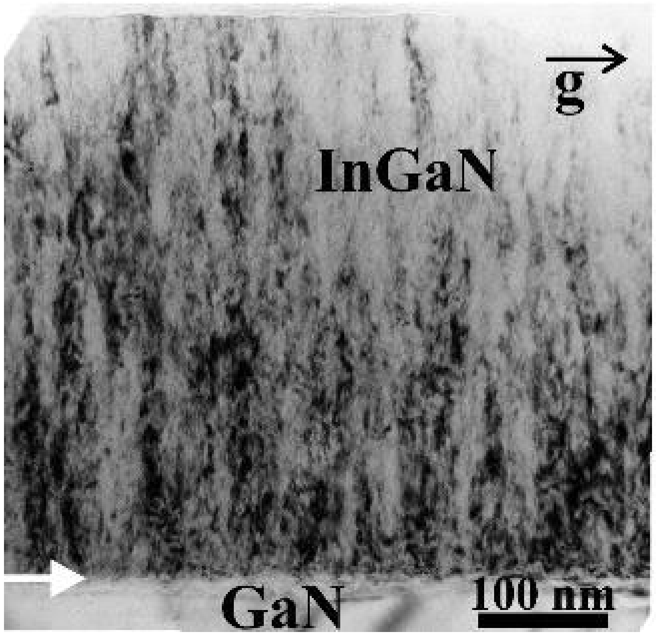
Integrated photocathode



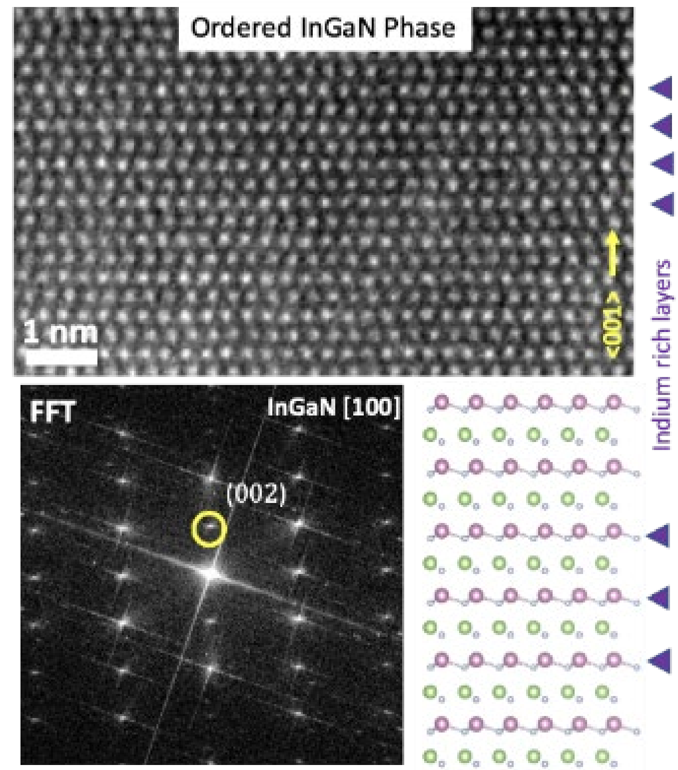
- We have investigated the design of InGaN/Si double-junction photocathode. The best performance is predicted for photoelectrode with a top $In_{0.46}Ga_{0.54}N$ (E_g ~1.8 eV) cell, with a photovoltage ~ 2 V and photocurrent density ~16.7 mA/cm^2, which promise a STH efficiency ~20%.

Accomplishments: *Controlled synthesis of Si-based tandem photoelectrodes*

We have demonstrated, for the first time, controlled synthesis of In-rich InGaN (E_g ~1.8 eV) directly on Si wafer with atomic ordering and low defect densities.



http://www.microscopy.cz/html/2233.html



Conventional InGaN

- Large dislocation densities
- Low PEC efficiency

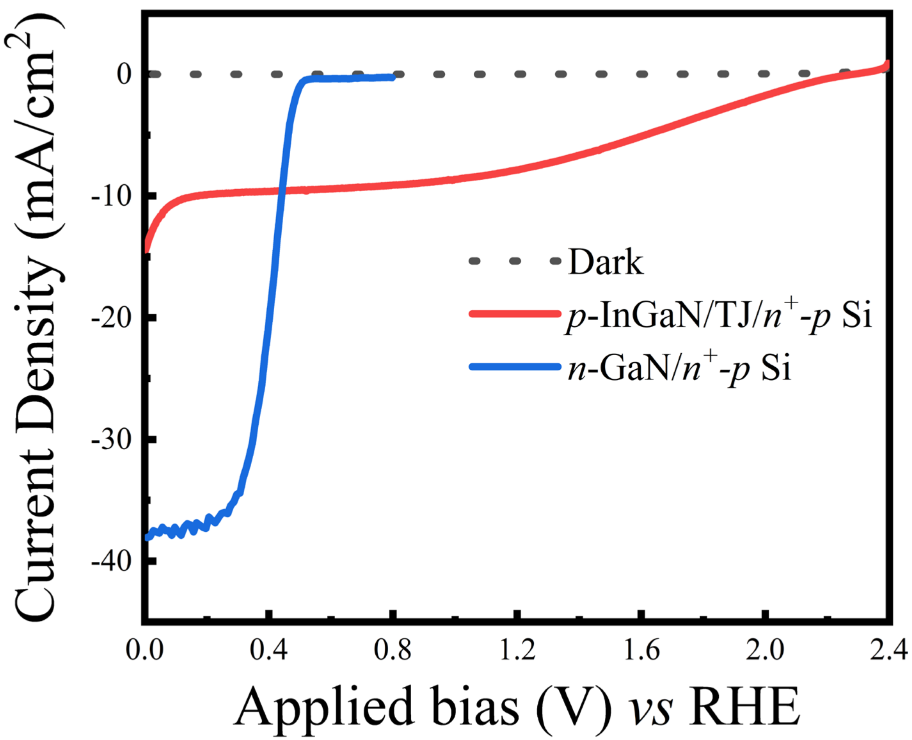
Atomically ordered InGaN

- Low defect densities
- High PEC efficiency

TEM/STEM images provided by R. Hovden at Univ. of Michigan.

