

Molybdenum Disulfide as a Protection Layer and Catalyst for Gallium Indium Phosphide Solar Water Splitting Photocathodes

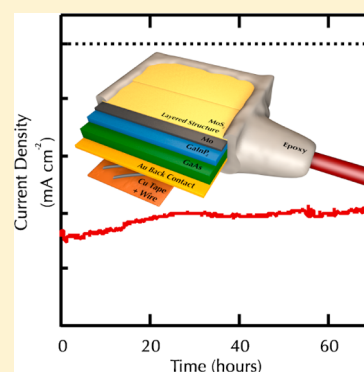
Reuben J. Britto,[†] Jesse D. Benck,[†] James L. Young,[‡] Christopher Hahn,[†] Todd G. Deutsch,[‡] and Thomas F. Jaramillo^{*,†}

[†]Department of Chemical Engineering, Shriram Center, Stanford University, 443 Via Ortega, Stanford, California 94305, United States

[‡]Chemistry and Nanoscience Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, Colorado 80401, United States

S Supporting Information

ABSTRACT: Gallium indium phosphide (GaInP₂) is a semiconductor with promising optical and electronic properties for solar water splitting, but its surface stability is problematic as it undergoes significant chemical and electrochemical corrosion in aqueous electrolytes. Molybdenum disulfide (MoS₂) nanomaterials are promising to both protect GaInP₂ and to improve catalysis because MoS₂ is resistant to corrosion and also possesses high activity for the hydrogen evolution reaction (HER). In this work, we demonstrate that GaInP₂ photocathodes coated with thin MoS₂ surface protecting layers exhibit excellent activity and stability for solar hydrogen production, with no loss in performance (photocurrent onset potential, fill factor, and light-limited current density) after 60 h of operation. This represents a 500-fold increase in stability compared to bare p-GaInP₂ samples tested in identical conditions.



One pathway toward economical and sustainable hydrogen production is to use the energy in sunlight to split water into hydrogen and oxygen. Designing a device that accomplishes this task efficiently and with long-term stability has been deemed the “Holy Grail” of electrochemistry.¹ Realizing this holy grail would not only significantly reduce the carbon footprint of the 50 billion kg a year hydrogen production industry but could also open up the hydrogen economy as a feasible and sustainable alternative to our current fossil-fuel-based economy.²

Gallium indium phosphide (GaInP₂) is a nearly ideal large band gap semiconductor for application as the top absorber in a dual-junction tandem absorber water-splitting device.^{3,4} It has been used in conjunction with a gallium arsenide (GaAs) bottom absorber in an overall water-splitting cell with 12.4% solar-to-hydrogen (STH) efficiency, one of the highest STH efficiencies for an integrated photoelectrochemical (PEC) water-splitting device reported to date.^{5,6} However, this device showed significant instability within hours of testing due to the corrosion of GaInP₂ in the acidic conditions optimal for the hydrogen evolution reaction (HER).⁵ Instability due to corrosion is prevalent among many semiconductor photoelectrodes, and thin-film protection schemes have been developed to address this issue.⁷ While substantial progress has been made protecting several semiconductors including Si, GaAs, GaN, InP, and CdTe, photoelectrodes of GaInP₂ have remained particularly challenging to stabilize.⁷

Earth-abundant molybdenum sulfide nanomaterials have the potential to enhance both stability and catalysis in GaInP₂

photocathodes through a thin-film protection scheme. Due to the low permeability through the basal planes of its layered structure, its excellent stability in acidic electrolyte, and the high activity of its edge sites for the HER, a thin coating of crystalline MoS₂ can provide effective surface protection while boosting catalytic activity.^{8–10} Recent studies have demonstrated the effectiveness of MoS₂ as a protection layer and catalyst on silicon photocathodes.^{10,11}

Herein, we report the use of a thin coating of MoS₂ as a surface protection layer to create highly active, precious-metal-free, stable GaInP₂ photocathodes. After 60 h of testing, there was no loss in activity (photocurrent onset potential, fill factor, and light-limited current density), and the MoS₂ and GaInP₂ materials remained largely unchanged in the system. This is in contrast to a bare GaInP₂ system, which showed catastrophic failure and complete corrosion of GaInP₂ within a few hours of testing. This study, in concert with our previous results on Si photocathodes,¹¹ highlights the promise of molybdenum disulfide as a catalytically active thin-film protection scheme for many different unstable semiconductor water-splitting devices.

