# Supporting Information for

# "Particulate $(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$ photocathode modified with CdS and ZnS for sunlight-driven overall water splitting"

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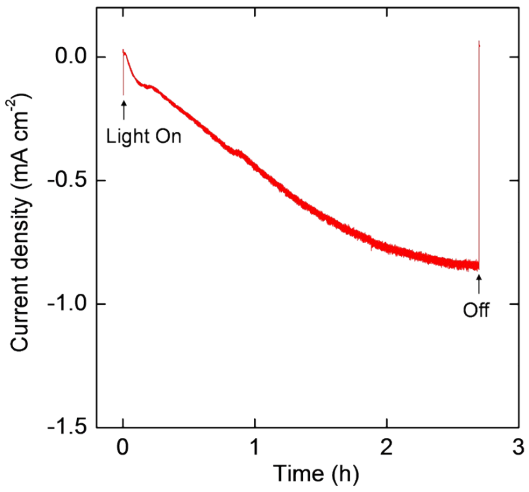


**Figure S1**. Current density versus time curve for the representative ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ photocathode in Pt deposition process at a potential of –0.3 V vs. Ag/AgCl. The solution containing 10 μM $H_2PtCl_6$, 50 μM NaOH, and 0.1 M $Na_2SO_4$, and an AM 1.5G solar simulator were used as the electrolyte and light source, respectively.

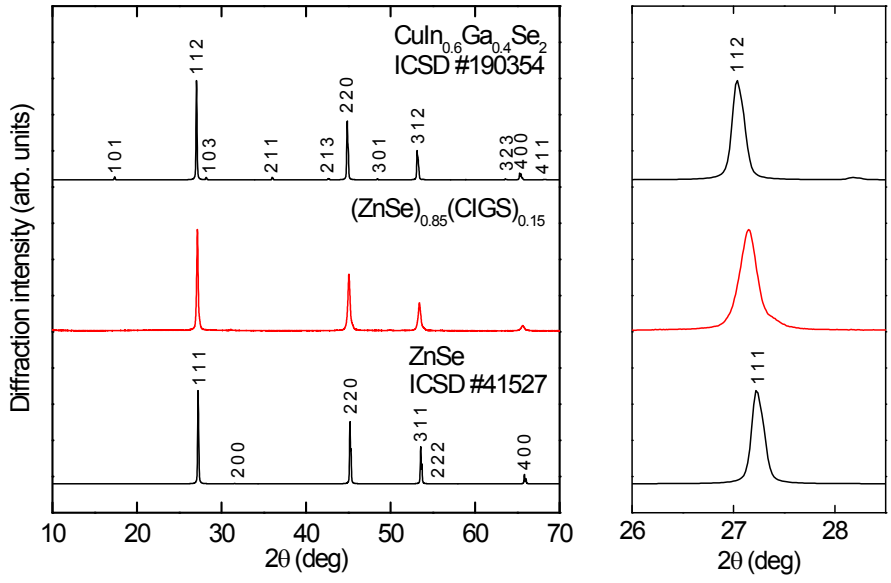


**Figure S2.** XRD pattern of prepared $(ZnSe)_{0.85}(CIGS)_{0.15}$ powder. The XRD patterns for ZnSe and $CuIn_{0.6}Ga_{0.4}Se_2$ were also shown as the references.