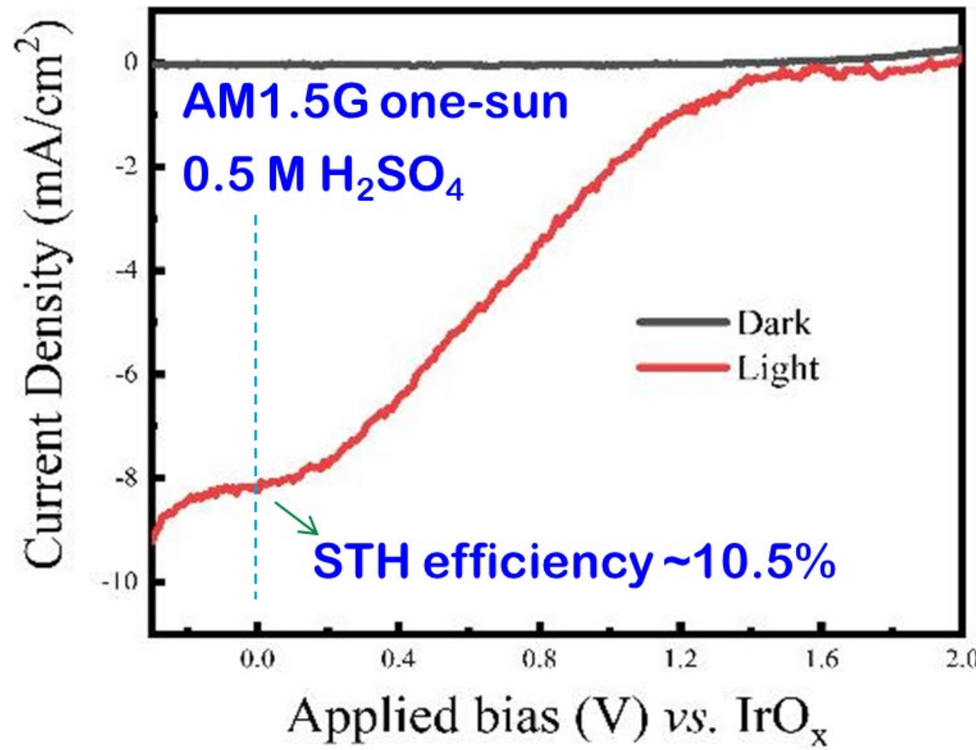
Accomplishments: *The first demonstration of Si-based double-junction photoelectrodes with STH efficiency >10%*

Three electrode measurement



Si/InGaN tandem electrode (red) shows a light-limited current density ~10 mA/cm^2, which can be further improved to >16 mA/cm^2 through optimization.

Two electrode measurement



Demonstrated a true STH efficiency ~10.5% in two-electrode, which meets part of the Go/No Go Criteria of Budget Period 2.

Accomplishments

Outlook and Projected Outcomes

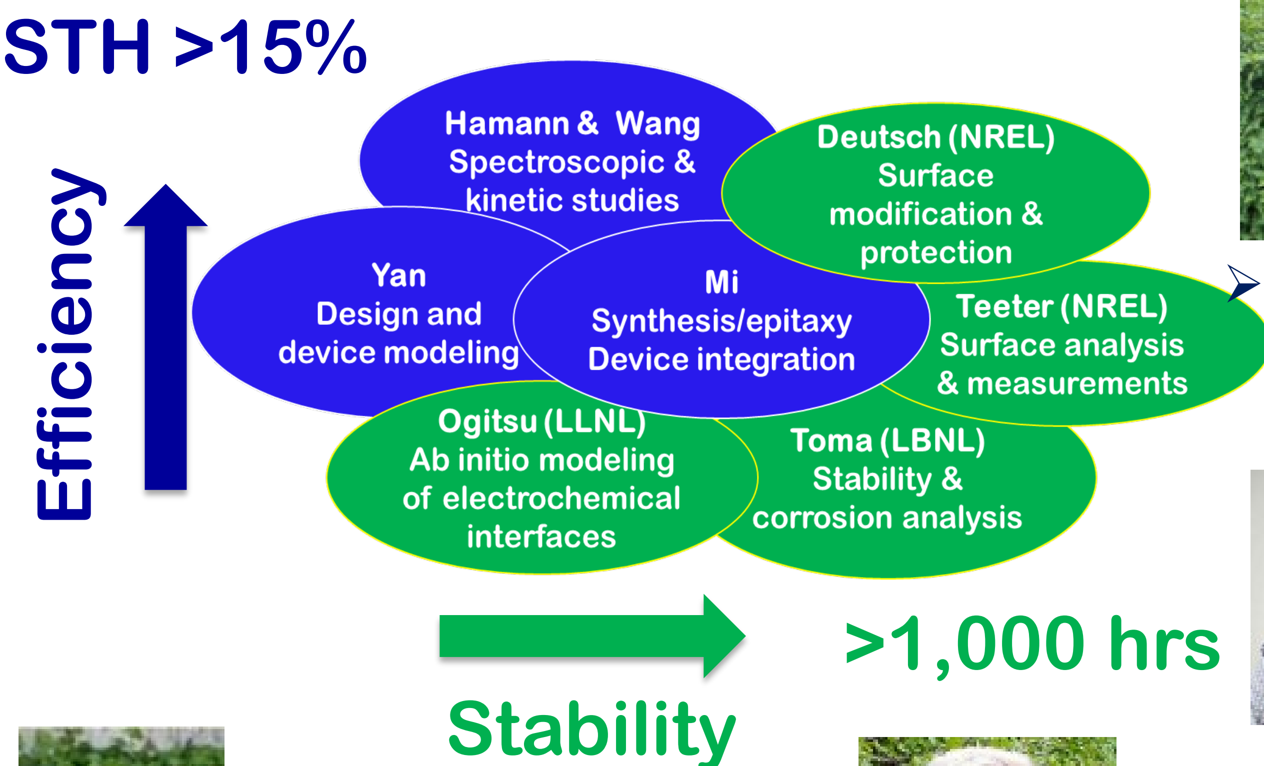
- Perform detailed spectroscopic and kinetic studies and further improve the STH efficiency.
- Perform a detailed investigation of the stability of InGaN and Si photoelectrodes, with the goal to achieve stable operation >500 hrs for the constituting single junction devices and >50 hrs for double-junction devices.

Confidence in meeting the Go/ No Go milestones: High

Major Impact

- This project will be instrumental to establish a Si-based platform for high efficiency PEC tandem water splitting devices and systems, which, to date, can only be achieved using prohibitively expensive GaAs-based materials.
- The stability of PEC water splitting devices will be fundamentally improved by utilizing N-terminated GaN protection layer.
- The semiconductor photoelectrodes are synthesized using industry ready materials, *e.g.,* Si and GaN based on standard semiconductor processing, and therefore the manufacture is controllable and scalable.

Collaboration effectiveness: *Role of the team members and nodes*



- **Francesca Toma, LBNL:** Photoelectrochemical AFM and STM

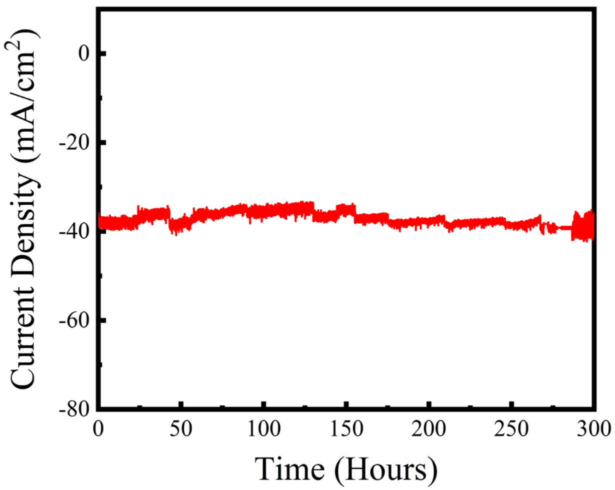
- **Todd Deutsch, NREL:** Surface modifications and protection

