Supplementary Information

Interfacial Engineering of Gallium Indium Phosphide Photoelectrodes for Hydrogen Evolution with Precious Metal and Non-Precious Metal Based Catalysts

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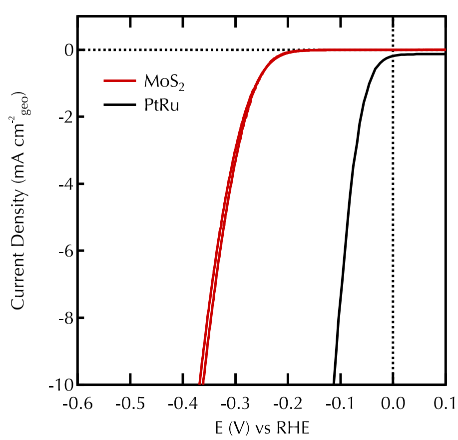

Figure S1. Electrochemical characterization of an MoS_2 film deposited on a degenerately doped n^+-Si wafer in an identical manner to the pn^+-$GaInP_2/MoS_2$ photocathode presented in this work and a PtRu catalyst deposited on fluorine doped tin oxide (FTO) in an identical manner to the pn^+-$GaInP_2$/PtRu photocathode presented in this work. LSVs were taken in 3M sulfuric acid.

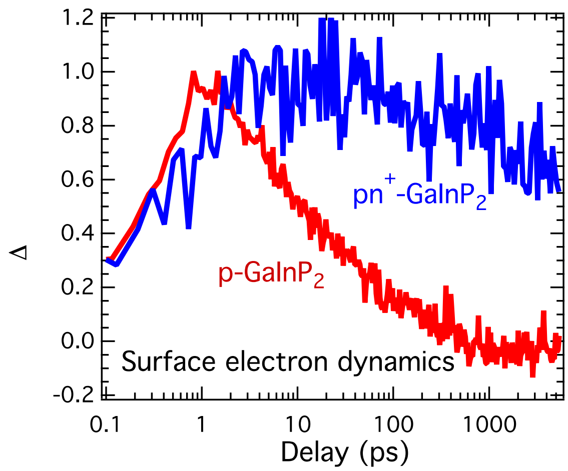

Figure S2. The surface electron dynamics of pn^+-$GaInP_2$ and p-$GaInP_2$. These kinetic traces are obtained by monitoring the broad non-oscillatory features above band gap (discussed in the main text) from transient photoreflectance (TPR) spectra, attributed to the band filling effect and band gap renormalization primarily due to the surface electrons.[1]

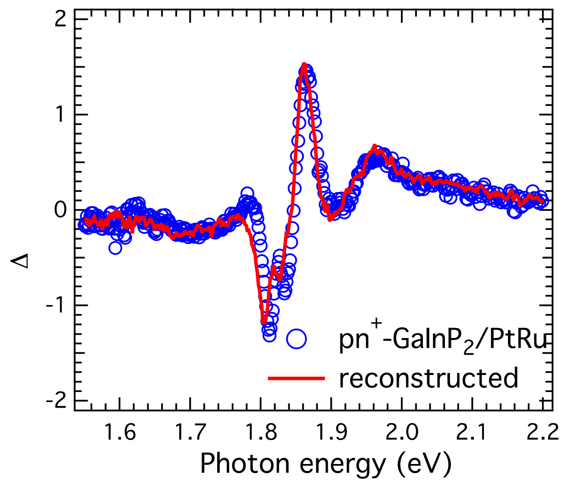

Figure S3. Comparison of the original TPR spectra of pn$^+$-$GaInP_2$/PtRu and that reconstructed from TPR spectra of pn$^+$-$GaInP_2$ and pn$^+$-$GaInP_2$/MoS_2. The TPR spectrum of pn$^+$-$GaInP_2$/PtRu can be reconstructed by adding linearly scaled spectra of pn$^+$-$GaInP_2$ and pn$^+$-$GaInP_2$/MoS_2 with scaling factors of 0.65 and 0.35, respectively. This spectral analysis indicates 35% of electrons transferred to the PtRu and the rest are localized near the surface, which coincides with the surface coverage fraction (~30%) by PtRu.[2]

Table S1. Photocathodes for hydrogen evolution

Photocathode	*E* (onset at 1 mA cm^{-2}) vs RHE (V)	Average *J* (mA cm^{-2})	Reported Stability (h)	Charge Passed (Coulombs)	Year	Ref #
pn^+-$GaInP_2/MoS_2$	0.91	13	100	4320	2018	N/A
pn^+-$GaInP_2$/PtRu	0.83	15	6	540	2018	N/A
n^+p-Si/MoS_2	0.33	10	120	4320	2013	15
n^+p-Si/MoS_2	0.35	17	100	6120	2014	16
p-$GaInP_2/MoS_2$	0.271	6.3	70	1587	2016	17
p-Si/Pt	0.29	4	1440	20736	1996	43
n^+p-Si/TiO_2	0.47	20	720	51840	2013	44
p-Si/nc-Si/TiO_2/Pt	0.58	18	984	63763	2017	45
p-Si/$SrTiO_3$	0.45	30	35	3780	2015	46
n^+p-Si/TiO_2/Pt	0.51	20	72	5184	2013	47
nip a-Si/TiO_2/Pt	0.93	11	12	475	2013	48
p-Si/Ti/Ni	0.3	10	12	432	2015	49
p-InP/TiO_2/Pt	0.8	24	2	172	2015	50
p-InP/TiO_2/Ru	0.73	35	4	504	2012	51
p-InP/RuRhPt	0.8	60	24	3600	1982	52
p-$CuGaSe_2$	0.1	10	4	144	2008	53
p-Cu(In,Ga)Se_2/n-CdS/Pt	0.5	9	16	518	2010	54
p-$CuGaSe_2$/CdS/Pt	0.6	4	288	4147	2013	55
p-CuO/AZO/TiO_2/ Pt/MoS_x	0.45	4.5	10	162	2014	56
p-Cu_2O/AZO/TiO_2/RuO_2	0.55	5	8	144	2014	57

n^+p-Si/MoS_2	0.28	11.5	1538	63673	2017	58
p-$CuGaSe_2$/CuGa	0.3	11.7	408	17000	2018	59
p-(Ag,Cu)$GaSe_2$/ $CuGa_3Se_5$CdS/Pt	0.62	7.5	480	12960	2015	60
p-CIGS/CdS/Ti/Mo/Pt	0.6	19.5	240	16848	2015	61
n^+p-Si/$MoSe_2$	0.4	27	120	11664	2018	62
p-Si-NWs/MoS_2	0.26	16.5	48	2851	2018	63
n^+p-Si-MWs/MoS_2	0.54	9.3	288	9590	2018	64
p-$GaInP_2$/TiO_2/$MoS2_x$	0.4	11	20	792	2017	65

REFERENCES

1. Yang Y, Gu J, Young JL, Miller EM, Turner JA, Neale NR*, et al.* Semiconductor interfacial carrier dynamics via photoinduced electric fields. *Science* 2015, **350**(6264)**:** 1061.

2. Young JL, Steiner MA, Döscher H, France RM, Turner JA, Deutsch Todd G. Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures. *Nature Energy* 2017, **2:** 17028.