Supplementary Information

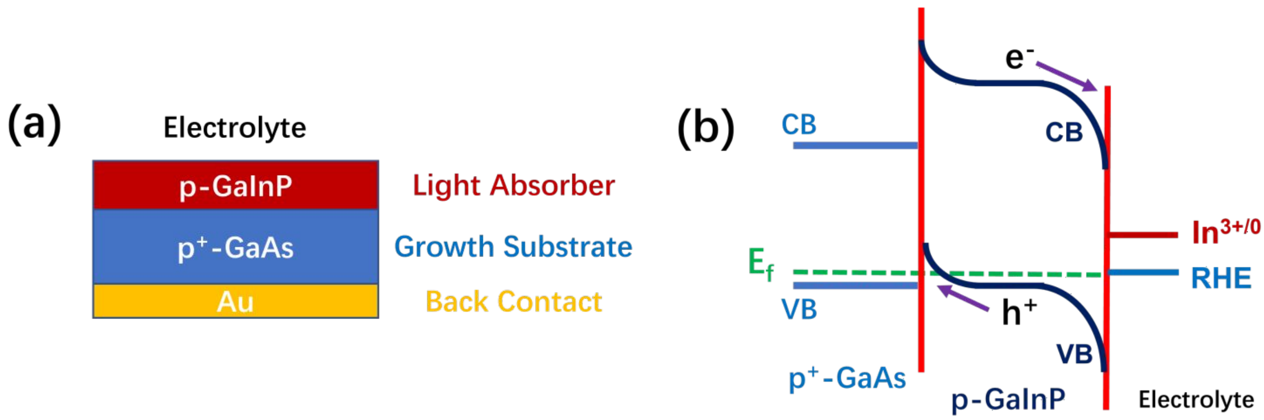
Understanding the Stability of Etched or Platinized p-GaInP Photocathodes for Solar-driven H_2 Evolution

Weilai Yu[1], James L. Young[2], Todd G. Deutsch[2], Nathan S. Lewis[1*]

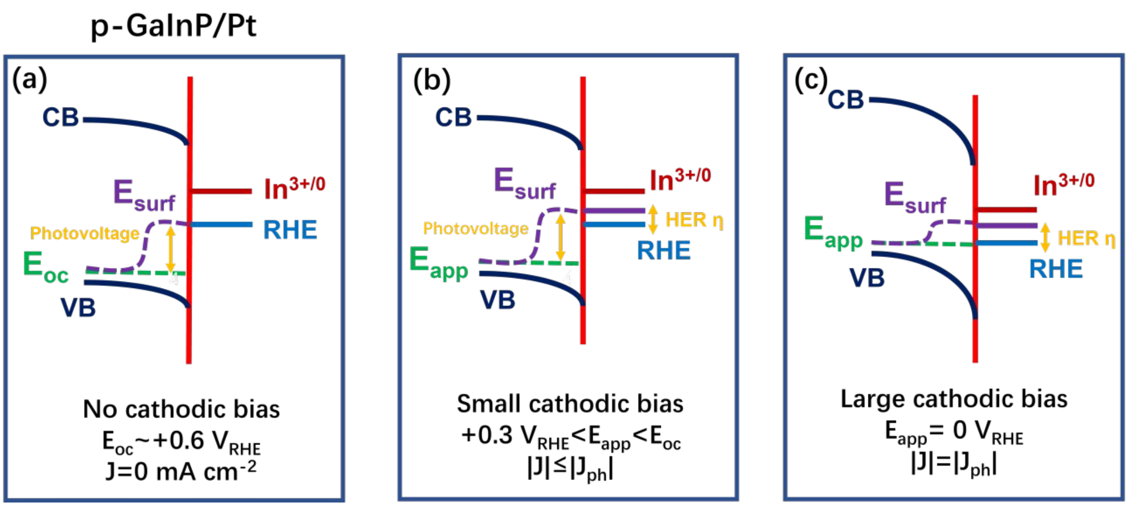
[1]Division of Chemistry and Chemical Engineering and Beckman Institute, California Institute of Technology, Pasadena, CA 91125, United States

