

SUPPORTING INFORMATION

Investigation of the photocorrosion of n-GaP photoanodes in acid with in-situ UV-Vis spectroscopy

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Photoelectrochemical energy-conversion behavior

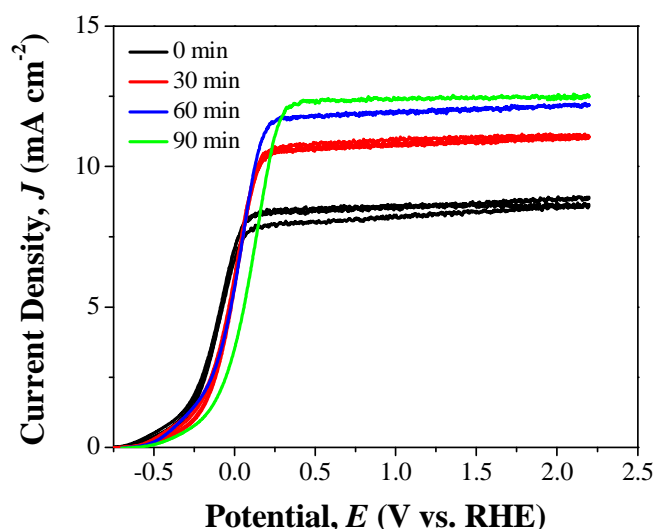


Fig. S1. Current density vs. potential (J - E) behavior for n-GaP in 1 M H_2SO_4 under 2 Suns AM1.5 illumination. The legend refers to how long the photoanode was under applied bias at 1.5 – 2.0 V vs. RHE.

In-situ UV-Vis spectroscopy

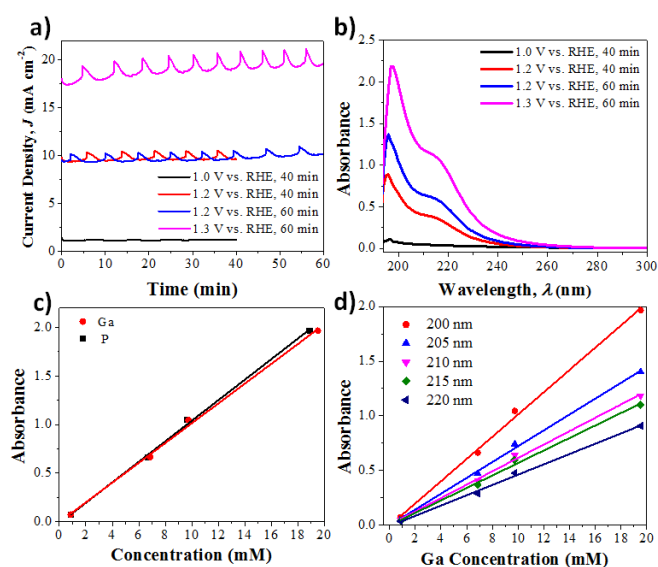


Fig. S2. Calibration for p^+ -GaP in-situ UV-Vis spectroscopy. (a) Current density vs. time for p^+ -GaP photoanodes at 1.2 V vs. RHE in 1 M H_2SO_4 and corresponding (b) absorbance vs. wavelength data. (c) Concentration of dissolved Ga and P in the electrolyte as measured by ICP-MS. (d) Resulting absorbance vs. Ga concentration calibration data.

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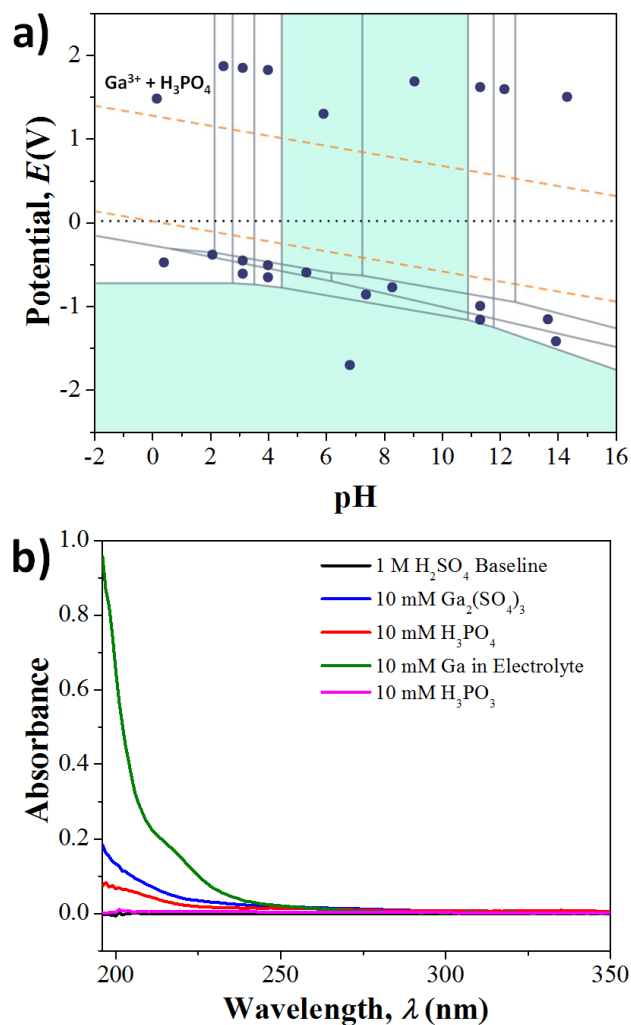