A diagram of the p-GaInP₂/MoS₂ photocathode is shown in Figure 1a. The MoS₂ coating was synthesized by a partial thermal sulfidization of a sputtered thin film of Mo metal (see

Received: March 10, 2016

Accepted: May 4, 2016

Published: May 19, 2016

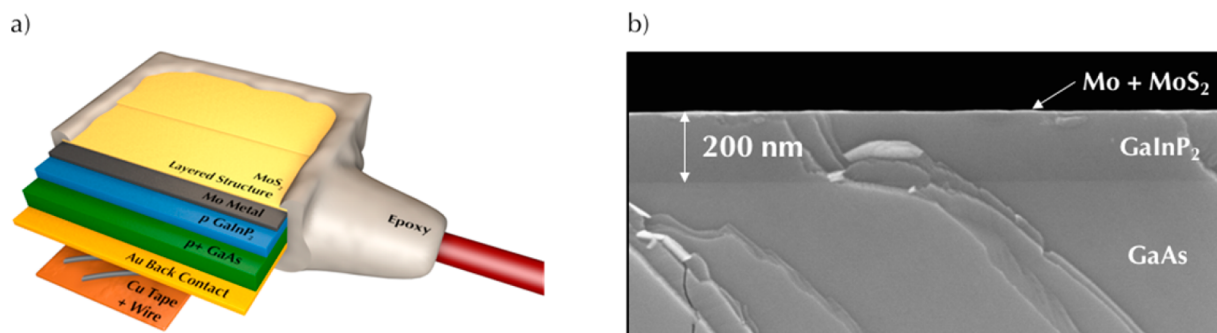


Figure 1. p-GaInP₂/MoS₂ device structure. (a) Schematic of a fully synthesized p-GaInP₂/MoS₂ photocathode. (b) Cross-sectional SEM image of the p-GaInP₂/MoS₂ surface region. These images illustrate that the surface of the device consists of a thin Mo + MoS₂ layer, a ~200 nm-thick p-GaInP₂ layer, and a substrate layer of degenerately-doped p-GaAs.

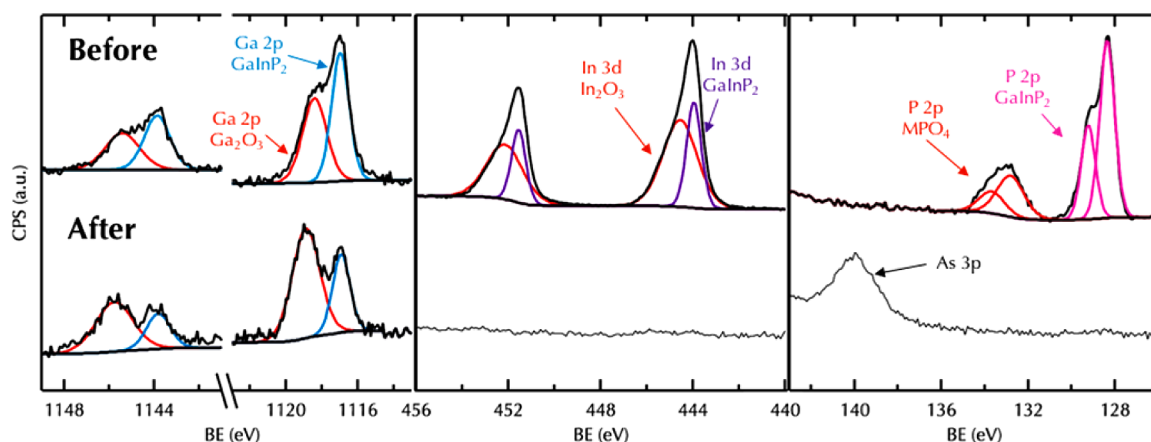


Figure 2. XPS measurements of the bare p-GaInP₂ device before and after the electrochemical stability measurement. Before testing, the structure contains Ga and In in the 3+ oxidation state, corresponding to p-GaInP₂, Ga₂O₃, and In₂O₃, indicating the presence of a surface oxide. The structure also contains P in both the 3- and 5+ oxidation states, corresponding to p-GaInP₂ and the metal phosphate, respectively. After testing, the In and P peaks are no longer present and there exists a new As peak. This indicates the complete removal of the p-GaInP₂ layer exposing the GaAs substrate.

the [Experimental Methods](#) section). This method was chosen to create a thin, conformal surface coating of MoS₂ that provides a barrier to the electrolyte, catalyzes the HER, and minimizes parasitic light absorption.¹¹

To confirm that the desired structure was successfully fabricated, we performed cross-sectional scanning electron microscopy (SEM), as shown in [Figure 1b](#). The SEM image reveals three layers. The bottom layer is the degenerately-doped GaAs substrate used for epitaxial growth of the p-type GaInP₂ layer above it. Above the p-type GaInP₂ layer is the thin layer of Mo metal and MoS₂, which can be seen as the bright contrast region atop the surface in [Figure 1b](#). Our synthesis is identical to one performed previously¹¹ on a crystalline silicon substrate that was characterized with cross-sectional transmission electron microscopy (TEM). On the basis of these studies, we expect the MoS₂ layer on our devices to consist of several conformal stacked basal planes of MoS₂ parallel to the GaInP₂ surface. These reside on top of a thin layer of Mo metal, and the entire thickness of the layers above the crystalline p-type GaInP₂ is expected to be ~5 nm.