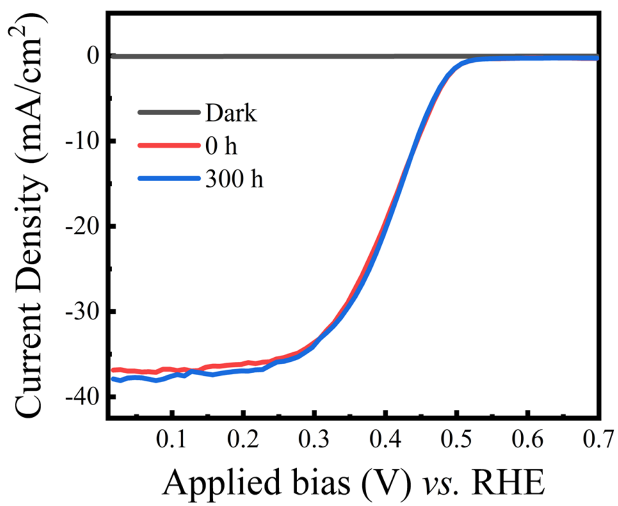
- **Tadashi Ogitsu, LLNL:** Ab initio modeling of electrochemical interfaces

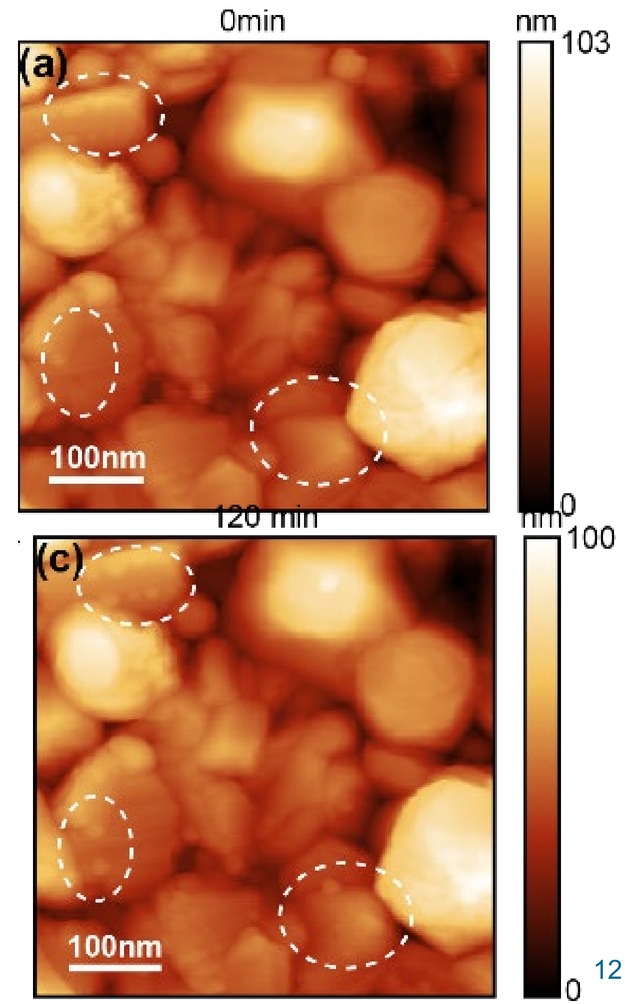
- **Glenn Teeter, NREL:** Surface analysis cluster tool, surface measurements

Collaboration Effectiveness

Teeter, Toma, Deutsch, Mi, and Wang studied the band alignment between GaN and Si, co-catalyst deposition, and PEC performance and demonstrated excellent stability of GaN/Si without extra surface protection.







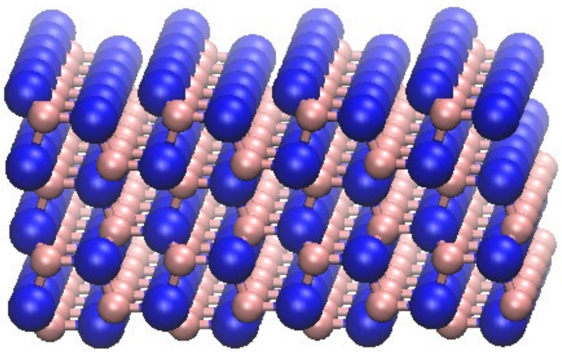
- **No performance degradation was observed for 300 hrs continuous solar water splitting.**
- **No change in morphology (other than some Pt particles) was measured during *in situ* AFM studies.**

Nano Lett., vol. 18, 6530, 2018.

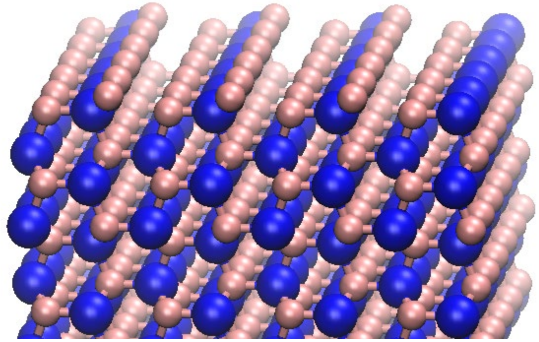
Collaboration Effectiveness

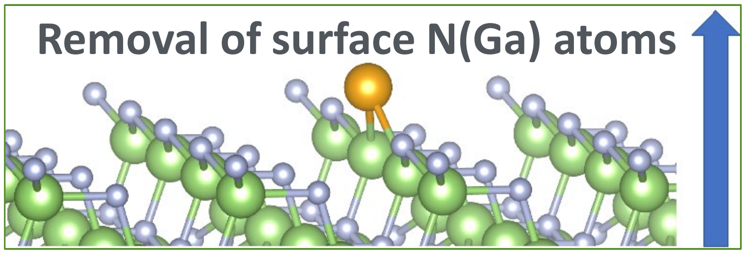
Inspired by experiments of Toma and Mi, Ogitsu conducted first-principles calculations and studied the origin for the stability of N-rich GaN.

