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Electronic Supplementary Information

Development of Highly Efficient CuIn_{0.5}Ga_{0.5}Se₂-based Photocathode and

Application to Overall Solar Driven Water Splitting

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Figure S1 (a) XRD patterns and (b) lattice constants for a series of CIGS films with various x (= Ga/(In+Ga)) values. Data were acquired using CuK α radiation at 0.1541 nm.



Figure S2 SIMS profile in the depth direction for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ sample with x = 0.4, indicating the local Ga/(In+Ga) ratio along the depth direction. The shaded regions labeled "unreliable" are associated with unstable signals resulting from the roughness of either the CIGS surface or the CIGS/Mo interface.



Figure S3 UV-vis transmission spectra of a series of CIGS films with various x (= Ga/(In+Ga)) values. The thickness of each CIGS layer formed directly on SLG was adjusted to 1.8 μ m.



Figure S4 Photocurrent density versus potential plots for a CIGS (x = 0.3) photocathode surface modified with CdS, Ti, Mo and Pt (Pt/Mo/Ti/CdS/CIGS) under simulated AM1.5G light in a 0.5 M Na₂SO₄ + 0.25 M Na₂HPO₄ + 0.25 M NaH₂PO₄ (aq.) electrolyte adjusted to pH 6.8 with NaOH. The potential sweep rate was +10 mV s⁻¹ (from negative to positive).

Band alignment at solid-liquid interface

The band diagram at the solid-liquid interface was calculated by solving Poisson's equation through the finite element method (FEM). Poisson's equations for CdS and CIGS layers are given by equations (S1) and (S2), respectively.

$$\frac{\mathrm{d}^2 \phi}{\mathrm{d}x^2} = -\frac{eN_\mathrm{D}}{\varepsilon_r \varepsilon_0} \tag{S1}$$

$$\frac{\mathrm{d}^2 \phi}{\mathrm{d}x^2} = \frac{eN_\mathrm{A}}{\varepsilon_r \varepsilon_0} \tag{S2}$$

Here, ϕ , x, e and ε_0 are the built-in potential, position, electron charge of 1.602×10^{-19} C, and vacuum permittivity of 8.85×10^{-12} F m⁻¹, respectively. The values of the relative dielectric constant, ε_r , for CdS and CIGS were assumed to be 10 and 13.6, respectively.^{1,2} The donor density, N_D , in the CdS layer and the acceptor density, N_A , in the CIGS layer were both set at 10^{16} . The band gaps for CIGS specimens having x = Ga/(Ga+In) = 0.3 and 0.5 and of CdS were 1.18, 1.32 and 2.4 eV, respectively. The parameters used for calculating the band alignment are provided in Table S3.

The difference between the Fermi level (E_F) and the conduction band minimum (CBM) for CdS, and the difference between E_F and the valence band maximum (VBM) for CIGS were assumed to be 0.2 eV.^{1,2} The VBM offsets between CdS and CIGS were 0.88 eV for both x = 0.3 and 0.5 and the flat band potential for CdS was $-0.255 V_{RHE}$.^{3,4}

Parameters	CdS	CuIn _{0.7} Ga _{0.3} Se ₂	CuIn _{0.5} Ga _{0.5} Se ₂
Thickness t (nm)	70	_	_
Donor density $N_{\rm D}~({\rm cm}^{-3})$	1.0×10 ¹⁶	_	_
Acceptor density $N_{\rm A}~({\rm cm}^{-3})$	_	1.0×10^{16}	1.0×10 ¹⁶
Band gap E_{g} (eV)	2.4	1.18	1.32
Relative dielectric constant ε	10	13.6	13.6

Table S1Parameters used to calculate band diagrams.