The cross-sectional SEM further reveals the thickness of the p-type GaInP₂ layer to be ~200 nm. While this is below the thickness needed (>2 μm) for maximal absorption of the AM1.5G spectrum at 1 sun illumination (see [Supporting Information Figure S1](#)), the ~200 nm GaInP₂ film is sufficient for the focus of this study, investigating the activity and stability of p-GaInP₂/MoS₂ photocathodes. Improvements in semi-

conductor performance could be achieved through a number of strategies, including thicker films of p-GaInP₂ that can reach its theoretically attainable ~19 mA cm⁻² photocurrent and fabricating surface n⁺p emitter junctions to maximize the photovoltage.^{12–14} Furthermore, detailed studies of the energetics of the GaInP₂ and the GaInP₂/Mo/MoS₂ interface would provide a greater understanding of the device that could be leveraged to improve its activity and its stability.

To further characterize the composition and chemical state of the MoS₂ coating and bare p-GaInP₂ surface, we performed X-ray photoelectron spectroscopy (XPS) on the photocathodes. [Figure 2](#) shows the peaks for an as-received bare p-GaInP₂ sample. The peaks observed in the Ga 2p, In 3d, and P 2p regions can each be deconvoluted into two spin-orbit doublets. The Ga 2p_{5/2} peak with a binding energy of 1117 eV and the In 3d_{5/2} peak with a binding energy of 444 eV indicate that both Ga and In exist in a 3+ oxidation state, corresponding to GaInP₂. The Ga 2p_{3/2} and In 3d_{3/2} peaks with slightly higher binding energies (1118.4 and 444.6 eV, respectively) indicate the presence of Ga and In in another 3+ oxidation state, corresponding to their native surface oxides.^{15,16} The P 2p peaks indicate the presence of P in both the 3- and 5+ oxidation states, corresponding to GaInP₂ and a metal phosphate, respectively.^{17,18} These XPS peaks verify the existence of a conformal bare GaInP₂ film on GaAs.

[Figure 3](#) shows peaks for a freshly synthesized p-GaInP₂/MoS₂ photocathode before testing. The peaks observed in the

