Electronic Supplementary Information

Powder-based $(CuGa_{1-y}In_y)_{1-x}Zn_{2x}S_2$ solid solution photocathode with a largely positive onset potential for solar water splitting

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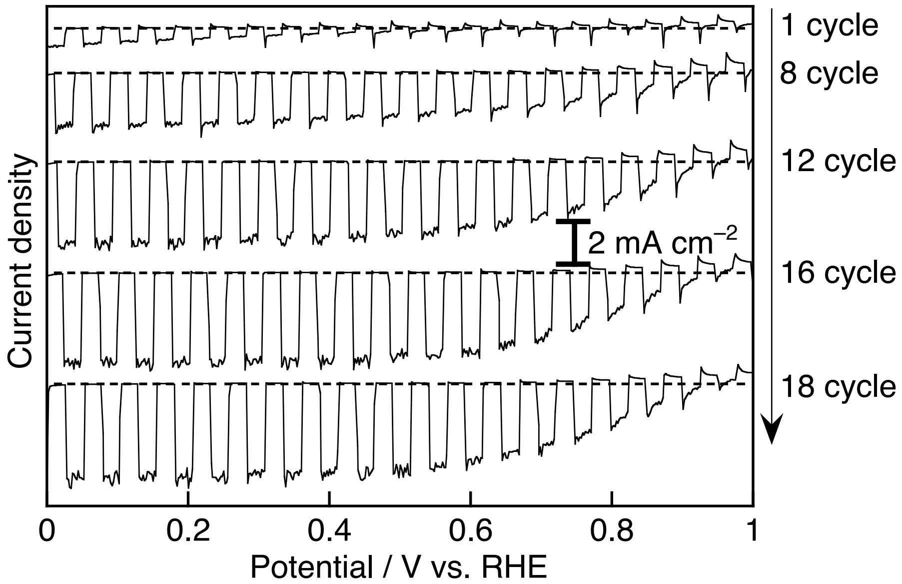

Figure S1. Typical *I-V* curves of a Pt/CdS/CGIZS photocathode in an activation process before use by performing cyclic voltammetry between 0.0-1.0 V vs. RHE in an aqueous phosphate buffer solution (pH 6.4) under irradiation of simulated sunlight (AM 1.5G). The CGIZS represents $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ (Ga 20% excess) prepared by a flux method using LiCl-KCl (3:2) mixture at 823 K for 15 h.

