HydroGEN Seedling: Monolithically Integrated Thin-Film/Silicon Tandem Photoelectrodes for High-Efficiency and Stable Photoelectrochemical Water Splitting

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Contract No: DE-EE0008086

Subcontractors:
- Michigan State University, East Lansing, MI
- Boston College, Boston, MA
- University of Toledo, Toledo, OH

Project Start Date: October 1, 2017
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop monolithically integrated Si-based tandem photoelectrodes to achieve both high solar-to-hydrogen (STH) efficiency (>15%) and long-term stability (>1,000 hours) in spontaneous water splitting systems.

Fiscal Year (FY) 2019 Objectives

- Demonstrate InGaN/Si photoelectrodes with STH >10% under standard one-sun illumination.
- Demonstrate ultra-high stability (>500 h) using GaN/Si photocathode under standard one-sun illumination.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- **Materials Durability—Bulk and Interface:** Identify intrinsically durable and efficient materials for photoelectrochemical (PEC) hydrogen generation.
- **Integrated Device Configurations:** Develop efficient, stable integrated devices to meet the ultimate targets in PEC hydrogen generation.
- **Synthesis and Manufacturing: Develop s**calable manufacturing of PEC materials and devices.

Technical Targets

This project is developing monolithically integrated tandem photoelectrodes on low-cost, large-area Si wafer. The success of this project will provide the materials platform for PEC water splitting devices that help meet the following DOE PEC hydrogen production targets:

- STH energy conversion ratio: 20%
- PEC electrode cost: $200/m^2$.

FY 2019 Accomplishments

- Demonstrated InGaN/Si double-junction photocathode that can exhibit unassisted solar water splitting with STH >10%, the best performance ever achieved for a Si-based photoelectrode.
- Demonstrated that, without any extra surface protection, GaN/Si photocathode can exhibit ultrahigh stability of 3,000 h without any performance degradation at high photocurrent density >35 mA/cm^2 under one-sun illumination in a three-electrode cell, which is the best stability ever achieved for a PEC water splitting device.
- Demonstrated that double junction GaN/Si photocathode using surface-modified (with Pt and Al_2O_3) at 0 V vs. IrO_x, can exhibit high stability of 100 h without any performance degradation at photocurrent density ~8.4 mA/cm^2 under one sun illumination which corresponds to an STH efficiency ~10.3%.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

INTRODUCTION

The DOE STH conversion efficiency and cost targets for purified, 300 psi compressed hydrogen gas are 20% STH and $5.70/kg hydrogen 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 photo-corrosion severely limited their 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 1.7–2.0 eV top light absorber. High performance top photoelectrode will be fabricated on large-area Si wafer using nanowire tunnel junction and will be passivated by an ultrathin N-rich GaN to protect against photo-corrosion 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) in STH conversion through PEC water splitting. This project will be instrumental in establishing an 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 the 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. The success of this project will help meet the DOE technical target for hydrogen production from PEC water splitting.

APPROACH

In this project, we aim to address the challenges of achieving efficient, cost-effective, PEC water splitting systems by combining the following unique approaches.

- **We use Si as the bottom light absorber** to reduce the cost of the tandem water splitting devices, given its narrow energy bandgap and prevalence in the industry
- **We use a wide-bandgap GaN nanowire tunnel junction** to fabricate the top photoelectrodes on the Si platform. The GaN nanowire tunnel junction not only exhibits remarkably low resistivity but also further reduces the formation of defects and dislocations in the top light absorber because of the effective lateral surface stress relaxation
- **We use Ta_3N_5, BCTSSe, and $In_{0.5}Ga_{0.5}N$ semiconductors** as the top light absorber of the double-junction photoelectrodes. These materials have bandgaps in the range of 1.7–2.0 eV, can be controllably doped n or p-type, and exhibit large light absorption coefficients and superior charge carrier transport properties. Recent studies have further shown that the conduction and valence band edge positions of Ta_3N_5 and $In_{0.5}Ga_{0.5}N$ straddle the water splitting potentials, promising photovoltages larger than 1.23 V
- **We use surface treatment and catalyst loading** to protect electrodes from corrosion and optimize water oxidation efficiency. We will incorporate a non-oxide coating (e.g., GaN) to eliminate this detrimental effect. We also have developed the chemistry and expertise at integrating a variety of water oxidation co-catalysts with photoanodes, which we have shown to improve the Von by several hundred millivolts, which will be employed to optimize the performance of the proposed systems

