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Efficient hydrogen evolution on $(CuInS_2)_x(ZnS)_{1-x}$ solid solution-based photocathode under simulated sunlight

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Experimental section

Preparation of $(CuInS_2)_x(ZnS)_{1-x}$ solid solution thin films by electrodeposition method

Metallic Cu, In and Zn layers were deposited successively onto Mo-coated soda-lime glass substrates under potentiostatic control using a potentiostat (HSV-100, Hokuto Denko). Cu deposition was performed at -0.4 V vs. Ag/AgCl reference electrode in 75 mL of an aqueous solution containing 10 mM $CuSO_4 \cdot 5H_2O$ (Wako, 99.5%) and 10 mM citric acid (Wako, 98%). In deposition onto the Cu layer was performed at -0.8 V vs. Ag/AgCl reference electrode in 75 mL of an aqueous solution containing 30 mM $InCl_3 \cdot 4H_2O$ (Wako, 99.9%), 36 mM trisodium citrate (Wako, 99%) and 10 mM citric acid with the pH adjusted to 2.2-2.3. Zn was deposited onto the In layer at -1.2 V vs. Ag/AgCl reference electrode in 75 mL of an aqueous solution containing 0.1 M $ZnSO_4$ (Wako, 99.9%), 0.5 M K_2SO_4 (Wako, 99%), and 20 mM trisodium citrate. The amount of Cu and In deposited was controlled by adjusting the total electric charge to 522 mC/cm^2 and 600 mC/cm^2, respectively, using a coulomb/ampere-hour meter (HF-301, Hokuto Denko). The amount of Zn was controlled as 20 mC/cm^2, 50 mC/cm^2, and 100 mC/cm^2, then the compositional ratio of Cu:In:Zn was fixed at 1.3:1:0.05, 1.3:1:0.125, and 1.3:1:0.25, respectively. Sulfurization of the as-prepared Cu/In/Zn film was performed by a two-step process. First, the film was heated to 110°C in N_2, and kept for 1 h. After this pre-heat treatment, the film was heated to 500°C in 10 min, and sulfurized for 20 min under a H_2S flow rate of 5 mL/min. Finally, the film was cooled to room temperature in N_2. The excess Cu_xS phase was selectively etched by immersing the as-sulfurized $(CuInS_2)_x(ZnS)_{1-x}$ film in an aqueous KCN solution (10%) for 2 min and then a NH_4OH solution (10%) for 10 min.

Chemical bath deposition (CBD) of CdS layer on $(CuInS_2)_{0.81}(ZnS)_{0.19}$ surface

A solution containing 7.5 mM $Cd(CH_3COO)_2$ (Kanto, 98%), 0.375 M $SC(NH_2)_2$ (Kanto, 98%) and 2 M NH_4OH was used as the chemical bath. The total CBD time was 5.5 min, during which the bath temperature increased from 0°C to 60°C. After deposition, the electrode was annealed in air at 200°C for 1 h.

In situ photoelectrochemical deposition of Pt

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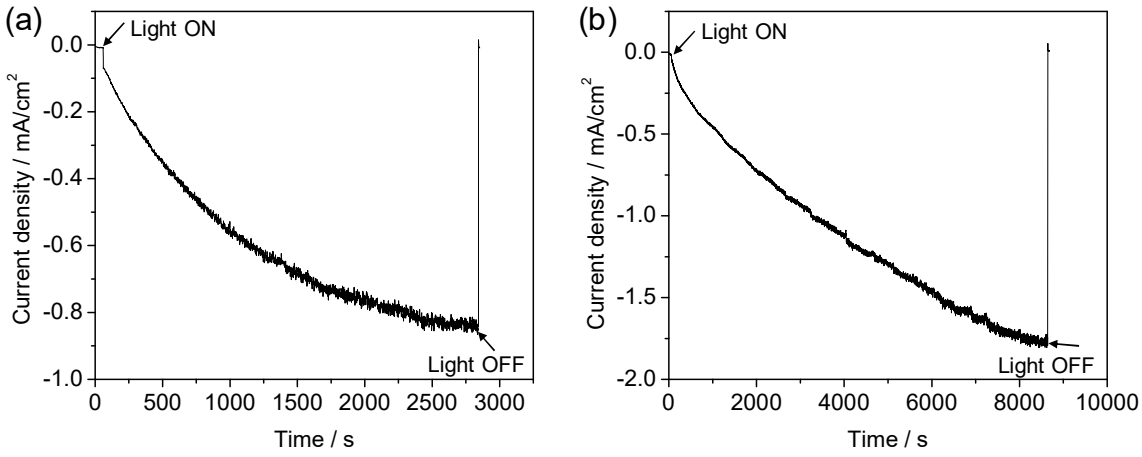
Pt deposition was performed at the potential of -0.66 V vs. Ag/AgCl in a 0.1 M aqueous Na_2SO_4 (Wako, 99%) solution (pH 9.5) containing 15 μmol H_2PtCl_6 (Kanto, 98.5%). The electrode was irradiated under simulated sunlight illumination (AM 1.5G) until the saturation of photocurrent. The in situ photoelectrochemical deposition curves of Pt co-catalyst for $CdS/CuInS_2$ (a) and $CdS/(CuInS_2)_{0.81}(ZnS)_{0.19}$ (b) electrodes were shown herein.