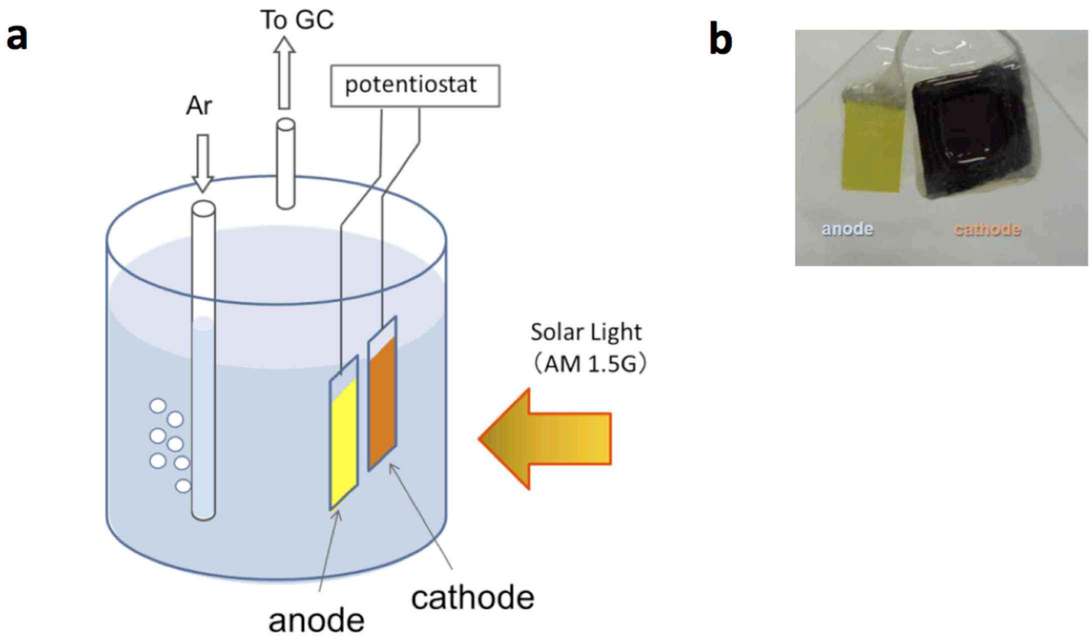

Figure S2. (a) Photoelectrochemical system equipped with on-line gas chromatography, two-electrode type. The photoanode and photocathode existed side by side in the same plane. (b) Photograph of Pt/TiO_2/CdS/CGIZS/Au photocathode (0.231 cm^2) and $CoFeO_x$/$BiVO_4$/ITO photoanode (0.272 cm^2) used for overall water splitting.

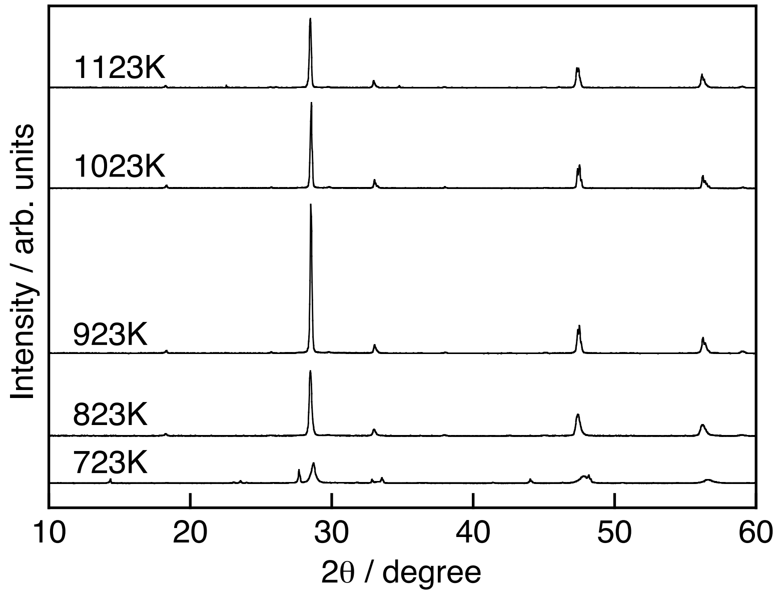

Figure S3. XRD patterns of $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ photocatalysts (Ga 20% excess) prepared by a flux method using LiCl-KCl (3:2) mixture for 3 h at 723 K, 823 K, 923 K, 1023 K, and 1123 K.

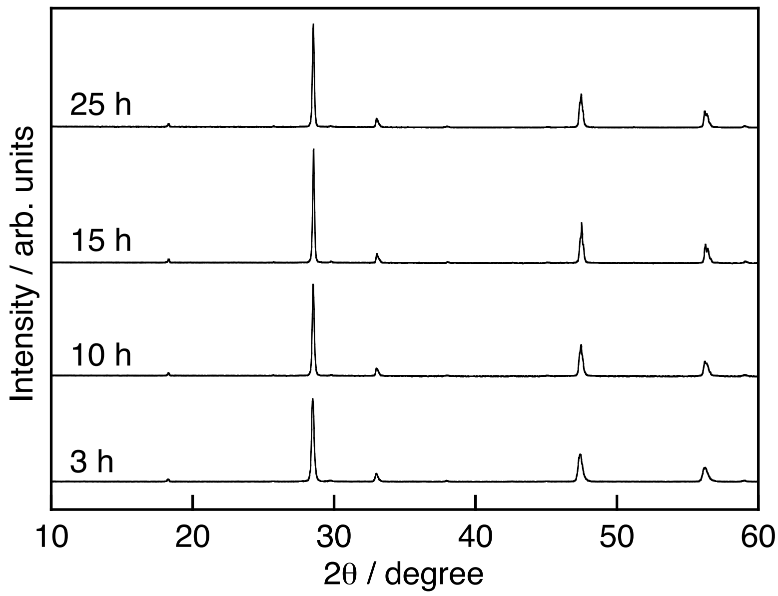

Figure S4. XRD patterns of $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ photocatalysts (Ga 20% excess) prepared by a flux method using LiCl-KCl (3:2) mixture at 823 K for 3 h, 10 h, 15 h and 25 h.