[2]Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States

Email: nslewis@caltech.edu



Scheme S1. (a) device structure and (b) band diagram of the p^+-GaAs/p-GaInP photoelectrode used in this study.[1–3]



Scheme S2. Comparison of band energy diagram for an illuminated p-GaInP/Pt photocathode under increasing cathodic biases.[4] (a) At E_{oc}, E_{surf} equilibrates with the RHE potential due to the fast HER kinetics of Pt; the E_{oc} value represents the photovoltage produced by p-GaInP; (b) under small applied cathodic bias (+0.3 V_{RHE}<E_{app}<E_{oc}), the band bending of p-GaInP increases and E_{surf} becomes more negative than RHE to drive cathodic J due to the HER overpotential (η); (c) When E_{app} = 0 V_{RHE}, E_{surf} stays between the RHE potential and E(In^{3+}/In^0), which equals the η of HER to drive J_{ph}.

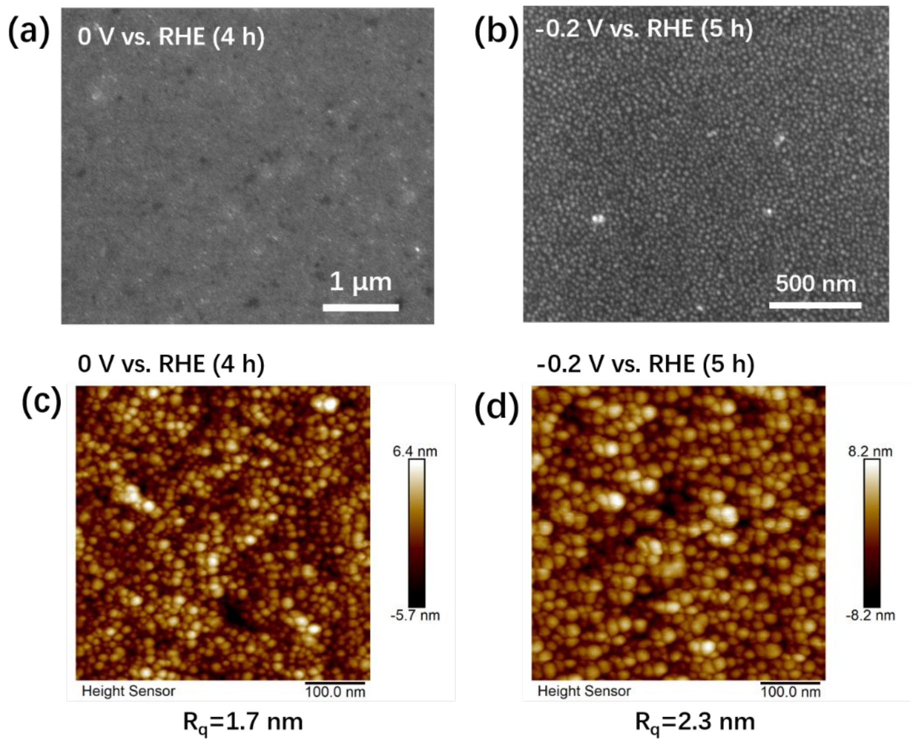


Figure S1. Comparison of (a-b) SEM images and (c-d) AFM images of etched p-GaInP electrodes evaluated at (a,c) 0 V vs. RHE for 4 h and (b,d) -0.2 V vs. RHE for 5 h, in 1.0 M KOH(aq) under 1-sun illumination. R_q is the surface roughness.