PEC measurement

The PEC performances were investigated in a three-electrode PEC configuration, using the prepared $Pt/CdS/(CuInS_2)_{0.81}(ZnS)_{0.19}$ as a photocathode, a Pt wire as a counter electrode, and an Ag/AgCl electrode as a reference electrode. The measured potentials vs. the Ag/AgCl reference electrode were converted into the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.197 \quad (1)$$

A 0.5 M, pH 7 aqueous KPi solution (the mixture of 0.25 M K_2HPO_4 and 0.25 M KH_2PO_4 with certain amounts of 8 M aqueous KOH solutions) was prepared as electrolyte. The electrolyte was stirred and purged with Ar gas for 15 min before and during the PEC measurements. An AM 1.5G simulated solar light at 100 mW cm^{-2} (SAN-EI electronic, XES40S1) was used as the light source for measuring current-potential curves

and gas evolution. Half-cell solar-to-hydrogen (HC-STH) conversion efficiency was calculated using the following equation:

$$\eta_{\text{HC-STH}} = [\,|J_{\text{ph}}| \times (E_{\text{RHE}} - E_{H^+/H2}) / P_{\text{sun}}] \times 100\% \quad (2)$$

where J_{ph} is the photocurrent density obtained under the applied bias of E_{RHE}, and $E_{H^+/H2}$ is the equilibrium potential of hydrogen evolution noted as 0 V_{RHE}. The wavelength dependence of incident photo-to-current efficiency (IPCE) was measured under monochromatic irradiation from a Xe lamp (MAX-301, Asahi Spectra) equipped with bandpass filter (with a FWHM of about 10 nm). For calibration of the light intensity at wavelengths below 750 nm, a visible light module was used, and for calibration light at wavelength above 750 nm, a visible-infrared module was used. The photon flux was determined using a calibrated Si photodiode (S2281-01, Hamamatsu). The IPCE at each wavelength (λ) was calculated using the equation:

$$\text{IPCE} = (|J_{\text{ph}}| \times 1239.8 / P_{\text{light}} / \lambda) \times 100\% \quad (3)$$

Table S1. The EDS analysis of $(CuInS_2)_x(ZnS)_{1-x}$ films with different deposition amount of Zn.

In:Zn	Atomic %				*x*
	S	Cu	In	Zn	
1:0.25	47.58	25.67	21.75	4.99	0.81
1:0.125	47.51	25.76	24.48	2.26	0.92
1:0.05	47.01	27.12	24.92	0.95	0.96

