

Electronic Supplementary Information (ESI)

## **Highly efficient and durable III-V semiconductor-catalyst photocathodes via a transparent protection layer**

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## Experimental details

**Chemicals.** Red P (98.9%, Alfa Aesar), Ni ingot (99.99%, Kurt J lesker), TiN target (99.5%, Kurt Lesker), H<sub>2</sub>SO<sub>4</sub> (99.99%, Sigma-Aldrich), Triton X100 Omnipur grade (Sigma) Chemicals were used without further purification.

### **Metal Organic Vapor Pressure Epitaxy (MOVPE) for buried junction n<sup>+</sup>p-GaInP<sub>2</sub> growth.**

Semiconductor samples (MQ535 and MQ956) were grown by atmospheric pressure MOVPE on a custom-built reactor. The GaAs substrates were cleaved into ~25 mm x 25 mm squares and then etched in NH<sub>4</sub>OH : H<sub>2</sub>O<sub>2</sub> : H<sub>2</sub>O (2:1:10 by volume) for two minutes before loading into the reactor. The source gases included trimethylgallium, triethylgallium, triethylindium and trimethylaluminum for the group-III elements; phosphine and arsine for the group-Vs; diethylzinc and carbon tetrachloride for the p-type dopants; and dilute hydrogen selenide for the n-type dopant. Films were grown at 700°C and at growth rates of ~2-4.5 μm/hr, in a total hydrogen carrier flow of ~6 slpm. The reactor was heated to growth temperature under an arsine overpressure, and at the end of the growth cooled back to room temperature under a phosphine overpressure.

Starting from the substrate, the layer structure included a GaAs/Al<sub>0.3</sub>Ga<sub>0.7</sub>As seed layer; a 200 nm p<sup>+</sup> Al<sub>0.27</sub>Ga<sub>0.24</sub>In<sub>0.49</sub>P minority carrier confinement layer; a 1 μm p-type GaInP<sub>2</sub> base layer; and a ~25 nm n<sup>++</sup> GaInP<sub>2</sub> emitter layer. The compositions and thicknesses are nominal, but based on regular calibrations of the reactor. Due to the thinner thickness of the base layer than that of full optimized GaInP<sub>2</sub> buried junction solar cell, the photovoltage and photocurrent are expected to be slightly lower than state-of-the-art GaInP<sub>2</sub> PV cell.<sup>1</sup>

After growth, a gold back contact was electroplated to the substrate, after a short etch in NH<sub>4</sub>OH : H<sub>2</sub>O<sub>2</sub> : H<sub>2</sub>O (2:1:10 by volume) to remove any accumulated residue from the growth.

**Pulsed laser deposition of TiN.** GaInP<sub>2</sub> on GaAs substrates were cleaned with Buffered Oxide Etchant (BOE) 6:1 vol. NH<sub>4</sub>F/HF for 30 s prior to introduction into the PLD vacuum chamber. Pulsed laser ablated the TiN target using a KrF excimer laser Compex 205 (λ = 248 nm d = 7 cm, 10 Hz, 2.5 – 5 J cm<sup>-2</sup>; Coherent). Base pressure and temperature were kept at 5-6 × 10<sup>-4</sup> Pa, 130°C, respectively.

**Thermal evaporation of nickel.** Custom built thermal evaporator was used with W boat (Kurt J. Lesker). 3 nm of Ni deposition carried out at a rate of 1.0-1.5 Å/s as determined by quartz crystal microbalance (QCM).

**Chemical vapor phosphidation.** Evacuated quartz ampoule with red P (3-5 mg) was sealed at 1 × 10<sup>-3</sup> Pa similar to previous work.<sup>2</sup> The quartz ampoule was heated to 380 °C at 10 °C/min with a hold for 40 min and quenching at 280 °C.

**PtRu deposition.** The PtRu benchmark catalyst was deposited by “flash” sputtering in a custom-built vacuum chamber. A 1.3 Pa UHP argon background was established and sputtering

performed at 20 W. The sample was occluded by a shutter during a 2-minute break-in period. The brief duration, “flash” sputtering of PtRu was executed through pneumatic actuation of the shutter to expose the sample to the sputtering plume for a 2-second period.

**Optical measurements.** All reflectance spectra were measured with a 300 W Xe arc lamp (Newport) as the light source and collected by Flame S spectrometer (Ocean Optics) equipped with integrating sphere (SI photonics). BaSO<sub>4</sub> and PTFE was used as a reference standard. Transmittance spectra were measured with an HP-8452A Diode Array spectrophotometer.