The research team consists of four investigators, including Profs. Z. Mi at the University of Michigan, T. Hamann at Michigan State University, D. Wang at Boston College, and Y. Yan at the University of Toledo. During this project, we have established effective collaborations with the following nodes at the HydroGEN Energy Materials Network (EMN) to advance the proposed project.

1. “Surface Analysis Cluster Tool,” Glenn Teeter, National Renewable Energy Laboratory (NREL). Surface characterization and in-operado X-ray photoelectron spectroscopy (XPS) measurements are being performed on the various top photoelectrodes.

2. "Probing and Mitigating Chemical and Photochemical Corrosion of Electrochemical and Photoelectrochemical Assemblies," Francesca Toma, Lawrence Berkeley National Laboratory (LBNL). With the unique in situ techniques, including photoelectrochemical atomic force microscopy (AFM) and scanning tunneling microscopy (STM), Toma has provided services to understand the behaviors of our top electrode materials, and this information proves invaluable to our optimization efforts.
3. "Surface Modifications for Catalysis and Corrosion Mitigation," Todd Deutsch, NREL. This collaboration helps to identify the best strategy to protect the surface against photocorrosion and oxidation.
4. "Ab Initio Modeling of Electrochemical Interfaces," Tadashi Ogitsu, Lawrence Livermore National Laboratory (LLNL). This collaboration provides important insights into electrochemical interface and PEC device optimization through ab-initio modeling and computational materials diagnostics.

RESULTS

Design of High-Efficiency InGaN/Si Double-Junction Photocathodes

In Year 2, we used SCAPS software to simulate the device performance of InGaN/Si double-junction tandem photocathodes. To model the performance of our tandem photoelectrode, we constructed the tandem device using two subcells, including a p-InGaN top subcell and a p-Si/n-InGaN bottom subcell, connected by a p^{++}/n^{++} InGaN tunnel junction (TJ). Figure 1a shows the SCAPS simulated energy band diagram for an InGaN/Si double junction photoelectrode. For SCAPS modeling, the two subcells were coupled optically, and the current-voltage behavior of individual cell was simulated individually under an assumption that the TJ had the Ohmic contact with both subcells. The performance of the tandem photoelectrode was then calculated by considering the two diodes connected in series following the Kirchhoff's Law. The optical and electrical properties of materials used for the experiments were adopted to simulate the performance of real devices. Variations in InGaN nanowires were considered to optimize the power output of the tandem photoelectrodes.

To identify the optimal design for the InGaN top photoelectrode, researches calculated photocurrent-voltage curves for the tandem devices with various bandgaps (1.7–2.3 eV) and thicknesses (300–1,500 nm) for the p-InGaN top cell. Figure 1b shows the contour plot of the theoretical power conversion efficiency of InGaN/Si double junction photoelectrodes. For wide-bandgap p-InGaN (E_g >2.0 eV, %In = 40%), the photocurrent of the tandem photocathode is limited by the p-InGaN subcell. Increasing the thickness of the top absorber layer increases the total photocurrent and thus the efficiency. In contrast, for low bandgap p-InGaN (E_g <1.7 eV, %In = 50%), the photocurrent of the tandem photocathode is limited by the Si subcell. Increasing the p-InGaN thickness decreases the total current of the tandem device. For the p-InGaN with a bandgap of ~1.8 eV (%In = 46%), optimal thicknesses of 600 nm to 900 nm are identified. This configuration shows a promise to achieve a theoretical power conversion efficiency of 33.3% and provide a guideline for tuning the bandgap of InGaN nanowires for achieving such high efficiency.