Fig. S3. (a) Calculated Pourbaix diagram for GaP predicting stable phases of Ga^{3+} and H_3PO_4 for oxidative potentials in strong acid. (b) UV-Vis absorbance spectra for electrolyte from n-GaP under illumination at 1.4 V vs. RHE corresponding to a Ga concentration of 10 mM (green), a 10 mM solution of $Ga_2(SO_4)_3$ (blue), a 10 mM solution of H_3PO_4 (red), and a 10 mM solution of H_3PO_3 (pink), all in aqueous 1 M H_2SO_4 .

The Pourbaix diagram for GaP was generated using the online platform of the Materials Project,^{1,2} specifically the Pourbaix Diagram application.³

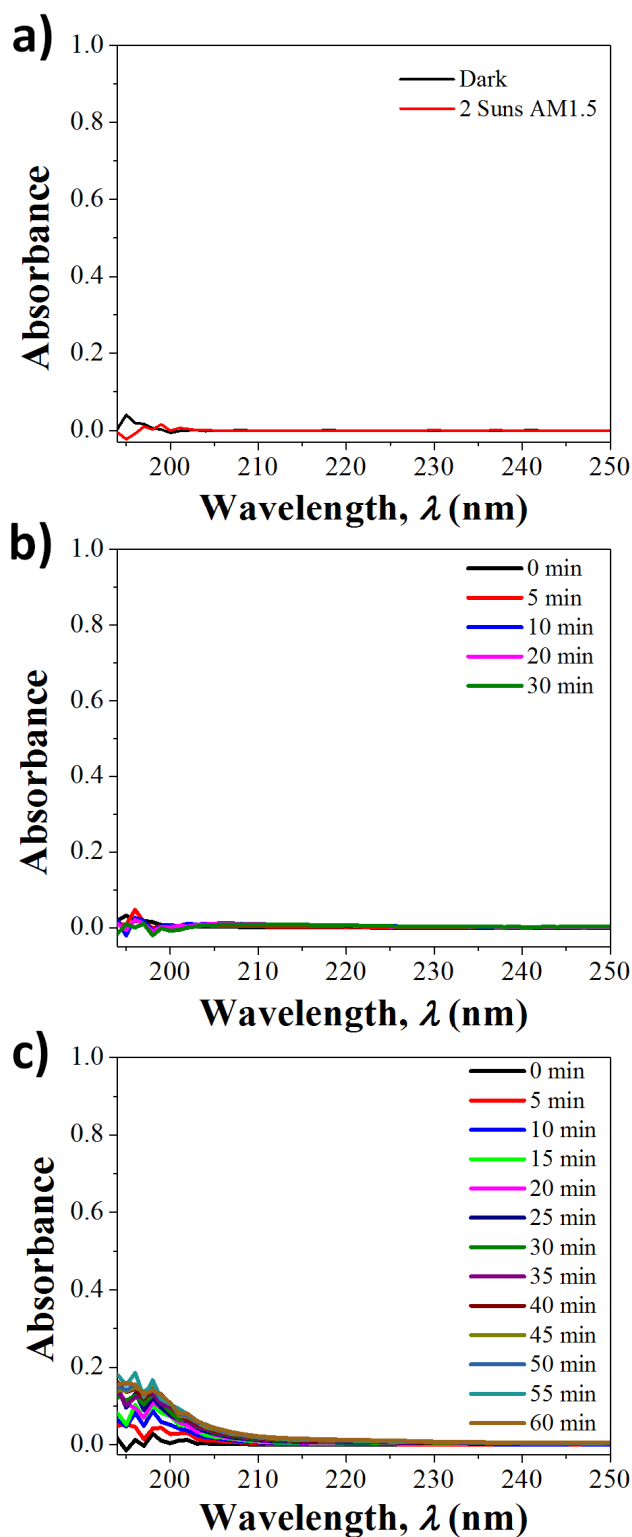