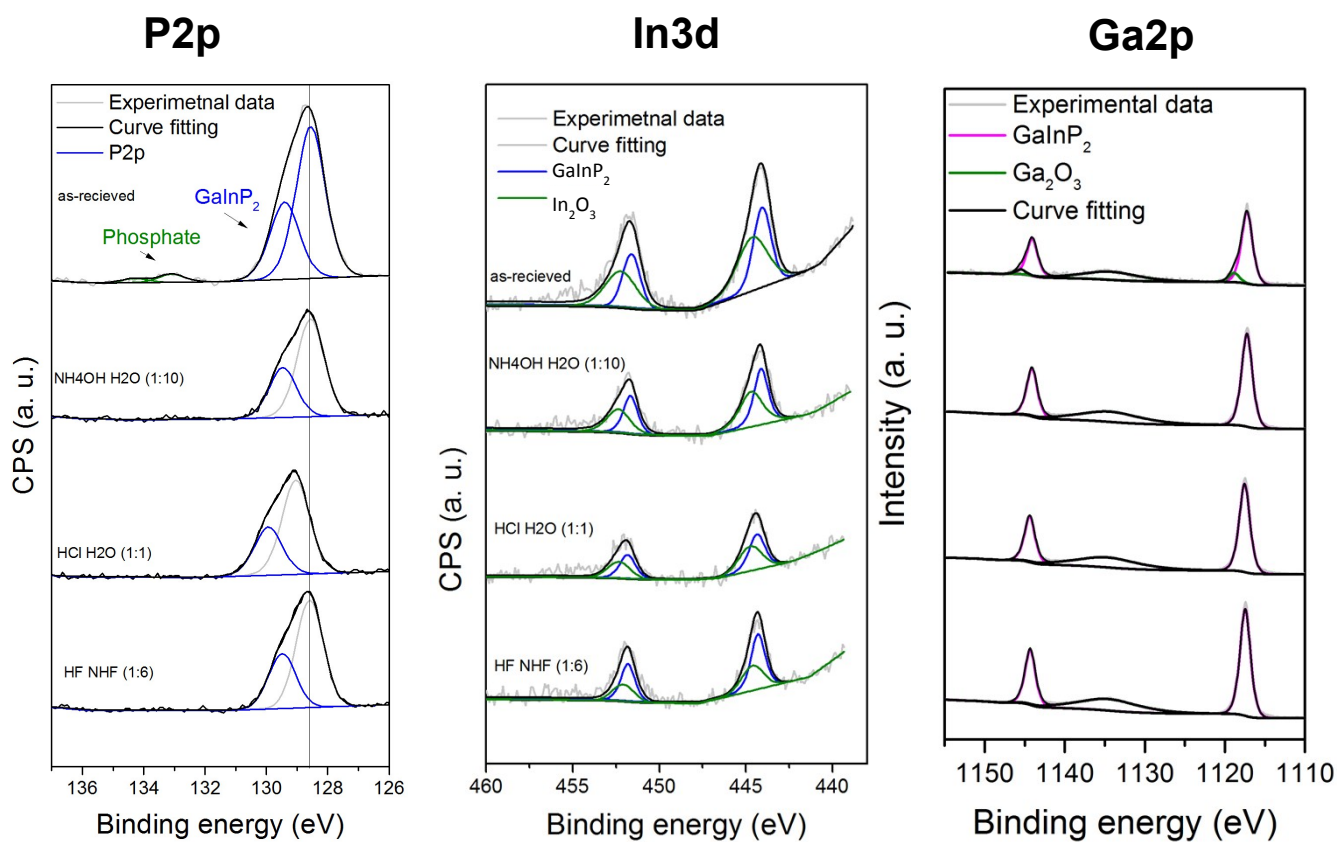
**Physical characterizations** Helium ion microscopy images were collected by an Orion Plus Helium Ion Microscope (ZEISS) operating at a 30 kV acceleration voltage and an ion beam current around 1 pA. X-ray photoelectron spectra were collected by a Thermo K-Alpha spectrometer with a flood gun for charge compensation. All spectra energy was calibrated against adventitious carbon (284.8eV). The TEM specimen was prepared using the Helios focused ion beam. A ~500 nm thick amorphous carbon protection layer was first deposited by electron beam on the surface of Ni<sub>5</sub>P<sub>4</sub> to ensure ideal contrast during HAADF imaging. STEM/EDS mappings were performed on the Themis Z S/TEM, operating at 300 kV with a probe current of ~450 pA. Pixel size and dwell time is 0.1\*0.1 nm<sup>2</sup> and 24 μs, respectively. High-resolution HAADF/STEM images were taken from the Nion UltraSTEM with an acceleration voltage of 60 kV. Probe convergence half angle was 30 mrad. HAADF signal was collected from 80 mrad and above.

**Electrode assembly** The electrical contact of the prepared electrodes was made on the back side of the Au coated GaAs substrate with copper wire using silver paint (SPI supplies). The wire was then inserted into a Pyrex glass tube, and sealed with a mixture of epoxy resin (Loctite Hysol 1C or Loctite EA e-120HP). Electrode areas were defined by epoxy area and measured with a digital photograph and ImageJ analysis. Typical electrode areas ranged between 0.1–0.2cm<sup>2</sup>.

