

Supporting Information

Photoelectrochemical Water Reduction over Wide Gap (Ag,Cu)(In,Ga)S₂ Thin Film Photocathodes

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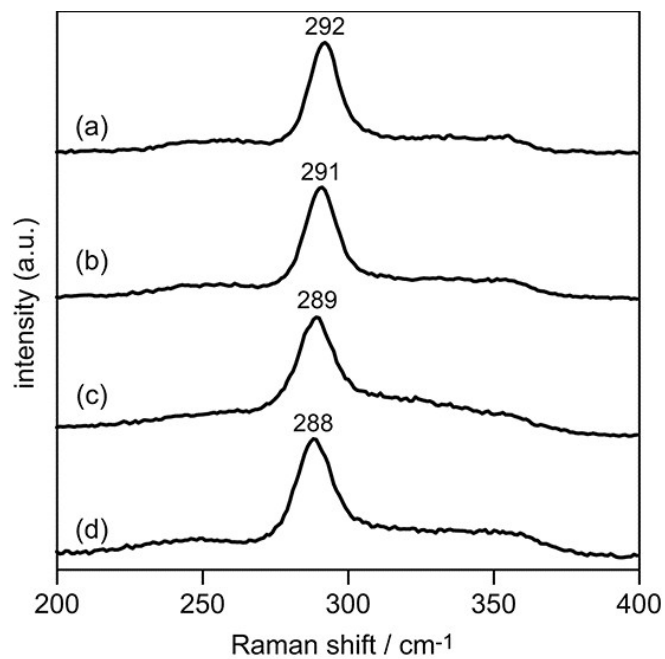


Figure S1. Raman spectra of (a) A(0)CIGS, (b) A(0.1)CIGS, (c) A(0.2)CIGS, and (d) A(0.3)CIGS films.

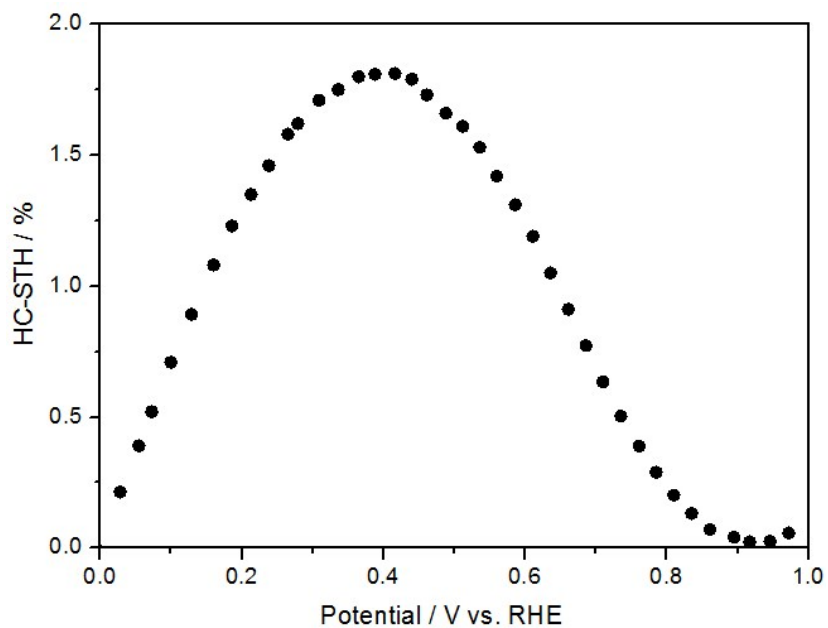


Figure S2. HC-STH spectrum of Pt-CdS/A(0.2)CIGS extracted from its $J-V$ curve.

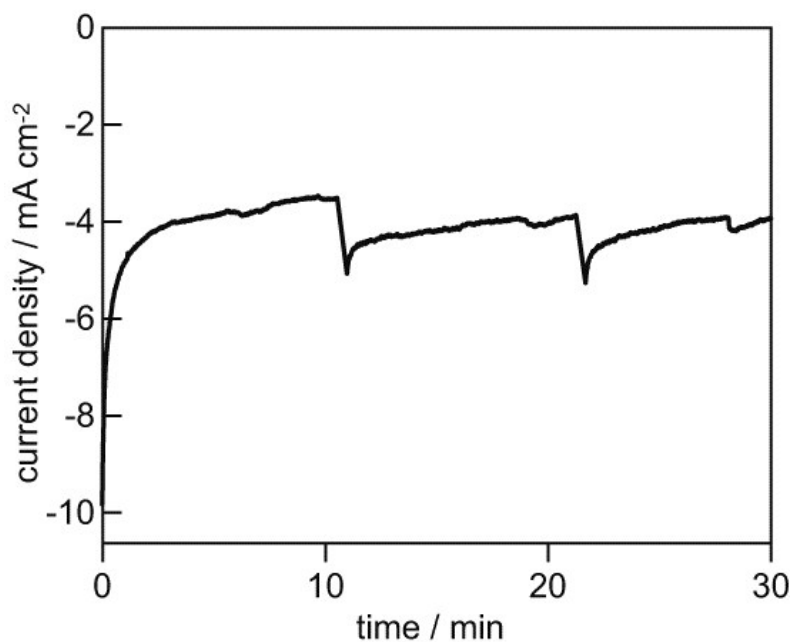


Figure S3. Time-course profile of Pt-CdS/A(0.2)CIGS measured in a sulfate-phosphate solution (pH 6.5) at 0 V vs. RHE under constant illumination from AM 1.5G solar simulator. The sudden drops of the photocurrent at *ca.* 10 min and 22 min were caused by removal of H₂ bubbles attached in the sample.

Table S1. Elemental compositions of sulfurized A(x)CIGS films obtained from various Ag/(Ag+Cu) ratio in the precursor solution.

Sample	Ag (%at.)	Cu (%at.)	In (%at.)	Ga (%at.)	S (%at.)	Ag/(Ag+Cu) in the films
A(0)CIGS	0	23.39	17.20	5.26	54.14	0
A(0.1)CIGS	2.15	21.31	18.82	5.25	52.46	0.09
A(0.2)CIGS	4.62	18.92	19.65	5.18	51.65	0.20
A(0.3)CIGS	6.87	17.43	19.14	5.60	50.95	0.28

Table S2. Resistivity of A(x)CIGS films with various Ag contents deposited on a glass substrate

ACIGS Samples	Resistivity (Ω .cm)
A(0)CIGS	5.9×10^6
A(0.1)CIGS	1.9×10^5
A(0.2)CIGS	3.6×10^6
A(0.3)CIGS	2.4×10^7