

*Supporting Information for:*

## **Photoelectrochemical Study of *p*-GaP(100)|ZnO|Au-NP Devices: Strategies for Enhanced Electron Transfer and Aqueous Catalysis**

Owen M. Williams, Justin W. Shi, and Michael J. Rose

*Department of Chemistry, The University of Texas at Austin, Austin, TX 78712, USA*

### **Experimental Procedures**

#### *Wafer Preparation.*

Zn doped GaP(100) wafers were purchased from ITME with a carrier concentration of  $4.7 \times 10^{17}$  and a resistivity of  $2 \times 10^{-1} \Omega \text{ cm}$ . The wafers were degreased sequentially with acetone, methanol, dichloromethane, methanol, and deionized water under sonication and etched in a 15% aqueous ammonium hydroxide solution, followed by washing with copious amounts of deionized MilliQ water. For ALD procedures, the etched wafers were introduced immediately into the ALD chamber.

#### *Atomic Layer Deposition*

Alumina was deposited using trimethylaluminum (TMA) and H<sub>2</sub>O as precursors. Zinc oxide was deposited using diethyl zinc (DEZ) and H<sub>2</sub>O as precursors. Thirty total cycles were performed at a substrate temperature of 150 °C, and precursor pulses of 0.015 seconds, followed by a 5 second purge. To construct the mixed ZnO/Al<sub>2</sub>O<sub>3</sub> interface, sixteen total cycles of ZnO deposition were followed by four cycles of alumina deposition, resulting in a nominal layer thickness of ~3.0 nm.

#### *Self-Assembled Monolayer Deposition*

Self-assembled monolayers were formed by soaking either the *p*-GaP(100)|Al<sub>2</sub>O<sub>3</sub> or *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4) wafers in a 1 mM solution of the corresponding monomer (dodecanethiol, dodecanephosphonic acid, or 12-mercaptododecanephosphonic acid) in EtOH for 18 h. The samples were then washed with copious amounts of methanol prior to characterization and further functionalization.

#### *Gold Nanoparticle Deposition*

A solution of gold nanoparticles was prepared by diluting a 1 OD Au(citrate) nanoparticles (~10 nm, PDI < 0.2, Sigma Aldrich) in pH 9.3 carbonate/bicarbonate buffer (1:9). The AuNPs were adsorbed to the wafer by immersion in this solution for 18 h. Following Au functionalization, the wafers were washed with copious amounts of water and dried under a nitrogen stream. These as-synthesized samples are stable under ambient light and atmosphere for periods > 1wk.

### *Wafer Characterization*

The surface composition and morphology of the wafer pieces were investigated by SEM on a Hitachi S5500 SEM system with a cold probe at a current of 10 mA and voltage of 10 kV. The elemental composition was determined by X-ray photoelectron spectroscopy on a Kratos Axis Ultra with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1486.5$  eV). Photoelectron take-off angle was 45° with respect to the X-ray beam, and the analysis chamber pressure remained at *ca.*  $2 \times 10^{-9}$  Torr during measurements. Some non-conductive samples required the use of a charge neutralizer to obtain a suitable signal. Typical region spectra used a pass energy of 20 eV, with the exception of Au 4f scans, for which the pass energy was 40 eV. All signals were standardized to the signal for adventitious carbon fixed at 284.6 eV. The obtained spectra were analyzed using Casa XPS software (version 2.3.15).

### *Electrode Fabrication*

The functional GaP electrodes were fabricated by threading a copper wire through a thick walled glass tube. The backside of each sample was scratched with a diamond scribe and GaIn eutectic applied to the freshly exposed surface of each sample. The samples were further affixed to the copper wire by means of Ag-epoxy (MG Chemicals 8331). The epoxy was allowed to set in a 65 °C furnace for 20-30 min. All of the contacts were then encased in blue epoxy paste (Loctite 615 Hysol) that was again set in a 65 °C furnace for 30 min. Electrode areas were determined by optical imaging with ImageJ and were typically 0.075 – 0.25 cm<sup>2</sup>.

## Electrochemistry

Electrochemical measurements were performed in a three electrode cell, with a modified semiconductor working electrode (*vide supra*), a platinum wire counter electrode, and either a Ag/Ag<sup>+</sup> (organic) or standard calomel (aqueous) reference electrode. The data were acquired using a Gamry Interface1000 potentiostat. The semiconductor electrodes were illuminated with a 150 W Xenon lamp (Newport, Co.) with an AM1.5G solar filter affixed. Currents are shown as current densities as determined by the surface area determined for each electrode. All non-aqueous PEC experiments were conducted in 5 mM ethyl viologen in 0.1 M LiClO<sub>4</sub>/MeCN electrolyte, while aqueous experiments were conducted in 0.5 M KCl electrolyte. Bulk electrolysis experiments were conducted in an airtight cell with a quartz window and constant stirring.

