Supporting Information

Low-Cost, Efficient and Durable H_2 Production by Photoelectrochemical Water Splitting with $CuGa_3Se_5$ Photocathodes

Christopher P. Muzzillo,[1,*] W. Ellis Klein,[1] Zhen Li,[1] Alexander Daniel DeAngelis,[2] Kimberly Horsley,[2] Kai Zhu[1,*] and Nicolas Gaillard.[2]

[1]National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO 80401

[2]Hawaii Natural Energy Institute, University of Hawaii, 1680 East-West Rd POST 109, Honolulu, HI 96822

*Corresponding authors: (C.P.M.) christopher.muzzillo@nrel.gov; (K.Z.) Kai.Zhu@nrel.gov

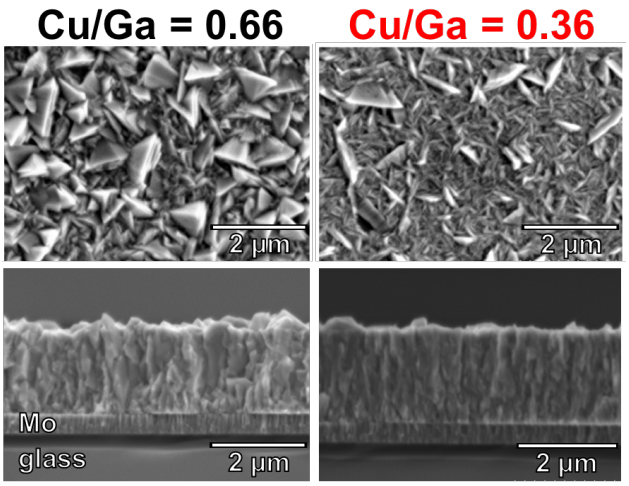

Figure S1. Plan view (top) and cross-sectional (bottom) SEM micrographs of glass/Mo/Cu-Ga-Se films with Cu/Ga compositions of 0.66 (left) and 0.36 (right).

Table S1. Champion PV performance efficiency, open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) for Cu-Ga-Se absorbers with varied Cu/Ga compositions.

Cu/Ga	Eff. (%)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)
0.31	0.4	721	2.0	24.6
0.31	0.2	581	1.0	27.7
0.33	1.8	720	6.1	40.3
0.34	1.5	753	6.5	30.4
0.35	0.6	570	3.8	25.4
0.36	1.0	652	6.0	26.6
0.36	1.4	652	6.4	33.4
0.38	1.0	596	6.7	26.2
0.39	1.6	650	6.9	35.5
0.52	3.0	661	8.1	56.8
0.66	3.7	615	11.8	50.5

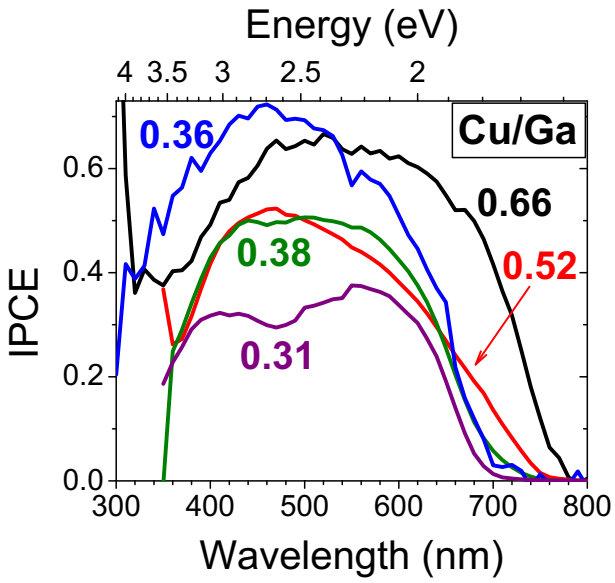

Figure S2. IPCE data (at -0.8 V vs. RHE) for Cu-Ga-Se photocathodes with Cu/Ga compositions of 0.66 (black), 0.52 (red), 0.38 (green), 0.36 (blue), and 0.31 (purple).

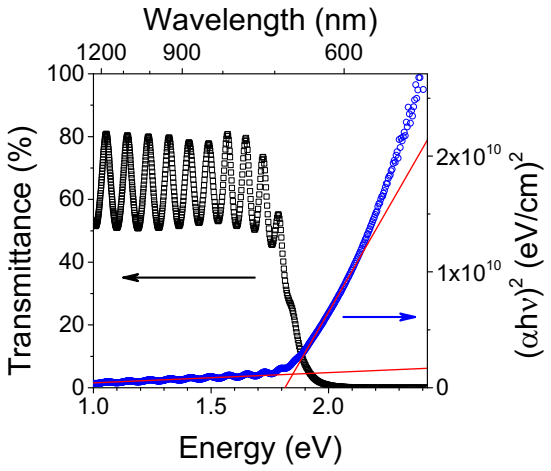

Figure S3. Transmittance of a $CuGa_3Se_5$ film with Cu/Ga of 0.32 (left axis; black squares) and Tauc plot (right axis; α is absorptivity, h is Planck's constant and ν is photon frequency) data (blue circles) and linear extrapolations to 1.85 eV (red lines).

Table S2. Overall film compositions by XRF before and after PEC degradation. Mean values from 8 measurements caused a shift away from nominal Cu/Ga; standard deviations are in parentheses.