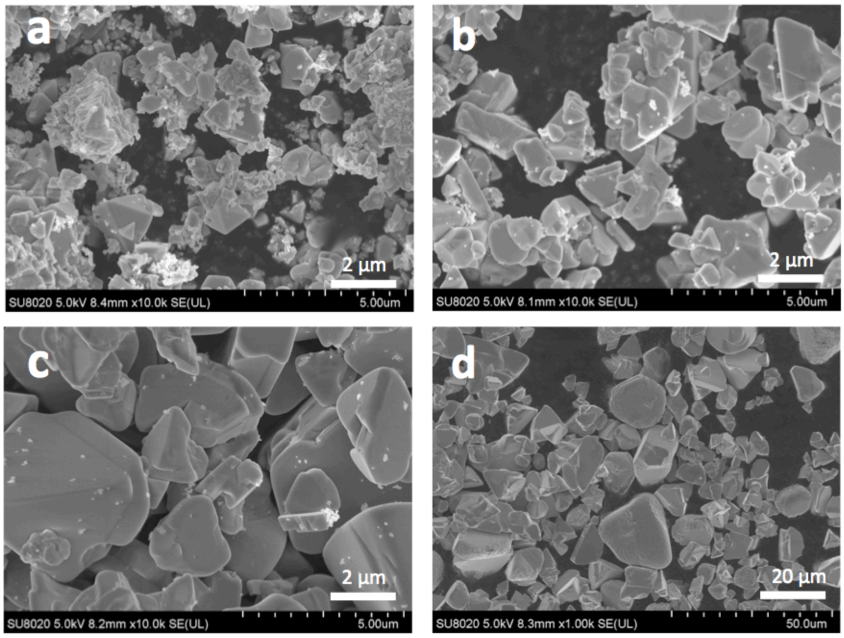

Figure S5. SEM images of $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ photocatalysts (Ga 30% excess) prepared by a flux method using LiCl-KCl (3:2) mixture for 15 h at (a) 723 K, (b) 823 K, (c) 923 K, and (d) 1023 K.

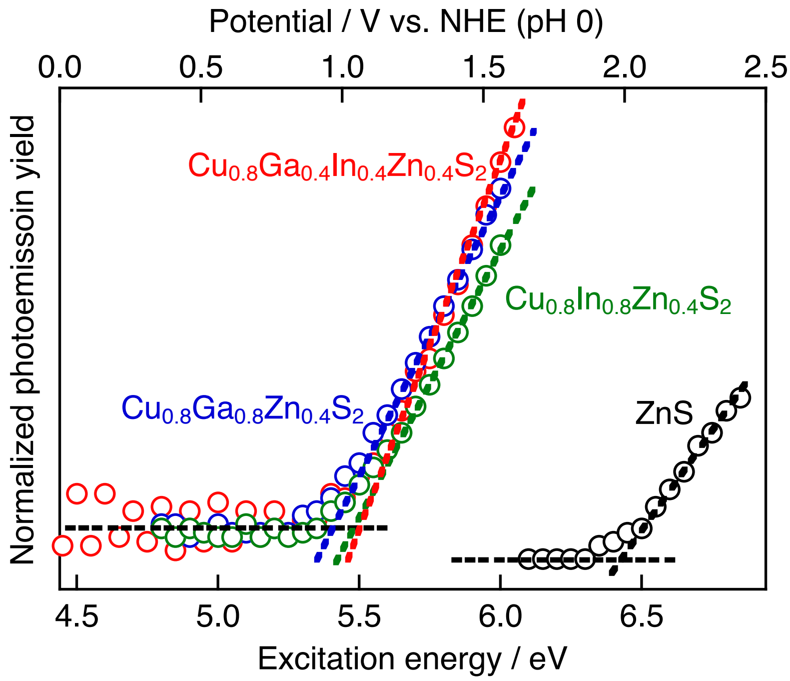

Figure S6. PESA (photoelectron spectroscopy in air) of $(CuGa_{1-y}In_y)_{1-x}Zn_{2x}S_2$ photocatalysts (Ga 20% excess) prepared by a flux method using LiCl-KCl (3:2) mixture at 823 K for 15 h; x=0.2, y=0.0, $Cu_{0.8}Ga_{0.8}Zn_{0.4}S_2$ (red), x=0.2, y=0.5, $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ (blue), x=0.2, y=1.0, $Cu_{0.8}In_{0.8}Zn_{0.4}S_2$ (green), and x=1, ZnS (black).