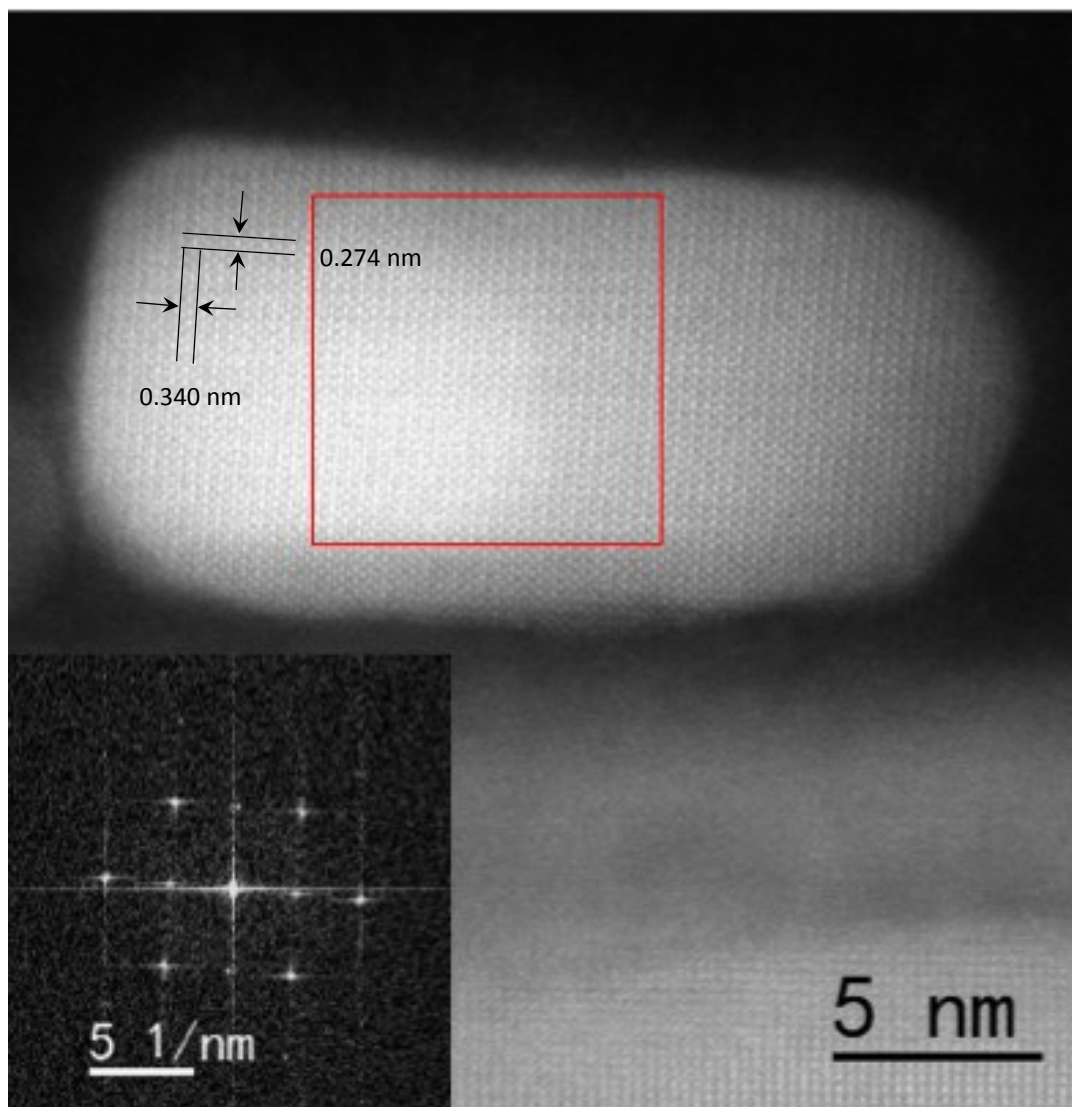
**Photoelectrochemical measurements** LSVs were performed in a 1x5cm<sup>2</sup> glass cuvette cell (FireflySci, Inc.) in 0.5 M H<sub>2</sub>SO<sub>4</sub> with 1mM Triton X-100 using a Solartron potentiostat. Durability measurements were performed in a custom built three-electrode glass cell in 0.5 M H<sub>2</sub>SO<sub>4</sub> using a Bio-logic potentiostat (VSP-300). The working electrodes were illuminated by 300W Xe arc lamp which is calibrated against the GaInP<sub>2</sub> reference cell (NREL) before each measurement. For the durability test, the photoelectrode (working electrode) locates 5mm away from the quartz viewport. For counter and reference electrode, a IrO<sub>x</sub> wire electrode (Alfa Aesar) and mercury/mercury sulfate reference electrode (single junction Hg/Hg<sub>2</sub>SO<sub>4</sub>, saturated K<sub>2</sub>SO<sub>4</sub>, BASi) were used.

**IPCE measurements** The detailed procedure is reported elsewhere.<sup>3</sup> Briefly, a 300 W xenon arc lamp (67005, Newport) was used and monochromatic illumination provided by a monochromator (SP-50, Acton) with 10-nm increments from 300 to 750 nm. The light intensity was measured at each wavelength using a calibrated Si photodiode (S1336-8BQ, Hamamatsu). The averaged illuminated current was used and the dark current subtracted to obtain the photocurrent at each wavelength.