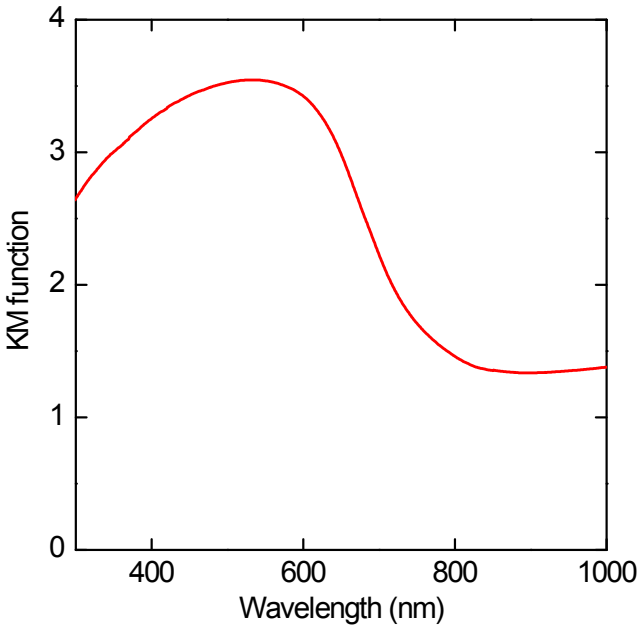


**Figure S3.** UV-Vis-NIR DRS spectrum of $(ZnSe)_{0.85}(CIGS)_{0.15}$ powder.

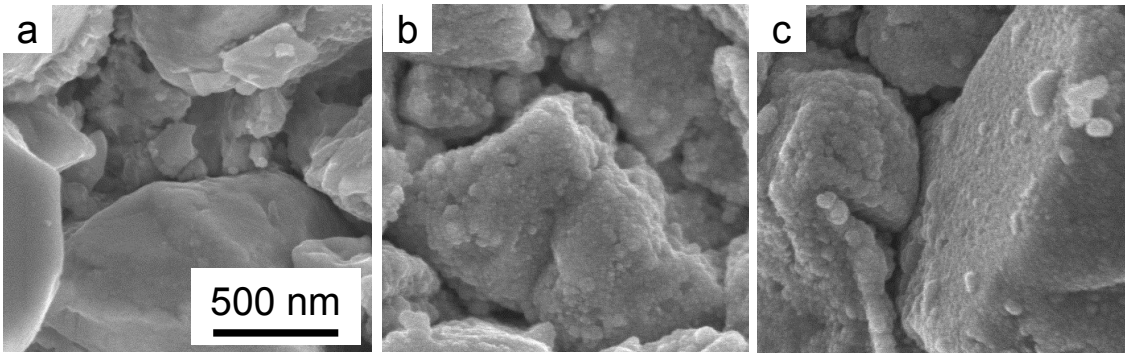


**Figure S4.** SEM images of (a) $(ZnSe)_{0.85}(CIGS)_{0.15}$, (b) CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$, and (c) ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ electrodes.

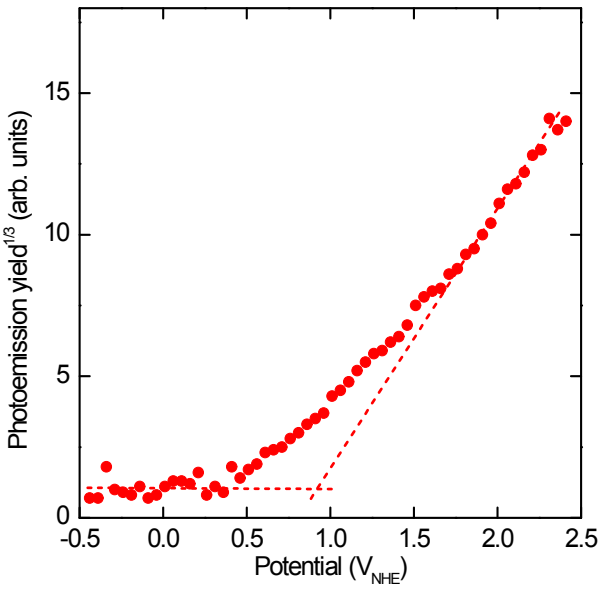


**Figure S5.** PESA spectrum of $(ZnSe)_{0.85}(CIGS)_{0.15}$ electrode.

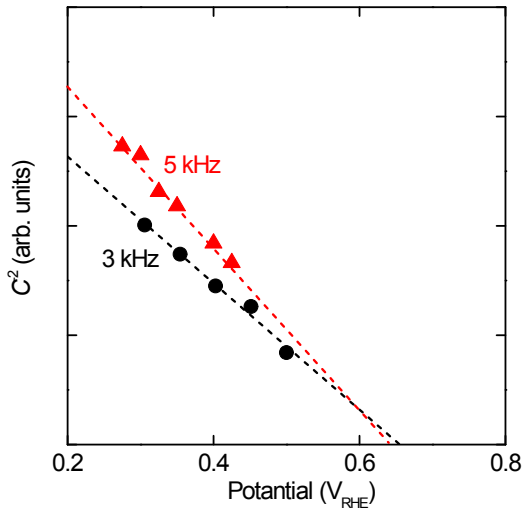


**Figure S6.** Mott-Schottky plot of $(ZnSe)_{0.85}(CIGS)_{0.15}$ electrode. A 1.0 M potassium phosphate buffer solution (pH 7.0) was used as the electrolyte.