Nominal Cu/Ga	Film	Cu (at. %)	Ga (at. %)	Se (at. %)	Cu/Ga
0.52	Orig.	15.8(1)	29.6(1)	54.5(2)	0.535(5)
	Degr.	15.9(2)	29.7(2)	54.3(3)	0.537(7)
0.36	Orig.	11.8(2)	32.0(2)	56.2(4)	0.368(5)
	Degr.	12.0(2)	31.7(1)	56.3(3)	0.378(4)

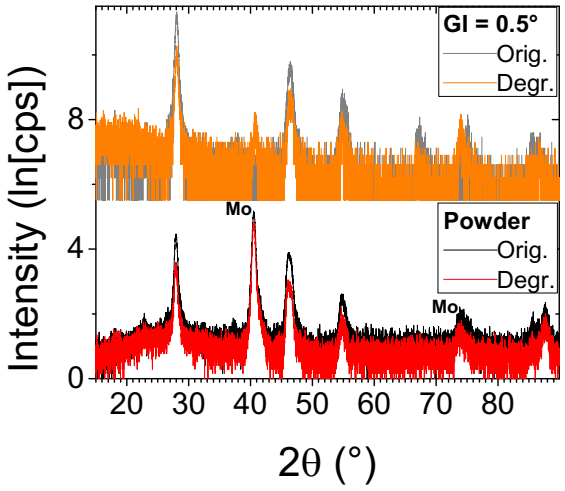

Figure S4. XRD (bottom) and GIXRD with a 0.5° incidence angle (top) for the original (black; gray) and PEC degraded (red; orange) films with Cu/Ga of 0.52. Mo peaks are labeled; all other peaks belong to the $CuGaSe_2$ and $CuGa_3Se_5$ phases. The degraded sample had areas with exposed Mo, causing more intense Mo peaks in the GIXRD scan.

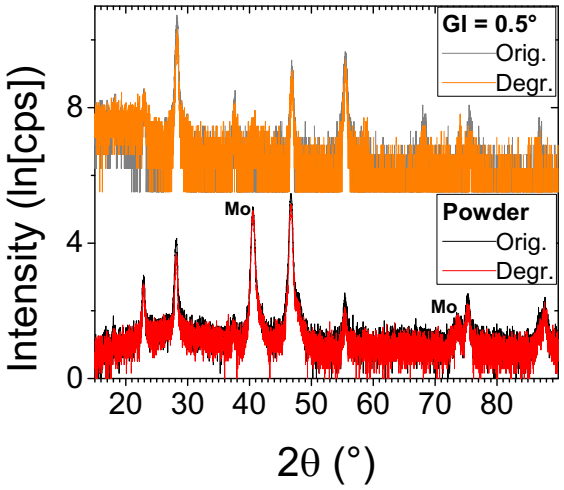

Figure S5. Powder (bottom) XRD and GIXRD with a 0.5° incidence angle (top) for the original (black; gray) and PEC degraded (red; orange) film with Cu/Ga of 0.36. Mo peaks are labeled; all other peaks belong to $CuGa_3Se_5$. The degraded sample had areas with exposed Mo, causing more intense Mo peaks in the GIXRD scan.

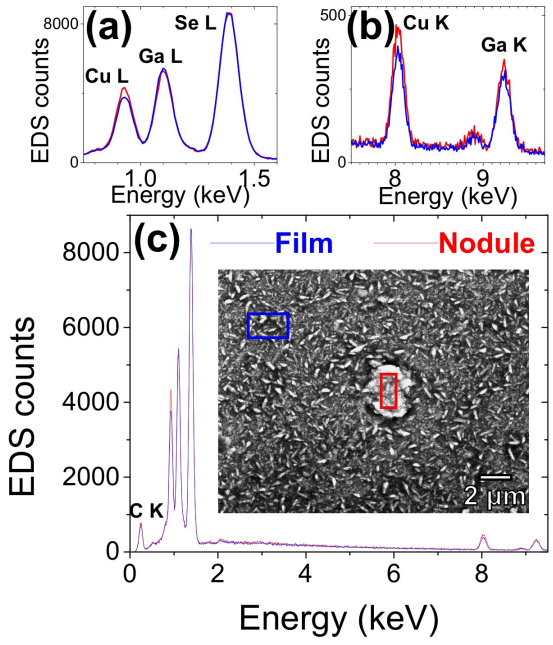

Figure S6. EDS spectra of the photocathode with Cu/Ga of 0.52 after PEC degradation at the L emission energies (a), K emission energies (b), and broad spectrum energies (c) for the film (blue) and nodule (red) locations (indicated on inset secondary electron micrograph). Quantitative compositions are in Table S3.

Table S3. EDS compositions of photocathodes with Cu/Ga of 0.52 and 0.36 after PEC degradation of the films and nodules that appeared on the films' surfaces after degradation.

Nominal Cu/Ga	Location	Cu (at. %)	Ga (at. %)	Se (at. %)	C (at. %)	Cu/Ga
0.52	Film	10.5(7)	18.9(1)	34.0(1.1)	36.6(2)	0.556(35)
	Nodule	12.7(8)	18.7(0)	34.8(1.1)	33.8(2)	0.678(43)
0.36	Film	10.2(2)	25.9(2.1)	44.5(3.1)	19.5(5.3)	0.395(25)
	Nodule	12.6(2)	20.3(1.6)	35.2(2.4)	31.9(8.6)	0.620(39)