

# Phosphonic Acid Modification of GaInP<sub>2</sub> Photocathodes Toward Unbiased Photoelectrochemical Water Splitting

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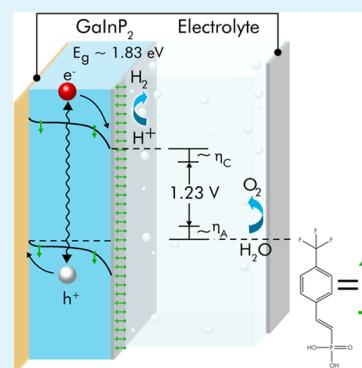
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## S Supporting Information

**ABSTRACT:** The p-type semiconductor GaInP<sub>2</sub> has a nearly ideal bandgap (~1.83 eV) for hydrogen fuel generation by photoelectrochemical water splitting but is unable to drive this reaction because of misalignment of the semiconductor band edges with the water redox half reactions. Here, we show that attachment of an appropriate conjugated phosphonic acid to the GaInP<sub>2</sub> electrode surface improves the band edge alignment, closer to the desired overlap with the water redox potentials. We demonstrate that this surface modification approach is able to adjust the energetic position of the band edges by as much as 0.8 eV, showing that it may be possible to engineer the energetics at the semiconductor/electrolyte interface to allow for unbiased water splitting with a single photoelectrode having a bandgap of less than 2 eV.



**KEYWORDS:** water splitting, photoelectrochemical cell, renewable energy, gallium indium phosphide, phosphonic acid

## INTRODUCTION

In 1998, Khaselev and Turner showed that an integrated photovoltaic-biased (tandem) p-type gallium indium phosphide (GaInP<sub>2</sub>) photoelectrochemical cell (PEC) was capable of a 12.4% solar–hydrogen conversion, providing proof that high-efficiency PEC water splitting is possible if high-efficiency semiconductors are used and the energetics are properly engineered.<sup>1</sup> The GaInP<sub>2</sub> top cell material in that configuration has a bandgap (1.83 eV) that is near ideal for water splitting, and the potential of photogenerated electrons at the conduction band edge of GaInP<sub>2</sub> is sufficient to drive the hydrogen evolution reaction (HER); however, the electrochemical potential of photogenerated holes is several hundred millivolts too negative to drive the oxygen evolution reaction (OER) at the counter electrode, and hence, the top cell cannot spontaneously split water under illumination on its own.<sup>2</sup> Adding the GaAs solar cell in a tandem configuration provides the extra bias to overcome the energetic mismatch. Photoelectrolysis from GaInP<sub>2</sub> photoelectrodes without tandem photovoltaic biasing has yet to be realized. When the energetic position of the band edges of GaInP<sub>2</sub> are engineered via surface modification, it may be possible to affect spontaneous water splitting with a single semiconductor having a bandgap of less than 2 eV.

In prior band edge engineering work on GaInP<sub>2</sub>, Kocha and Turner treated the surface of GaInP<sub>2</sub> with quinoline and showed a significant shift in the flatband potential (measured in

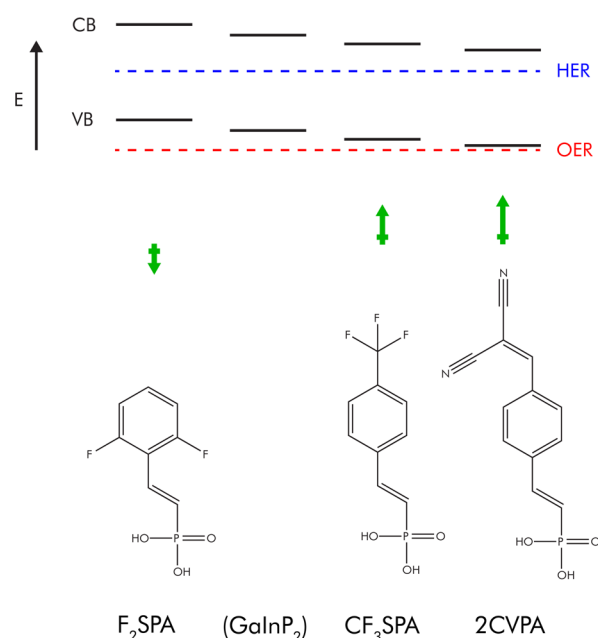
the dark by Mott–Schottky analysis) but failed to achieve water splitting under illumination because of poor kinetics and a so-called band edge migration.<sup>3</sup> Following this work, Bansal and Turner showed a small improvement in the flatband potential with the use of transition metal ions, but it was not sufficient for water splitting with an unbiased photoelectrode.<sup>4</sup>