References

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- T. Schulmeyer, R. Kniese, R.Hunger, W. Jaegermann, M. Powalla and A. Klein, Influence of Cu(In,Ga)Se₂ band gap on the valence band offset with CdS. *Thin Solid Films*, 2004, 451–452, 420–423.
- 4. T. Watanabe, A. Fujishima, K. Honda, POTENTIAL VARIATION AT THE SEMICONDUCTOR-ELECTROLYTE INTERFACE THROUGH A CHANGE IN pH OF THE SOLUTION. *Chem. Lett.* 1974, 897-900.



Figure S5 Quantum efficiency for an Al-ZnO/CdS/CuIn_{1-x}Ga_xSe₂(x = 0.4)/Mo/SLG photovoltaic as a function of the incident light wavelength. The film thickness was 1.8 µm. In the region below 600 nm, the incident light was partly absorbed by the Al-ZnO and CdS layers.

Electrolyte	Conductivity / mS cm ⁻¹
$0.04 \text{ M} \text{ Na}_2 \text{SO}_4 + 0.04 \text{ M} \text{ Na}_2 \text{HPO}_4 + 0.04 \text{ M} \text{ Na}_2 \text{PO}_4$	14
$0.1\ M\ Na_2SO_4+0.1\ M\ Na_2HPO_4+0.1\ M\ NaH_2PO_4$	29
$0.2 \text{ M} \text{ Na}_2 \text{SO}_4 + 0.2 \text{ M} \text{ Na}_2 \text{HPO}_4 + 0.2 \text{ M} \text{ Na}_2 \text{PO}_4$	47
$0.4~M~Na_2SO_4+0.4~M~Na_2HPO_4+0.4~M~NaH_2PO_4$	72

Table S2Conductivity of sodium phosphate/sulfate (pH 6.8) based electrolytes.

Table S3Conductivity of potassium phosphate/sulfate (pH 6.8) based electrolytes.

Electrolyte	Conductivity / mS cm ⁻¹
$0.04 \text{ M K}_2 \text{SO}_4 + 0.04 \text{ M K}_2 \text{HPO}_4 + 0.04 \text{ M KH}_2 \text{PO}_4$	18
$0.1 \text{ M K}_2 \text{SO}_4 + 0.1 \text{ M K}_2 \text{HPO}_4 + 0.1 \text{ M KH}_2 \text{PO}_4$	38
$0.2 \text{ M K}_2 \text{SO}_4 + 0.2 \text{ M K}_2 \text{HPO}_4 + 0.2 \text{ M KH}_2 \text{PO}_4$	68
$0.4 \ M \ K_2 SO_4 + 0.4 \ M \ K_2 HPO_4 + 0.4 \ M \ KH_2 PO_4$	117

Table S4Conductivity of potassium borate (pH 9.5) based electrolytes.

Electrolyte	Conductivity / mS cm ⁻¹
0.1 M H ₃ BO ₃	5.3
0.2 M H ₃ BO ₃	9.4
0.4 M H ₃ BO ₃	17
0.5 M H ₃ BO ₃	20
1.0 M H ₃ BO ₃	26

Figure S6: (see next page for caption)





Figure S6 Photocurrent density versus potential plots for Pt/CdS/CIGS (x = 0.5) in (a) a sodium phosphate buffer with pH adjusted to 6.8 with NaOH, (b) a potassium phosphate buffer with pH adjusted to 6.8 with KOH, and (c) a potassium borate solution with pH adjusted to 9.5 with KOH, all under simulated AM1.5G irradiation. The conductivities of these electrolytes are summarized in Tables S1, S2 and S3.



Figure S7 H₂ and O₂ evolution rates for Pt/CdS/CIGS (x = 0.5, in red, light acceptance area: 2.1 cm²) and NiFeO_x/BiVO₄ (in blue, 2.4 cm²) using dual-electrode parallel configurations in a 0.5 M K₃BO₃ buffer solution (pH adjusted to 9.5 with KOH), under AM 1.5G irradiation. The amount of H₂ and O₂ generated in a closed vessel was monitored by gas chromatography (sampling rate once per 10 min.). These data points represent the molar quantities accumulated in the vessel, normalized by the larger electrode area (2.4 cm² for BiVO₄). The dashed lines were generated by integrating the simultaneously-recorded chronoamperometric curve and normalized according to the molar quantities, using e⁻/2 for H₂ and e⁻/4 for O₂. Faradaic efficiency of the PEC cell for H₂ and O₂ evolution are virtually 100%.