PESA is similar to XPS and UPS. During the measurements, a sample is irradiated with a monochromatic ultraviolet light with energy of 4.0-7.0 eV. When the energy is larger than the work function of the sample, photoelectrons are emitted from the sample. In other words, photoelectrons start to emit at a certain energy level, when the energy of the irradiated ultraviolet light is gradually raised. The energy level corresponds to the valence band maximum in a semiconductor material.

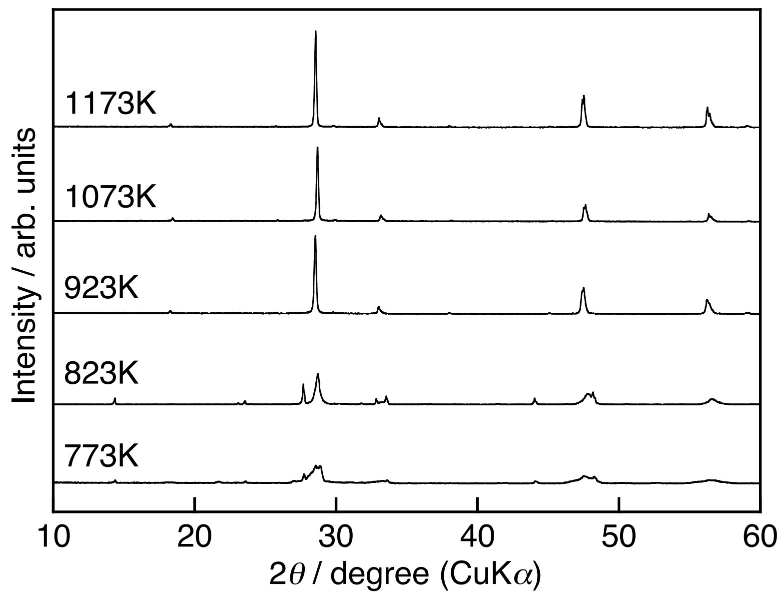

Figure S7. XRD patterns of $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ photocatalysts (Ga 20% excess) prepared by solid-state synthesis at 773 K, 823 K, 923 K, 1073 K, and 1173 K for 10 h.

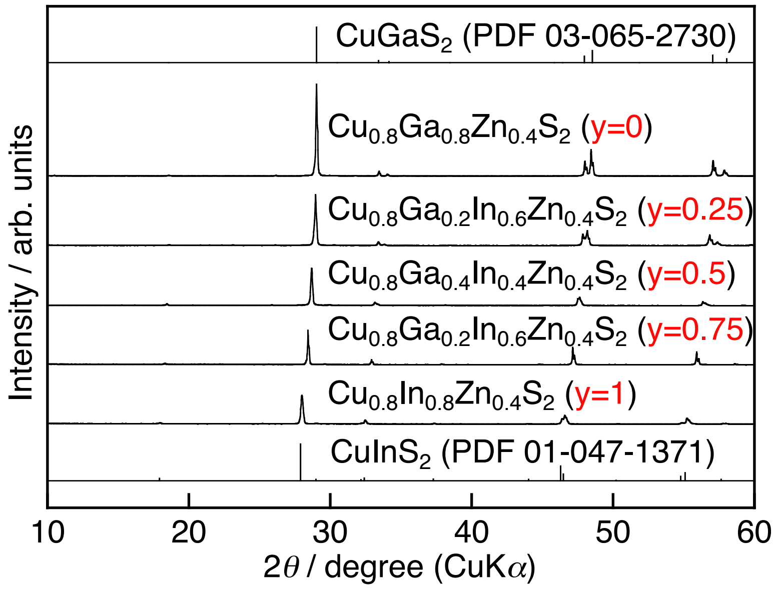

Figure S8. XRD patterns of $(CuGa_{1-y}In_y)_{0.8}Zn_{0.4}S_2$ photocatalysts (y=0.0, 0.25, 0.5, 0.75, 1.0 and Ga 20% excess) prepared by solid-state synthesis at 1073 K for 10 h.