Fig. S4. Control measurements for in-situ UV-Vis spectroscopy with PEC characterization. (a) Absorbance spectra for pure 1 M H_2SO_4 electrolyte in the dark (the condition for background correction) and with 2 Suns AM1.5 illumination orthogonal to the monochromatic UV-Vis signal. (b) Absorbance spectra for n-GaP at 1.8 V vs. RHE in the dark. (c) Absorbance spectra over time for pure 1 M H_2SO_4 with 2 Suns AM1.5 illumination orthogonal to the monochromatic UV-Vis signal with no n-GaP present.

Corrosion of n-GaP photoanodes

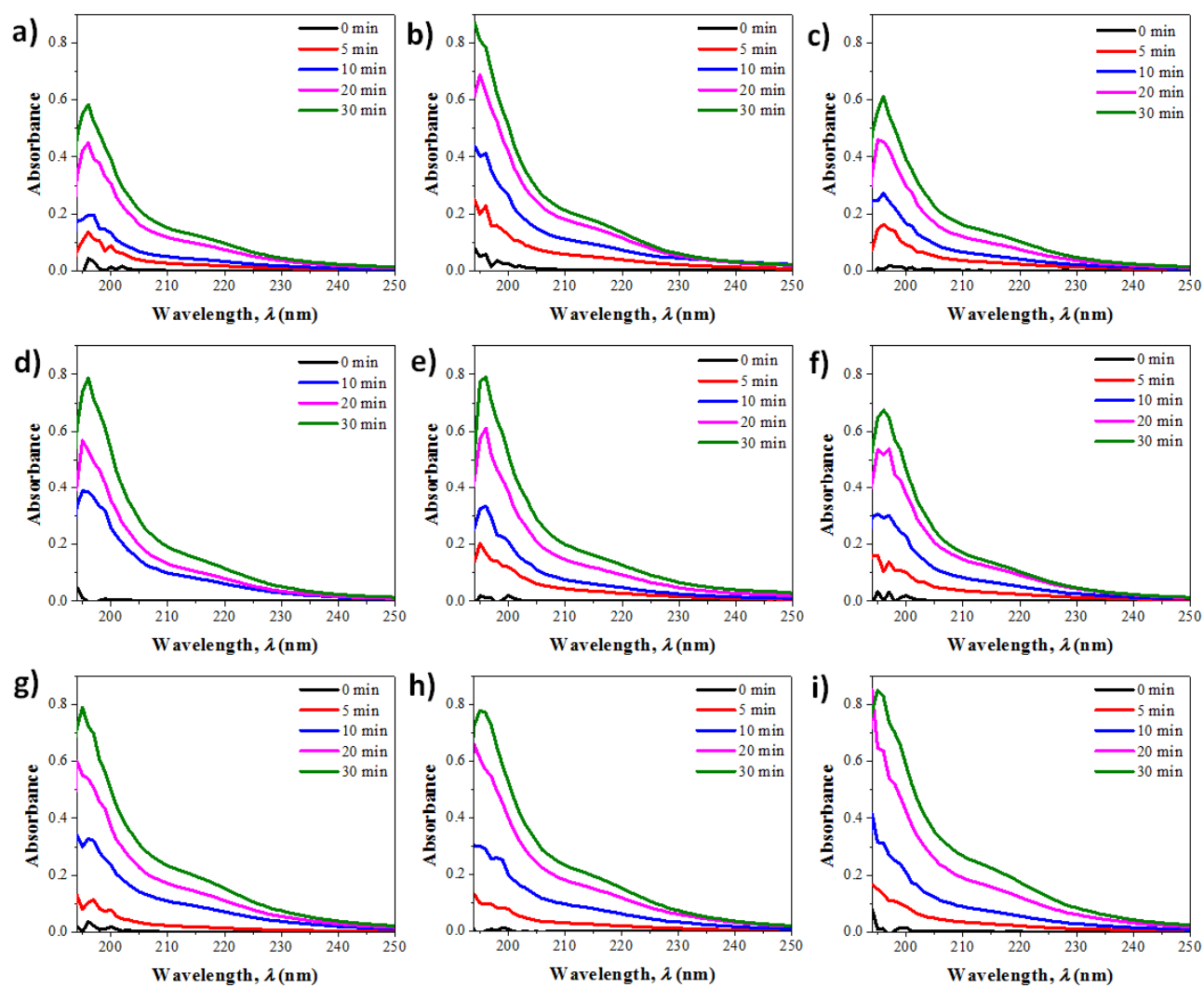


Fig. S5. Example absorbance data vs. time for n-GaP under 2 Suns AM1.5 illumination in 1 M H₂SO₄, operating potentiostatically at (a) 0.4 V, (b) 0.6 V, (c) 0.8 V, (d) 1.0 V, (e) 1.2 V, (f) 1.4 V, (g) 1.6 V, (h) 1.8 V, and (i) 2.0 V vs. RHE.