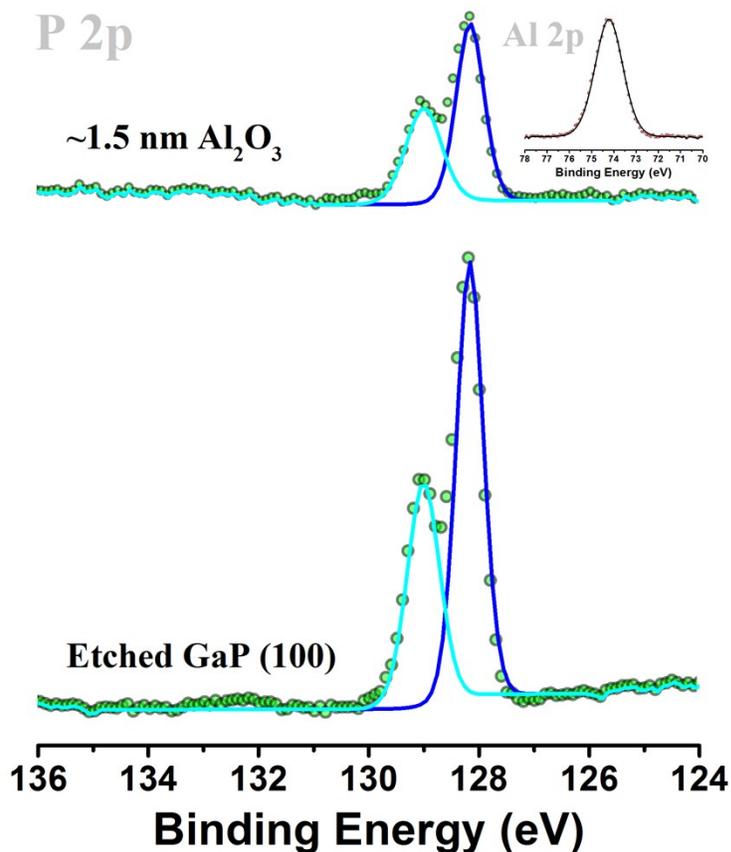
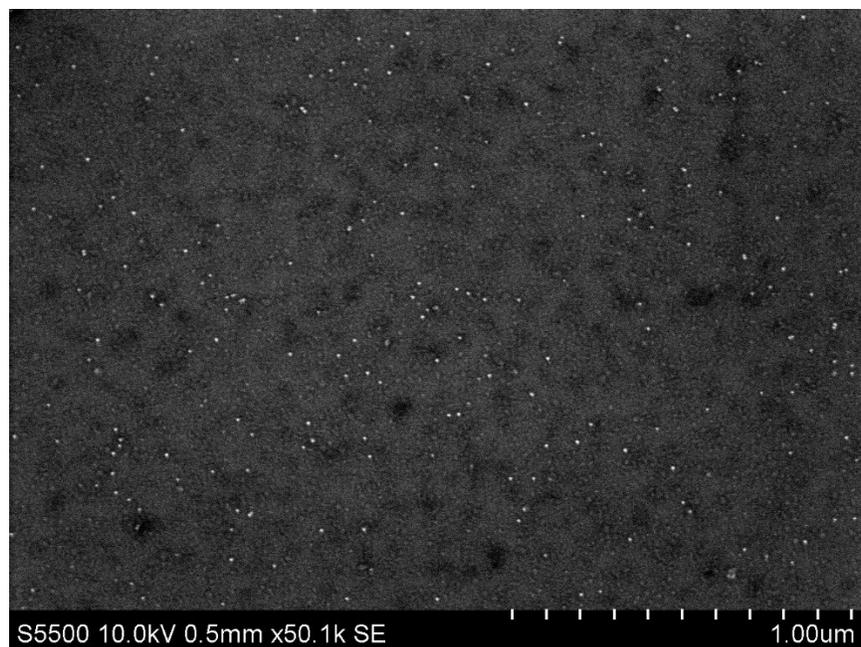
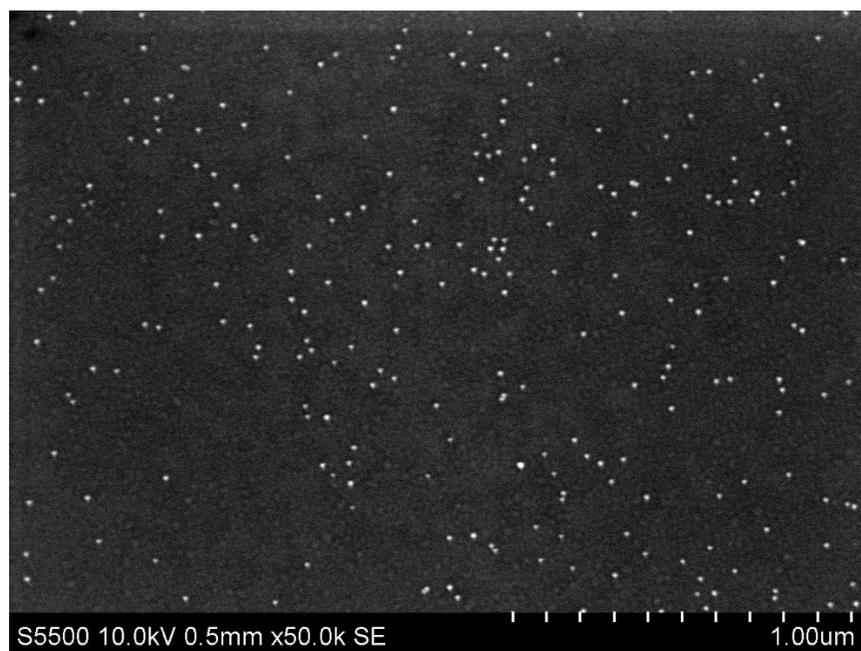