N-rich surface



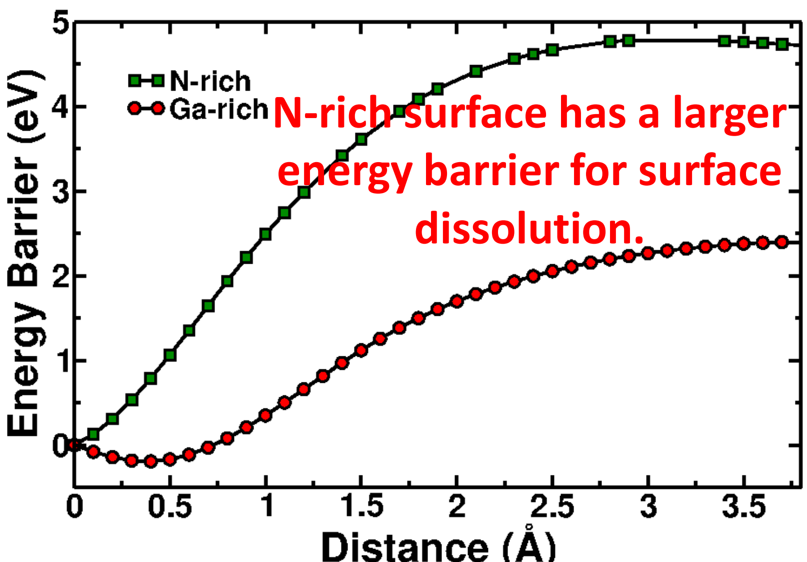
Ga-rich surface





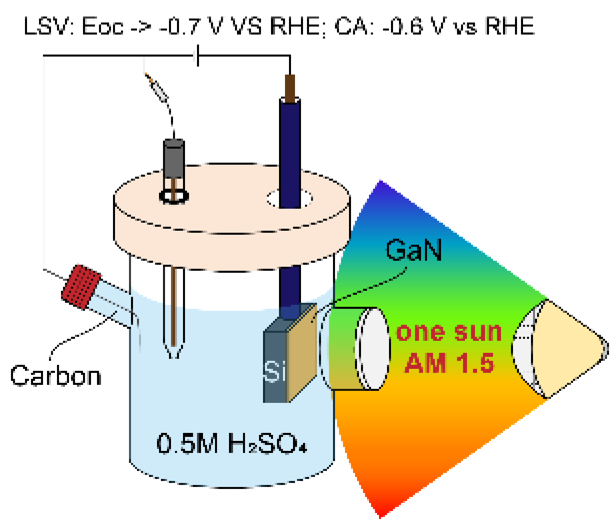
Nitrogen **Gallium**

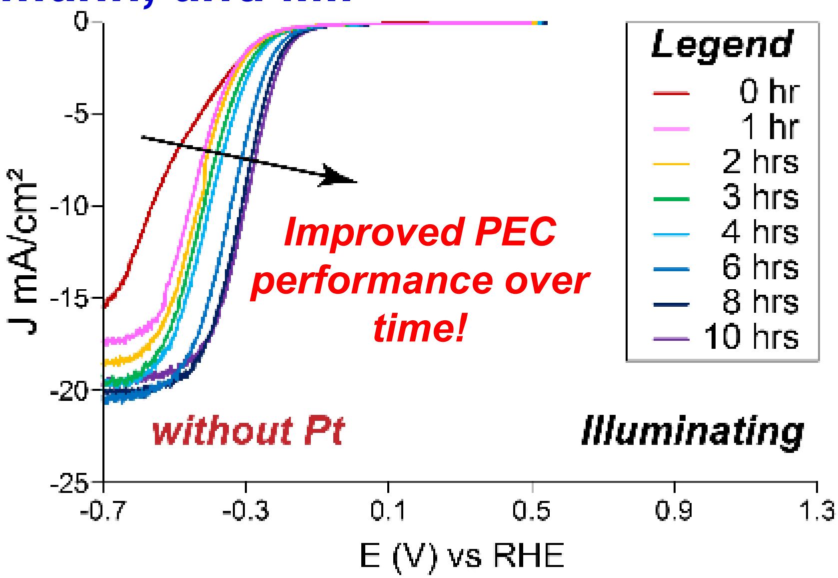
- **Ga-N bond length of the N-rich surface is almost 10% shorter than that of the Ga-rich one, indicating that the N-rich surface is more stable**
- **Similar conclusion is obtained by considering the energy barrier for dissolution of N- and G-rich surfaces**



Accomplishments

Toma and Mi discovered, for the first time, that a GaN/Si photocathode can exhibit improved performance, instead of performance degradation, under continuous solar water splitting. The underlying origin is being studied theoretically by Ogitsu and experimentally by Toma, in collaboration with Teeter, Wang, Hamann, and Mi.





- **GaN / Si photocathode showed continuous improvement in performance, i.e., positive shift of turn on voltage and fill factor, while is in stark contrast to the rapid degradation for conventional photocathode in solar water splitting.**

Collaboration: Effectiveness

- **Specific activities and accomplishments incorporating project data in the HydroGEN data hub.**

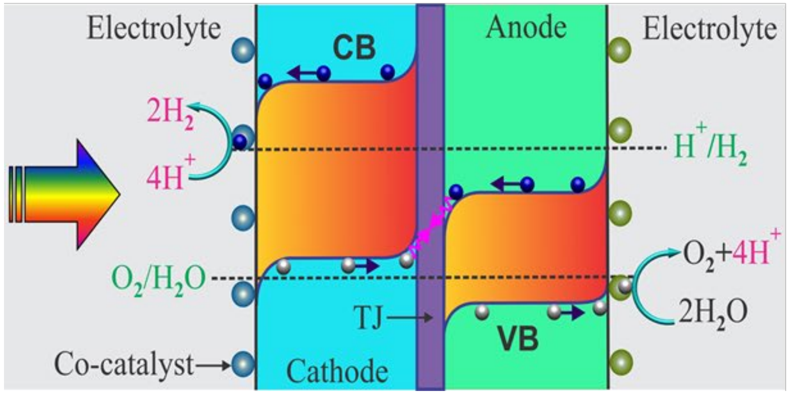
Project data, including materials design, synthesis, characterization, and testing results are incorporated in the HydroGEN data hub and shared among team members. The shared data include images, figures, and videos taken in the lab. These activities have proved to be effective and efficient in promoting collaboration and advancing the progress of this project.

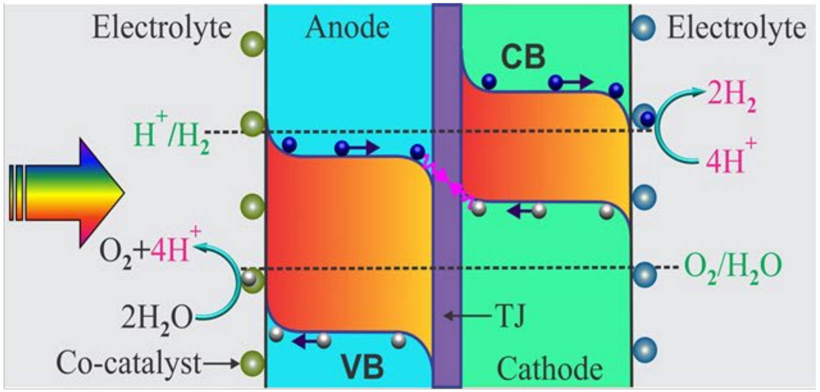
- **Expected benefits to the HydroGEN Consortium and the broader water-splitting R&D community**

To date, stable and efficient PEC water splitting devices do not exist. This project is focused on the use of industry-ready materials, e.g., Si and GaN to manufacture low cost, high efficiency PEC tandem water splitting devices and systems. We have achieved the most efficient Si-based double-junction photoelectrode. Moreover, we have discovered that N-terminated GaN can effectively protect against photocorrosion and oxidation, leading to highly stable solar water splitting that was difficult for conventional Si and III-V based photoelectrodes. Significantly, the semiconductor photoelectrodes are synthesized using standard semiconductor processing, and therefore the manufacture is controllable and scalable.