In this work, we modify the surface of GaInP<sub>2</sub> with conjugated phosphonic acids (shown in Figure 1) to shift the band offset with the water redox half reactions to be more favorable for unbiased water splitting. Previously, benzylphosphonic acids have been synthesized with a range of molecular dipole moments by varying the position of electron-withdrawing fluorine substitutions in the aromatic ring,<sup>5</sup> and the molecules readily self-assemble on metal oxide surfaces via the phosphonate group. The most notable applications have been on indium tin oxide and zinc oxide surfaces, because of their extensive use as transparent conducting electrodes in photovoltaic and light-emitting diode applications.<sup>6,7</sup> The adsorbed molecular dipoles generate a vacuum level offset with band energies that is experimentally measured as a shift in the work function ( $\Delta\Phi$ ) of the respective metal oxide and was shown to span a range of up to 1.5 eV.<sup>8–10</sup>

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**Figure 1.** (Top) Cartoon energy diagram of the band energies of the (un)modified GaInP<sub>2</sub> surfaces relative to the water redox reaction potentials. (Bottom) Chemical structures of the conjugated phosphonic acids used in this study: 2,6-difluorostyrylphosphonic acid (F<sub>2</sub>SPA), 4-(trifluoromethyl)styrylphosphonic acid (CF<sub>3</sub>SPA), and 4-(2,2-dicyanovinyl)styrylphosphonic acid (2CVPA). Relative intensity and direction of the dipole moment of each molecule are depicted with green arrows. Density functional theory calculations of molecular dipole moments will be reported elsewhere.<sup>15</sup>

This  $\Delta\Phi$  was demonstrated to have a correlated effect on many device properties in organic electronics. When implemented in organic light-emitting diodes, electroluminescence has been enhanced because of the lowered turn-on voltage<sup>8,11</sup> and enhanced built-in electric field.<sup>9</sup> When implemented in organic photovoltaics, the open-circuit voltage ( $V_{OC}$ ) could be increased for improved power conversion efficiency because of the increased quasi-Fermi level splitting.<sup>10,12–14</sup>

More recently, Braid et al. reduced the ZnO work function upon surface modification with a conjugated 2,6-difluorostyrylphosphonic acid (F<sub>2</sub>SPA; Figure 1) and an unconjugated 2,6-difluorophenylvinylphosphonic acid. It was shown that the surface modification with the F<sub>2</sub>SPA molecule produced larger  $\Delta\Phi$ , as a result of the conjugated linkage between the headgroup and the binding group in the molecule.<sup>12</sup> This finding suggests that these styrylphosphonic acids could possibly tune semiconductor surface energetics spanning a range greater than had previously been reported for modifications of metal oxides, by inserting the conjugation between the aromatic headgroup and the phosphonate binding group, in addition to providing better electrical conduction through a conjugated linkage.<sup>12,15</sup>

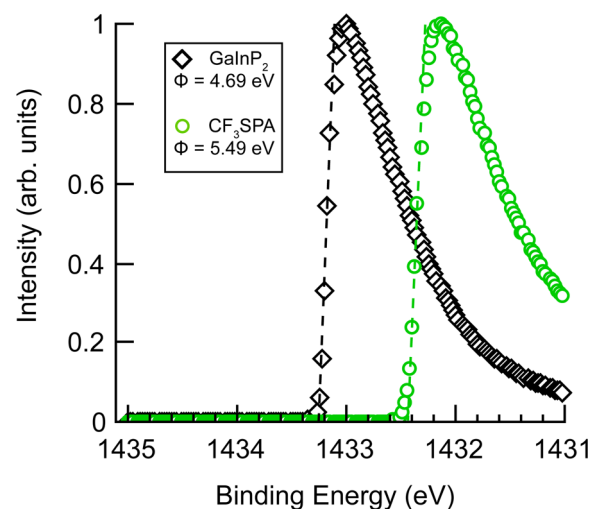
Building upon the advancements in photovoltaics and light-emitting devices, we apply conjugated styrylphosphonic acids to the working electrodes in photochemical cells. We modify the surface of GaInP<sub>2</sub>, inducing an offset in band energies, relative to the local vacuum level (measured as  $\Delta\Phi$ ), and retain some of this offset during operation in an illuminated photoelectrochemical cell. With the fluorine-substituted motif, we are able to increase or decrease the work function and have also