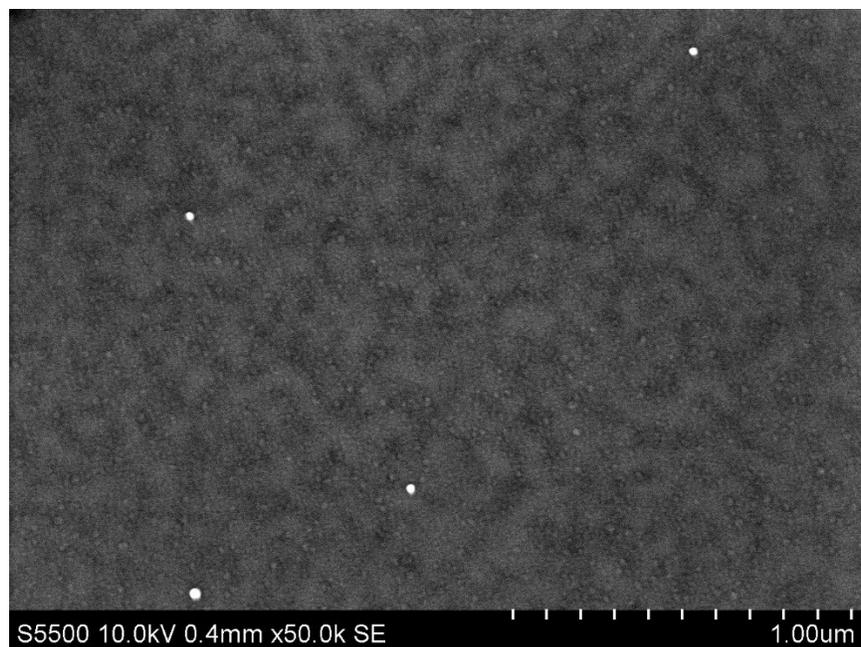
Figure S1. P 2p and Al 2p region spectra of etched (bottom) and ALD-Al<sub>2</sub>O<sub>3</sub> protected (top) gallium phosphide wafers showing the appearance of an aluminum signal and the attenuation of the phosphorous signal.



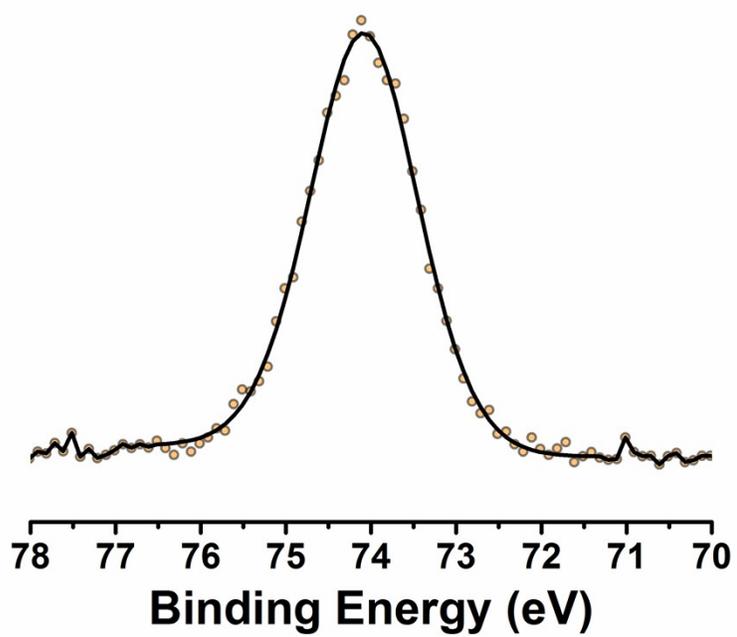
**Figure S2.** SEM image of GaP|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP(5nm) at 50K × magnification.