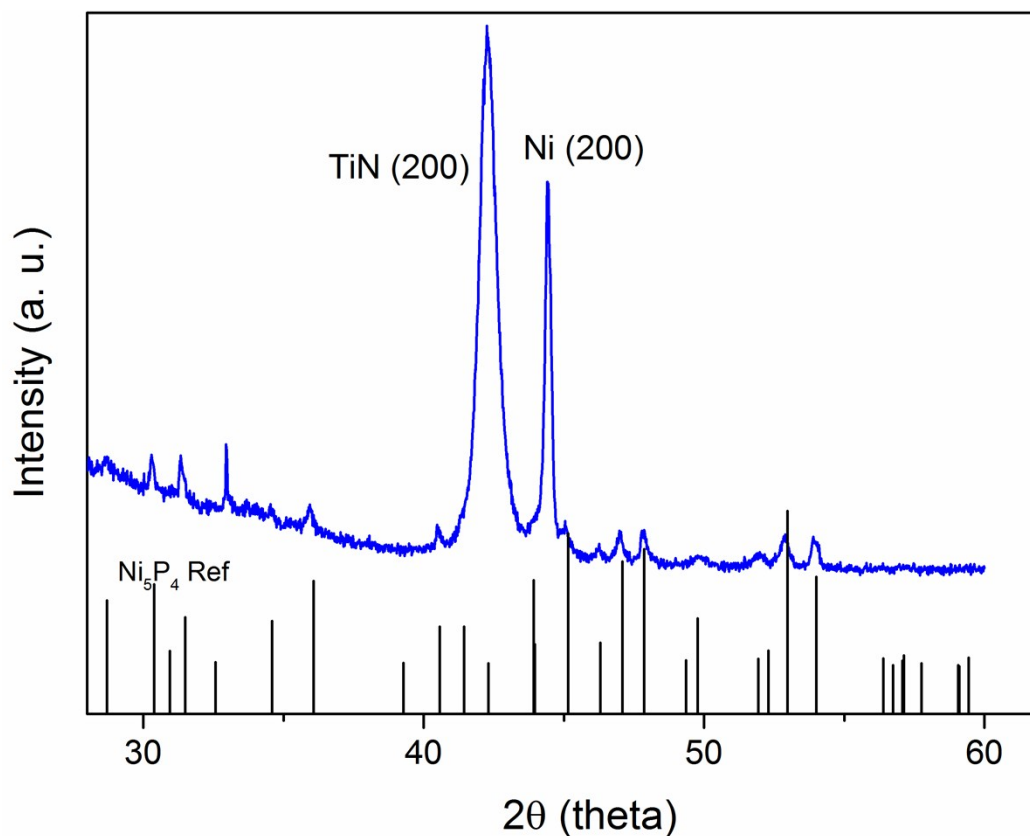
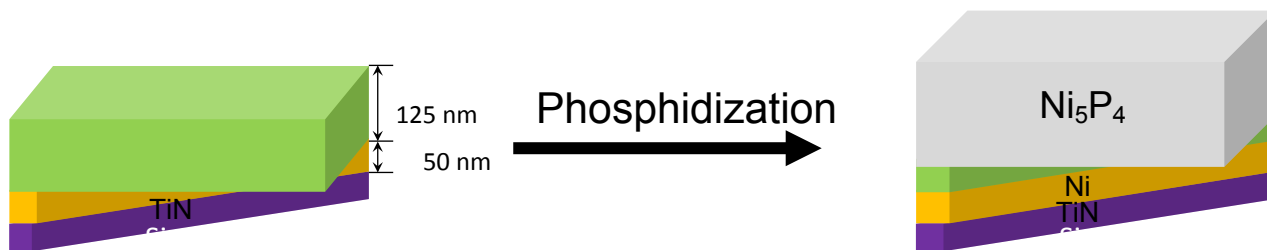
**Faradaic Efficiency Measurement.** The detail method was described elsewhere.<sup>1</sup> Briefly, hydrogen was quantified on an automated online GC (HP 5890 Series II). N<sub>2</sub> was used as a carrier gas. The calibration curve was constructed from constant current electrolysis of water (0.5M H<sub>2</sub>SO<sub>4</sub> electrolyte) with flame-annealed Pt foil as working electrode and IrO<sub>x</sub> mesh as counter electrode, separated by a Nafion membrane. At steady state, samples of the headspace were taken (averaged, n=3 at 10-minute intervals). The faradaic efficiency of the HER for Ni<sub>5</sub>P<sub>4</sub>/TiN/GaInP<sub>2</sub> was measured in a similar fashion at -1mA. The value reported corresponds to the average (n=3) of the headspace hydrogen concentration.