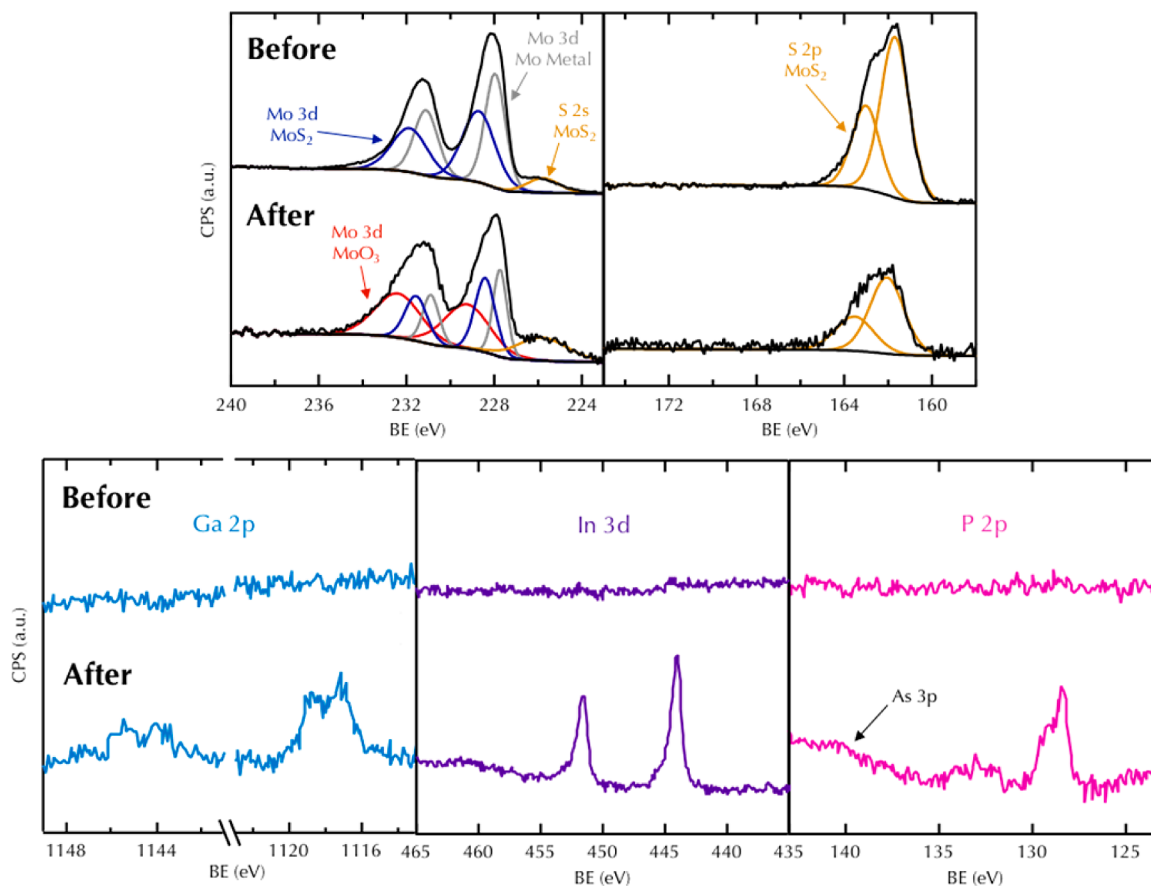


Figure 3. XPS measurements of the p-GaInP₂/MoS₂ device before and after the electrochemical stability measurement. Before testing, the structure contains Mo in the 4+ oxidation state corresponding to MoS₂. The second doublet arises from Mo metal. The sulfur binding energy matches the expected value for MoS₂. There is no presence of Ga, In, or P peaks before testing. After testing, the composition and chemical state remain very similar. Most of the molybdenum still exists as MoS₂ and Mo metal, but there is a new peak corresponding to Mo 6+ indicating the presence of MoO₃. The sulfur also still exists in a similar oxidation state. Ga, In, P, and As peaks are now present in the spectra, indicating the exposure of the GaInP₂ layer and its corrosion to further expose the GaAs substrate.

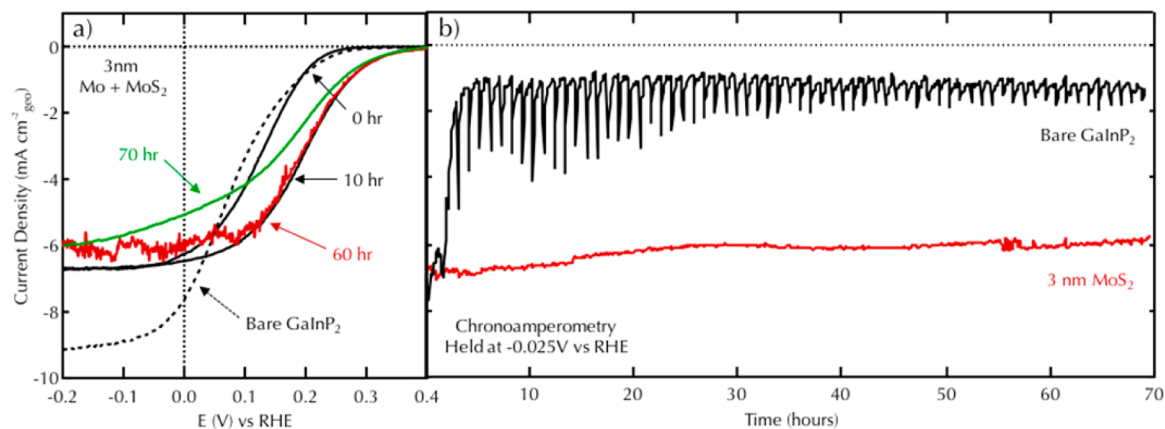


Figure 4. Electrochemical stability measurements of the bare p-GaInP₂ and p-GaInP₂/MoS₂ photocathodes. (a) LSVs collected at 0 and 60 h for the p-GaInP₂/MoS₂ photocathodes indicated no loss in performance and an increase in onset potential relative to the bare p-GaInP₂ photocathode. The LSV at 70 h indicates a decline in fill factor for the p-GaInP₂/MoS₂ device. (b) Chronoamperometry (CA) measurements at $E = -0.025$ V versus RHE. These indicate a loss of light-limited photocurrent for the bare p-GaInP₂ device within a few hours of testing while the light-limited photocurrent for the p-GaInP₂/MoS₂ device remains stable for 70+ hours.

Mo 3d region indicate that the molybdenum exists in both the reduced metallic state and the 4+ oxidation state, which is consistent with MoS₂. There is no evidence of molybdenum in the 6+ state corresponding to MoO₃.^{8,19} The S 2p region shows a single spin-orbit splitting doublet with a binding energy

corresponding to sulfur in MoS₂.^{8,19} These XPS peaks verify the existence in our system of the Mo/MoS₂ layer as observed in the TEM characterization of MoS₂-Si photocathodes.¹¹