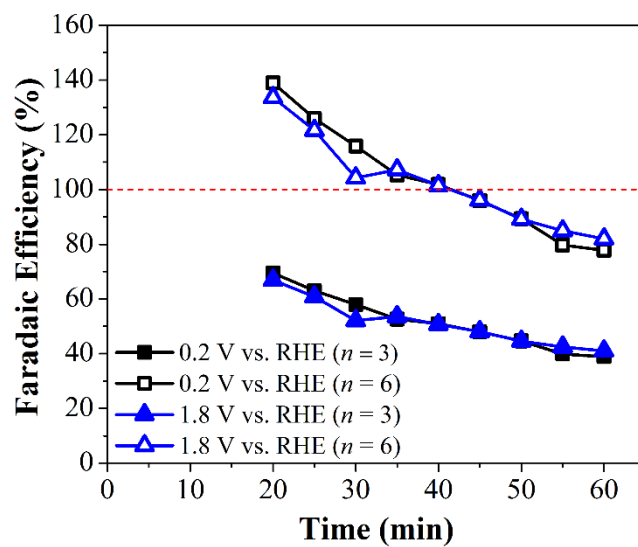


Fig. S6. Extended 1 h measurements of n-GaP under 2 Suns. Calculated faradaic efficiency for GaP oxidation using either $n = 3$ (filled markers) or $n = 6$ (open markers), from Ga concentration determined with in-situ UV-Vis spectroscopy.

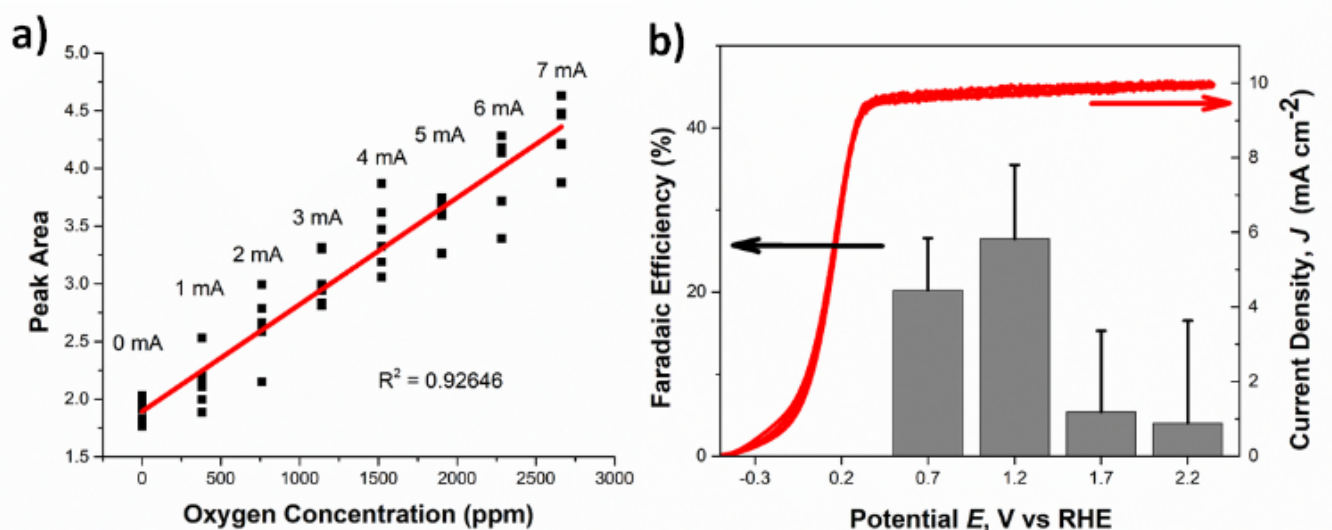


Fig. S7. Characterization of gaseous oxygen in the reactor headspace. (a) O_2 calibration curve produced with a Pt anode for water-splitting. (b) Calculated faradaic efficiency for OER (grey, left scale) vs. potential based on measured O_2 concentration and the charge passed, and corresponding n-GaP current density (red, right scale) vs. potential. Bare n-GaP was measured in 1 M H_2SO_4 under 2 Suns AM1.5 illumination.