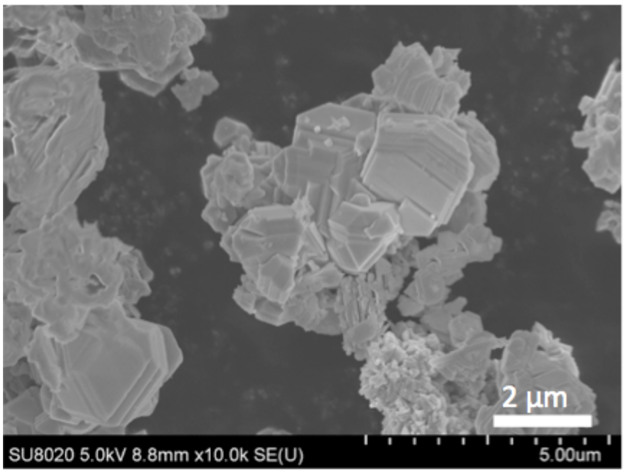

Figure S9. SEM image of $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ photocatalyst (Ga 20% excess) prepared by solid-state synthesis at 1073 K for 10 h.

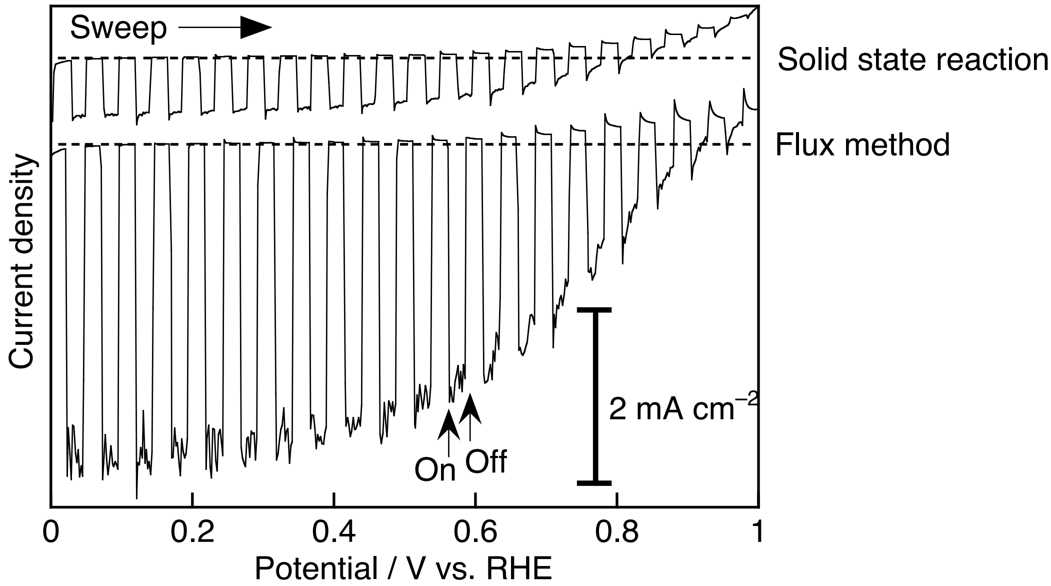

Figure S10. *I-V* curves of Pt/CdS/CGIZS photoelectrodes under simulated sunlight irradiation. The CGIZS photocatalysts ($Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$, Ga 20% excess) were prepared by a flux method using LiCl-KCl (3:2) mixture at 823 K for 15 h and by a solid-state synthesis at 1073 K for 10 h. Electrolyte, aqueous phosphate buffer solution (0.5 mol L^{-1} of Na_2SO_4 + 0.25 mol L^{-1} of NaH_2PO_4 + 0.25 mol L^{-1} of Na_2HPO_4) with pH 6.4; light source, solar simulator (AM 1.5G).