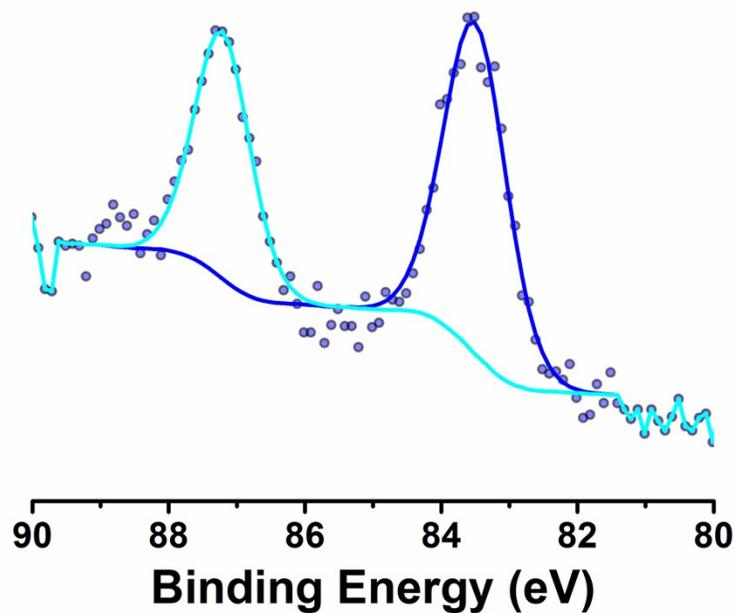
**Figure S3.** SEM image of GaP|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP(10nm) at 50K × magnification.



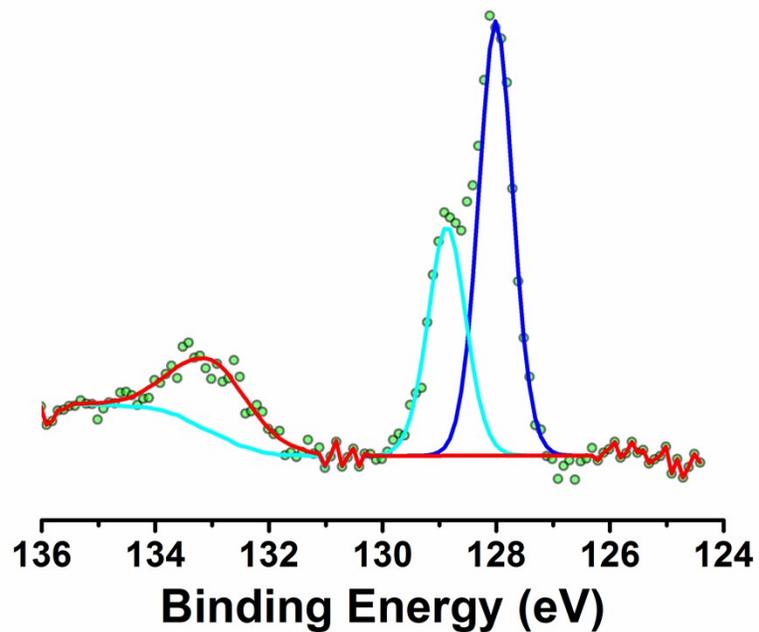
**Figure S4.** SEM image of GaP|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP(20nm) at 50K × magnification.



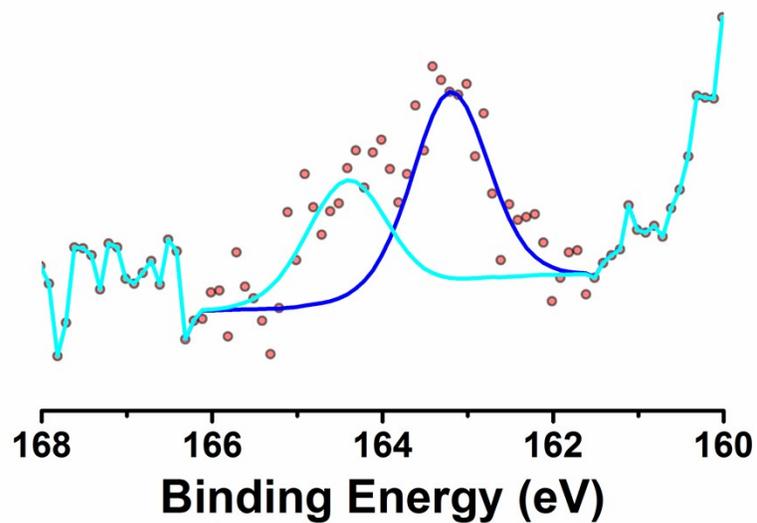
**Figure S5.** Al 2p region spectrum of *p*-GaP(100)|Al<sub>2</sub>O<sub>3</sub>|SAM|AuNP device.