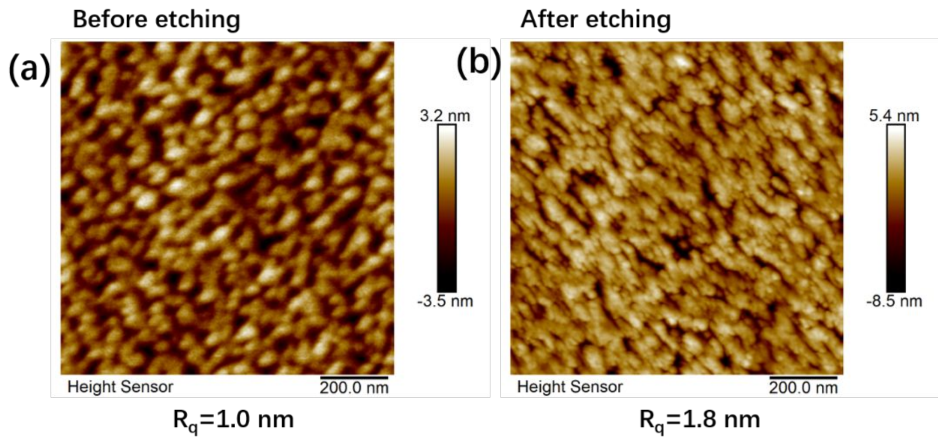


Figure S2. Comparison of AFM images of p-GaInP samples (a) before and (b) after etching. R_q is the surface roughness.

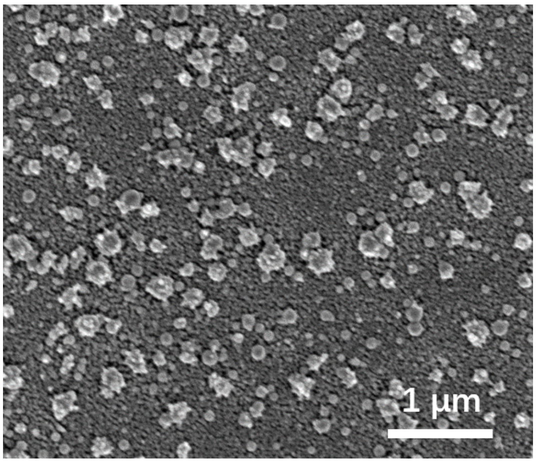


Figure S3. SEM image of a p-GaInP/Pt electrode after 213 h of CA at 0 V vs. RHE in 1.0 M H_2SO_4(aq) under 1-sun illumination.

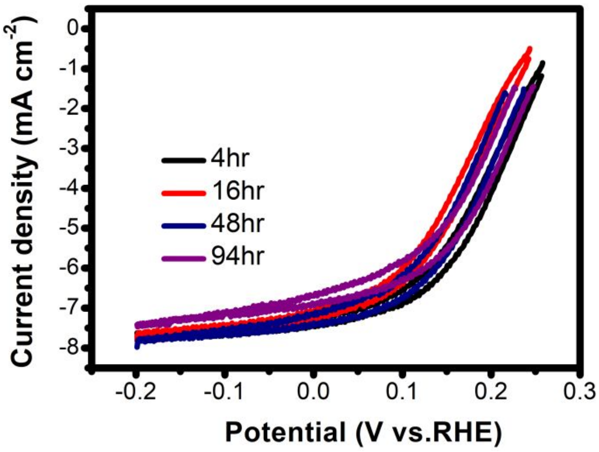


Figure S4. Comparison of the *J*-E behavior of a p-GaInP/Pt electrode during CA at 0 V vs. RHE in 1.0 M KOH(aq) under 1-sun illumination.

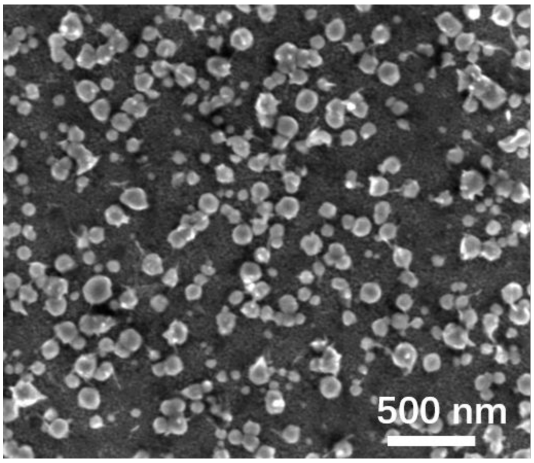


Figure S5. SEM image of a p-GaInP/Pt electrode after 139 h of CA at 0 V vs. RHE in 1.0 M KOH(aq) under 1-sun illumination.