increased the work function with a new, non-fluorine-based motif. To our knowledge, this is the first demonstration of a surface modification on GaInP<sub>2</sub> that allows for improved energetics in an operating electrolytic cell, demonstrating a methodology toward achieving unbiased photoelectrochemical water splitting with a GaInP<sub>2</sub> electrode.

## RESULTS AND DISCUSSION

To achieve the goal of spontaneous OER at the counter electrode of a GaInP<sub>2</sub> photoelectrochemical cell, the potential for photocurrent onset must be shifted positive (with respect to the Ag/AgCl reference) by  $\sim 1$  eV. This can only be achieved when there is significant overpotential for the water OER, which requires the valence band of GaInP<sub>2</sub> to be shifted further below the vacuum level. Therefore, to achieve the desired positive shift in photocurrent onset potential within a photoelectrochemical cell, the phosphonic-acid-modified GaInP<sub>2</sub> surface must demonstrate a positive  $\Delta\Phi$ , as measured in vacuum, and this is the metric that we test prior to testing modified GaInP<sub>2</sub> electrodes in electrolytic cells.

Previously, Kocha et al. showed that etching of GaInP<sub>2</sub> in concentrated sulfuric acid for 120 s was optimal for removal of surface oxide species, which results in reduced surface recombination and better photocatalytic activity.<sup>16</sup> We adopt this protocol, verifying the significantly reduced presence of native oxide species by X-ray photoelectron spectroscopy (XPS; see the Supporting Information), prior to adsorption of the phosphonic acids. Etched GaInP<sub>2</sub> was then modified with the self-assembling molecule 4-(trifluoromethyl)styrylphosphonic acid (CF<sub>3</sub>SPA; Figure 1), and the surface work functions were measured by XPS (Figure 2), revealing

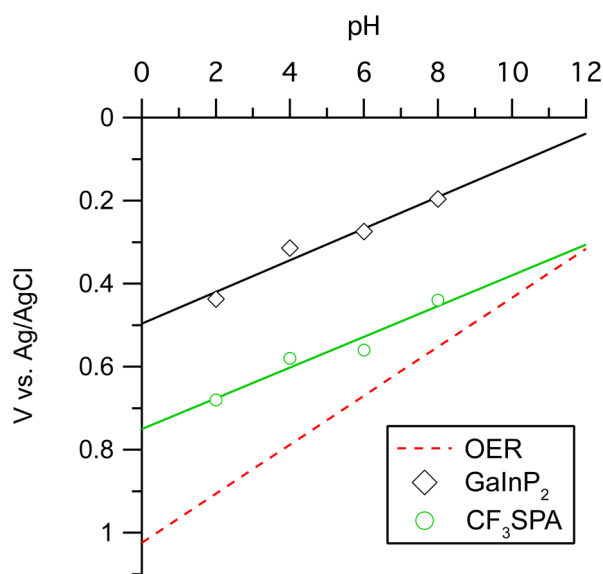


**Figure 2.** Normalized XPS secondary electron cutoff region for the GaInP<sub>2</sub> surface etched with sulfuric acid (black diamonds) and subsequently reacted with the CF<sub>3</sub>SPA modifier (green circles), resulting in  $\Delta\Phi = +0.8$  eV (from 4.69 to 5.49 eV). Dashed lines represent linear regression to the spectral cutoff feature.