Relevance & Impact

- The STH conversion efficiency and cost targets for purified, 300 psi compressed H_2 gas are 20% STH and \$5.70 per kg H_2 by 2020. The tandem PEC device concept of stacking wide-bandgap and narrow-bandgap semiconductors is a proven method that can achieve the targeted STH efficiency. To date, all efficient tandem PEC devices are based on the state-of-the-art III-V semiconductor tandem photoelectrodes. However, the expensive GaAs substrates and photocorrosion severely limited its ability to achieve the cost goal.
- We aim to tackle the challenges of achieving efficient, cost-effective PEC water splitting devices by developing tandem photoelectrodes, which consist of a bottom Si light absorber and a 1.7-2 eV top light absorber (Ta_3N_5, BCTSSe, or InGaN). *High performance top photoelectrode is fabricated on large area Si wafer using nanowire tunnel junction, and is passivated by an ultrathin N-rich GaN to protect against photocorrosion and oxidation.*
- The outcome of this project is to develop monolithically integrated Si-based tandem photoelectrodes, with the objective to achieve high efficiency (up to 20%) and long-term stability (>1,000 hours) solar-to-H_2 conversion through PEC water splitting. The success of this project will help meet the DOE technical target for H_2 production from PEC water splitting.





Relevance & Impact

This project leverages the existing unique expertise and capabilities of HydroGEN Energy Materials Network (EMN). We have been working closely with the following to advance the proposed project:

1) Probing and Mitigating Chemical and Photochemical Corrosion of Electrochemical and Photoelectrochemical Assemblies, Francesca Toma, LBNL. With the unique *in situ* techniques, including photoelectrochemical AFM and STM, Toma revealed that GaN/Si photoelectrodes, without any extra surface protection, showed no sign of any performance degradation during continuous PEC water splitting, which is in stark contrast for the rapid degradation of conventional high efficiency photoelectrodes.
2) Surface Analysis Cluster Tool, Glenn Teeter, NREL. Dr. Teeter and his team members have performed surface characterization and XPS measurements of InGaN on Si wafer and have studied the band alignment between GaN nanostructures and Si and the photovoltage of various single and double-junction devices, which forms the basis for the design of high efficiency photoelectrodes.
3) Ab Initio Modeling of Electrochemical Interfaces, Tadashi Ogitsu, LLNL. This collaboration provides important insights of electrochemical interface and PEC device optimization through ab-initio modeling and computational materials diagnostics. Preliminary studies revealed the underlying mechanism for the extraordinary stability of N-rich GaN-based photoelectrodes.
4) Surface Modifications for Catalysis and Corrosion Mitigation, Todd Deutsch, NREL. Dr. Deutsch and his team members have been working on the co-catalyst deposition and surface protection to identify the best strategy to protect the surface against photocorrosion and oxidation.

Proposed Future Work

Proposed Scope:

- Budget Period 3 (M25-M36): (1) Detailed studies on the PEC performance and stability test of double-junction photoelectrodes and the correlation with the design and synthesis parameters. (2) Double-junction photoelectrodes with STH efficiency >15% and stable operation (>1,000 hrs)

Estimated Budget (excluding cost share): $375,000

Intended Outcomes:

- Double-junction photoelectrodes with efficiency >15% and stable operation (>1,000 hrs) under standard solar light illumination.

Impacts:

- Establish a Si-based low cost and scalable platform for high efficiency and highly stable PEC water splitting devices and systems.

Any proposed future work is subject to change based on funding levels.

Project Summary

- This project is focused on the development of Si-based high efficiency PEC tandem water splitting devices, with major innovations including:
  - The use of defect-free nanowire tunnel junction to fabricate 1.7-2.0 eV top photoelectrode directly on low cost, large area Si wafer.
  - The discovery of N-terminated GaN to protect against photocorrosion.
- Major achievements to date:
  - Established productive collaborations with four EMN nodes.
  - Demonstrated, for the first time, Si-based double junction photoelectrode with STH ~10%.
  - Discovered N-rich GaN and has demonstrated efficient and stable PEC water splitting without using any extra surface protection.
- The project is on the right track to meet Year 2 milestones.
- Success of this project will be instrumental to establish a low cost and scalable platform for high efficiency and highly stable PEC water splitting devices and systems by using industry ready materials, *e.g.,* Si and GaN.

Publications & Presentations

Journal publications since last AMR:

1. Y. Wang, S. Vanka, J. Gimb, Y. Wu, R. Fan, Y. Zhang, J. Shi, M. Shen, R. Hovden, and Z. Mi, "An In0.42Ga0.58N tunnel junction nanowire photocathode monolithically integrated on a nonplanar Si wafer," Nano Energy, vol. 57, 405, 2019.
2. S. Vanka, E. Arca, S. Cheng, K. Sun, G. A. Botton, G. Teeter, and Z. Mi, "A High Efficiency Si Photocathode Protected by Multi-Functional GaN Nanostructures," Nano Lett., vol. 18, 6530, 2018.
3. B. Zhou, X. Kong, S. Vanka, S. Chu, P. Ghamari, Y. Wang, N. Pant, I. Shih, H. Guo, and Z. Mi, "GaN nanowire as an outstanding linker of MoSx and planar silicon for photoelectrocatalytic water splitting", Nature Communications, vol. 9, 3856, 2018.
4. Y. He, S. Vanka, T. Gao, D. He, J. Espano, Y. Zhao, Q. Dong, C. Lang, Y. Wang, T. W. Hamann, Z. Mi, D. Wang, "Dependence of Interface Energetics and Kinetics on Catalyst Loading in a Photoelectrochemical System," Nano Res., accepted. DOI: 10.1007/s12274-019-2346-3.
5. Y. He, T. Hamann, D. Wang, "Thin Film Photoelectrodes for Solar Water Splitting," Chem. Soc. Rev., accepted, 2019. DOI: 10.1039/C8CS00868J.
6. Y. Wang, D. He, H. Chen, D. Wang, "Catalysts in Electro-, Photo- and Photoelectrocatalytic CO2 Reduction Reactions," J. Photochem. Photobio. C: Photochem. Rev., accepted, 2019. DOI: 10.1016/j.jphotochemrev.2019.02.002.
7. Y. Wang, C. Niu, D. Wang, "Metallic Nanocatalysts for Electrochemical CO2 Reduction in Aqueous Solutions," J. Colloid Inter. Sci., vol. 527, 95-106, 2018.
8. Y. He, D. Wang, "Toward Practical Solar Hydrogen Production," Chem., vol. 4, 405-408, 2018.
9. H. Hajibabaei, D. J. Little, A. Pandey, D. Wang, Z. Mi, T. W. Hamann; "Direct Deposition of Crystalline Ta3N5 Thin-Films on FTO for PEC Water Splitting" ACS Applied Materials and Interfaces, under revision.