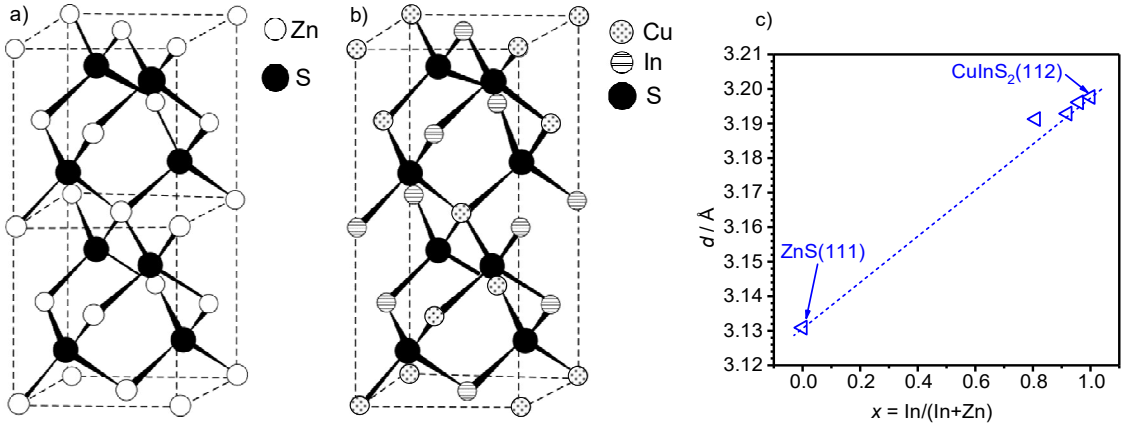


Fig. S1 Unit cells of a) ZnS and b) $CuInS_2$,[15] and c) variation of *d*-spacing obtained from the XRD peak at around 2Θ = 28º. The linear variation of *d*-spacing supports formation of alloy between ZnS and $CuInS_2$ because of the similar crystal structures.

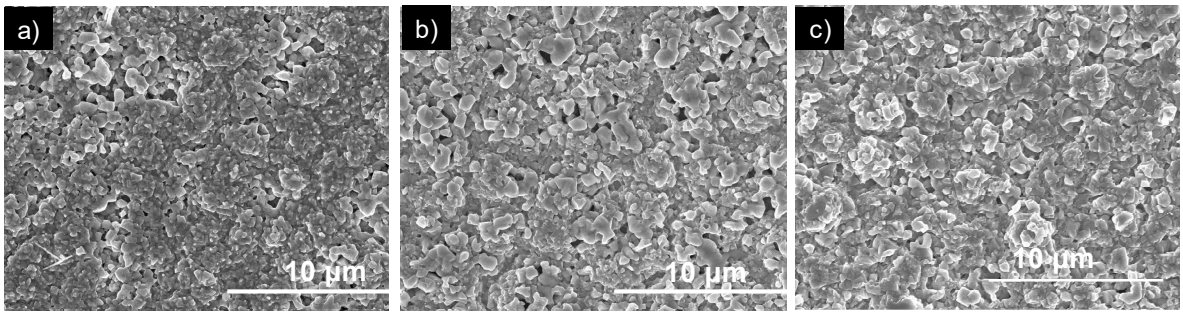


Fig. S2 SEM images of the $(CuInS_2)_x(ZnS)_{1-x}$ films surface, a) x=0.81, b) x=0.92 and c) x=0.96.

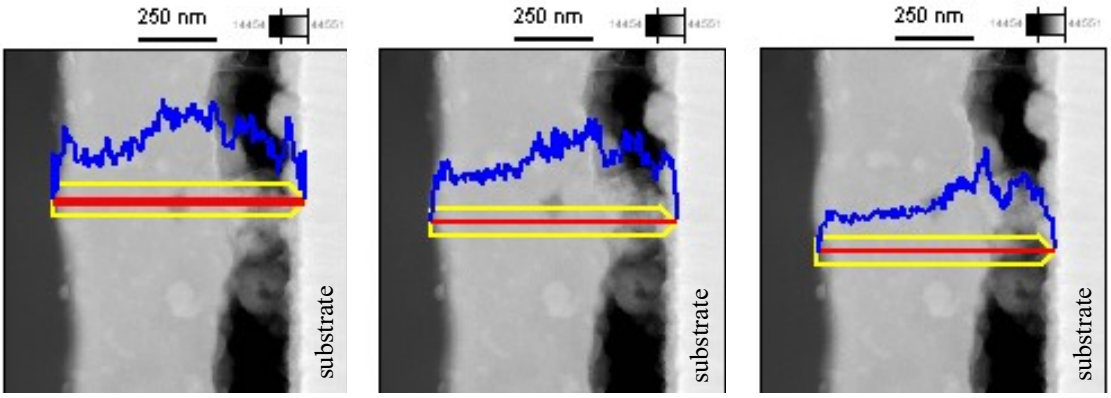


Fig. S3 Cross-sectional STEM-DF images of $(CuInS_2)_{0.81}(ZnS)_{0.19}$ film. The atomic ratio of Zn along the scan line was indicated as blue curves, which revealed a gradual increase of Zn content from the surface-side to the back-contact-side.