$\Delta\Phi = +0.8$  eV. This value is similar to previous reports using the analogous 4-(trifluoromethyl)benzylphosphonic acid (CF<sub>3</sub>BnPA), which showed  $\Delta\Phi = +0.5$ – $1.1$  eV for indium tin oxide (ITO)<sup>5,10</sup> and  $\Delta\Phi = +0.9$  eV for ZnO.<sup>14</sup>

As further verification of favorable energetics at the working electrode, we measured the same working electrodes by Mott–Schottky analysis in several pH buffer solutions; these values

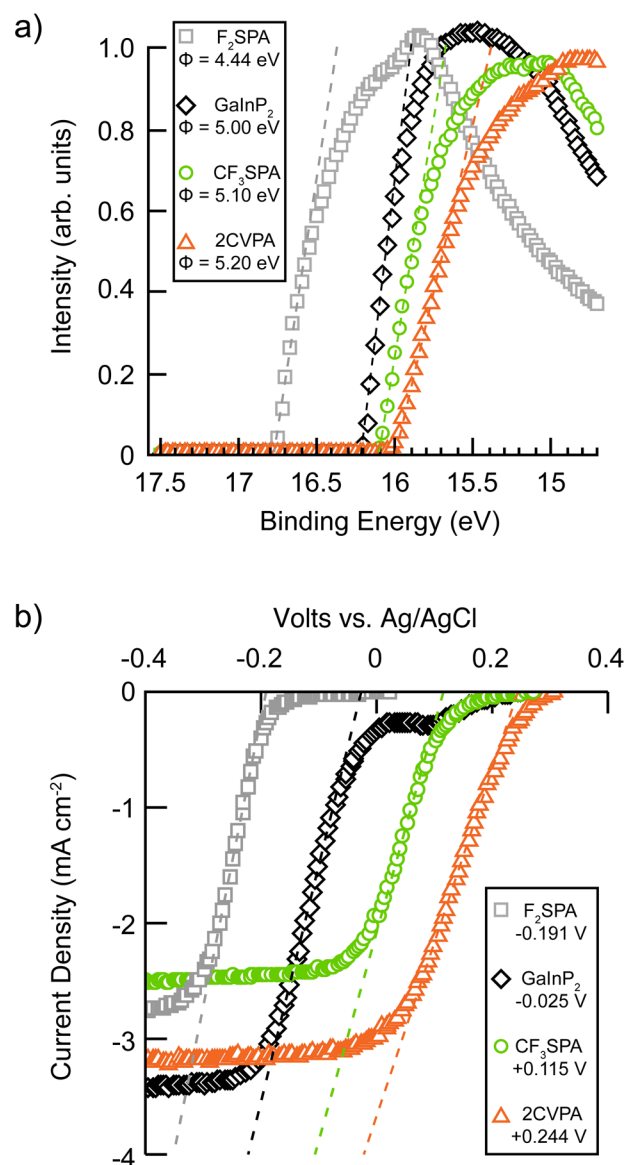
are plotted in Figure 3. Indeed, the CF<sub>3</sub>SPA-modified electrode exhibits a  $\sim 250$  mV increase in the flatband potential across the



**Figure 3.** Flatband potential of working electrodes against Ag/AgCl reference electrode using a Pt counter electrode, measured in various pH buffer solutions. Unmodified GaInP<sub>2</sub> is shown in black diamonds with linear regression (slope =  $-0.038$  V pH<sup>-1</sup>); CF<sub>3</sub>SPA-modified GaInP<sub>2</sub> is shown in green circles with linear regression (slope =  $-0.037$  V pH<sup>-1</sup>); and the OER is shown as a red dashed line for reference (slope =  $-0.059$  V pH<sup>-1</sup>). Data that fall below the red dashed line would indicate photoelectrodes that are capable of spontaneously driving the OER at the counter electrode without the need for external biasing.

pH range tested. Both electrodes exhibit a dependence upon pH that are slightly reduced from Nernstian, as apparent from the reduced slope of the linear regression in Figure 3. We hypothesize that the flatband potential offset measured in the electrolyte may be significantly reduced from the measured  $\Delta\Phi$  ( $+0.8$  eV) because of the polarization of the electrolyte in the Helmholtz layer. Still, the sub-Nernstian dependence suggests that this modification or a similar modification that provides a larger increase in flatband potential could drive the OER at a sufficiently high pH. Unfortunately, both electrodes were irreversibly damaged when tested in pH 10 buffer. With evidence of improved energetics for a phosphonic-acid-modified electrode, we next incorporated an electrodeposited Pt particle catalyst to investigate the effect of  $\Delta\Phi$  on the catalyzed photocurrent response of cells tested in electrolyte solution under broadband illumination.