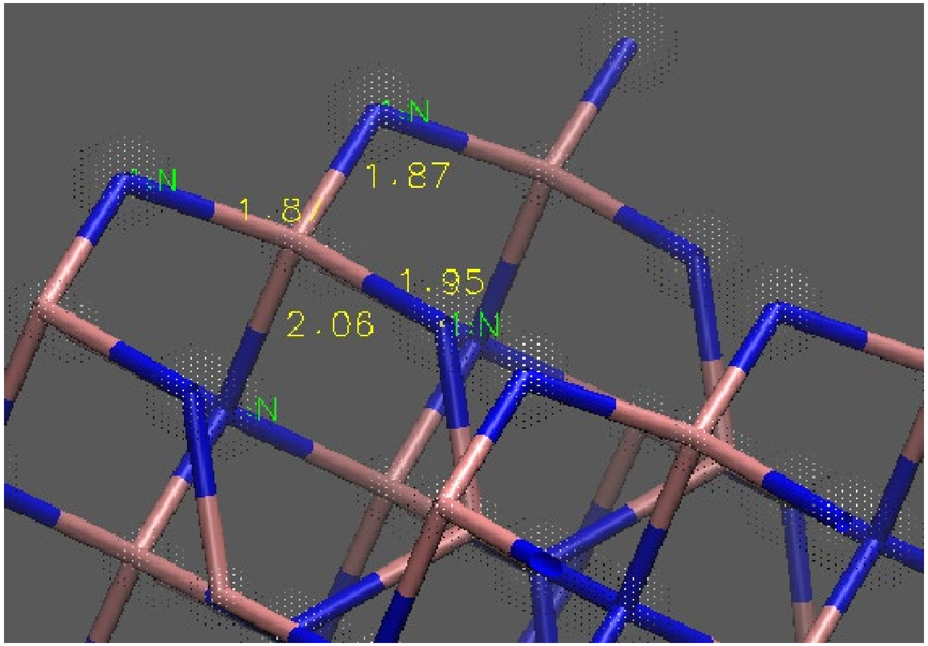
Conference presentations since last AMR:

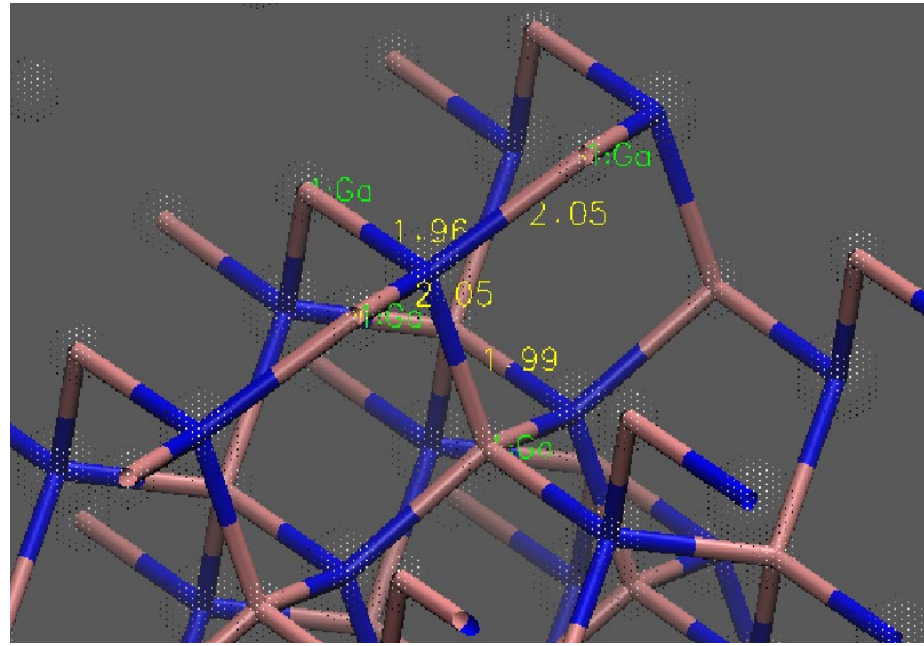
1. (Invited talk) Z. Mi, "Monolithically Integrated InGaN/Si Tandem Photoelectrodes for Efficient and Stable Photoelectrochemical Water Splitting," MRS Spring Meeting, Apr. 22-26, 2019, Phoenix, AZ.
2. F. A. Chowdhury, H. Guo and Z. Mi, "Surmounting the Carrier-transport and Stability-bottleneck of III-Nitride Nanowire Solar Water-splitting Device for Efficient and Sustainable Hydrogen Generation," MRS Fall Meeting, Boston, MA, Nov. 25-30, 2018.
3. S. Vanka, E. Arca, G. Teeter, and Z.M, "Photoelectron Spectroscopy Investigation of GaN/Si Heterostructures for Photoelectrochemical Water Splitting," MRS Fall Meeting, Boston, MA, Nov. 25-30, 2018.
4. F. A. Chowdhury, and Z. Mi, "Stable, Efficient and Industry-Friendly III-Nitride Nanowire Device for Visible Light Driven Sustainable Solar Hydrogen Generation," International Workshop on Nitride Semiconductors, Kanazawa, Japan, Nov. 11-16, 2018.
5. S. Vanka, S. Chu, Y. Wang, I. Shih, and Z. Mi, "High Efficiency, Monolithically Integrated (In)GaN/Si Photocathode for Stable Generation of Solar Fuels," 60th Electronic Materials Conference, Santa Barbara, CA, June 27-29, 2018.

