Electronic Supplementary Information (ESI) for:

Overall Water Splitting by Photoelectrochemical Cells Consisting of $(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$ Photocathodes and $BiVO_4$ Photoanodes

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Preparation and surface modification of the $(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$ (ZnSe-CIGS/Ti-foil) photocathodes

ZnSe-CIGS/Ti-foil photocathodes were prepared following previously reported procedures, using modified Ti foil as the substrate.[1-3] In the initial step, a 10 nm-thick soda lime glass (SLG) layer and a 500 nm-thick Mo layer were sequentially deposited on a 20 μm-thick Ti foil (99.5%, Nilaco) by radio frequency (RF) magnetron sputtering to prepare the substrate. This substrate was subsequently loaded into a vacuum chamber equipped with Knudsen cells containing elemental Cu, In, Ga, Zn and Se. A bilayer-structured ZnSe-CIGS thin film with a thickness ranging from 1.5 to 2.5 μm was deposited on the substrate by vacuum co-evaporation. Prior to subsequent surface modifications, the ZnSe-CIGS film was etched for 1 min in an aqueous solution containing 0.1 M KCN (98.0%, Wako) and 0.8 M KOH (Kanto) to remove excess Cu_xSe phase. Following this, the film was sequentially modified by applying a 60 nm-thick CdS layer and a In_2S_3 layer with a thickness of several nm, using chemical bath deposition (CBD).[4-6] The CdS deposition was accomplished by immersing the sample for 14 min in an aqueous solution containing 25 mM $Cd(CH_3COO_2)_2 \cdot 2H_2O$ (98.0%, Kanto), 375 mM CH_4N_2S (98.0%, Kanto) and 8 M NH_4OH (Wako), using a water bath held at 333 K to heat the solution. The In_2S_3 was deposited by immersion in an aqueous solution containing 25 mM $In_2(SO_4)_3$ (Wako), 100 mM CH_3CSNH_2 (98.0%, Wako) and 100 mM CH_3COOH (99.7%, Wako) for 15 min, with heating in a water bath at 343 K. Following the CdS deposition, the thin film was annealed at 473 K for 1 min in air. The surface of the CdS and In_2S_3-modified ZnSe-CIGS thin film was further modified by the sequential deposition of 3 nm-thick Ti and Mo layers, acting as the electron mediators, by RF sputtering. Prior to processing and measurements, a Pt catalyst for the hydrogen evolution reaction was deposited on the surface of the resulting film via the thermal evaporation of Pt wire (99.98%, Nilaco). Herein, we refer to the final surface-modified ZnSe-CIGS thin film prepared on Ti foil as ZnSe-CIGS/Ti-foil.

The samples were analyzed by X-ray diffraction (XRD; RINT-Ultima3, Rigaku), X-ray photoelectron spectroscopy (XPS; JPS-9000, JEOL), scanning electron microscopy (SEM; S-4700, Hitachi).

Preparation and surface modification of the $BiVO_4$ (BVO) photoanodes

BVO photoanodes were prepared using a previously reported method.[7] Briefly, a Bi precursor film was deposited on an ITO glass plate (Geomatec, sheet resistivity ~5 Ω sq^{-1}, 10 mm × 10-30 mm × 1 mm in thickness) by electrodeposition in a mixture of a 0.1 M $Bi(NO_3)_3$ (99.9%, Wako) solution in acetic acid and a 0.3 M *p*-benzoquinone (98.0%, Wako) ethanol solution for 7 min at 2.3 V vs. Ag/AgCl. Following this, a solution of 0.2 M vanadyl diacetylacetonate ($VO(acac)_2$; 98.0%, Aldrich) in a mixture of DMSO and ethanol (1:1 v/v) was drop-painted onto the Bi precursor film. The $VO(acac)_2$/Bi precursor film was then calcined in a muffle furnace at 793 K for 2 h, resulting in a $BiVO_4$ thin film. Excess VO_x was removed by immersion in a 1 M NaOH solution for 10 min, after which the $BiVO_4$ film was rinsed with copious amounts of milli-Q water and dried at room temperature.