Following the sulfuric acid etch procedure, Pt was electrodeposited both before and after the deposition of the phosphonic acid modifiers. The highly acidic electrodeposition conditions for depositing the Pt catalyst were too harsh for the electrodes on which phosphonic acids were deposited first; therefore, we focus the discussion on the more promising electrodeposition procedure: when Pt is electrodeposited prior to the phosphonic acid modifier. Figure 4a shows ultraviolet photoemission spectra for these electrodes, both unmodified and modified with the phosphonic acids shown in Figure 1, with calculated work functions ( $\Phi$ ) of each given in the legend.  $\Delta\Phi = -0.56$ ,  $+0.10$ , and  $+0.2$  eV for the electrodes modified with F<sub>2</sub>SPA, CF<sub>3</sub>SPA, and 4-(2,2-dicyanovinyl)-styrylphosphonic acid (2CVPA; Figure 1), respectively.



**Figure 4.** Ultraviolet photoelectron spectroscopy (UPS) and photocurrent response of electrodes: unmodified GaInP<sub>2</sub> (black diamonds), F<sub>2</sub>SPA-modified GaInP<sub>2</sub> (gray squares), CF<sub>3</sub>SPA-modified GaInP<sub>2</sub> (green circles), and 2CVPA-modified GaInP<sub>2</sub> (orange triangles). Electrodes in this figure are similar to but differ from the samples in Figures 2 and 3, in that they were modified with Pt particles (prior to any phosphonic acid treatment). (a) Normalized ultraviolet photoemission spectra in the secondary electron cutoff region, with work functions of each electrode listed in the legend. Dashed lines represent linear regression to the spectral cutoff feature. (b) Photocurrent as a function of the applied bias for the same electrodes, as in (a), illuminated at  $\sim 0.2$  sun intensity, at pH 2. Dashed lines represent linear regression to the onset of the photocurrent.

As expected from the orientation of the molecular dipole that is derived from the position of electron-withdrawing groups on the aromatic ring, CF<sub>3</sub>SPA gives a positive  $\Delta\Phi$ , while F<sub>2</sub>SPA gives a negative  $\Delta\Phi$ . The 2CVPA molecule acts similarly to CF<sub>3</sub>SPA, also producing a positive  $\Delta\Phi$ , but in this case because of the electron-withdrawing dicyanovinyl group. However,  $\Delta\Phi$  for the CF<sub>3</sub>SPA-modified surface (Figure 4a) is significantly smaller than the same molecule deposited on the freshly etched GaInP<sub>2</sub> surface without electrodeposited Pt (Figure 2). We assume that the platinum particles displace phosphonate

binding sites on the GaInP<sub>2</sub> surface, and the high heat of platinum oxide formation prevents Pt–O–P bonds from forming in platinum-covered regions of the electrode,<sup>17</sup> lowering the coverage density of phosphonic acids. The reduced coverage density would mean significant reduction in magnitude of  $\Delta\Phi$ , because of the linear relationship of the two properties.<sup>18</sup>

Figure 4b shows the photocurrent response of the same electrodes in Figure 4a, tested in pH 2 electrolyte solution. The magnitude and direction of the shift in photocurrent onset potentials for each of the modified electrodes agrees well with  $\Delta\Phi$ , as measured by UPS. Although a sufficient shift in the band edge potentials for spontaneous water splitting was not achieved, this agreement suggests that attachment of ordered molecular dipoles improves the energetics of the electrode/electrolyte interface. To drive spontaneously the OER at the counter electrode, the photocurrent onset would need to shift positive another  $\sim 700$  mV beyond that of the 2CVPA-modified electrode measured here.