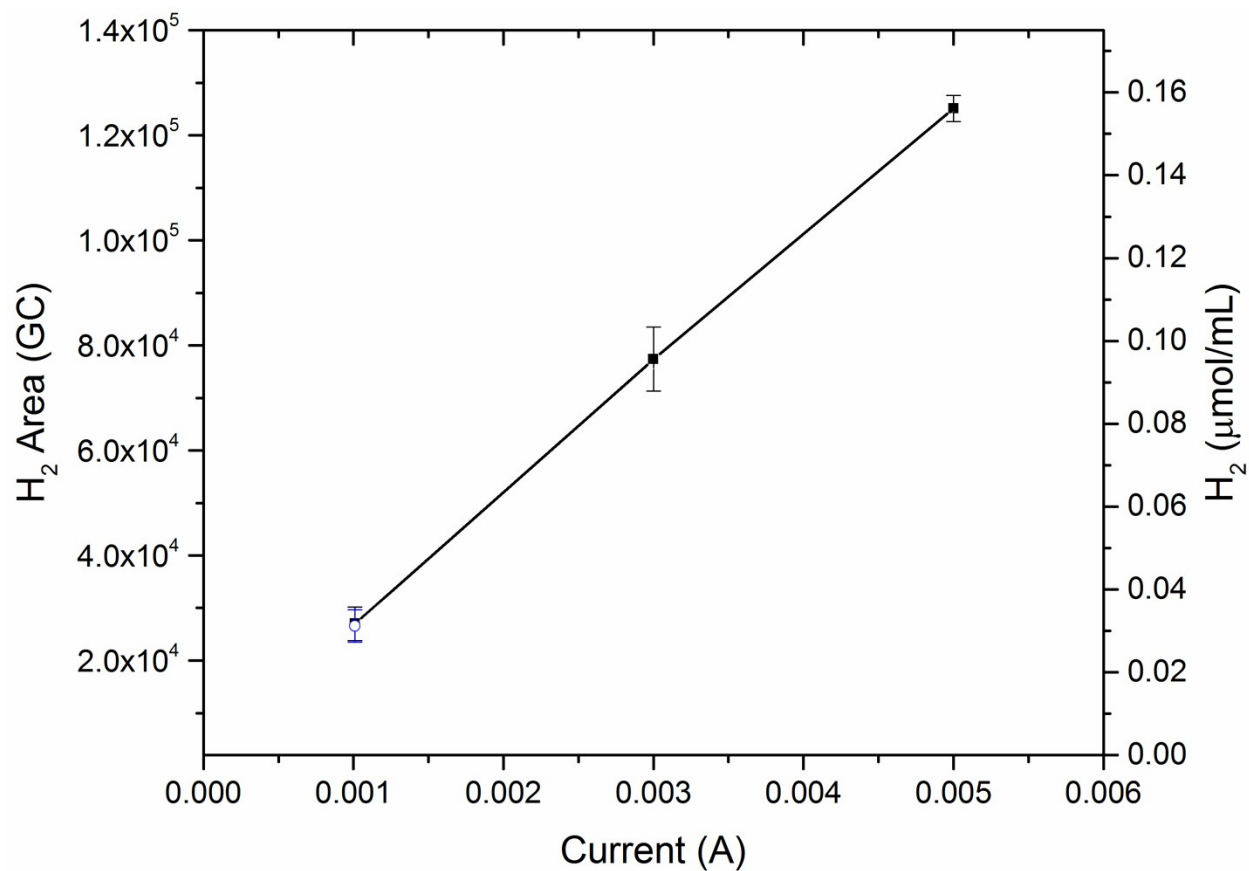
**Figure S1** XPS core level spectra (P2p, In3d, and Ga2p) of GaInP<sub>2</sub> surface after etching the surface oxide using different etching solutions: As-received, diluted NH<sub>4</sub>OH, concentrated HCl, and NH<sub>4</sub>/HF buffered oxide etchant.



**Figure S2** High-magnification STEM-HAADF image of a representative  $\text{Ni}_5\text{P}_4$  island. The measured d-spacing are 0.340 and 0.274 nm, which are matched with (110), and (004) planes of  $\text{Ni}_5\text{P}_4$ . The inset image is FFT of STEM image which is well matched with [1-10] zone axis.