The $BiVO_4$ film was immersed in an aqueous solution containing 10 mM $Co(NO_3)_2$ (Wako) and 10 mM NH_4OH at pH 8.4 for 0.5 h to deposit CoO_x, followed by washing with milli-Q water and annealing in air at 523 K for 0.5 h. A NiO catalyst was then added to the $BiVO_4$ surface using atomic layer deposition (ALD), employing 300 cycles. Herein, we refer to the $BiVO_4$ surface modified with NiO and CoO_x as BVO. Bis-(2,2,6,6-tetramethylheptane-3,5-dionate) nickel(II) ($Ni\text{-}(thd)_2$; Wako) and H_2O were used as the ALD precursors, heated to 438 and 288 K, respectively. The temperature in the deposition chamber was held at 533 K. One ALD cycle consisted of a 6 s H_2O pulse, a 3 s N_2 purge, a 3 s pressurization of the $Ni\text{-}(thd)_2$ container with N_2 gas (500 sccm), a 6 s $Ni\text{-}(thd)_2/N_2$ pulse, and a 3 s N_2 purge. Prior to the ALD process, the CoO_x/BVO was cleaned with an ozone plasma for 5 min to increase its surface wettability with respect to hydroxyl ions.

Preparation of integrated photoelectrodes (*i*-PE) and parallel PEC cell

The ZnSe-CIGS/Ti-foil photocathode was processed into sections approximately 0.1 × 1 cm by mechanical cutting. These pieces were arrayed on the top surface of a BVO photoanode to prepare a striped structure with photocathode lines approximately 1 mm wide and photoanode lines 2 to 3 mm wide. The photocathode pieces were fixed on the photoanode surface using epoxy resin. The head of ZnSe-CIGS pieces about 0.1 × 0.1 cm parts were removed to expose the Ti-foil parts, and then these Ti-foil parts and ITO part in the side of BVO photoanode were connected using In solder. Unused regions were covered with epoxy resin. This PEC cell having a striped structure is referred to herein as an integrated photoelectrode (*i*-PE) unit. Subsequently, parallel PEC cells were also fabricated based on ZnSe-CIGS/Ti-foil photocathodes and BVO photoanodes, placed side-by-side and connected using a lead wire.

A solar simulator (XES-70S1, SAN-EI Electric Co., Ltd.) was employed as the light source. PEC measurements for the photoelectrodes were performed with a three-electrode configuration, using a Ag/AgCl/saturated KCl reference electrode, a coiled Pt wire counter electrode and a potentiostat (HSV-110, Hokuto).

Overall water splitting was performed using the *i*-PE and the parallel PEC cell without the application of an external bias voltage. The resulting photocurrents and the quantities of evolved gases were determined using a multimeter and a micro gas chromatograph (microGC; GC3000A, Agilent).

Solar-to-hydrogen energy conversion efficiency (STH) of the PEC cells

The half-cell solar-to-hydrogen energy conversion efficiency (HC-STH) values of the photocathodes were calculated from the *i-E* curves using the equation:

$$\text{HC-STH}\ (\%) = J \times V \times 100 / P \qquad (1)$$

where J is the photocurrent density (mA cm^{-2}), V is the electrode potential vs. RHE, and P is the intensity of the simulated AM 1.5G light (100 mW cm^{-2}).

The STH for the parallel PEC cell without the application of an external bias voltage was calculated from the *i-t* curve using the equation:

$$\text{STH}\ (\%) = J \times 1.23\ \text{V} \times 100 / P \qquad (2)$$

where J is the photocurrent density (mA cm^{-2}), and P is the intensity of the simulated AM 1.5G light (100 mW cm^{-2}). Note that the effective electrode area for the parallel PEC cell was equal to the total geometrical areas of the photocathode and photoanode.

The STH for the *i*-PE was calculated from the rate of hydrogen evolution using the equation:

$$\text{STH}\ (\%) = (R(\text{H}_2) \times \Delta G_\text{r}))/(P \times S) \times 100 \qquad (3)$$

where $R(\text{H}_2)$, ΔG_r, P and S are the rate of hydrogen evolution during the water splitting reaction, the Gibbs energy (237 kJ mol^{-1}) for the reaction $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{ (g)} + 1/2\ \text{O}_2\text{(g)}$, the intensity of the simulated AM 1.5G light (100 mW cm^{-2}), and the total effective area of the photoelectrodes, respectively.