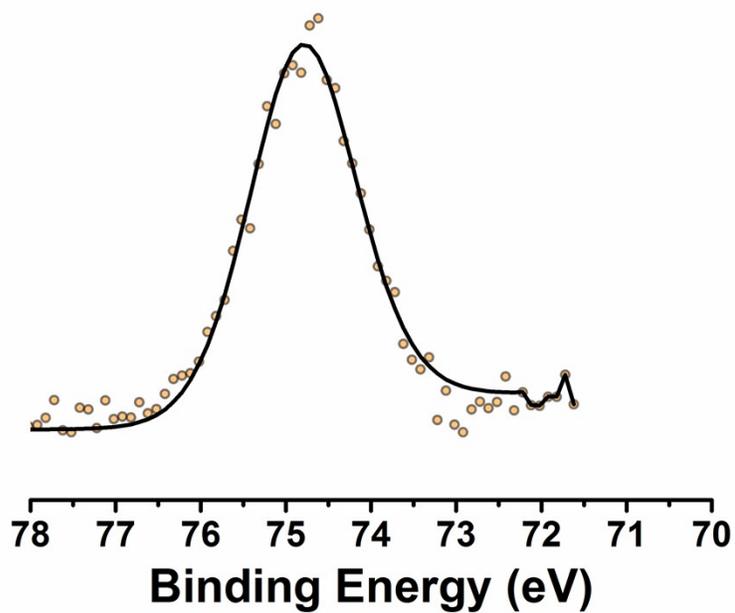
**Figure S6.** Au 4*f* region spectrum of *p*-GaP(100)|Al<sub>2</sub>O<sub>3</sub>|SAM|AuNP device.



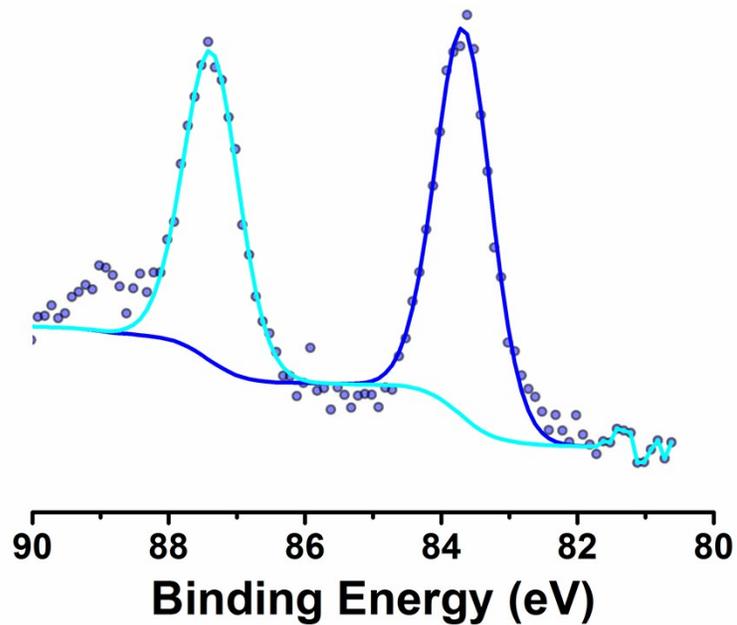
**Figure S7.** P 2*p* region spectrum of *p*-GaP(100)|Al<sub>2</sub>O<sub>3</sub>|SAM|AuNP device.