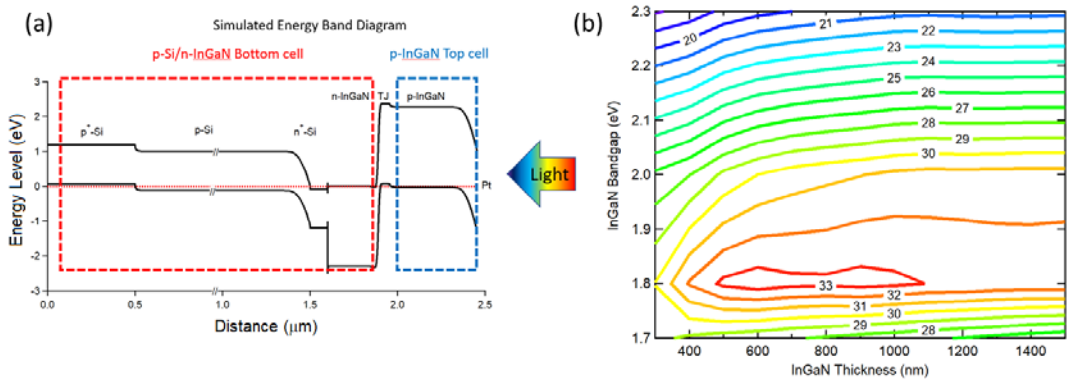

Figure 1. (a) Simulated energy band diagram for an InGaN/Si double junction photoelectrode. (b) Theoretical power conversion efficiencies of the tandem photoelectrodes with various InGaN thickness and bandgap values.

Synthesis, Performance and Long-Term Stability Studies of InGaN/Si Double-Junction and GaN/Si Photocathodes

Experimentally we have investigated the synthesis, performance, and long-term stability of InGaN/Si photocathodes. The stability studies of GaN/Si photocathode, schematically shown in Figure 2a, is first described. Pt was incorporated as co-catalyst. Unique to the GaN/Si heterointerface is that the conduction band edges are near-perfectly aligned between GaN and Si (a recent discovery through collaborations between Mi and G. Teeter at NREL), which leads to efficient extraction of photo-generated charge carriers (electrons) from the underlying Si absorber [1]. This is the foundation for the achievement of high-efficiency photoelectrodes using InGaN and Si. Shown in Figure 2b, Pt-decorated n^+-GaN nanowires on n^+-p Si photocathode can exhibit ultrahigh stability of 3,000 h at a large photocurrent density (>35 mA/cm^2) without any performance degradation, which is the best-reported stability at such high current level for any photoelectrodes without any extra surface protection. The stability experiments are conducted in 0.5M H_2SO_4 solution under AM 1.5G one-sun illumination at 0 V *vs.* RHE. Figure 2c shows that the *J-V* curves after 3,000 h experiment is nearly the same as the 0th h curve. The underlying mechanisms for such unprecedented long-term stability in photoelectrochemical water splitting are due to the N-terminated surfaces of GaN nanostructures, which can protect the underlying Si absorber against photo-corrosion and oxidation [2,3]. Detailed stability studies performed by F. Toma at LBNL are further described in Section 3.

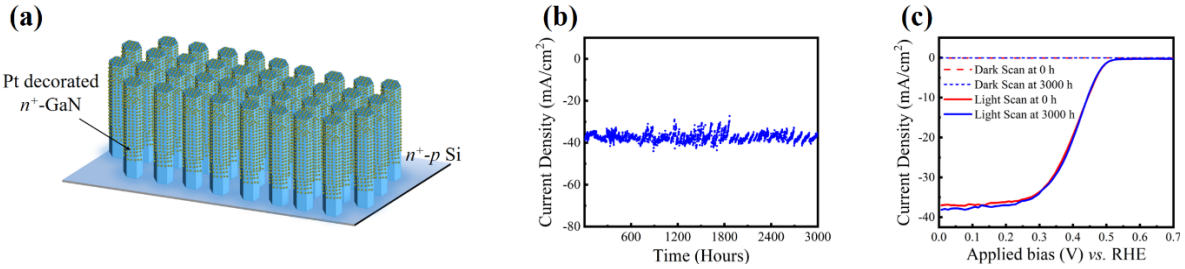

Figure 2. (a) Schematic of Pt decorated GaN/Si photocathode. (b) Chronoamperometry long-term stability measurements for platinized n+- GaN nanowires/n+-p Si photocathode at 0 V *vs.* RHE in 0.5M H_2SO_4 under AM 1.5G one sun illumination. (c) *J-V* comparison between 0 h (red) and 3,000 h (blue) under AM 1.5G one-sun illumination and dark (red and blue dotted).