Oxygen concentration calibration was performed with a three-electrode setup using a Pt mesh working electrode, a Pt mesh counter electrode and a Ag/AgCl reference electrode in a four-neck flask containing 1 M H_2SO_4 . The counter electrode was separated from the rest of the cell with a glass frit to avoid hydrogen gas from mixing into the exhaust of the dynamic sampling loop of the gas chromatograph, and to prevent oxygen reduction at the cathode. N_2 carrier gas was bubbled through the electrolyte at 10 sccm, and the gas outlet stream was sampled in a 1 mL sampling loop. The GC was an SRI 6810C Gas Mix #3 configuration. Oxygen was detected by a thermal conductivity detector (TCD). The calibration was performed using chronopotentiometry at 0, 1, 2, 3, 4, 5, 6, and 7 mA with at least 6 measurements for each current level (Fig. S7a).

OER on n-GaP was performed in a similar fashion with the n-GaP as the working electrode and the position calibrated for 2 Suns intensity. OER faradaic efficiency was determined at a no bias (no sun) condition as well as 0.7, 1.2, 1.7, and 2.2 V vs. RHE. No oxygen beyond the baseline value was detected at the no bias condition. Each faradaic efficiency value measured consisted of an average of 6 oxygen measurements conducted sequentially over ~ 2 h.