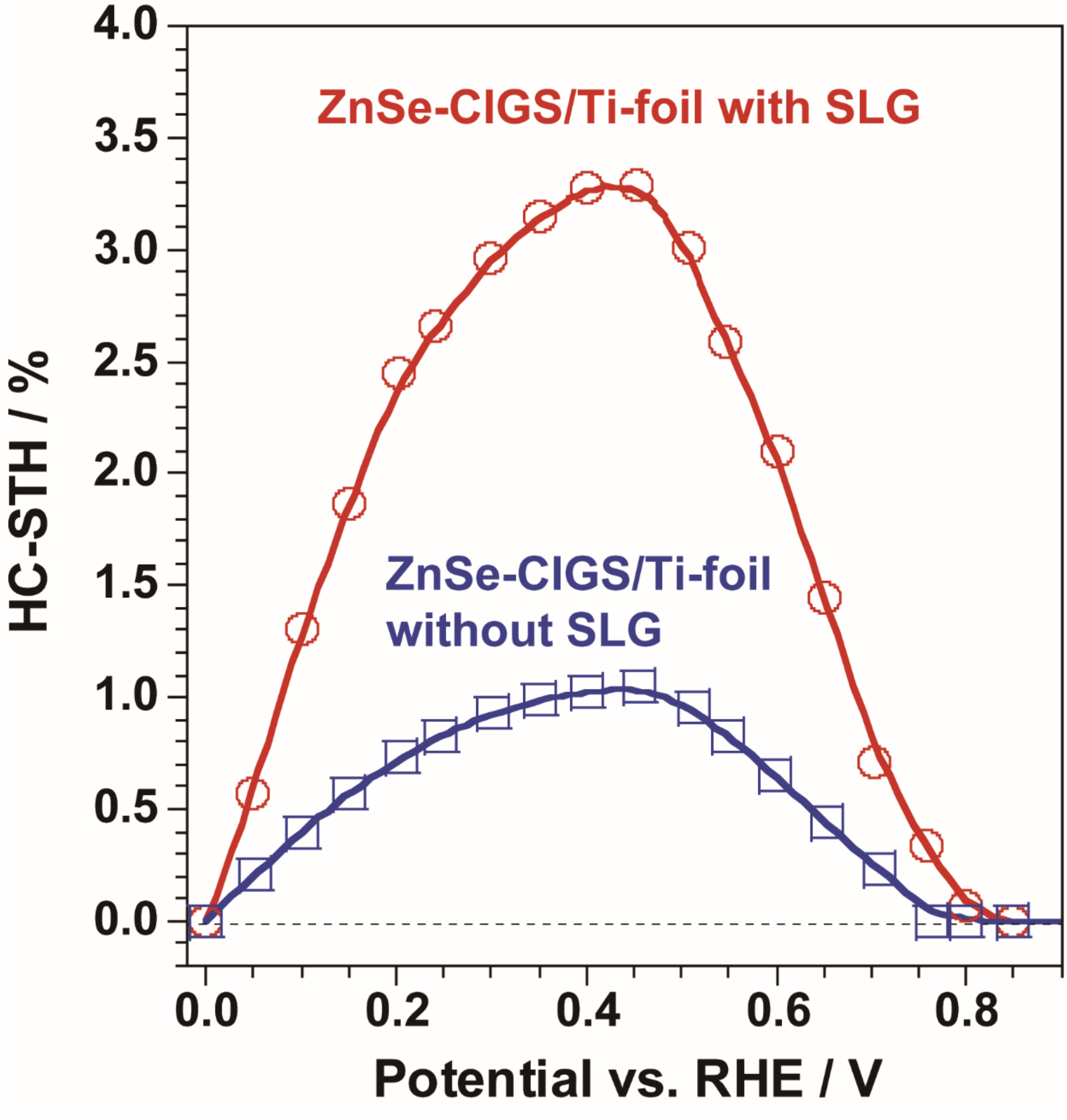

Figure S1. Half-cell solar-to-hydrogen energy conversion efficiency (HC-STH) for ZnSe-CIGS/Ti-foil photocathodes with and without an SLG layer on the Ti foil substrate under simulated AM 1.5G light. A 1.0 M potassium phosphate buffer solution (pH = 7.0) was used as the electrolyte.