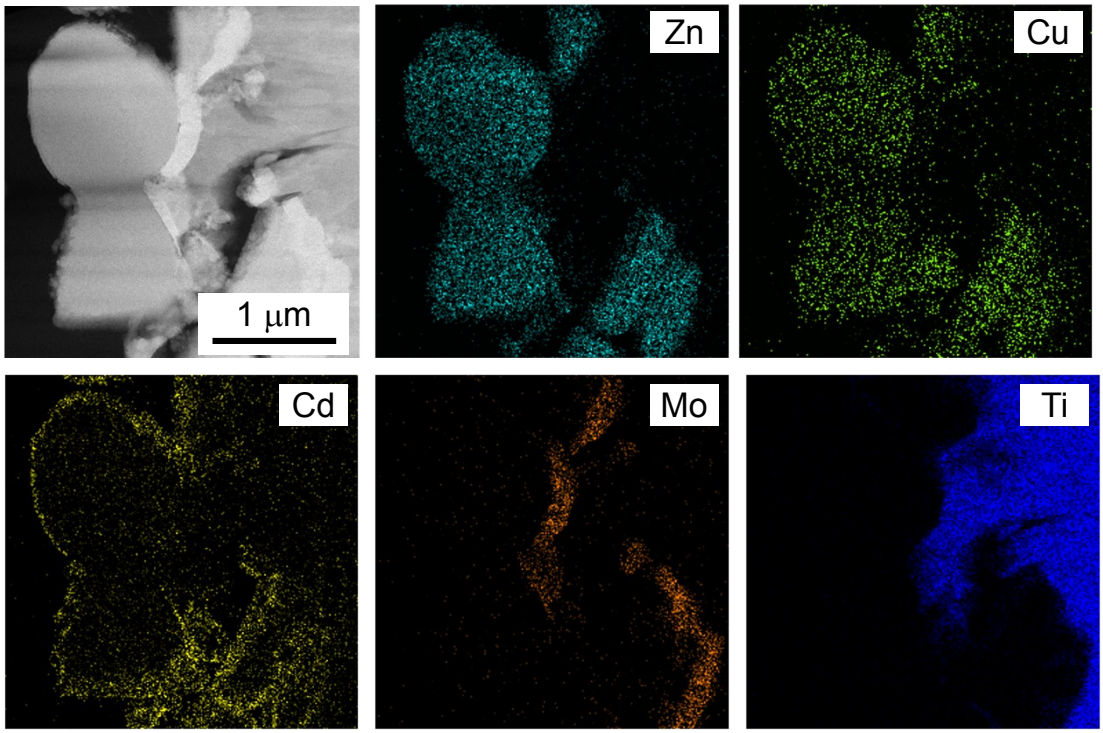


**Figure S7.** Cross-sectional STEM image and EDS elemental maps for ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$/Mo/Ti electrode.

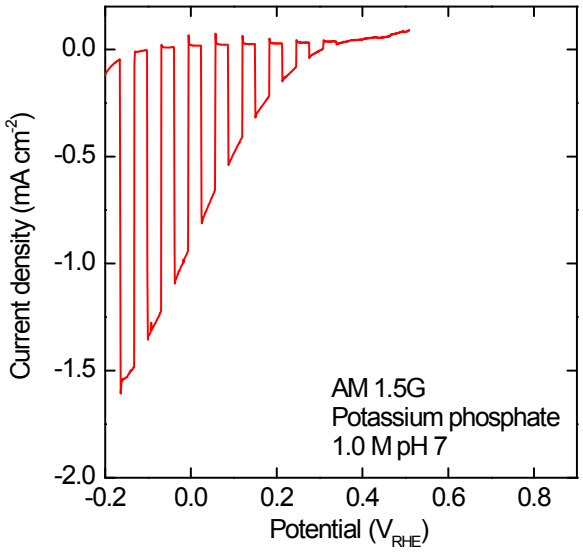


**Figure S8.** Current density versus potential curves for, Pt/ZnS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ under chopped simulated sunlight. A 1.0 M phosphate buffer solution (pH 7) was used as the electrolyte.