Technical Backup Slides

Surface Models of N(Ga)-rich (1010) GaN

T. Ogitsu, LLNL





N-terminated surfaces

Ga-N bond contraction

Stable

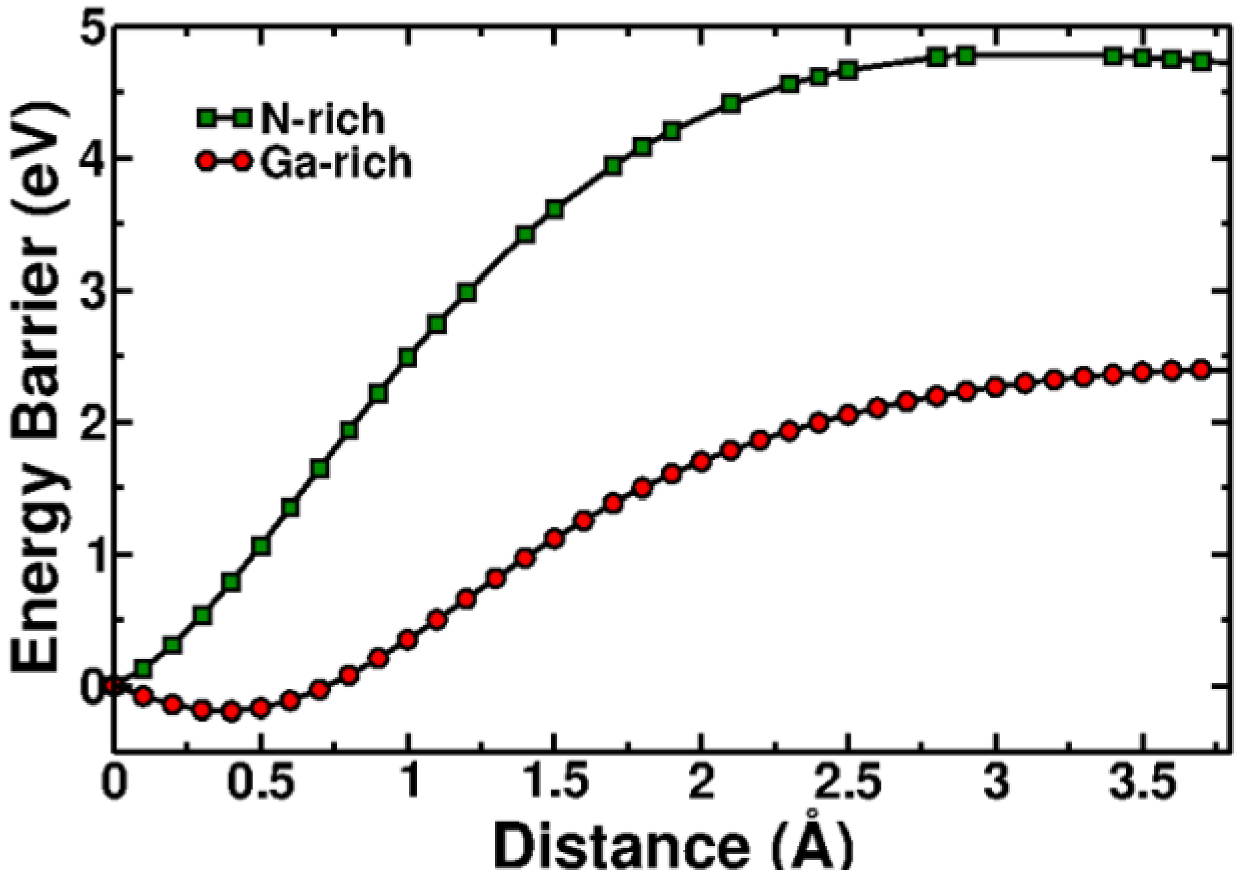
Ga-terminated surfaces

Larger Ga-N bond

Less stable

Surface Models of N(Ga)-rich (1010) GaN

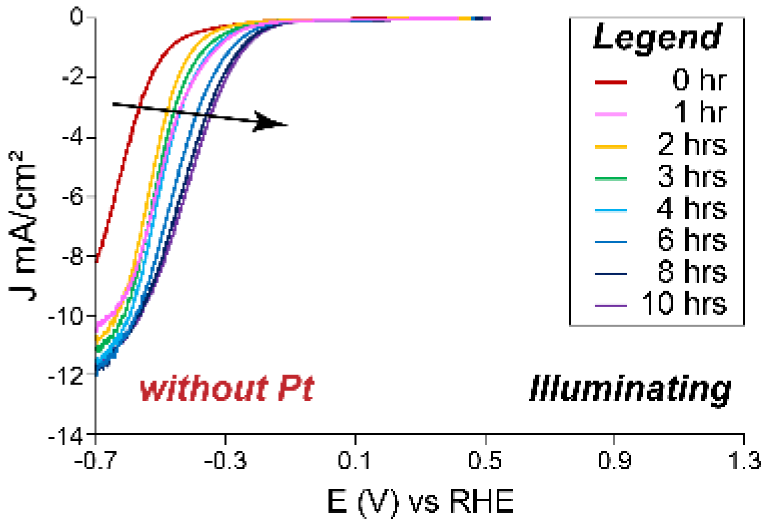
T. Ogitsu, LLNL

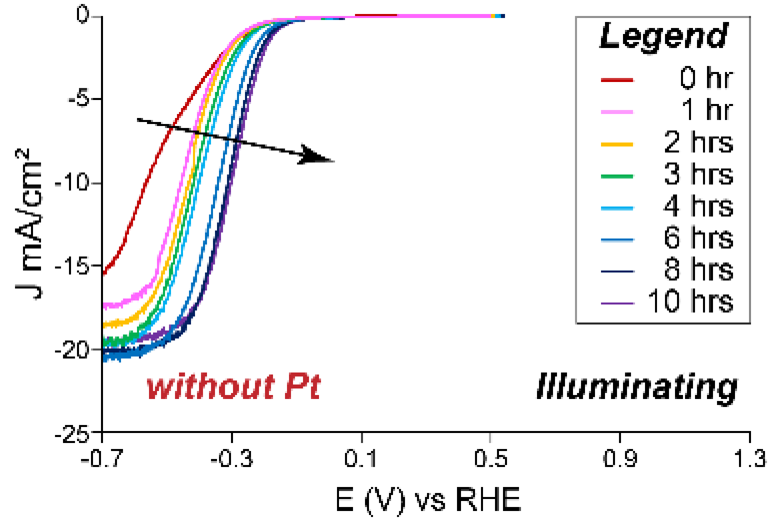


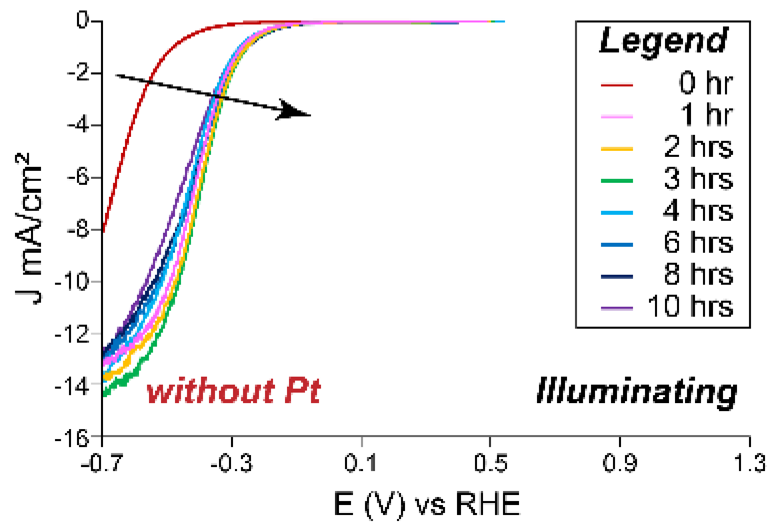
Preliminary studies by T. Ogitsu suggested that N-terminated surfaces are significantly more stable in aqueous solution, due to the extremely large energy barrier for dissociation.