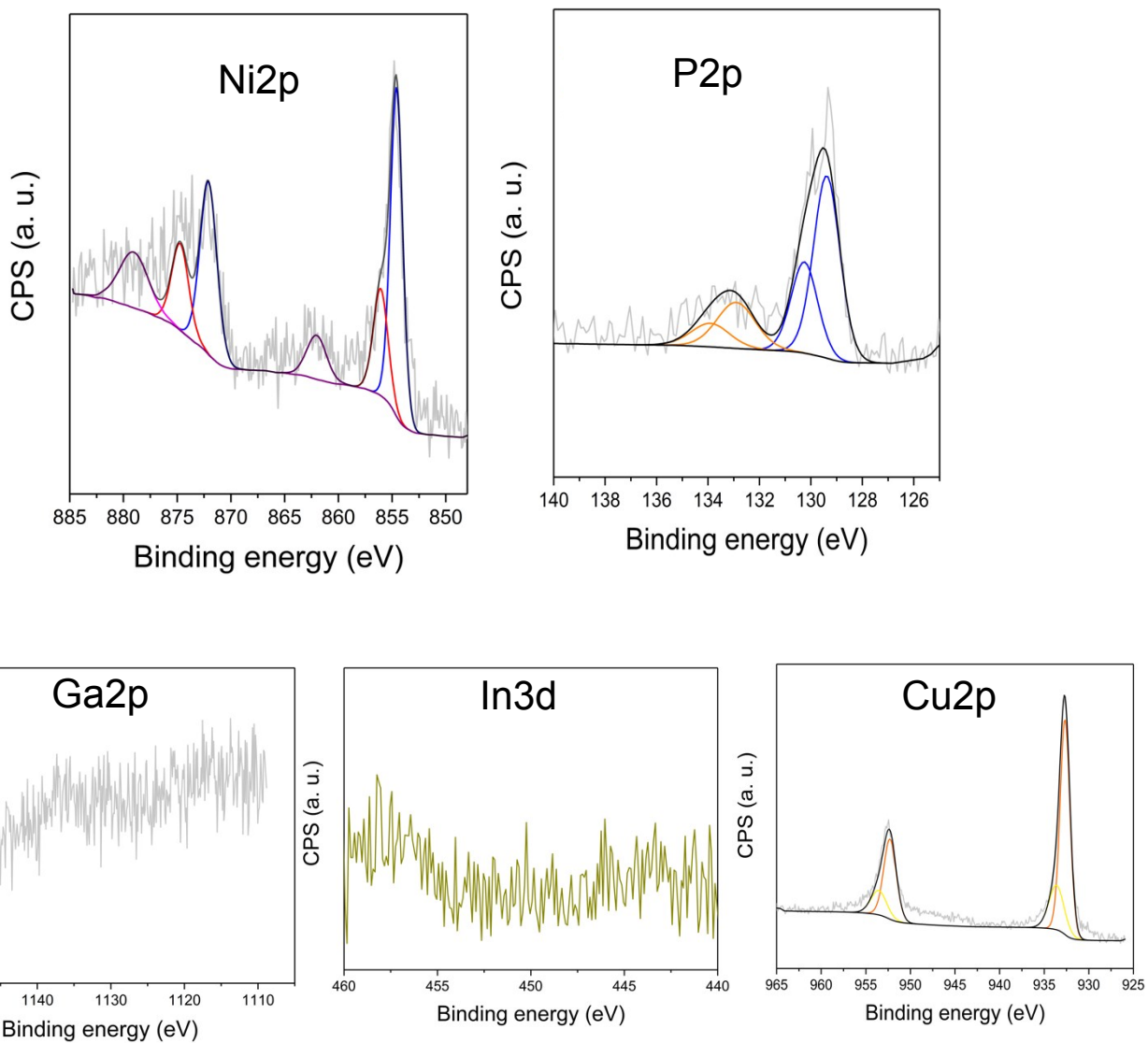


**Figure S3** Reaction scheme of thick (125nm)  $\text{Ni}_5\text{P}_4/\text{Ni}/\text{TiN}/\text{Si}$  sample preparation, and X-ray diffraction (XRD) pattern of the thick  $\text{Ni}_5\text{P}_4/\text{Ni}/\text{TiN}/\text{Si}$  sample. When thick  $\text{Ni}_5\text{P}_4$  films were fabricated, XRD patterns are well matched with reference pattern (PDF 01-089-2588). TiN shows a reflection (200) at  $42.2^\circ$ , and unreacted Ni shows a reflection (200) at  $44.5^\circ$ . Unreacted Ni expect to be fully consumed when phosphidation occur with thin-film of Ni ( $\sim 3\text{nm}$ ).