There are several potential improvements to this method of engineering the band energetics of GaInP<sub>2</sub> that may lead to the spontaneous OER. As mentioned above, the low coverage density of adsorbing the phosphonic acids after the platinum catalyst limits the magnitude of the band offset that can be achieved, regardless of the orientation and magnitude of the molecular dipole moment. Whereas some degree of optimization in depositing the catalyst prior to the phosphonic acid could achieve higher coverage densities, this route would not likely result in increases in coverage of the phosphonic acids that would be sufficient to generate a large enough band offset to spontaneously drive the OER at the counter electrode. When CF<sub>3</sub>SPA was deposited directly to GaInP<sub>2</sub>, without first depositing the platinum particles,  $\Delta\Phi$  was 0.8 eV; with larger molecular dipoles possible via the steryl phosphonic acid motif,<sup>15</sup> we expect  $\Delta\Phi$  greater than 0.8 eV should be possible when adsorbed to GaInP<sub>2</sub> that has not yet been treated with platinum particles. Because the untreated GaInP<sub>2</sub> surface provides the largest possible coverage density of phosphonic acid modifiers, this process is more likely to achieve the necessary band offset but would require a non-destructive method of applying the catalyst particles. In either of these modified deposition schemes, the performance of the electrode may still be limited by the metal oxide bond through the phosphonate groups (M–O–P).

## CONCLUSION

We have demonstrated improved energetics from a GaInP<sub>2</sub> photocathode via surface modification with self-assembling molecular dipoles. To our knowledge, this is the first example of concurrently improving the band edge energetics and the photocurrent onset of GaInP<sub>2</sub> by modifying the surface energetics alone. While the solution-based method of modifying GaInP<sub>2</sub> with phosphonic acids was rather facile, it appears to have a few drawbacks. Future efforts in surface modification by molecular dipole moments should focus on processing of both the adsorbed molecular dipole as well as the deposition of catalyst particles, to obtain sufficient overpotential for the OER at the counter electrode while retaining some of the inherent overpotential for the HER.

## EXPERIMENTAL SECTION

Epilayers of p-GaInP<sub>2</sub> were grown on p-GaAs (100) substrates miscut by 4° toward  $\langle 111 \rangle$  by organometallic vapor-phase epitaxy. Epilayers

were p-doped with Zn to  $\sim 2 \times 10^{17}$  cm<sup>-3</sup>.<sup>19,20</sup> Back contacts were formed on the GaAs substrate by electron-beam evaporation of a 10 nm layer of titanium, followed by 300 nm of gold. Because of the scarcity of high-quality GaInP<sub>2</sub> samples, the number of electrodes fabricated for this study was limited.

Standard treatment of the as-grown GaInP<sub>2</sub> sample includes an etch in concentrated sulfuric acid for 2 min,<sup>16</sup> followed by rinsing in deionized water and drying with N<sub>2</sub>(g) flow. For the samples to be used in photocurrent onset measurements, a Pt catalyst was electrodeposited from 9.4 mM chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) in 2 M HCl. The deposition consisted of applying a galvanic square wave (2 Hz and  $-1$  mA<sup>-2</sup>) to an illuminated electrode until reaching a cumulative charge of approximately  $-18$  mC<sup>-2</sup>.

Details on the synthesis and characterization of the phosphonic acids used here will be reported elsewhere.<sup>15</sup> Dry purified methanol was used to dissolve CF<sub>3</sub>SPA, F<sub>2</sub>SPA, or 2CVPA at 10 mM for the attachment of phosphonic acids to the GaInP<sub>2</sub> surface. GaInP<sub>2</sub> samples were submerged in the phosphonic acid solution, sealed within borosilicate scintillation vials using polytetrafluoroethylene caps, heated to 120 °C, and allowed to react overnight ( $\sim 16$  h). After the heating duration, the reaction vials were cooled to ambient. To remove any residual physisorbed phosphonic acids, the samples were rinsed with a basic alcohol solution consisting of  $\sim 10$  vol % triethylamine in methanol, followed by rinsing with neat methanol, and finally, drying with N<sub>2</sub>(g) flow.

Electrodes were prepared for flatband potential measurements, without Pt catalyst deposition, by cleaving samples to  $\sim 0.2$  cm<sup>2</sup>, attaching to copper coils with silver paint, and sealing with insulating epoxy. Electrodes were measured against the Ag/AgCl reference electrode using a Pt counter electrode, in various pH buffer solutions (Hydrion buffer). Further details on electrode fabrication and testing conditions are described elsewhere.<sup>21</sup>

Photocurrent onset measurements were performed in a compression cell with an exposed area of 0.17 cm<sup>2</sup>. To minimize degradation during these measurements, illumination intensity was reduced and the magnitude of reverse bias with respect to open circuit and the time elapsed during biasing were both minimized. The intensity of the 250 W tungsten–halogen light source was set such that a GaInP<sub>2</sub> reference cell output 20% of the photocurrent as calibrated using the AM1.5 G reference spectrum. Calibration of the reference cell was performed by the Measurements and Characterization Group at the National Renewable Energy Laboratory. Photocurrent onset measurements were performed in a pH 2 electrolyte solution of K<sub>2</sub>SO<sub>4</sub> with Zonyl FSN-100 (a surfactant) additive.