The PEC performance of bare p-GaInP₂ and p-GaInP₂/MoS₂ photocathodes was evaluated in a three-electrode electro-

chemical cell with 3 M sulfuric acid electrolyte. The working electrodes were illuminated with simulated solar irradiance calibrated to “one sun” based on the AM1.5G standard.²⁰ The performance of the photocathodes was measured using chronoamperometry (CA) holding the potential at -0.025 V versus the reversible hydrogen electrode (RHE) and periodically (every hour) performing linear sweep voltammetry (LSV). As shown in Figure 4, the photocurrent onset potential, defined here as the potential required to reach -0.1 mA cm⁻², is 0.28 V versus RHE for the bare p-GaInP₂ photocathode. The p-GaInP₂/MoS₂ photocathode had a similar onset potential to begin with but over the course of 10 h showed consistent improvement until it stabilized at 0.36 V versus RHE for the next 50 h. This improvement in onset is most likely due to exposure of MoS₂ edges sites, which are more active for HER relative to the basal plane sites.²¹ The exact mechanism for this improvement is unclear but may be due to a number of factors, including the corrosion of any MoO₃ that may be present in trace amounts in the Mo/MoS₂ layer. MoO₃ is unstable in sulfuric acid and would dissolve rapidly during the beginning of the experiment, exposing any concealed MoS₂ edge sites.⁸ Another factor could be modification of the energetics of the semiconductor/catalyst junction to mitigate effects such as Fermi level pinning as the catalyst is exposed to the electrolyte.²² The improved onset of the p-GaInP₂/MoS₂ photocathode compared to the bare p-GaInP₂ photocathode demonstrates the advantage of using a protection layer that doubles as a catalyst. However, the as-deposited MoS₂ thin film is not optimized to expose the active edge sites, which are present in densities orders of magnitude lower than those which can be achieved with three-dimensional nanostructured MoS₂ materials. As a result, we expect to see an increase in HER activity for our p-GaInP₂/MoS₂ photocathodes versus our bare p-GaInP₂ photocathodes, but this activity should not be as high as what could be achieved using the best MoS₂ catalysts.^{8,23,24}

Figure 4 shows that the light-limited current density of the bare p-GaInP₂ is -9.5 mA cm⁻². This value represents the yield of incident photons that are converted into current. An optimally thick (>2 μm) and perfectly absorptive GaInP₂ semiconductor (no reflection or recombination losses) can attain a maximum light-limited current density of ~ 19 mA cm⁻² under 1 sun illumination (see the Supporting Information). A 200 nm thick perfectly absorptive GaInP₂ semiconductor can be expected to attain a maximum light-limited current density of ~ 12 mA cm⁻² (see Supporting Information, Figure S1), suggesting that our bare p-GaInP₂ photocathode may be subject to reflective losses. This result is expected given that no antireflective or light-trapping strategies were used in these electrodes. Work on a similar GaInP₂ PEC system established that Fresnel normal incidence reflectance can account for 20–30% loss in maximal achievable external quantum efficiency.²⁵ The light-limited current density of the p-GaInP₂/MoS₂ is ~ 6 mA cm⁻², indicating that the Mo/MoS₂ layer is responsible for parasitic absorption and/or interfacial recombination losses. Optical absorbance measurements were performed on a Mo/MoS₂ layer deposited on a quartz slide (see Supporting Information, Figure S2). The Mo/MoS₂ layer was synthesized in an identical manner to that of the p-GaInP₂/MoS₂ photocathodes and absorbed approximately 40% of the incident light with photon energies above the band gap of GaInP₂. A similar percentage drop ($\sim 40\%$) was observed in the light-limited current density of the p-GaInP₂/MoS₂ photo-

cathode compared to bare p-GaInP₂, indicating that optimizing the Mo/MoS₂ to minimize losses in light penetration could lead to improved photocathode performance. Previous work on Si/MoS₂ photocathodes also suggests that parasitic absorption in the Mo-containing layers is the primary culprit for the reduced light-limited current.¹¹ Future work will focus on minimizing this parasitic absorption by attempting to make the Mo/MoS₂ layer thinner.

The onset potential, fill factor, and light-limited current density are examined as metrics of stability for bare and p-GaInP₂/MoS₂ over the course of 60 h (Figure 4). The bare p-GaInP₂ showed a decrease in onset potential, fill factor, and light-limited current density within minutes, and a complete catastrophic failure (loss of most of the light-limited current) of the device within several hours. This occurs because most of the p-GaInP₂, the photoactive material, has dissolved into the electrolyte (see the XPS analysis above). On the other hand, the p-GaInP₂/MoS₂ demonstrated stability of the onset potential, fill factor, and light-limited current density for 60 h. The onset potential showed an increase, and the fill factor remained nearly unchanged, while the slight decrease and noise in the light-limited current density can be attributed to an accumulation and sporadic detachment of bubbles around the working electrode. The light-limited current density does remain stable well beyond 60 h, suggesting no catastrophic failure, but the onset and fill factor start decreasing after 60 h. The p-GaInP₂/MoS₂ photocathodes maintained ($>90\%$ of initial) their light-limited current density over 500× longer than the bare p-GaInP₂ photocathodes.