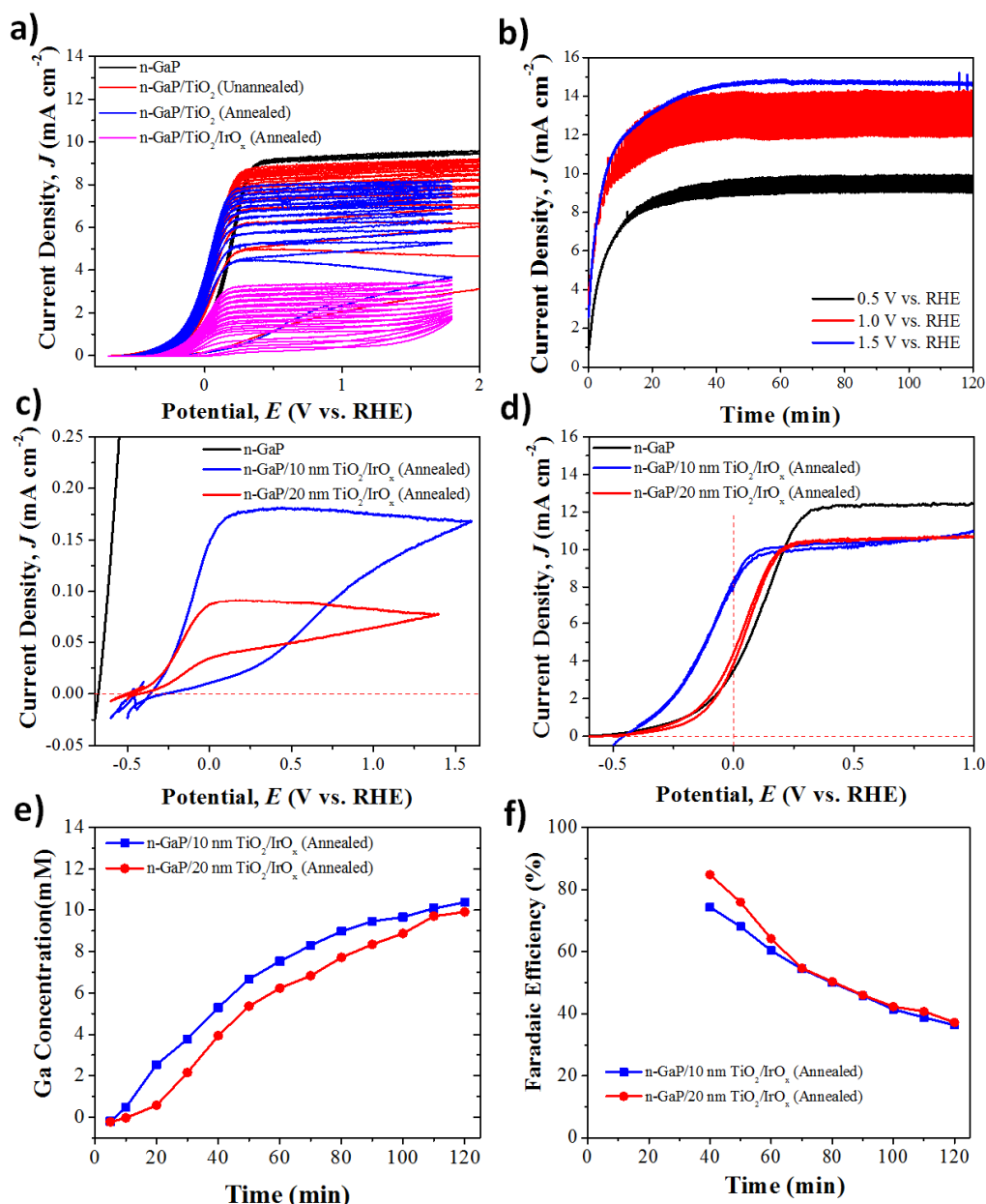
Effect of TiO₂ protective layer

Fig. S8. n-GaP photocorrosion under 2 Suns with variable ALD TiO₂ thickness. (a) Current density vs. potential (*J-E*) behavior for multiple cycles for n-GaP with different protective layers. (b) Chronoamperometric behavior for n-GaP/TiO₂/IrO_x (Annealed) at different potentials. TiO₂ in (a-b) was 4 nm thick. (c-d) *J-E* behavior (c) before and (d) after 2 h at 2 V vs. RHE, and corresponding time dependence for (e) Ga concentration and (f) faradaic efficiency for GaP oxidation.