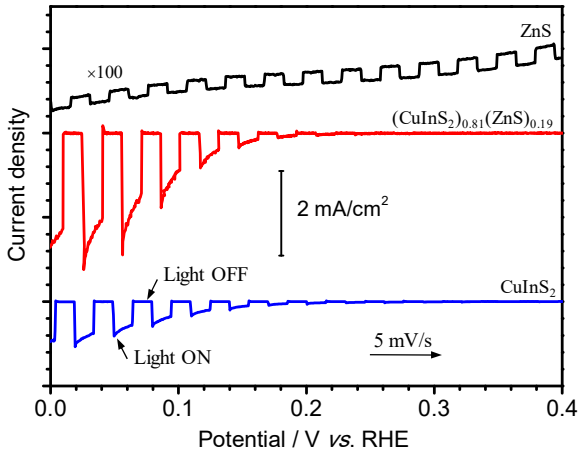


Fig. S4 Photocurrent density–potential curves of bare ZnS, $CuInS_2$, and $(CuInS_2)_{0.81}(ZnS)_{0.19}$ electrodes. The curves were measured under chopped AM 1.5G illumination in an aqueous 0.5 M KPi electrolyte with pH 7.

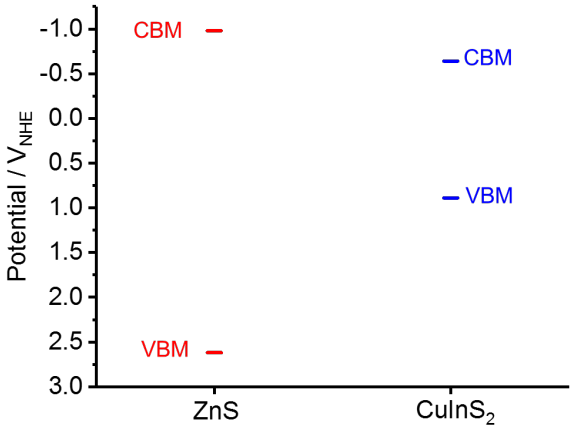


Fig. S5 Band edge potentials of ZnS and $CuInS_2$.[19] ZnS has clearly deeper VBM potenial than that of $CuInS_2$.

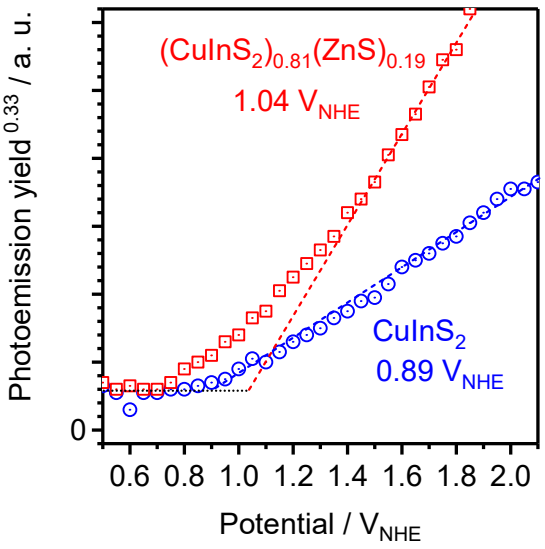


Fig. S6 PESA spectra of the $CuInS_2$ and $(CuInS_2)_{0.81}(ZnS)_{0.19}$ films.

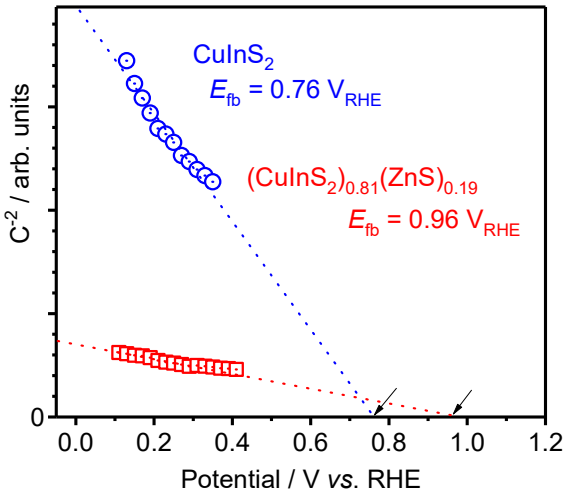


Fig. S7 Mott-Schottky plots of $CuInS_2$ and $(CuInS_2)_{0.81}(ZnS)_{0.19}$ measured in 0.5 M KPi electrolyte with pH 7 at frequency of 10 kHz.