As shown in Figures 2 and 3, the XPS spectra collected after the stability test explain why the bare p-GaInP₂ catastrophically fails while the p-GaInP₂/MoS₂ does not. The XPS spectra obtained for the bare p-GaInP₂ photocathodes after the 100 h stability test show no peaks in the In 3d or P 2p regions and only peaks in the Ga 2p and As 3p regions (Figure 2). This indicates that the p-GaInP₂ corrodes away, revealing the GaAs epitaxial growth substrate. The loss of the light-limited current density within a few hours most likely correlates with the complete corrosion of the bare p-GaInP₂ photocathodes. For the p-GaInP₂/MoS₂, the peaks for the Mo metal and MoS₂ remain, but there are now Mo 6+ oxidation peaks. The large full width half-max (FWHM) of these peaks suggests the presence of Mo 5+ species as well.⁸ This indicates that the MoS₂ may be subject to corrosion over very long-term operation, exposing the Mo metal underneath, which oxidizes to MoO₃. MoO₃ is unstable in sulfuric acid and dissolves rapidly; therefore, it most likely formed upon exposure to air after the test.⁸

Furthermore, we see small peaks in the Ga 2p, In 3d, and P 2p regions and faint peaks in the As 3p region that were absent in the XPS spectra of the samples prior to testing. This indicates that p-GaInP₂ was exposed and subsequently corroded to expose the GaAs growth substrate over the course of this 100 h experiment. The strong Mo and S XPS peaks and the presence of the In and P XPS peaks indicate that most of the Mo/MoS₂ and p-GaInP₂ remain, which explains why the light-limited photocurrent is maintained well past 60 h (the time after which the onset potential and fill factor started declining). This suggests that instability of the p-GaInP₂/MoS₂ photocathodes may be caused by small-scale failure (e.g., pinholes) of the MoS₂. These small-scale failures expose the p-GaInP₂, which may quickly corrode away, exposing the degenerately doped GaAs substrate. The exposed GaAs may

act as a shunt for the device, impairing both the fill factor and onset potential of the device without significantly affecting the light-limited photocurrent density.²⁶ The details of this mechanism are currently being studied. Mitigation of these failure mechanisms could significantly extend the lifetimes of these devices.

The p-GaInP₂/MoS₂ devices presented in this work are highly active and stable precious-metal-free photocathodes for solar hydrogen production from water. They demonstrate that a very thin, conformal coating of MoS₂ can significantly improve the stability of p-GaInP₂ photocathodes, maintaining >90% of their initial light-limited current density over 500× longer than that of bare p-GaInP₂ photocathodes. As this protection scheme has been used successfully on silicon photocathodes, this work further highlights the potential for MoS₂ to be used as a thin-film protection scheme for many different semiconductor water splitting devices that are unstable in acid. Future efforts to engineer the catalyst layer, for example, thickness, morphology, and interfaces, offer opportunities to further improve photoelectrode activity and stability.

■ EXPERIMENTAL METHODS

Device Synthesis. Bare p-GaInP₂ and MoS₂-coated p-GaInP₂ (p-GaInP₂/MoS₂) photocathodes were synthesized from single-crystal zinc-doped (10¹⁷ cm⁻³) p-type GaInP₂ films grown on GaAs wafers. These films were grown by organometallic vapor-phase epitaxy to a thickness of ~200 nm on a 3 in. diameter degenerately p-doped GaAs(100) substrate wafers 4° offcut toward 111B. Ohmic back contacts were made to the substrate back by evaporation of Ti/Au (20 nm/350 nm).

The wafers to be coated with MoS₂ were diced and then cleaned with two 5 min sonications in standard acetone and isopropanol solvents (J.T. Baker). Following cleaning, the wafers were transferred, within 10 min, to a DC magnetron sputter coater. A thin layer of Mo metal with a nominal thickness of 3.6 nm was deposited onto the cleaned wafers at a rate of 7.2 nm min⁻¹. After Mo deposition, the wafers were sulfidized in 90% H₂/10% H₂S gas in a tube furnace held at 250 °C for 1 h to create the surface MoS₂ layer.

Physical and Chemical Characterization. X-ray photoelectron spectra of the bare p-type GaInP₂ wafers and newly synthesized p-GaInP₂/MoS₂ photocathodes were collected using a Phi VersaProbe Spectrometer with an Al K α source. Binding energies were calibrated to the adventitious C 1s peak at 284.6 eV.

SEM cross-sectional images were obtained using an FEI Magellan XHR microscope operated with a beam voltage of 5.0 kV.

Electrochemical Characterization. Back contacts to the p-GaInP₂ electrodes were made by connecting a stranded wire to the rear Au layer using copper tape as a conductive adhesive and a Ga–In eutectic (Aldrich) to ensure electrical contact was made. The electrodes were mounted in inert epoxy (Loctite Hysol 9462) and cured for at least 24 h to protect the back contact from exposure to electrolyte before testing. The working electrode area of each sample was measured using a digital photograph and was 0.1–0.2 cm².