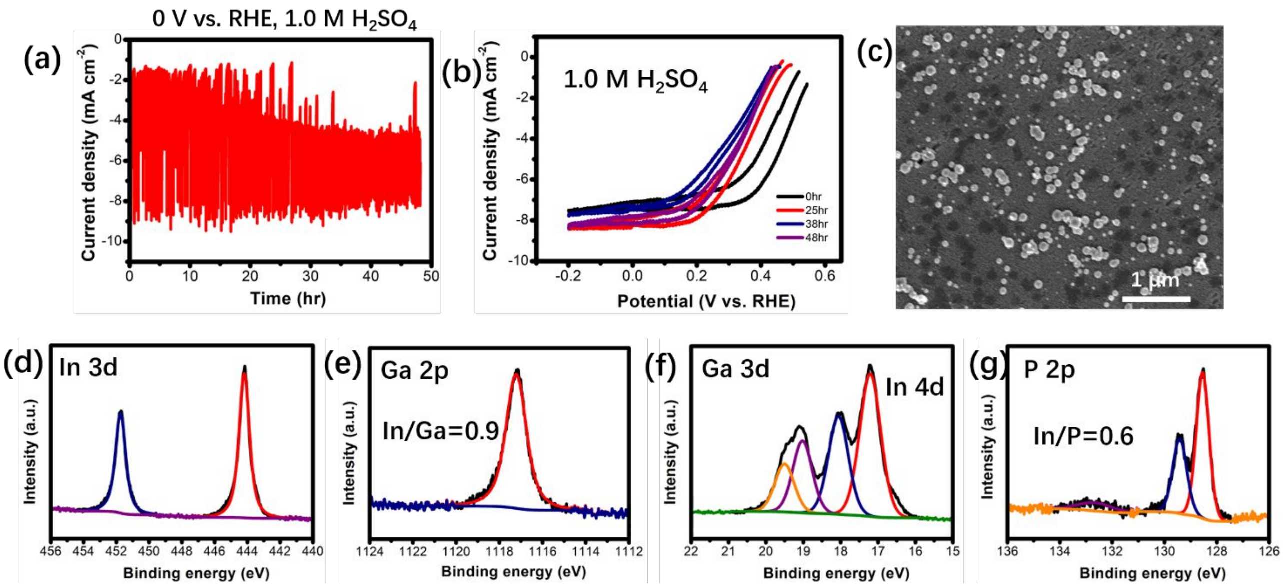


Figure S6. Repeated stability test of a p-GaInP/Pt electrode in an aqueous acidic electrolyte. (a) CA of p-GaInP/Pt at 0 V vs. RHE in 1.0 M H_2SO_4(aq) under 1-sun illumination. (b) *J-E* behavior of a p-GaInP/Pt photoelectrode during the CA in (a). (c) SEM image of p-GaInP/Pt after CA in (a). (d-g) XP spectra of the (e) In 3d, (f) Ga 2p, (g) Ga 3d/In 4d and (h) P 2p regions for p-GaInP/Pt after the CA in (a).