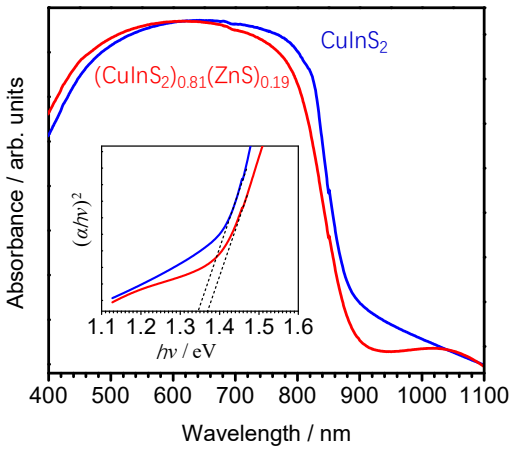


Fig. S8 UV-vis diffuse reflection spectra of the $(CuInS_2)_{0.81}(ZnS)_{0.19}$ and $CuInS_2$ films on Mo-coated soda-lime glass substrates. Inset is the plot of $(\alpha h\nu)^2$ versus $h\nu$ based on the direct gap.

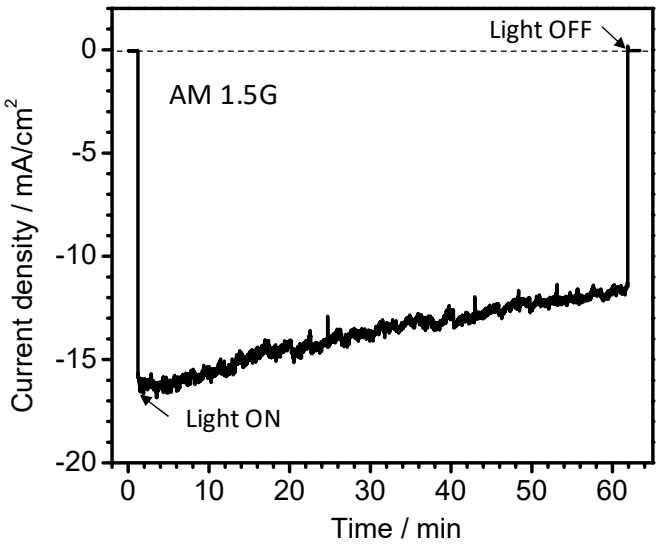


Fig. S9 Photocurrent density–time curves for Pt/CdS/$(CuInS_2)_{0.81}(ZnS)_{0.19}$ electrode measured at 0 V_{RHE} under AM 1.5G illumination in an aqueous electrolyte of 0.5 M potassium phosphate (KPi) at pH 7.

Table S2. Comparison of the PEC performance of the state-of-the-art photocathodes based on chalcogenides photoelectrodes.

Photocathodes	Electrolyte[a]	*J* at 0 V_{RHE} (mA/cm^2)[b]	*J* at 0.6 V_{RHE} (mA/cm^2)[c]	Onset *E* (V_{RHE})[d]	HC-STH[e]	Stability test[f]	Reference
$Pt/CdS/(CuInS_2)_{0.81}(ZnS)_{0.19}$	pH 7	-16.7	-6.5	0.84	5.6%	1h	This work
$Pt/Mo/Ti/CdS/(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}(ZnSe)_{0.85}$	pH 7	-12	-4.9	0.89	3.6%	3h	ref 11
Pt/CdS/CIGS(25)	pH 9*	-6.8	<-1*	0.89	-	100min*	ref 17b
$Pt/In_2S_3/CdS/Cu_2ZnSnS_4$	pH 6.5	-9.3	-	0.63	1.63%	3h	ref 3b
Pt/Mo/Ti/CdS/CIGSe	pH 6.8	-30	~ -1*	0.70	8.5%	3h	ref 6
$Pt/TiO_2/CdS/CuInS_2$	pH 10	-13	-	0.60	1.82%	1h	ref 14
$Pt/In_2S_3/CuInS_2$	pH 6	-18	<-1*	0.72	2.9%	3h	ref 5c
$Pt/TiO_2/AZO/CdS/CuInS_2$	pH 5	-2.3	-	0.60	-	2h*	ref 20b
$Pt/TiO_2/CdS/CuInS_2(Bi)$	pH 6.1	-8	-	0.60	-	2h*	ref 20a

[a] Phosphate buffer electrolyte is used for all of the experiment, except for asterisk marked one with 0.1 M Na_2SO_4 electrolyte.

[b] Photocurrent density (J) at 0 V_{RHE} under light illumination.

[c] Photocurrent density (J) at 0.6 V_{RHE} under light illumination. The value estimated from the reported figure was marked with an asterisk.

[d] Onset potential of photocurrent with respect to V_{RHE}.

[e] Half-cell solar-to-hydrogen (HC-STH) conversion efficiency.

[f] The test time of the corresponding reports. The experiment performed under chopped light illumination was marked with an asterisk.