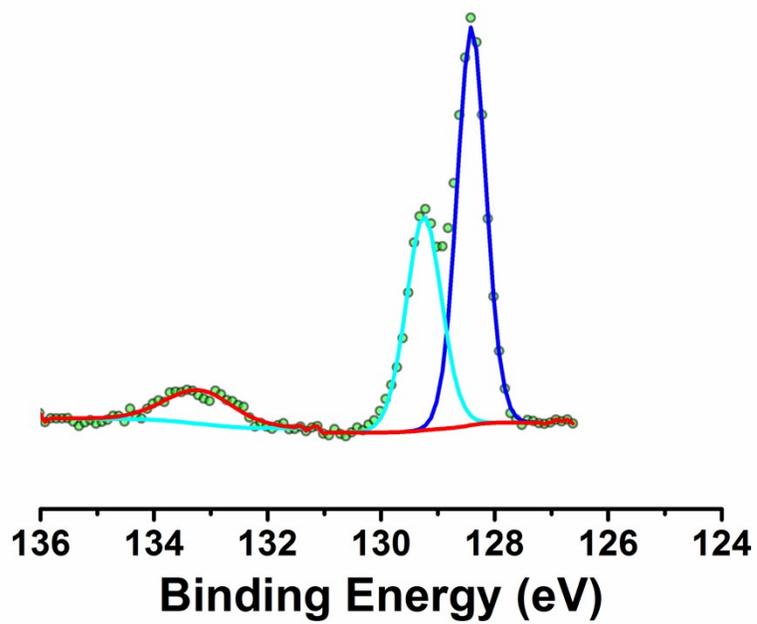
**Figure S8.** S 2p region spectrum of *p*-GaP(100)|Al<sub>2</sub>O<sub>3</sub>|SAM|AuNP device.



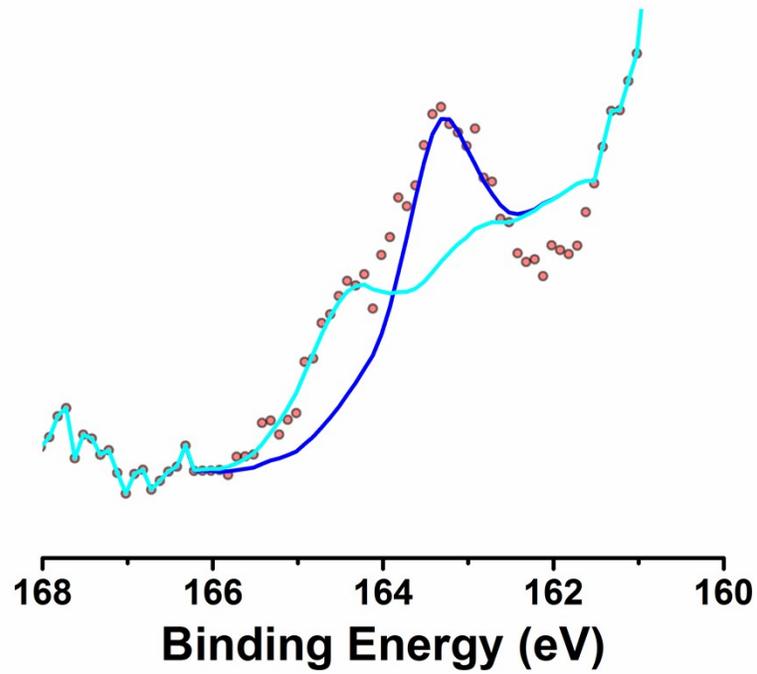
**Figure S9.** Al 2p region spectrum of *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP device.



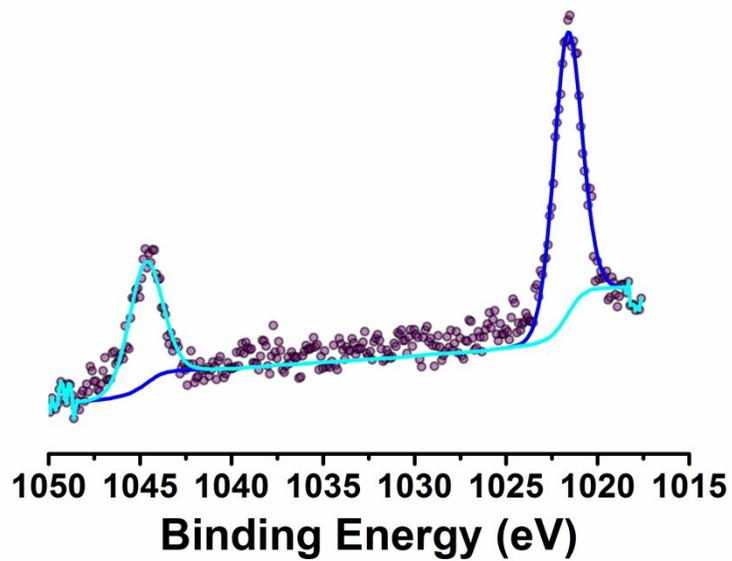
**Figure S10.** Au 4*f* region spectrum of *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP device.