UPS was performed in a Physical Instruments 5600 photoelectron spectrometer. Photoelectrons were generated using 21.2 eV ultraviolet light from a He plasma discharge. Samples were biased at  $-49$  V to remove background contributions to the spectra. Fermi calibration was performed on freshly sputtered gold foil. XPS was performed in the same instrument using monochromatic Al K $\alpha$  (1486.6 eV) as the excitation source. Binding energy calibration was performed following Seah for Cu 2p<sub>3/2</sub>, Ag 3d<sub>5/2</sub>, and Au 4f<sub>7/2</sub> peak positions.<sup>22</sup> Work function measurements were performed by either XPS or UPS, depending upon instrument availability.

## ASSOCIATED CONTENT

### Supporting Information

Additional XPS and photocurrent response data (PDF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01814.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic–Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* **1998**, *280*, 425–427.
- (2) Kocha, S. S.; Turner, J. A.; Nozik, A. J. Study of the Schottky Barrier and Determination of the Energetic Positions of Band Edges at the n- and p-type Gallium Indium Phosphide Electrode/Electrolyte Interface. *J. Electroanal. Chem.* **1994**, *367*, 27–30.
- (3) Kocha, S. S.; Turner, J. A. Displacement of the Band Edges of GaInP<sub>2</sub> in Aqueous Electrolytes Induced by Surface Modification. *J. Electrochem. Soc.* **1995**, *142*, 2625–2630.
- (4) Bansal, A.; Turner, J. A. Suppression of Band Edge Migration at the p-GaInP<sub>2</sub>/H<sub>2</sub>O Interface under Illumination via Catalysis. *J. Phys. Chem. B* **2000**, *104*, 6591–6598.
- (5) Hotchkiss, P. J.; Li, H.; Paramonov, P. B.; Paniagua, S. A.; Jones, S. C.; Armstrong, N. R.; Brédas, J.-L.; Marder, S. R. Modification of the Surface Properties of Indium Tin Oxide with Benzylphosphonic Acids: A Joint Experimental and Theoretical Study. *Adv. Mater.* **2009**, *21*, 4496–4501.
- (6) Hotchkiss, P. J.; Jones, S. C.; Paniagua, S. A.; Sharma, A.; Kippelen, B.; Armstrong, N. R.; Marder, S. R. The Modification of Indium Tin Oxide with Phosphonic Acids: Mechanism of Binding, Tuning of Surface Properties, and Potential for Use in Organic Electronic Applications. *Acc. Chem. Res.* **2011**, *45*, 337–346.
- (7) Lange, I.; Reiter, S.; Pätzelt, M.; Zykov, A.; Nefedov, A.; Hildebrandt, J.; Hecht, S.; Kowarik, S.; Wöll, C.; Heimel, G.; Neher, D. Tuning the Work Function of Polar Zinc Oxide Surfaces using Modified Phosphonic Acid Self-Assembled Monolayers. *Adv. Funct. Mater.* **2014**, *24*, 7014–7024.
- (8) Sharma, A.; Hotchkiss, P. J.; Marder, S. R.; Kippelen, B. Tailoring the Work Function of Indium Tin Oxide Electrodes in Electrophosphorescent Organic Light-Emitting Diodes. *J. Appl. Phys.* **2009**, *105*, 084507.
- (9) MacLeod, B. A.; Horwitz, N. E.; Ratcliff, E. L.; Jenkins, J. L.; Armstrong, N. R.; Giordano, A. J.; Hotchkiss, P. J.; Marder, S. R.; Campbell, C. T.; Ginger, D. S. Built-In Potential in Conjugated Polymer Diodes with Changing Anode Work Function: Interfacial States and Deviation from the Schottky–Mott Limit. *J. Phys. Chem. Lett.* **2012**, *3*, 1202–1207.