The synthesis, performance, and stability studies of high-efficiency InGaN/Si photocathode is subsequently described. As shown in Figure 3a, the double-junction photocathode consists of p-InGaN top light absorber, p^{++}-InGaN/n^{++}-InGaN tunnel junction, and n^+-p Si bottom light absorber. Photo-generated electrons from n^+-p Si wafer are extracted by n^+-InGaN nanowire arrays. The bottom n^+-InGaN acts as an active hole blocking layer for n^+-p Si. Photo-generated electrons from the bottom Si cell then recombine with the photo-generated holes from the top p-InGaN layer in the tunnel junction. Due to the unique polarization induced tunnel junction incorporated in the nanowires, the charge carriers from the top p-InGaN cell (photo-generated holes) can readily tunnel and recombine with charge carriers from bottom Si cell (photo-generated electrons) in the tunnel junction. The PEC reaction is conducted in 0.5M H_2SO_4 solution using surface-modified (with Pt and Al_2O_3) double-junction photocathode and IrO_x as the working and counter electrode, respectively. The maximum photocurrent density for the optimized double-junction photocathode (see Figure 3b), at 0 V *vs.* IrO_x, is ~ 8.4 mA/cm^2 under AM 1.5G one-sun illumination in 0.5M H_2SO_4, which corresponds to an STH efficiency ~10.3%, which is the highest reported STH value for a Si-based photoelectrode. As shown in Figure 3c, the stability of the photocathode is measured at 0 V *vs.* IrO_x for a duration of 100 h in 0.5M H_2SO_4 under AM 1.5G one-sun illumination without any degradation. The achievement of a record high STH value for Si-based photoelectrode is due to the superior quality InGaN nanostructures and the low resistivity tunnel junction. In addition, these nanostructures have N-terminated surfaces, which can protect against corrosion and oxidation to achieve long-term stability [2,3]. With the use of GaN surface protection, we have also demonstrated III-V photocathodes can exhibit STH efficiency >12% and unprecedented long-term stability.

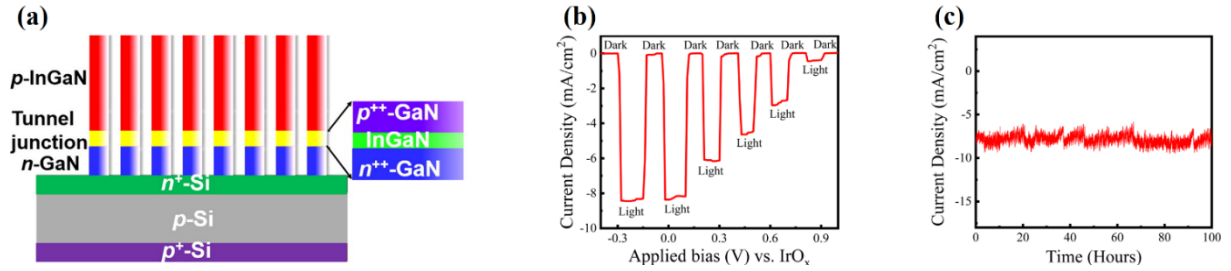

Figure 3. (a) Schematic of double junction photocathode consisting of p-InGaN top junction and an Si bottom junction. The InGaN and Si are connected through a tunnel junction. (b) Chopped *J-V* curve of double-junction photocathode under dark and AM 1.5G one-sun illumination. (c) Chronoamperometry measurements for double junction at 0 V vs. IrO_x in 0.5M H_2SO_4 under AM 1.5G one-sun illumination.