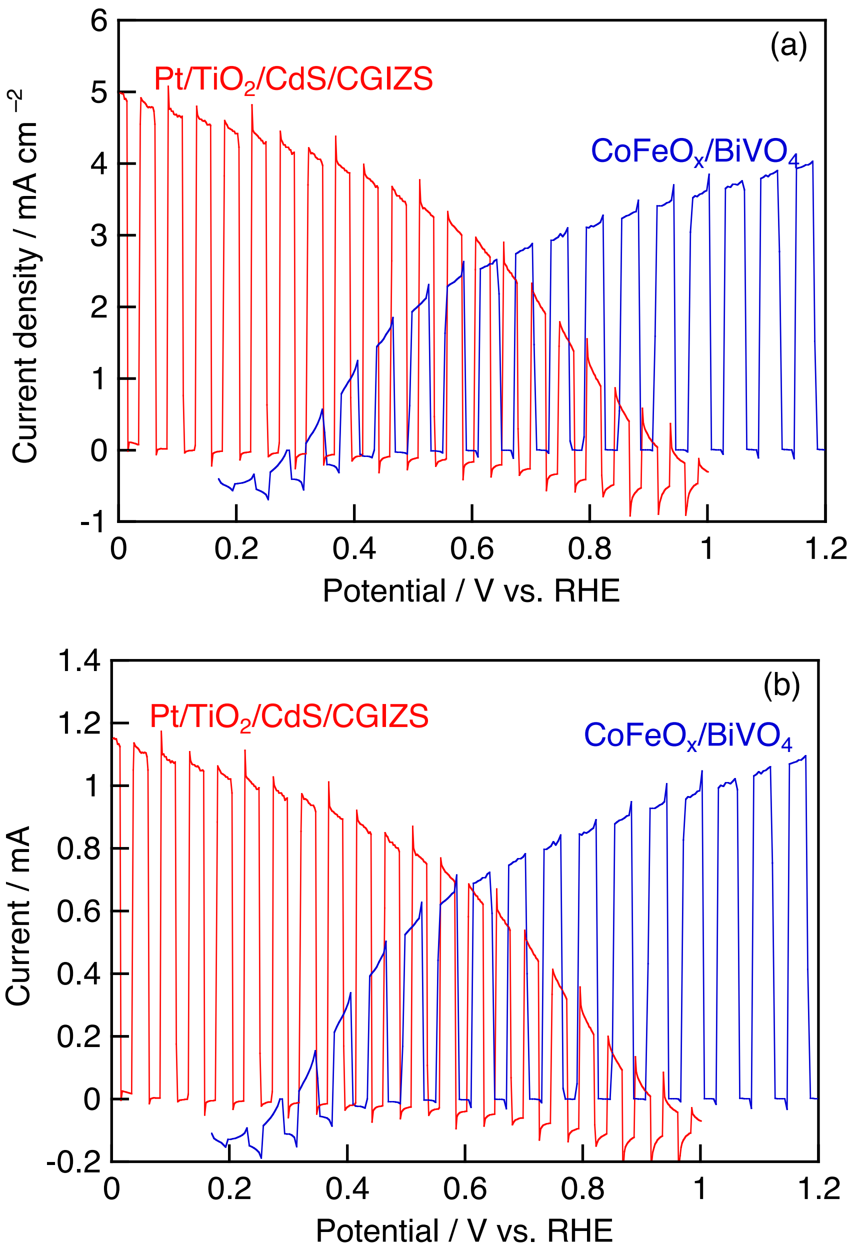

Figure S11. (a) Current density-potential and (b) current-potential curves of $Pt/TiO_2/CdS/CGIZS$ and $CoFeO_x/BiVO_4$ photoelectrodes under simulated sunlight irradiation. In (b), the irradiated areas of $Pt/TiO_2/CdS/CGIZS$ and $CoFeO_x/BiVO_4$ were considered to be 0.231 and 0.272 cm^2.

Electrolyte, aqueous phosphate buffer solution (0.5 mol L^{-1} of Na_2SO_4 + 0.25 mol L^{-1} of NaH_2PO_4 + 0.25 mol L^{-1} of Na_2HPO_4) with pH 7.0; light source, solar simulator (AM 1.5G).