Figure S8 Current–potential curves of Pt/CdS/CIGS (x = 0.5) in (a) 0.4 M K₂HPO₄ + 0.4 M KH₂PO₄ (aq.), (b) 0.4 M K₂SO₄ + 0.6 M K₂HPO₄ + 0.6 M KH₂PO₄ (aq.), and (c) 0.4 M K₂SO₄ + 0.4 M K₂HPO₄ + 0.4 M KH₂PO₄ (aq.) adjusted to pH 6.8 with KOH. The potential was swept toward the negative direction at 10 mV s⁻¹.

Table S5Conductivity of potassium phosphate/sulfate (pH 6.8) based electrolytes used offigure S8.

Electrolyte	Conductivity / mS cm ⁻¹
0.4 M K ₂ HPO ₄ + 0.4 M KH ₂ PO ₄	72
0.6 M K ₂ HPO ₄ + 0.6 M KH ₂ PO ₄	90
$0.4 \text{ M K}_2 \text{SO}_4 + 0.4 \text{ M K}_2 \text{HPO}_4 + 0.4 \text{ M KH}_2 \text{PO}_4$	114

Table S6 Series resistance of a series of CIGS films with various x = Ga/(In+Ga) values. Series resistances were calculated from the slope of the curve of Figure 2 (a) based on the equivalent circuit and formulae shown in Figure S9.

x = Ga/(Ga+In) ratio	Series resistance / Ω
x = 0	13.3
<i>x</i> = 0.3	16.4
x = 0.5	15.9
x = 0.7	20.8
x = 1.0	55.6



Figure S9 The equivalent circuit used for estimation of series resistance, R_s .



Figure S10 Slopes shown as dashed lines used for series resistance calculations of CIGS films with various x (= Ga/(In+Ga)) values on current-potential curves, Figure 2.



Figure S11 Pictures of (a) co-evaporation system, and (b) as-deposited CIGS film prepared on 50 x 50 mm sized Mo-coated soda-lime glass plate.



Figure S12 (a) Picture of tandem PEC cell for overall water splitting composed of 50 x 50 mm sized BiVO₄-based photoanode and 4 pcs of 20 x 20 mm sized CIGS-based photocathodes, and (b) time course of photocurrent under simulated sunlight (AM 1.5G) without application of bias-voltage. An aqueous solution of 0.5 M K_3BO_3 buffer solution with pH adjusted to 9.5 through KOH addition was used as an electrolyte.



Figure S13 Pictures of the tandem PEC cell exhibited >3% STH in Figure 6. During the measurement, an optical mask was equipped to minimize unexpected exposure of samples to scattering light.



Figure S14 Cross-sectional SEM images of Pt/CdS/CIGS photocathode for (a)before and (b)after PEC durability test for 4 days at 0 V_{RHE} in 0.5 M Na₂SO₄ + 0.25 M Na₂HPO₄ + 0.25 M Na₁PO₄ (aq.) under AM 1.5G light. CdS layer was partly removed.



Figure S15 Time course of the photocurrent for Pt/CdS/CIGS photocathode at 0 V_{RHE} under simulated AM 1.5G sunlight, using 0.5 M Na₂SO₄ + 0.25 M Na₂HPO₄ + 0.25 M NaH₂PO₄ (aq.) adjusted to pH 6.8 with NaOH as an electrolyte. Cathodic photocurrent recovered after the short interruption of irradiation at around 60 minutes.



Figure S16 Calculated band diagrams for solid liquid interfaces of CdS/CIGS at x = 0.5 without external voltage under dark condition (a) and AM 1.5G irradiation from right side on this figure (b).