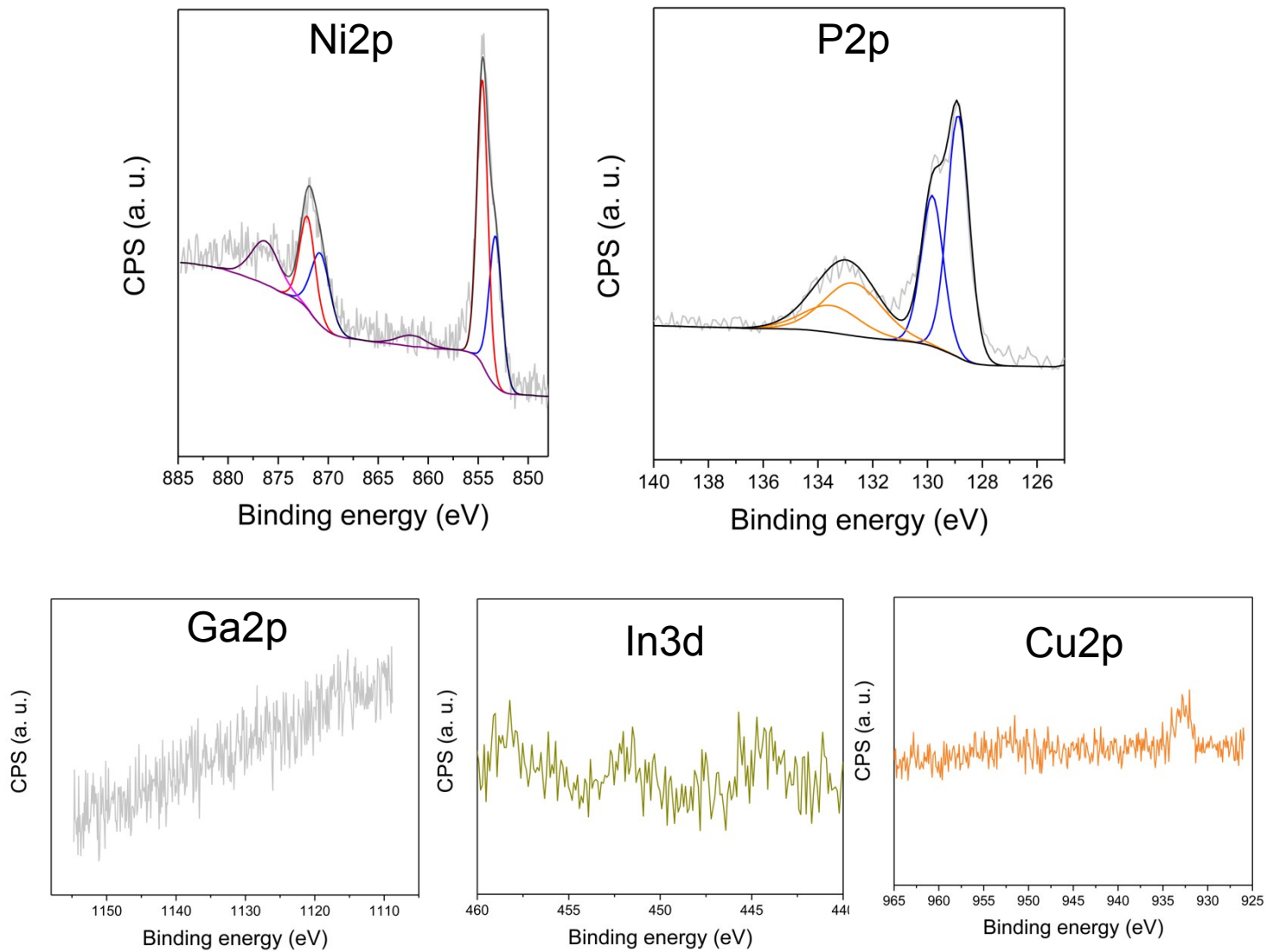


**Figure S4** Faradaic efficiency test of the calibration curve and Ni<sub>3</sub>P<sub>4</sub>/TiN/n<sup>+</sup>p-GaInP<sub>2</sub>. A calibration curve (Black, steady-state H<sub>2</sub> as a function of constant current density) was obtained with the Pt foil benchmark.<sup>2</sup> Blue circle corresponds to Ni<sub>3</sub>P<sub>4</sub>/TiN/n<sup>+</sup>p-GaInP<sub>2</sub> at a constant current at 0.001 A. The results overlapped with the Pt benchmark within the error bars.