Electrochemical measurements were performed in a three-electrode configuration using a Bio-Logic potentiostat (VSP) in a two-compartment glass cell (Adams and Chittenden Scientific Glassware). Both sides of the cell contained 3 M sulfuric acid prepared with Millipore water (18.2 M Ω -cm). The compartments were separated by a proton-conducting Nafion

membrane (50.8 μ m thick, Fuel Cells Etc.). The working electrodes were the bare p-GaInP₂ and p-GaInP₂/MoS₂ photocathodes, the reference electrode was Hg/Hg₂SO₄ in saturated K₂SO₄, and the counter electrode was an IrO_x/Ir wire. The working electrode and reference electrode were placed in the same compartment ~1 cm apart, and the counter electrode was placed in the other compartment to minimize cross-contamination. The working electrode was illuminated through a fused silica window, and the working electrode compartment was purged with H₂ gas prior to each measurement. Potentials were calibrated to the RHE scale using platinum working and counter electrodes in H₂-purged electrolyte.

The light source used for illuminated measurements was a 150 W xenon arc lamp (ABET, class ABA solar simulator) with a borosilicate slide to reduce output in the UV region. The irradiance incident on the electrode surface was measured using an Ocean Optics Jax EL 200-XR1 spectrometer and calibrated to 1 sun simulated solar illumination.²⁰

The PEC performance of the photocathodes was measured using LSV and CA. The activity of the photocathodes was measured periodically using linear sweep voltammograms from +0.5 to -0.4 V versus RHE at 10 mV s⁻¹. Between these measurements, the potential was held at -0.025 V versus RHE and the current was averaged in 300 s increments to study the light-limited photocurrent. The electrodes and electrolyte were not disturbed during the 100 h stability test except to refill the saturated K₂SO₄ solution in the reference electrode.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.6b00563.

Additional details on light absorption in the catalyst and the relation between light-limited current density and semiconductor thickness (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jaramillo@stanford.edu. Phone: (650) 498 6879.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This Letter presents results from an NSF project (Award Number CBET-1433442) competitively selected under the solicitation “NSF 14-15: NSF/DOE Partnership on Advanced Frontiers in Renewable Hydrogen Fuel Production via Solar Water Splitting Technologies”, which was cosponsored by the National Science Foundation, Division of Chemical, Bioengineering, Environmental, and Transport Systems (CBET) and the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office. R.J.B. acknowledges support from the National Science Foundation Graduate Research Fellowship Program. Characterization was performed at Stanford Nano Shared Facilities (SNSF). This work was supported by the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory. We would also like to acknowledge the MOCVD growth technician Alan Kibbler, as well as Thomas R. Hellstern and Pongkarn Chakhranont for technical assistance with optical and photoelectrochemical measurements.