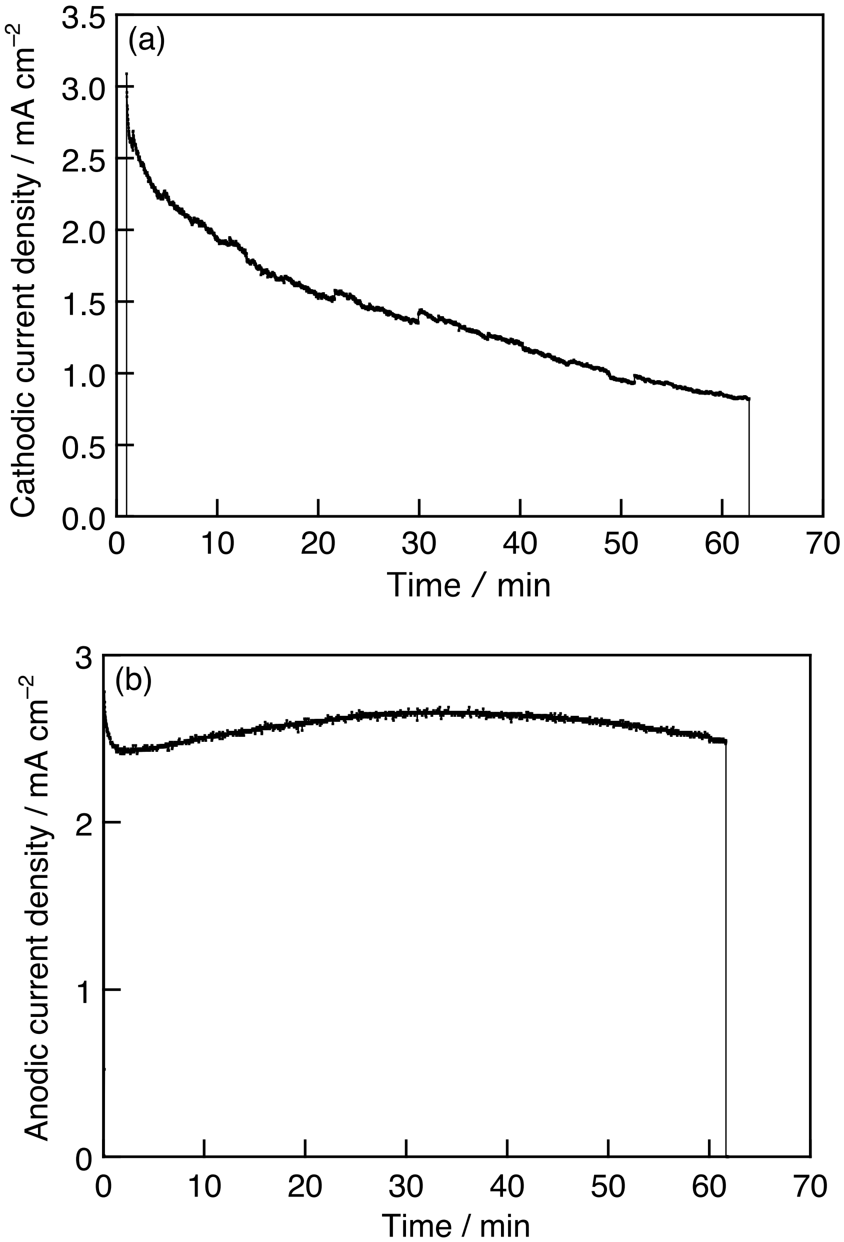

Figure S12. Durability test of (a) Pt/TiO_2/CdS/CGIZS/Au and (b) $CoFeO_x$/$BiVO_4$ photoelectrodes under simulated sunlight irradiation.
Electrolyte, aqueous phosphate buffer solution (0.5 mol L^{-1} of Na_2SO_4 + 0.25 mol L^{-1} of NaH_2PO_4 + 0.25 mol L^{-1} of Na_2HPO_4) with pH 7.0; light source, solar simulator (AM 1.5G).