Studies on the Underlying Mechanism for Ultrahigh Stable Ga(In)N/Si Photocathodes

Long-term stability tests and characterization have been carried out at LBNL node (F. Toma). The PEC results revealed that the performance of GaN protected Si photocathode exhibited a self-healing behavior, *i.e.*, the performance continuously improves (evidenced by that the on-set potential gradually shifting towards the positive side) along with the proceeding of the chronoamperometric test (Figure 4a). EIS (Figure 4b) suggested an improved charge transfer at the solid/liquid interface, while the equivalent circuit (Figure 4c) bears out the improvement of charge transfer efficiency. Such improved performance during PEC testing has never been observed in any other photoelectrodes and provides clear evidence that Ga(In)N/Si photoelectrodes are positioned to address the stability issues of conventional photoelectrodes.

To better understand the mechanism of such a self-healing effect, several state-of-the-art surface characterization techniques were employed to analyze the tested surface.

1. The photoconductive AFM was performed on both 10 h CA tested samples and pristine samples. The results indicated that after the test, under illumination, no bias was required to have measurable photocurrent, which is significantly better than the sample before PEC testing. Furthermore, the photocurrent originates from the sidewall of the GaN grain, indicating the m-plane has higher charge carrier extraction efficiency, which is consistent with previous studies [2].
2. Angle-resolved XPS was conducted to examine the top and the side surface of the GaN tested and pristine samples. TEM/EELS was also carried out on the tested sample to see the surface composition locally in nanoscale.

For future work, analysis from these measurements, along with theoretical studies conducted in LLNL node, will be used to further understand the unprecedented ultrahigh stability for GaN/Si photocathodes.

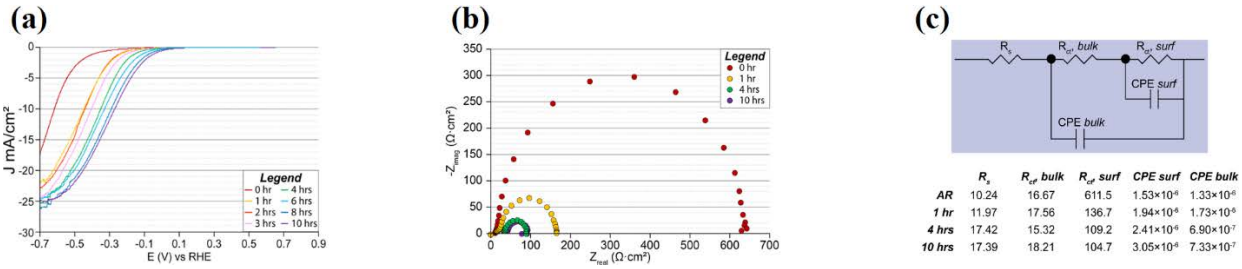

Figure 4. (a) *J-V* curves of GaN/Si after test with different durations; (b) EIS of GaN/Si after 1 h, 4 h, and 10 h; (c) equivalent circuit.

CONCLUSIONS AND UPCOMING ACTIVITIES

In conclusion, this project is focused on the development of Si-based high-efficiency PEC tandem water splitting devices, with major innovations including the use of nanowire tunnel junction to fabricate 1.7–2.0 eV top photoelectrodes on Si wafers, and the discovery of N-terminated GaN to protect against photo-corrosion. In