■ REFERENCES

- (1) Bard, A. J.; Fox, M. A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. *Acc. Chem. Res.* **1995**, *28*, 141–145.
- (2) *Quadrennial Technology Review*; U.S. Department of Energy: Washington, DC, 2015.
- (3) Pinaud, B. A.; Benck, J. D.; Seitz, L. C.; Forman, A. J.; Chen, Z.; Deutsch, T. G.; James, B. D.; Baum, K. N.; Baum, G. N.; Ardo, S.; et al. Technical and Economic Feasibility of Centralized Facilities for Solar Hydrogen Production Via Photocatalysis and Photoelectrochemistry. *Energy Environ. Sci.* **2013**, *6*, 1983–2002.
- (4) Doscher, H.; Geisz, J. F.; Deutsch, T. G.; Turner, J. A. Sunlight Absorption in Water - Efficiency and Design Implications for Photoelectrochemical Devices. *Energy Environ. Sci.* **2014**, *7*, 2951–2956.
- (5) Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production Via Water Splitting. *Science* **1998**, *280*, 425–427.
- (6) Ager, J. W.; Shaner, M. R.; Walczak, K. A.; Sharp, I. D.; Ardo, S. Experimental Demonstrations of Spontaneous, Solar-Driven Photoelectrochemical Water Splitting. *Energy Environ. Sci.* **2015**, *8*, 2811–2824.
- (7) Hu, S.; Lewis, N. S.; Ager, J. W.; Yang, J.; McKone, J. R.; Strandwitz, N. C. Thin-Film Materials for the Protection of Semiconducting Photoelectrodes in Solar-Fuel Generators. *J. Phys. Chem. C* **2015**, *119*, 24201–24228.
- (8) Chen, Z.; Cummins, D.; Reinecke, B. N.; Clark, E.; Sunkara, M. K.; Jaramillo, T. F. Core-Shell MoO₃-MoS₂ Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials. *Nano Lett.* **2011**, *11*, 4168–4175.
- (9) Keong Koh, E. W.; Chiu, C. H.; Lim, Y. K.; Zhang, Y.-W.; Pan, H. Hydrogen Adsorption on and Diffusion through MoS₂ Monolayer: First-Principles Study. *Int. J. Hydrogen Energy* **2012**, *37*, 14323–14328.
- (10) Laursen, A. B.; Pedersen, T.; Malacrida, P.; Seger, B.; Hansen, O.; Vesborg, P. C. K.; Chorkendorff, I. MoS₂—an Integrated Protective and Active Layer on n+p-Si for Solar H₂ Evolution. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20000–20004.
- (11) Benck, J. D.; Lee, S. C.; Fong, K. D.; Kibsgaard, J.; Sinclair, R.; Jaramillo, T. F. Designing Active and Stable Silicon Photocathodes for Solar Hydrogen Production Using Molybdenum Sulfide Nanomaterials. *Adv. Energy Mater.* **2014**, *4*, 1–8.
- (12) Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; et al. Photoelectrochemical Hydrogen Evolution Using Si Microwire Arrays. *J. Am. Chem. Soc.* **2011**, *133*, 1216–1219.
- (13) Seger, B.; Laursen, A. B.; Vesborg, P. C. K.; Pedersen, T.; Hansen, O.; Dahl, S.; Chorkendorff, I. Hydrogen Production Using a Molybdenum Sulfide Catalyst on a Titanium-Protected n+p-Silicon Photocathode. *Angew. Chem., Int. Ed.* **2012**, *51*, 9128–9131.
- (14) Warren, E. L.; Boettcher, S. W.; Walter, M. G.; Atwater, H. A.; Lewis, N. S. pH-Independent, 520 mV Open-Circuit Voltages of Si/Methyl Viologen^{2+/+} Contacts through Use of Radial n+p-Si Junction Microwire Array Photoelectrodes. *J. Phys. Chem. C* **2011**, *115*, 594–598.
- (15) Cossu, G.; Ingo, G. M.; Mattogno, G.; Padeletti, G.; Proietti, G. M. XPS Investigation on Vacuum Thermal Desorption of UV/Ozone Treated GaAs(100) Surfaces. *Appl. Surf. Sci.* **1992**, *56–58*, 81–88.
- (16) Faur, M.; Faur, M.; Jayne, D. T.; Goradia, M.; Goradia, C. XPS Investigation of Anodic Oxides Grown on p-Type InP. *Surf. Interface Anal.* **1990**, *15*, 641–650.
- (17) Sundararaman, C. S.; Lafontaine, H.; Poulin, S.; Mouton, A.; Currie, J. F. Reactive Sputtering of InP in N₂ and N₂/O₂ Plasmas. *J. Vac. Sci. Technol., B: Microelectron. Process. Phenom.* **1991**, *9*, 1433–1439.
- (18) Streubel, P.; Peisert, H.; Hesse, R.; Chassé, T.; Szargan, R. Chemical Bonding Studies on UV/Ozone- and (NH₄)₂S-treated InP(001) Surfaces by X-Ray Photoelectron Spectroscopy and X-Ray Induced Auger Electron Spectroscopy. *Surf. Interface Anal.* **1995**, *23*, 581–588.
- (19) Nielsen, J. H.; Bech, L.; Nielsen, K.; Tison, Y.; Jørgensen, K. P.; Bonde, J. L.; Horch, S.; Jaramillo, T. F.; Chorkendorff, I. Combined Spectroscopy and Microscopy of Supported MoS₂ Nanoparticles. *Surf. Sci.* **2009**, *603*, 1182–1189.
- (20) *Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface*; ASTM International, 2012.
- (21) Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts. *Science* **2007**, *317*, 100–102.
- (22) Thorne, J. E.; Li, S.; Du, C.; Qin, G.; Wang, D. Energetics at the Surface of Photoelectrodes and Its Influence on the Photoelectrochemical Properties. *J. Phys. Chem. Lett.* **2015**, *6*, 4083–4088.
- (23) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the Surface Structure of MoS₂ to Preferentially Expose Active Edge Sites for Electrocatalysis. *Nat. Mater.* **2012**, *11*, 963–969.
- (24) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. MoS₂ Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 7296–7299.
- (25) Doscher, H.; Young, J. L.; Geisz, J. F.; Turner, J. A.; Deutsch, T. G. Solar-to-Hydrogen Efficiency: Shining Light on Photoelectrochemical Device Performance. *Energy Environ. Sci.* **2016**, *9*, 74–80.
- (26) Benganem, M. S.; Alamri, S. N. Modeling of Photovoltaic Module and Experimental Determination of Serial Resistance. *Journal of Taibah University for Science* **2009**, *2*, 94–105.