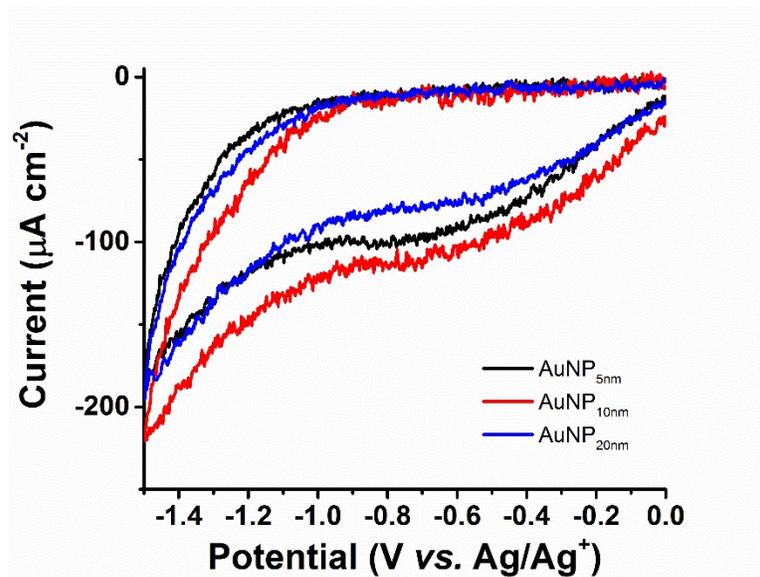
**Figure S11.** P 2*p* region spectrum of *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP device.



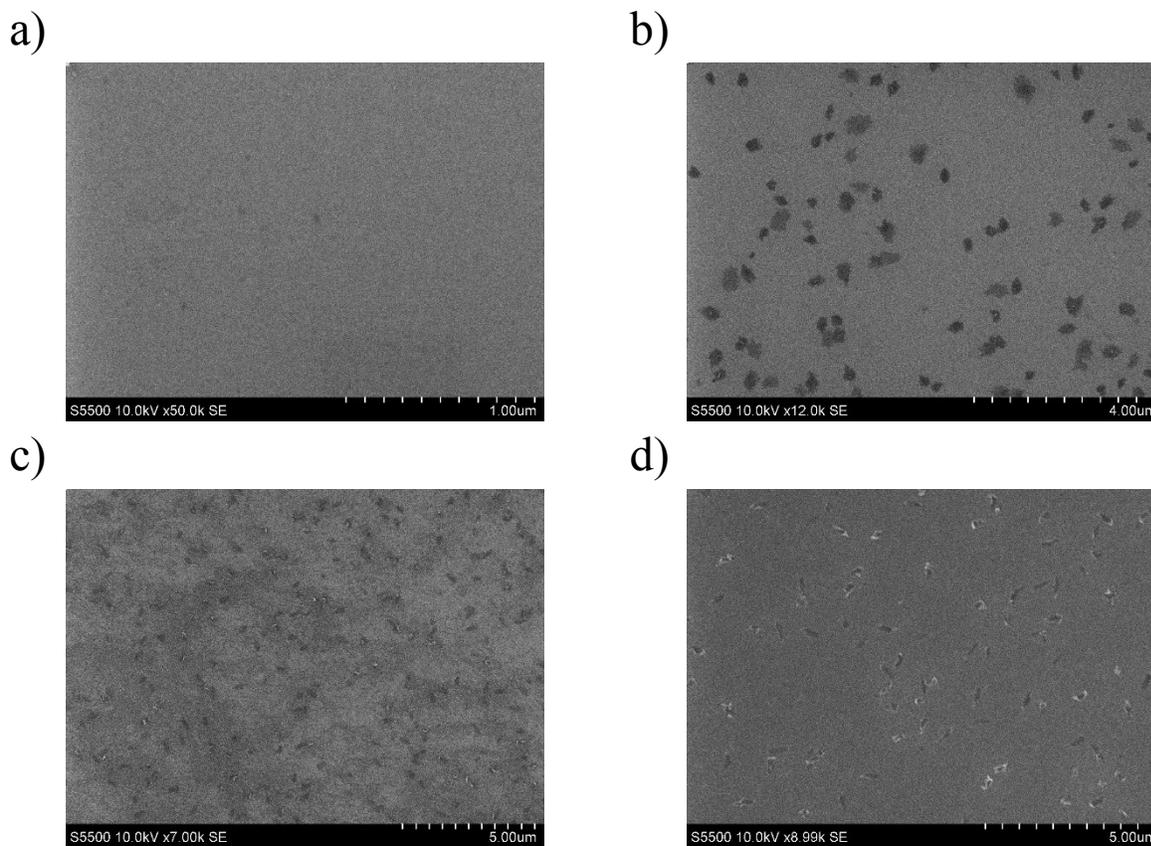
**Figure S12.** S 2*p* region spectrum of *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP device.