this project, we have demonstrated InGaN/Si double-junction photocathode with STH of >10% and further demonstrated photocathodes with a stability of ~3,000 h in AM 1.5G one-sun illumination in 0.5M H_2SO_4 without any performance degradation, *i.e.,* without any loss of photocurrent, onset potential, or efficiency, at a very high photocurrent density of >35 mA/cm^2 without using any extra surface protection. Detailed studies performed at LBNL further confirmed the unprecedented stability of such photoelectrodes.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. 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.* 12 (2019): 2378. https://doi.org/10.1007/s12274-019-2346-3.
2. H. Hajibabaei, D.J. Little, A. Pandey, D. Wang, Z. Mi, T.W. Hamann, "Direct Deposition of Crystalline Ta_3N_5 Thin-Films on FTO for PEC Water Splitting", *ACS Appl. Mater. Interfaces*, 11, 17, (2019): 15457-15466.
3. B. Shan, S. Vanka, T.T. Li, L.T. Gautier, M. K. Brennaman, Z. Mi, T.J. Meyer, "Binary molecular-semiconductor p–n junctions for photoelectrocatalytic CO_2 reduction", *Nature Energy*, 4, 4, (2019): 290-299.
4. Y. Wang, J. Schwartz, J. Gim, R. Hovden, Z. Mi, "Stable Unassisted Solar Water Splitting on Semiconductor Photocathodes Protected by Multifunctional GaN Nanostructures", *ACS Energy Lett.* 4, 7, (2019): 1541-1548.
5. Y. Wang, Y. Wu, J. Schwartz, S.H. Sung, R. Hovden, Z. Mi, "A Single-Junction Cathodic Approach for Stable Unassisted Solar Water Splitting", *Joule* (2019): DOI: https://doi.org/10.1016/j.joule.2019.07.022.
6. R. Fan, Z. Mi, M. Shen, "Silicon based photoelectrodes for photoelectrochemical water splitting", *Optics Express*, 27, 4, (2019): A51.
7. Y. Wang, S. Vanka, J. Gim, Y. Wu, R. Fan, Y. Zhang, J. Shi, M. Shen, R. Hovden, Z. Mi, "An $In_{0.42}Ga_{0.58}N$ tunnel junction nanowire photocathode monolithically integrated on a nonplanar Si wafer", *Nano Energ.* 57, (2019): 405–413.
8. R. Fan, S. Cheng, G. Huang, Y. Wang, Y. Zhang, S. Vanka, G.A. Botton, Z. Mi, M. Shen, "Unassisted solar water splitting with 9.8% efficiency and over 100 h stability based on Si solar cells and photoelectrodes catalyzed by bifunctional Ni–Mo/Ni", *J. Mater. Chem. A*, 7, (2019): 2200–2209.

Conference Presentations

1. **Invited:** Z. Mi and S. Vanka, "Monolithically Integrated InGaN/Si Tandem Photoelectrodes for Efficient and Stable Photoelectrochemical Water Splitting," MRS Spring Meeting, Phoenix, AZ, April 22-26, 2019.
2. **Plenary:** Z. Mi, "Emerging applications of III-nitride nanocrystals," International Conference on Nitride Semiconductors, July 7-12, 2019, Bellevue, Washington.
3. **Keynote:** Z. Mi, "Gallium nitride: A platform towards practical artificial photosynthesis," 102nd Canadian Chemistry Conference and Exhibition, Quebec City, Canada, June 3-7, 2019.
4. S. Vanka, E. Arca, G. Teeter and Z. Mi, "High Efficiency, Monolithically Integrated GaN/Si Photocathode for Stable Generation of Solar Fuels", MRS Fall Meeting & Exhibit Boston, MA, November 25-30, 2018.
5. S. Vanka, B. Zhou, N. Pant, A. Roberts, K. Kulkarni and Z. Mi, "InGaN/Si Tandem Photocathode for High Efficiency Unassisted Solar Water Splitting", Electronic Materials Conference, University of Michigan, Ann Arbor, MI, June 26-28, 2019.
6. S. Vanka, B. Zhou, N. Pant, A. Roberts, K. Kulkarni and Z. Mi, "InGaN/Si Tandem Photocathode for High Efficiency Unassisted Solar Water Splitting", International Conference on Nitride Semiconductors, July 7-12, 2019, Bellevue, Washington.

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3. M.G. Kibria, R. Qiao, W. Yang, I. Boukahil, X. Kong, F.A. Chowdhury, M.L. Trudeau, W. Ji, H. Guo, F.J. Himpsel, L. Vayssieres, Z. Mi, "Atomic-Scale Origin of Long-Term Stability and High Performance of p-GaN Nanowire Arrays for Photocatalytic Overall Pure Water Splitting." *Adv. Mater.* 28, no. 38 (2016): 8388–8397.