- (10) Ratcliff, E. L.; Garcia, A.; Paniagua, S. A.; Cowan, S. R.; Giordano, A. J.; Ginley, D. S.; Marder, S. R.; Berry, J. J.; Olson, D. C. Investigating the Influence of Interfacial Contact Properties on Open Circuit Voltages in Organic Photovoltaic Performance: Work Function Versus Selectivity. *Adv. Energy Mater.* **2013**, *3*, 647–656.
- (11) Knesting, K. M.; Hotchkiss, P. J.; MacLeod, B. A.; Marder, S. R.; Ginger, D. S. Spatially Modulating Interfacial Properties of Transparent Conductive Oxides: Patterning Work Function with Phosphonic Acid Self-Assembled Monolayers. *Adv. Mater.* **2012**, *24*, 642–646.
- (12) Braid, J. L.; Koldemir, U.; Sellinger, A.; Collins, R. T.; Furtak, T. E.; Olson, D. C. Conjugated Phosphonic Acid Modified Zinc Oxide Electron Transport Layers for Improved Performance in Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19229–19234.
- (13) Bulusu, A.; Paniagua, S. A.; MacLeod, B. A.; Sigdel, A. K.; Berry, J. J.; Olson, D. C.; Marder, S. R.; Graham, S. Efficient Modification of Metal Oxide Surfaces with Phosphonic Acids by Spray Coating. *Langmuir* **2013**, *29*, 3935–3942.
- (14) Cowan, S. R.; Schulz, P.; Giordano, A. J.; Garcia, A.; MacLeod, B. A.; Marder, S. R.; Kahn, A.; Ginley, D. S.; Ratcliff, E. L.; Olson, D. C. Chemically Controlled Reversible and Irreversible Extraction Barriers Via Stable Interface Modification of Zinc Oxide Electron Collection Layer in Polycarbazole-based Organic Solar Cells. *Adv. Funct. Mater.* **2014**, *24*, 4671–4680.
- (15) Koldemir, U.; Braid, J. L.; Morgenstern, A.; Eberhart, M.; Collins, R. T.; Olson, D. C.; Sellinger, A. *J. Phys. Chem. Lett.* **2015**, DOI: 10.1021/acs.jpcclett.5b00420.
- (16) Kocha, S. S.; Peterson, M. W.; Nelson, A. J.; Rosenwaks, Y.; Arent, D. J.; Turner, J. A. Investigation of Chemical Wet-Etch Surface Modification of Ga<sub>0.5</sub>In<sub>0.5</sub>P Using Photoluminescence, X-ray Photoelectron Spectroscopy, Capacitance Measurements, and Photocurrent–Voltage Curves. *J. Phys. Chem.* **1995**, *99*, 744–749.
- (17) Yagyu, S.; Yoshitake, M.; Tsud, N.; Chikyow, T. Adsorption of Phenylphosphonic Acid on Gold and Platinum Surfaces. *Jpn. J. Appl. Phys.* **2011**, *50*, 081606.
- (18) Li, H.; Brédas, J.-L. Theoretical Study of the Surface Modification of Indium Tin Oxide with Trifluorophenyl Phosphonic Acid Molecules: Impact of Coverage Density and Binding Geometry. *J. Mater. Chem.* **2010**, *20*, 2630.
- (19) Olson, J. M.; Kurtz, S. R.; Kibbler, A. E.; Faine, P. A. 27.3 Ga<sub>0.5</sub>In<sub>0.5</sub>P/GaAs Tandem Solar Cell. *Appl. Phys. Lett.* **1990**, *56*, 623.
- (20) Kurtz, S. R.; Olson, J. M.; Kibbler, A. E.; Bertness, K. A. Incorporation of Zinc in MOCVD Growth of Ga<sub>0.5</sub>In<sub>0.5</sub>P. *J. Cryst. Growth* **1992**, *124*, 463–469.
- (21) Deutsch, T. G.; Head, J. L.; Turner, J. A. Photoelectrochemical Characterization and Durability Analysis of GaInPN Epilayers. *J. Electrochem. Soc.* **2008**, *155*, B903–B907.
- (22) Seah, M. P. Post-1989 Calibration Energies for X-ray Photoelectron Spectrometers and the 1990 Josephson Constant. *Surf. Interface Anal.* **1989**, *14*, 488–488.