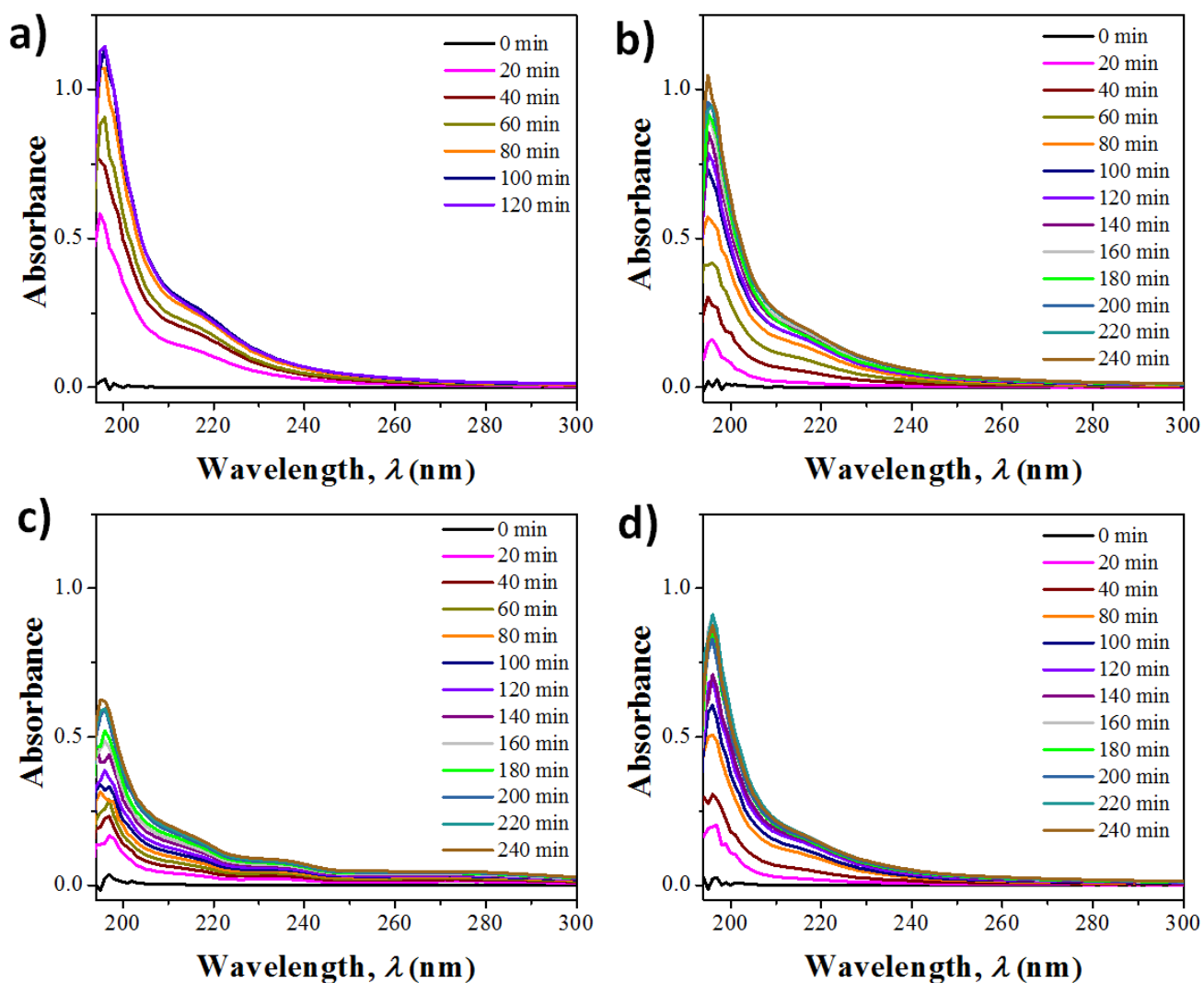


Fig. S9. In-situ UV-Vis spectroscopic measurement of absorbance over time at 0.2 V vs. RHE under 2 Suns for (a) n-GaP, (b) n-GaP/TiO₂ (Unannealed), (c) n-GaP/TiO₂ (Annealed), and (d) n-GaP/TiO₂/IrO_x (Annealed). The TiO₂ was 20 nm thick by ALD in (b-d).