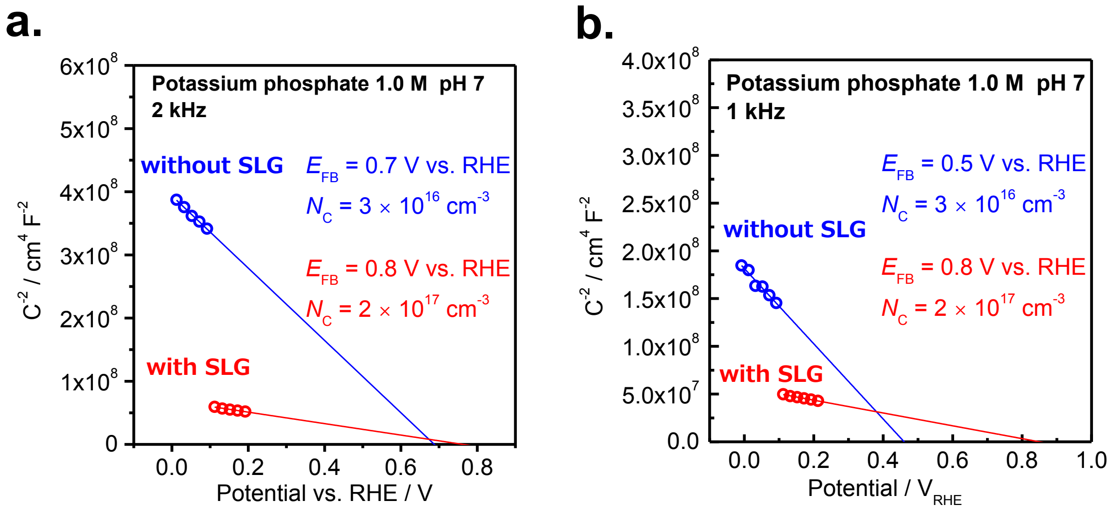

Figure S2. Mott-Schottky (MS) plots for ZnSe-CIGS/Ti-foil photocathodes with and without an SLG layer on the Ti foil substrate. The frequency of the potential modulation are 2 kHz (Fig. S2a) and 1 kHz (Fig. S2b). A 1.0 M potassium phosphate buffer solution (pH = 7.0) was used as the electrolyte. The ac amplitude was 20 mV.