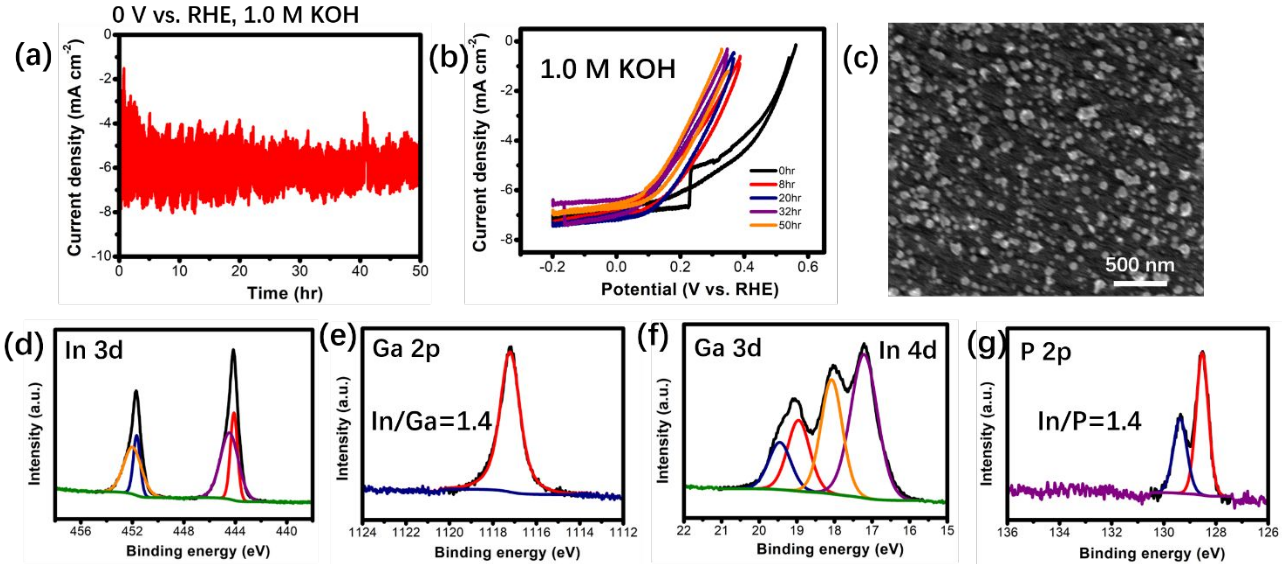


Figure S7. Repeated stability test of a p-GaInP/Pt electrode in an aqueous alkaline electrolyte. (a) CA of p-GaInP/Pt at 0 V vs. RHE in 1.0 M KOH(aq) under 1-sun illumination. (b) Comparison of the *J*-*E* behavior of p-GaInP/Pt photoelectrode during the CA in (a). (c) SEM image of a p-GaInP/Pt electrode after CA in (a). (d-g) XP spectra of the (e) In 3d, (f) Ga 2p, (g) Ga 3d/In 4d and (h) P 2p regions for a p-GaInP/Pt photoelectrode after the CA in (a). The XPS data collectively showed the formation of InO_x and surface enrichment of In relative to Ga and P atoms.