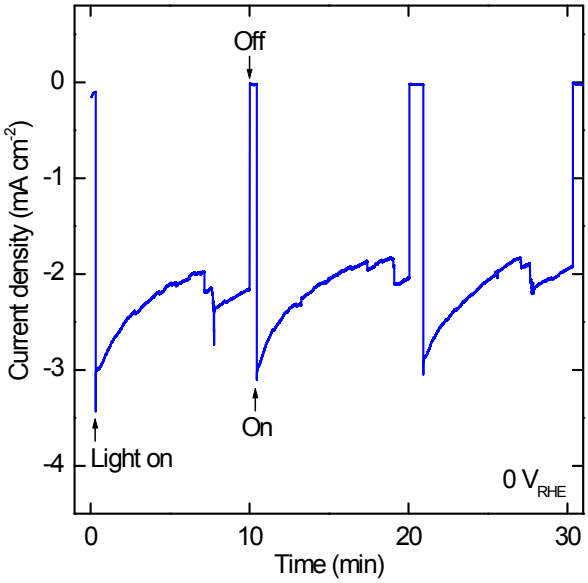


**Figure S9.** Current density versus time curve for Pt/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ at applied potential of 0 $V_{RHE}$ under simulated sunlight. During measurements, photocurrent was fluctuated due to adsorption and desorption of hydrogen bubbles. A 1.0 M phosphate buffer solution (pH 7) was used as the electrolyte.

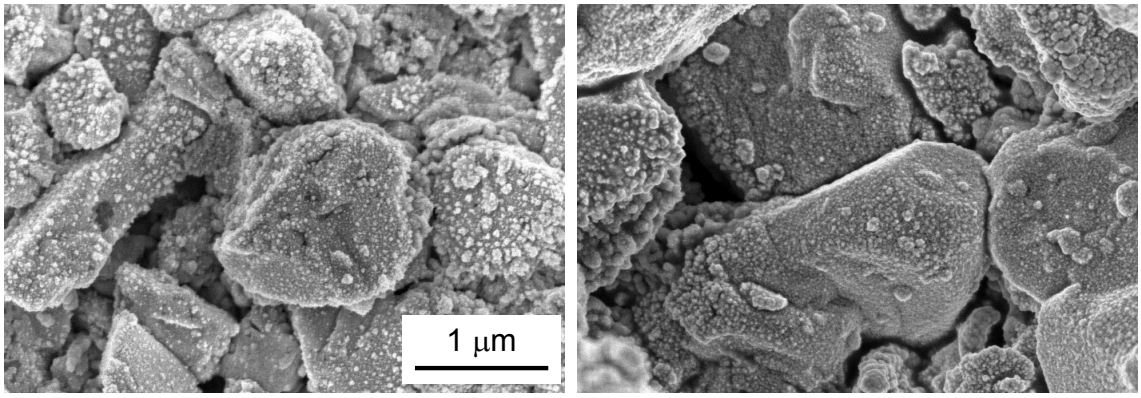


**Figure S10.** SEM images of Pt/ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ before (left panel) and after (right panel) PEC overall water splitting reaction shown in Fig. 6(b).