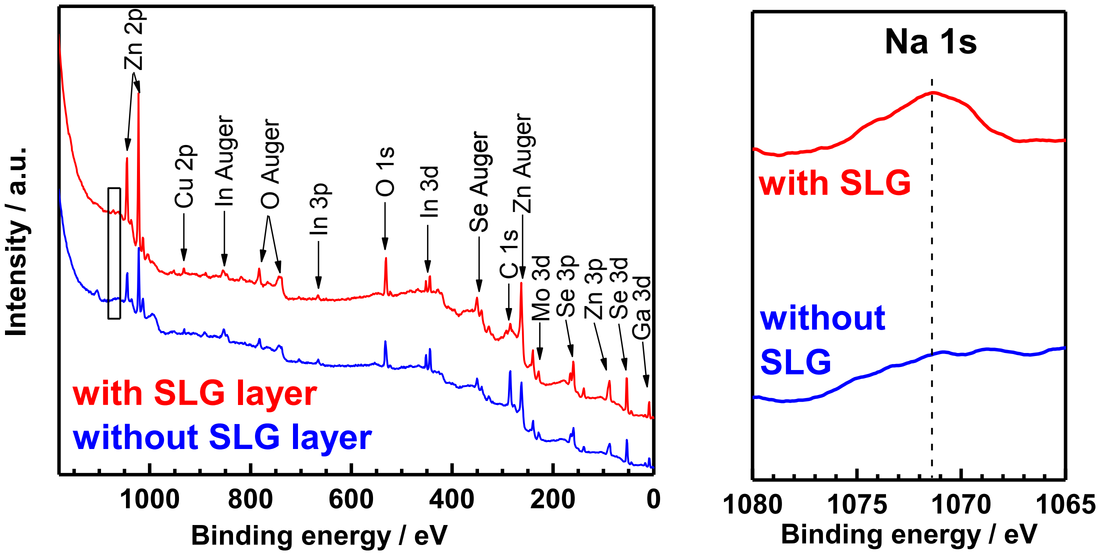

Figure S3. XPS spectra obtained from ZnSe-CIGS thin films on Ti-foil substrate with and without SLG layer. A Na 1s signal is evident following Na-doping of ZnSe-CIGS/Ti-foil photocathode with SLG layer.

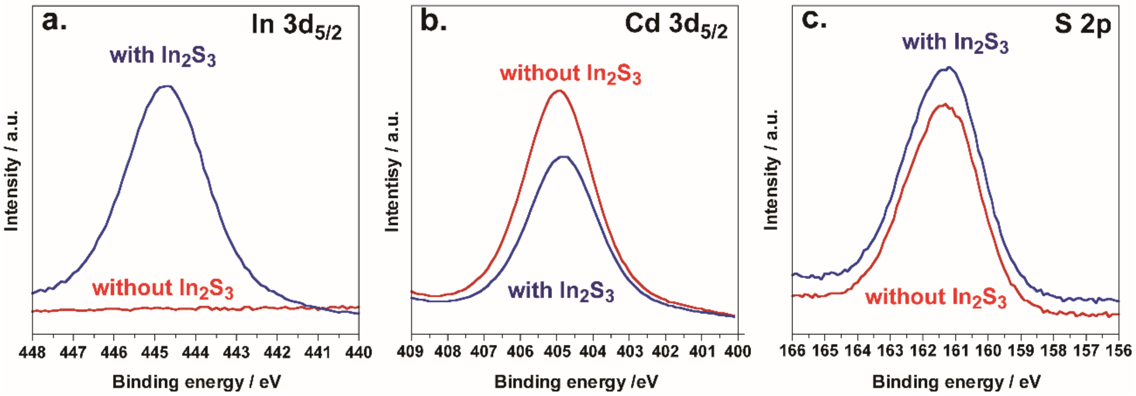

Figure S4. XPS spectra obtained from CdS-modified ZnSe-CIGS thin films with and without In_2S_3 deposition *via* CBD. An In $3d_{5/2}$ signal is evident following In_2S_3 deposition (Fig. S4a). The Cd $3d_{5/2}$ peak intensity was reduced (Fig. S4b) while the S 2p peak intensity was increased (Fig. S4c), indicating that a In_2S_3/CdS bilayer was successfully formed.