GaP electrode surface characterization

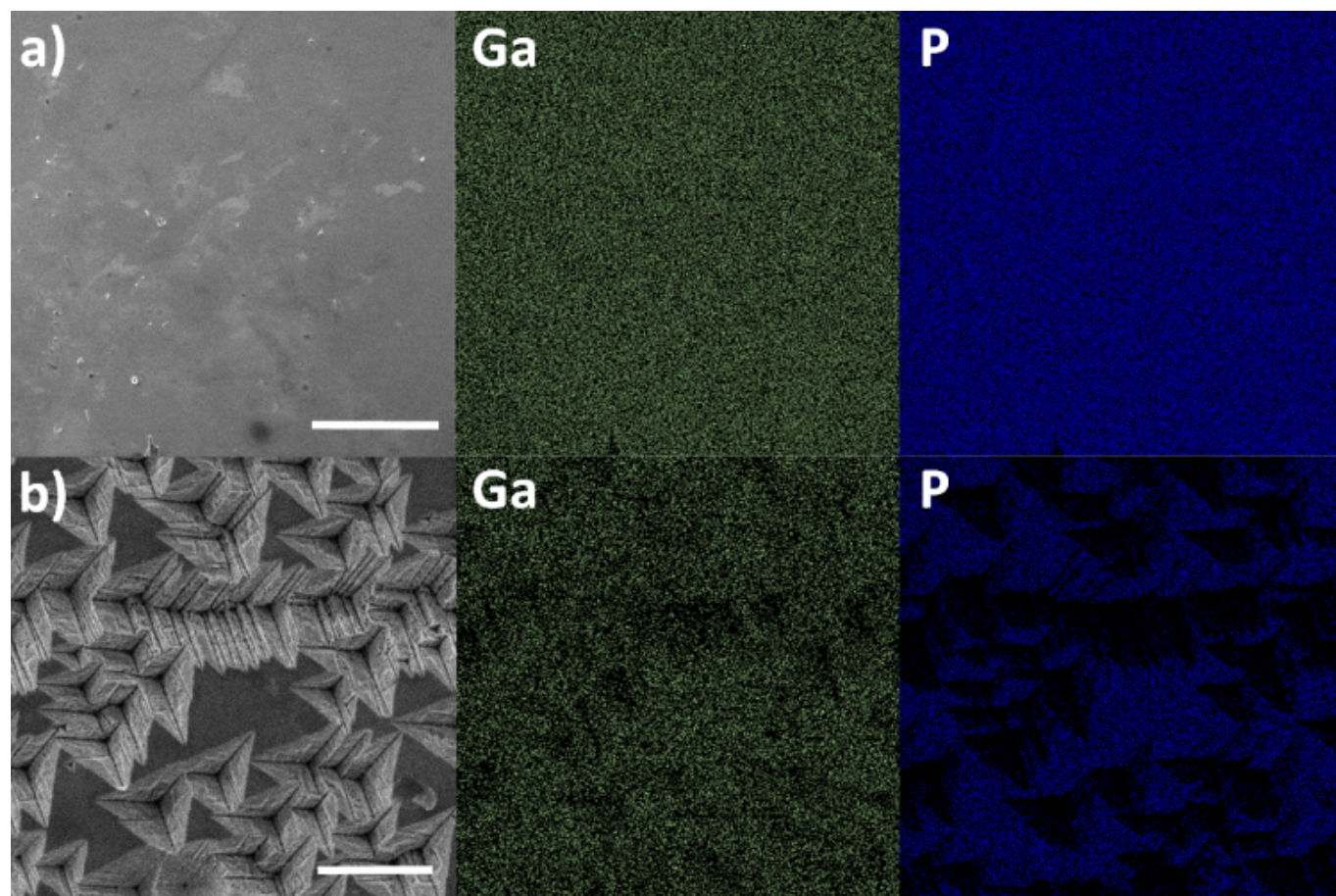


Fig. S10. SEM images (left) and EDS maps for Ga (center) and P (right) for annealed n-GaP/TiO₂ (a) before and (b) after 4 h at 0.2 V vs. RHE under 2 Suns. The scale bar is 500 μm in (a) and 100 μm in (b).

Energy dispersive X-ray spectroscopy (EDS) mapping measurements were conducted using a VEGA3 TESCAN microscope with an accelerating voltage of 20 kV.

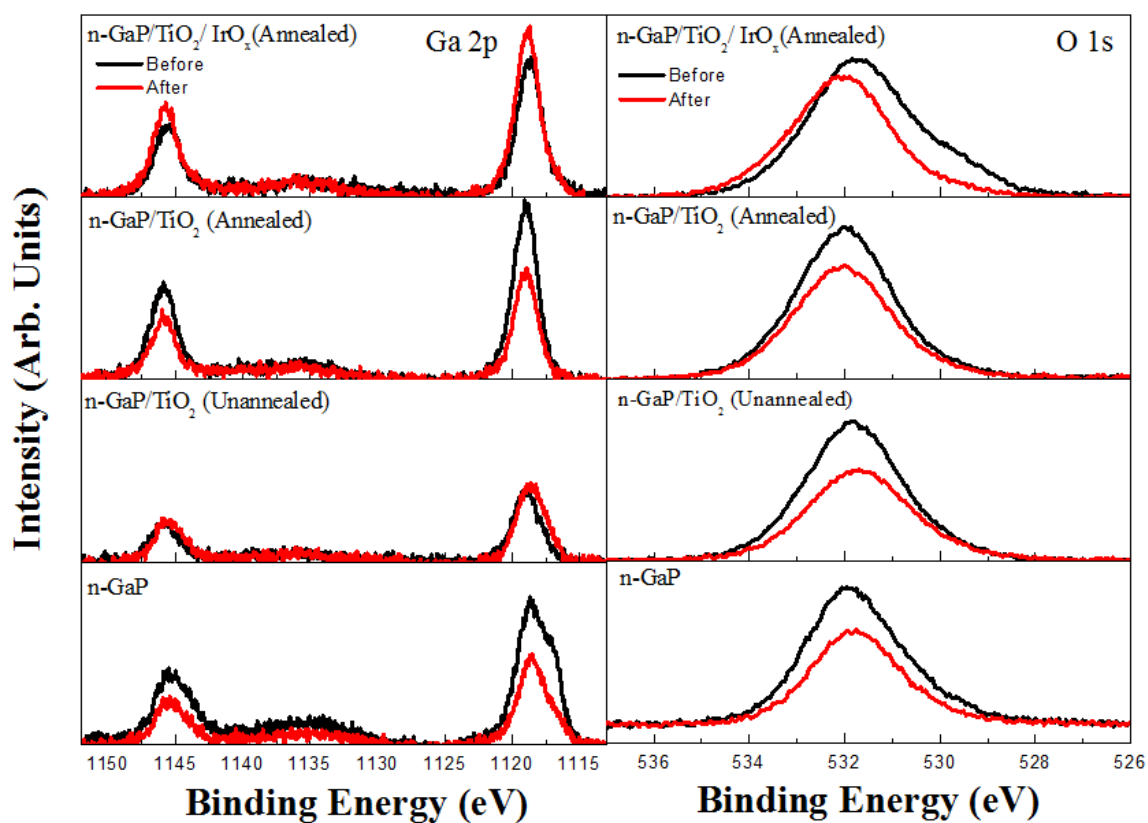


Fig. S11. XPS spectra for the n-GaP with and without protective layers before (black) and after (red) extended potentiostatic operation at 0.2 V vs RHE under 2 Suns for the Ga 2p (left) and O 1s (right) regions.

Notes and references

1. www.materialsproject.org.
2. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *Appl Materials*, 2013, **1**, 011002.
3. K. A. Persson, B. Waldwick, P. Lazic and G. Ceder, *Physical Review B*, 2012, **85**, 235438.