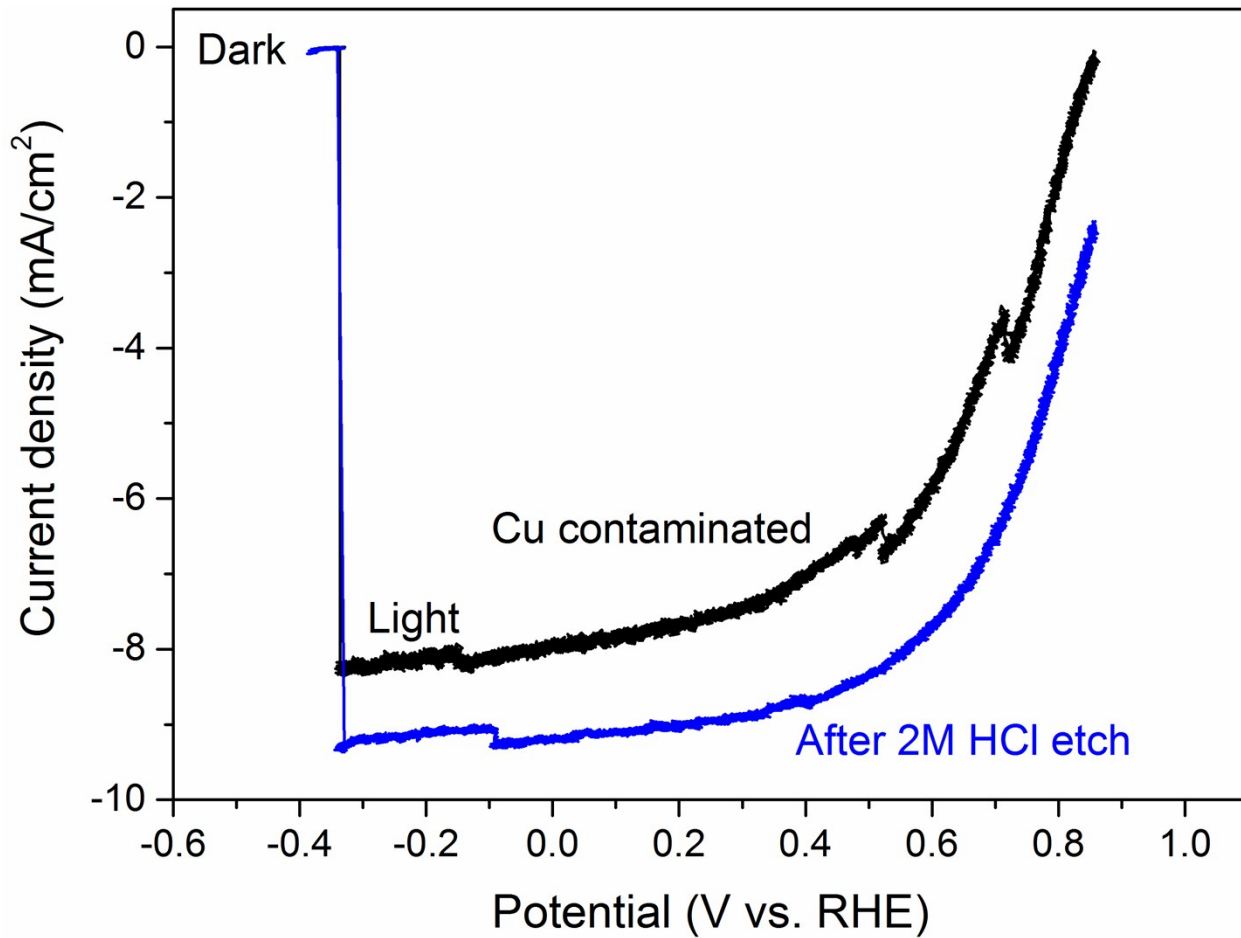




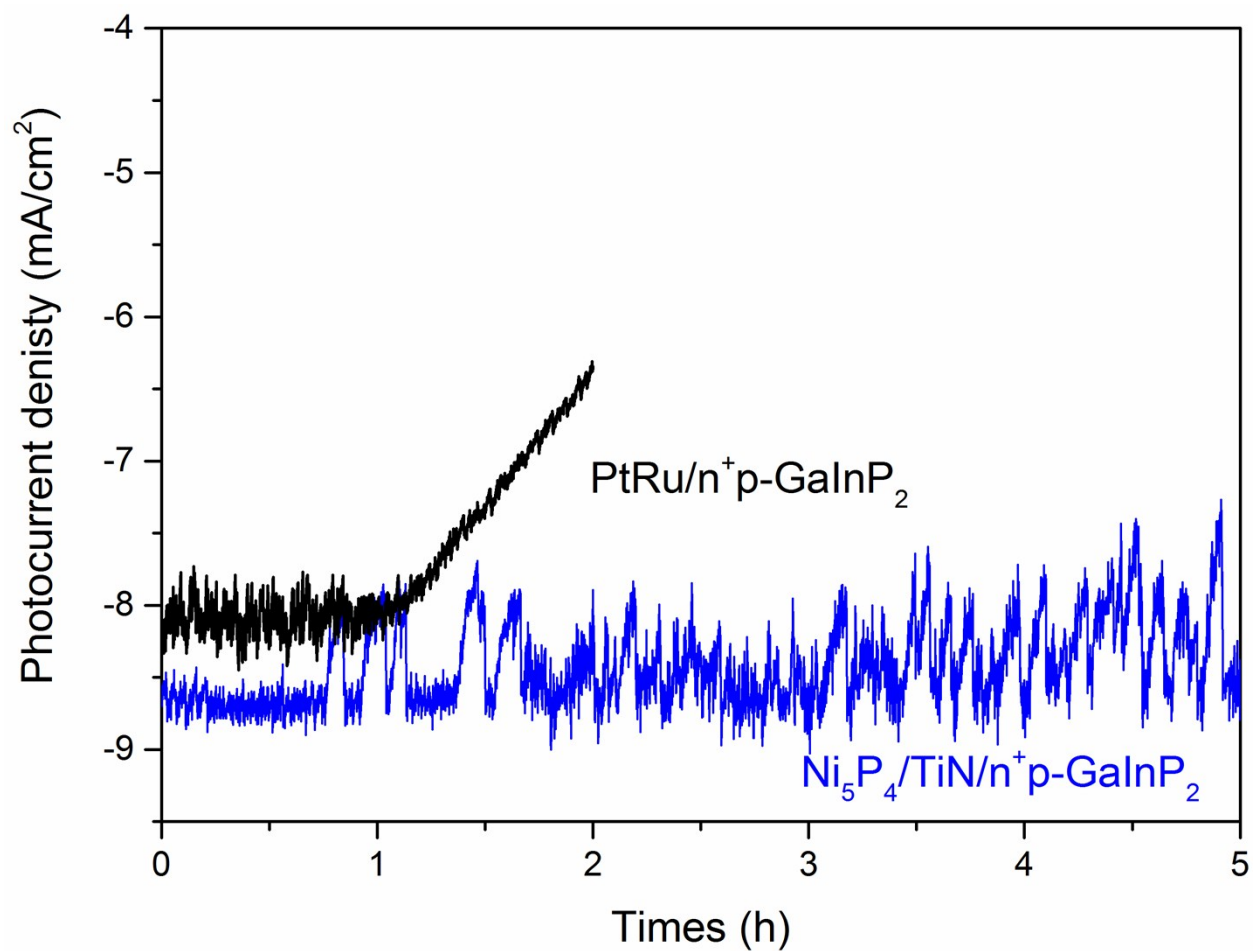
**Figure S5** X-ray photoelectron spectra of Cu contaminated  $\text{Ni}_5\text{P}_4/\text{TiN}/\text{n}^+\text{p-GaInP}_2$  sample after durability test. Cu2p core level spectra show a clear Cu signal while S/N ratio of Ni and P are decreased.



**Figure S6** X-ray photoelectron spectra of 2M HCl (3s) etched Cu contaminated  $\text{Ni}_5\text{P}_4/\text{TiN}/\text{n}^+\text{p-GaInP}_2$  sample. Cu signal is substantially decreased and Ni and P S/N ratios are recovered.



**Figure S7** LSVs of Cu contaminated Ni<sub>3</sub>P<sub>4</sub>/TiN/n<sup>+</sup>p-GaInP<sub>2</sub> (24 CA run) and after performing 2M HCl (3s) for etching.



**Figure S8** 5 hours chronoamperograms of PtRu/n<sup>+</sup>p-GaInP<sub>2</sub> and Ni<sub>5</sub>P<sub>4</sub>/TiN/n<sup>+</sup>p-GaInP<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Potential was held at -0.78 V vs. RHE, and +0.25 V vs. RHE for of PtRu/n<sup>+</sup>p-GaInP<sub>2</sub> and Ni<sub>5</sub>P<sub>4</sub>/TiN/n<sup>+</sup>p-GaInP<sub>2</sub>, respectively.

## References

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- 2 S. Hwang, S. H. Porter, A. B. Laursen, H. Yang, M. Li, V. Manichev, K. U. D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel and G. C. Dismukes, *J. Mat. Chem. A*, 2019, **7**, 2400–2411.
- 3 J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner and T. G. Deutsch, *Nature Energy*, 2017, **2**, 17028.