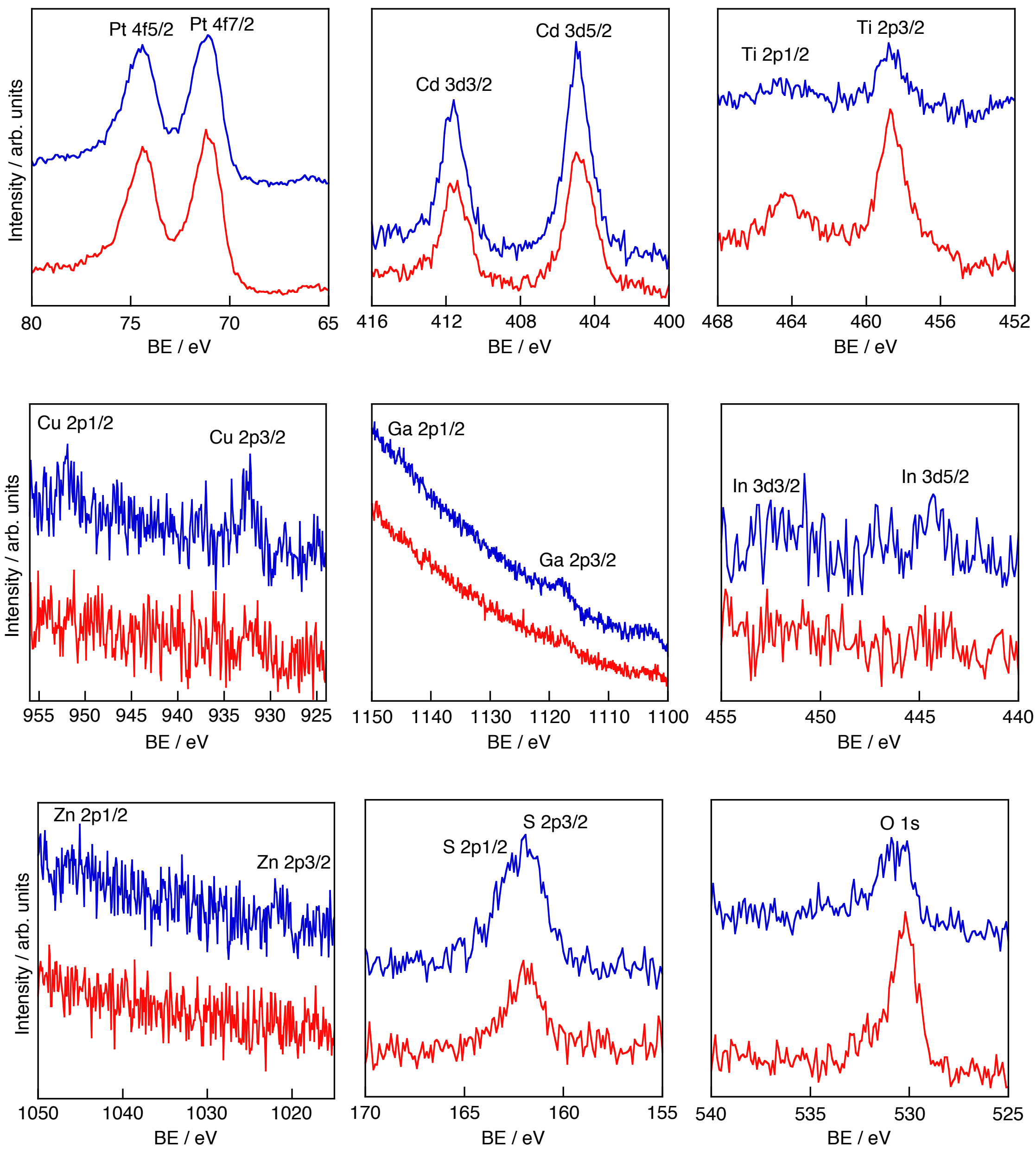

Figure S13. XPS spectra of Pt, Cd, Ti, Cu, Ga, In, Zn, S, and O in a $Pt/TiO_2/CdS/CGIZS/Au$ photoelectrode before (red) and after (blue) durability test (Figure S12).

Table S1. Current densities and onset potentials in j-V curves of various CGIZS photocathodes (Pt/CdS/CGIZS/Au) with excess elements under chopped simulated sunlight (AM 1.5G)

Excess elements / at%			Current density / mA cm^{-2}			Onset potential
Ga	In	Zn	0.0 V_{RHE}	0.4 V_{RHE}	0.8 V_{RHE}	$/V_{RHE}$
0	0	0	0.9	0.5	0.0	0.7
20	0	0	4.6	4.3	1.4	1.0
30	0	0	4.1	3.8	1.0	1.0
0	20	0	3.6	3.3	0.6	0.9
0	30	0	2.7	2.3	0.6	1.0
0	0	20	4.9	1.4	0.0	0.7
20	20	0	1.4	1.2	0.4	1.0
20	0	20	1.6	1.5	0.6	1.0
0	20	20	2.8	2.5	0.1	0.9

The CGIZS ($Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$) photocatalysts with various excess elements of Ga, In or Zn were prepared by a flux method using LiCl-KCl (3:2) mixture at 823 K for 15 h. An aqueous phosphate buffer solution (0.5 mol L^{-1} of Na_2SO_4 + 0.25 mol L^{-1} of NaH_2PO_4 + 0.25 mol L^{-1} of Na_2HPO_4) with pH 6.4 was used as the electrolyte.