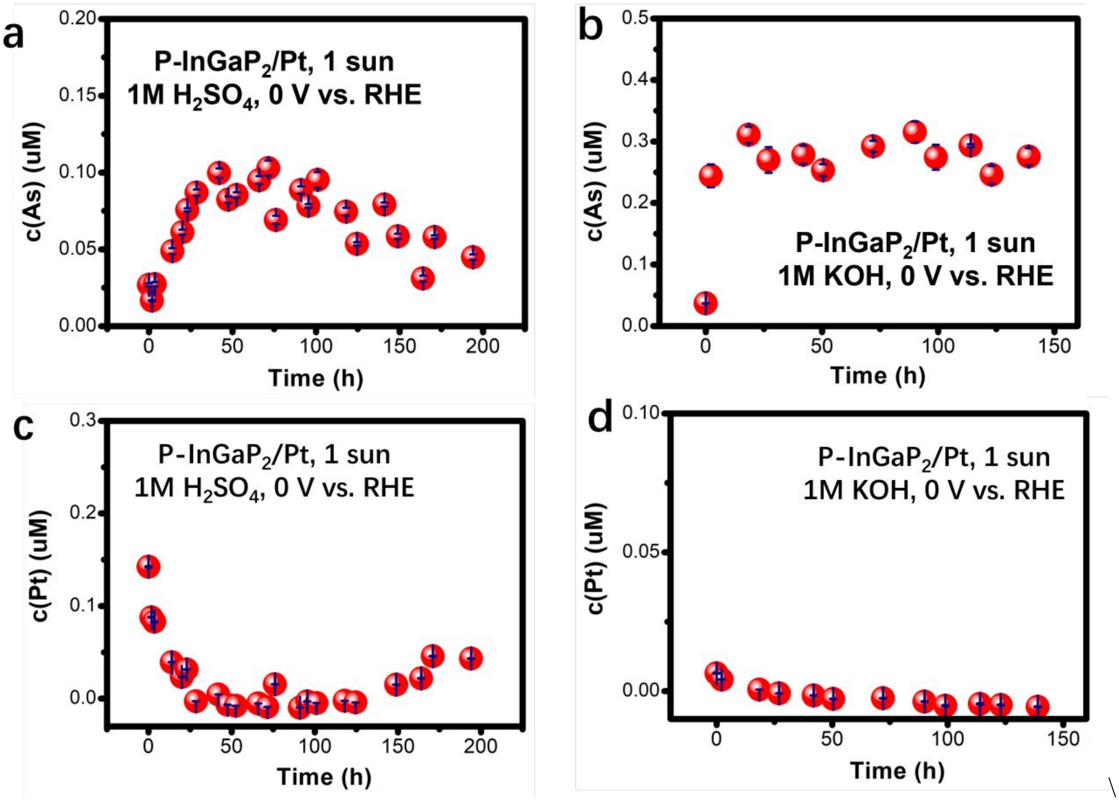


Figure S8. Comparison of the concentrations of (a-b) As ions and (c-d) Pt ions dissolved in electrolyte during long-term CA of p-GaInP/Pt photoelectrodes (1 sun) at 0 V vs. RHE in (a,c) 1.0 M H_2SO_4(aq) and (b,d) 1.0 M KOH(aq).

Table S1. Peak positions and peak assignment of XPS data. The numbers in bracket represent the full width at half maximum (FWHM) values of each peak. The peaks that are not denoted with any species are assigned to the In/Ga cations or P anions of p-GaInP.

Sample	Fig.	Electrolyte	E/V_{RHE}	Duration/h	In 3d/eV	P 2p/eV	Ga 3d/eV	In 4d/eV	Ga 2p/eV
p-GaInP	**1**	1M H_2SO_4	0	7	444.1 (0.6), 443.4 (0.6, In^0); 444.6 (2.2, InO_x)	128.5 (0.6)	19.0 (0.7)	17.2 (0.6); 16.3 (0.5, In^0)	1117.2 (1.0)
				Before	444.2 (0.7)	128.5 (0.6)	19.0 (0.6)	17.2 (0.6)	1117.2 (1.0)
p-GaInP	**3**	1M KOH	0	4	444.2 (0.6); 444.5 (1.4, InO_x)	128.5 (0.6)	19.0 (0.6)	17.2 (0.6)	1117.2 (1.1)
p-GaInP	**3**	1M KOH	-0.2	5	444.2 (0.6); 444.5 (1.6, InO_x); 443.6 (0.4, In^0)	128.5 (0.6)	18.9 (0.8)	17.2 (0.7); 16.5 (0.6, In^0)	1117.3 (1.1)
p-GaInP /Pt	**4**	As-prepared			444.1 (0.5); 444.6 (1.8, InO_x)	128.3 (0.6); 132.8 (1.8, PO_x)	18.8 (0.6)	17.0 (0.6)	1117.3 (1.1); 1118.4 (1.7, GaO_x)
	4	Outside			444.1 (0.7)	128.4 (0.6)	18.9 (0.6)	17.0 (0.6)	1117.2 (1.1)
p-GaInP /Pt	**5**	1M H_2SO_4	0	213	444.1 (0.8)	128.4 (0.5); 132.6 (1.8, PO_x)	18.9 (0.6)	17.1 (0.6)	1117.2 (1.3)
p-GaInP /Pt	**6**	1M KOH	0	139	444.2 (0.6); 444.4 (1.6, InO_x)	128.5 (0.6)	19.0 (0.7)	17.2 (0.8)	1117.3 (1.2)
p-GaInP	**S6**	1M H_2SO_4	0	48	444.2 (0.8)	128.5 (0.6)	19.0 (0.6)	17.2 (0.7)	1117.2 (1.1)

/Pt									
p-GaInP /Pt	**S7**	1M KOH	0	50	444.1 (0.6); 444.5 (1.6, InO_x)	128.5 (0.6)	19.0 (0.8)	17.2 (0.8)	1117.2 (1.1)

References

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