PEC Performance of GaN Protected Si Photocathodes

F. Toma, LBNL





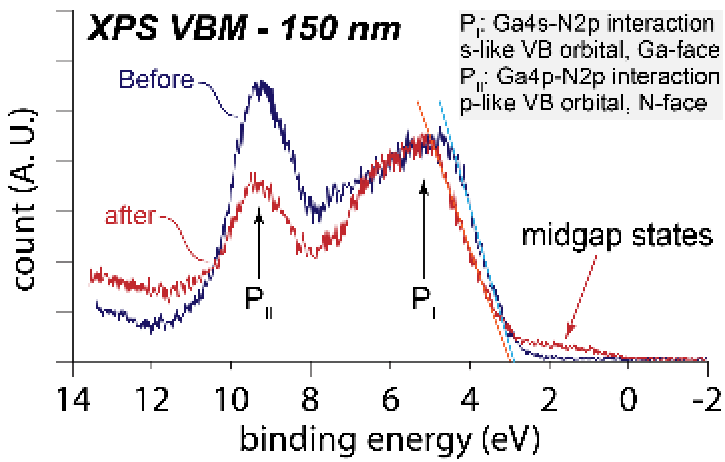


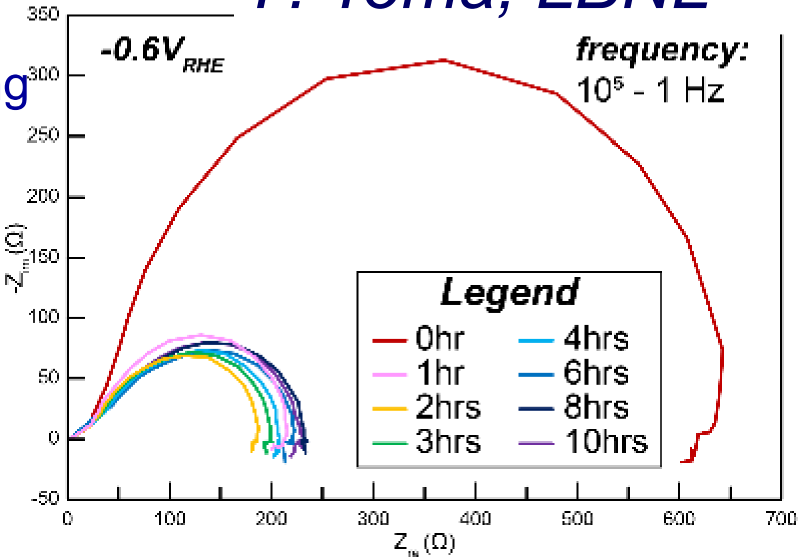
- GaN protected Si photocathodes with various thicknesses (5 to 150 nm) were studied and showed no degradation (initial performance improvement was observed).
- The performance is similar and has no dependence on the thickness of GaN, due the near-perfect conduction band alignment between GaN and Si. This is in direct contrast to conventional TiO_2 protection layer, which is compromises charge carrier transport.

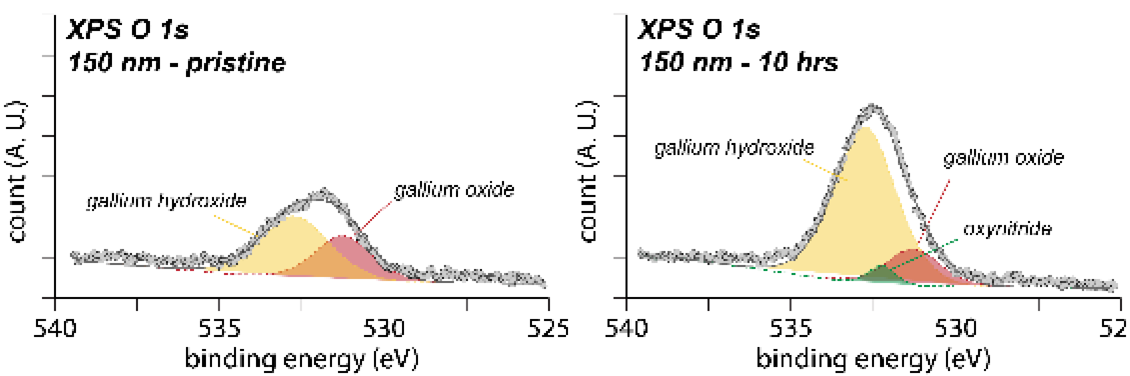
PEC Performance of GaN Protected Si Photocathodes

F. Toma, LBNL

GaN: Self-healing process for PEC water splitting



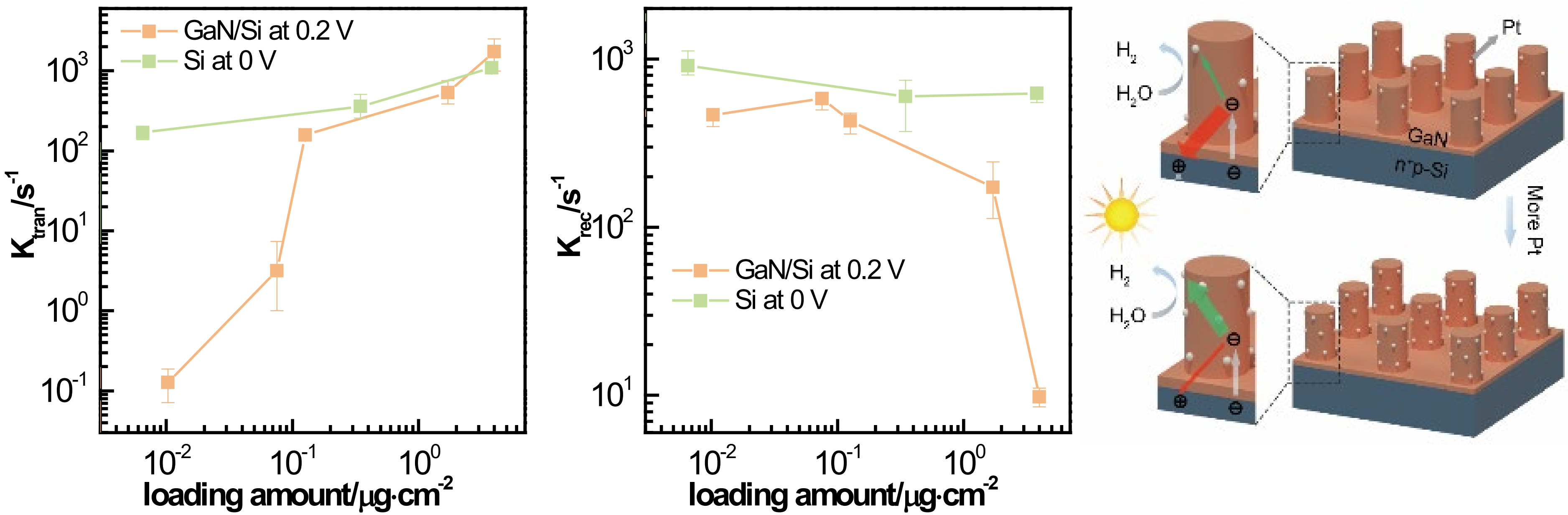




- It was evidenced by VBM that midgap states were formed after PEC testing. It is hypothesized that these midgap states correspond to the enhancement of PEC performance of GaN/Si, as a self-healing effect.
- Band edge was also modified, which also altered the surface band bending, giving rise to a more efficient charge transfer.
- Changing of the ratio between P_I and P_{II} together with O1s spectra also demonstrated that the surface got modified due to the photoelectrochemical reaction.
- EIS clearly evidenced that the surface of bare GaN/Si was modified during PEC testing, which is in consistent with LSV results, again suggesting a more efficient charge carrier extraction

The effect of co-catalyst loading: A direct comparison between Si and GaN/Si

D. Wang, BC



- Kinetic parameters under different Pt loading amount at GaN/Si interface were analyzed using IMPS.
- Higher Pt loading led to both faster charge transfer and reduced charge recombination at GaN/Si interface.
- Si without GaN only showed faster charge transfer with high Pt loading.