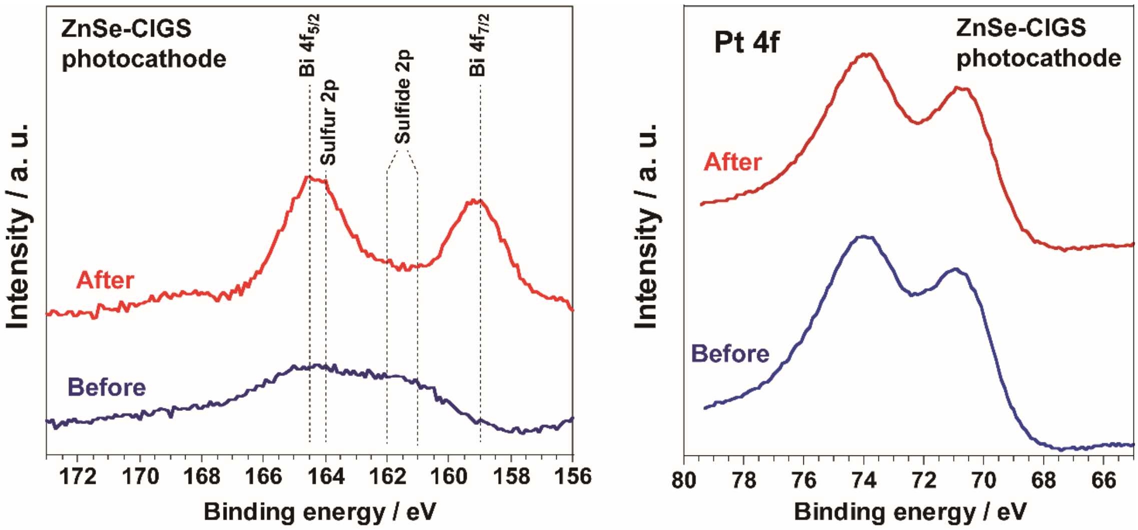

Figure S5. XPS spectra of a ZnSe-CIGS photocathode following the overall water splitting reaction by the combination of a BVO photoanode. The reaction proceeded in a PEC cell within a 0.5 M potassium borate buffer solution (pH = 9.5) over 6030 s. The surface Bi/Pt ratio was determined to be 0.24. The rate of Bi deposition was calculated to be 1.0×10^{-13} mol cm^{-2} s^{-1} based on the Pt surface density of 2.6×10^{-9} mol cm^{-2}. We note that the quantity of deposited Bi species would be equivalent to 0.33 monolayer (ML) and 1.0 ML on the Pt surface at 2.3 and 6.9 h, respectively.

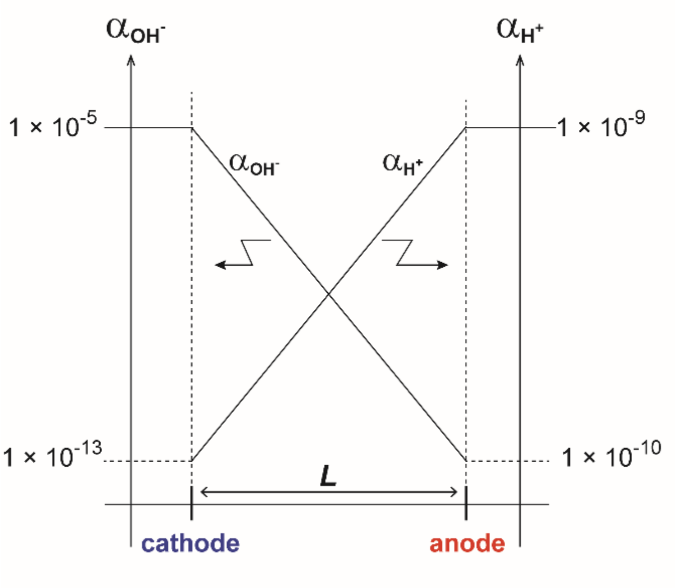

Figure S6. Diagram summarizing the concentration profiles for reactants at an arbitrary distance, *L*, between a hydrogen evolution site on the photocathode and an oxygen evolution site on the photoanode. The concentration of the reactants was assumed to vary linearly, and the activity of the reactants were regarded to be same as their concentration. The flux (*J*) of H^+ was calculated using an equation based on Fick's first law:

$J = D_{H^+} (d\alpha_{H^+} / dL)_{L=0}$,

where J is the H^+ flux, D_{H^+} is the H^+ diffusion coefficient, α_{H^+} is the H^+ activity, and L is as defined above.

The surface pH of the photocathode and photoanode and the bulk pH of the solution were assumed to be 13, 4 and 9, respectively. It has been reported that the photocathode and photoanode pH can change to ~13.5 and ~6.4, respectively, during the water splitting reaction, even in a borate buffer solution.[8] In this calculation, the variations in the surface pH values were estimated from the changes in the H^+ concentration calculated from the photocurrent density of 0.89 mA cm^{-2} at each photoelectrodes. The diffusion coefficient (D_{H^+}) was determined to be 9.31×10^{-5} cm^2 s^{-1}. From the plot above, J was evidently inversely proportion to L, and increased significantly at L values below 1 mm.

Reference.

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