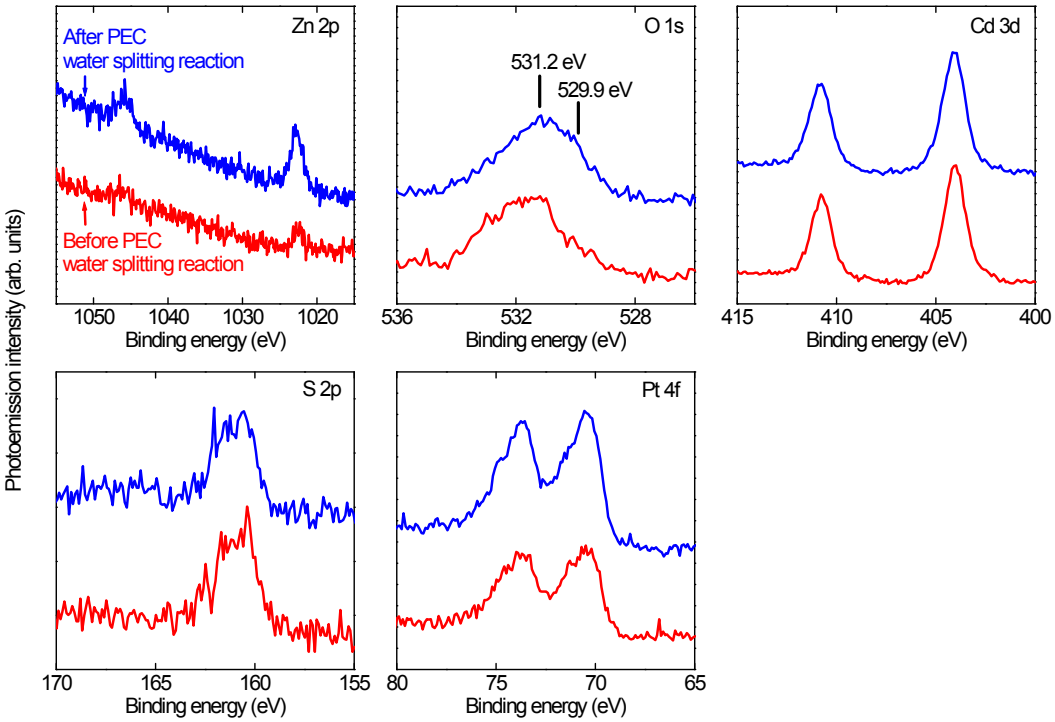


**Figure S11.** XPS spectra of Pt/ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ before (red) and after (blue) PEC overall water splitting reaction shown in Fig. 6(b). The XPS spectra exhibit photoemission peaks attributable to both Cd and Zn. This result indicates that the deposited ZnS layer was as thin as several nm and/or only partly covered the CdS, which is consistent with the EDS analysis. Vertical tick marks in O 1s XPS spectra corresponds to chemisorbed oxygen species (531.2 eV) and $O^{2-}$ ions in the ZnO lattice (529.9 eV)[1], suggesting that surface ZnS was oxidized into ZnO during PEC overall water splitting reaction. The Surface composition ratio estimated using XPS is shown in Table S2.

**Table S1.** Deposition conditions of back contact/conductor layer. Substrate temperature was set to be 200 °C.

| | Mo | C | Ti |
|---|---|---|---|
| RF power (W) | 100 | 50 | 200 |
| Deposition time (min) | 5 | 180 | 180 |
| Partial pressure of Ar (Pa) | $3 \times 10^{-1}$ | $4 \times 10^{-1}$ | $6 \times 10^{-1}$ |

**Table S2.** Parameters used to calculate the band alignments shown in Figure 4.

| | ZnS | CdS | $(ZnSe)_{0.85}(CIGS)_{0.15}$ |
|---|---|---|---|
| Thickness (nm) | 3 | 60 | >1000 |
| Donor density ($cm^{-3}$) | $1 \times 10^{16}$ | $1 \times 10^{16}$ | – |
| Acceptor density ($cm^{-3}$) | – | – | $1 \times 10^{16}$ |
| Band gap (eV) | 3.7 | 2.4 | 1.4 |
| Relative dielectric constant | 10 | 10 | 10 |
| Electron affinity (eV)[2,3] | 3.90 | 4.45 | 4.10 |

**Table S3.** Surface composition ratio estimated using XPS for the Pt/ZnS/CdS/$(ZnSe)_{0.85}(CIGS)_{0.15}$ before and after PEC overall water splitting reaction shown in Fig. 6(b).

| | Before reaction | After reaction |
|---|---|---|
| Cd/S | 0.80 | 0.87 |
| Zn/S | 0.04 | 0.19 |
| (Cd + Zn)/S | 0.84 | 1.06 |
| Zn/Cd | 0.05 | 0.22 |

**References**

(1) X. G. Han, H. Z. He, Q. Kuang, X. Zhou, X. H. Zhang, T. Xu, Z. X. Xie, L. S. Zheng, *J. Phys. Chem. C* **2009**, *113*, 584–589.

(2) W. E. Swank, P. G. Le Comber, *Phys. Rev.* **1967**, *153*, 844–849.

(3) Niemegeers, M. Burgelman, R. Herberholz, U. Rau, D. Hariskos, H.-W. Schock, *Prog. Photovoltaics Res. Appl.* **1998**, *6*, 407–421.