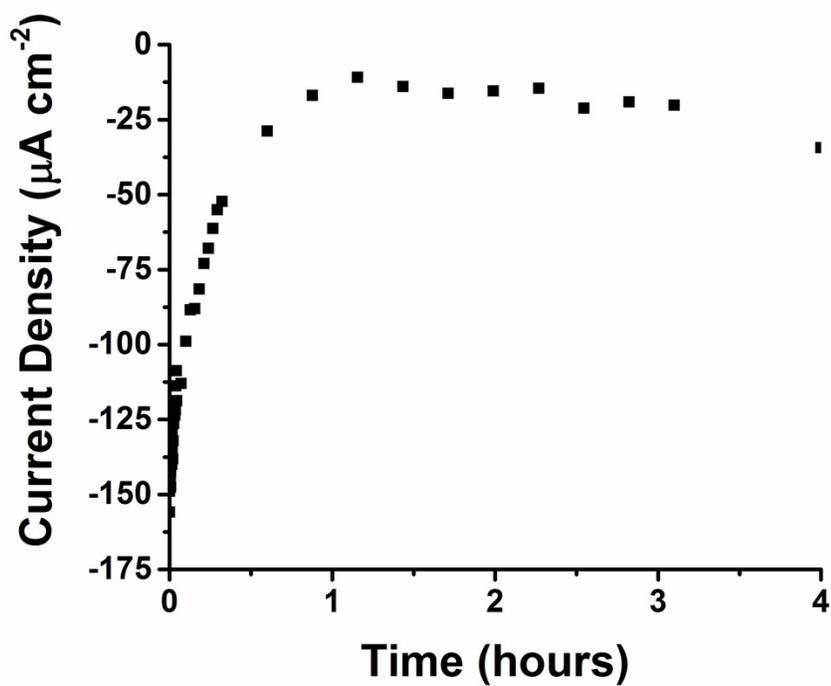
**Figure S13.** Zn 2*p* region spectrum of *p*-GaP(100)|ZnO(16)Al<sub>2</sub>O<sub>3</sub>(4)|SAM|AuNP device.



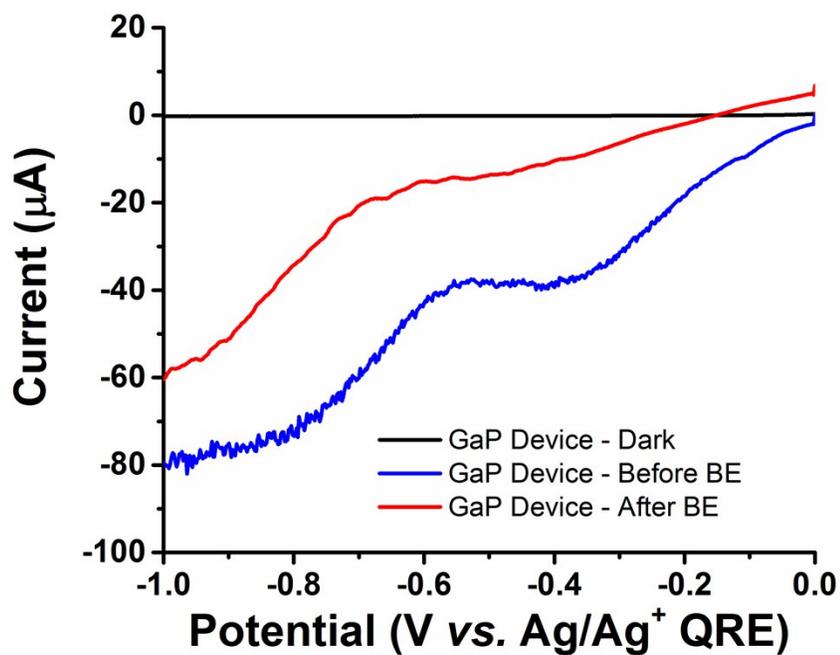
**Figure S14.** Organic electrochemistry in 5.0 mM  $\text{EtV}^{2+}$  in 0.1 M  $\text{LiClO}_4/\text{MeCN}$  electrolyte for  $\text{GaP}|\text{ZnO}(16)|\text{Al}_2\text{O}_3(4)|\text{SAM}|\text{AuNP}(5, 10, 20 \text{ nm})$  under AM1.5G illumination.



**Figure S15.** SEM images of pH experiments (18 hour soaking) conducted on  $\text{Si}|\text{Al}_2\text{O}_3|\text{SAM}$  substrates: a) pH  $\sim 9.0$ , b) pH  $\sim 9.5$ , c) pH  $\sim 10.0$ , d) pH  $\sim 10.5$ .



**Figure S16.** Current recorded in chronoamperometric bulk electrolysis over a four hour time period. GC samples showed the presence of both  $\text{H}_2$  and  $\text{CO}$ .



**Figure S17.** LSV graphs recorded before and after bulk electrolysis showing the decrease in observable current after electrolysis.