

Supporting information

Fabrication of CZTS and CZTSSe photocathode

CZTS photocathode was fabricated by sulfurization of a stacked film containing Cu, Zn and Sn. The stacked film was fabricated on Mo coated glass substrates by rf sputtering deposition and electron beam physical vapour deposition. The deposited multilayer films were sulfurized in tubular furnace at 580 °C and kept for 30min. Then they were cooled naturally to room temperature.

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) was fabricated by utilizing Mo coat glass treated with selenium. Mo coat glass was treated with Se by vacuum heating. Then stacked film containing Cu, Zn and Sn was fabricated on Mo glass as same as CZTS.

Fabricated CZTS and CZTSSe photocathode were soldered to a copper wire with indium, and then their edges were covered with silicone rubber. The area of photoelectrode was ca. 1 cm^2 .

Synthesis of $[\text{Ru}\{4,4'\text{-di}(1\text{-H-1-pyrrolylpropyl carbonate})\text{-}2,2'\text{-bipyridine}\}(\text{CO})(\text{MeCN})\text{Cl}_2]$ (RuCE1) and $[\text{Ru}(4,4'\text{-diphosphate ethyl-}2,2'\text{-bipyridine})(\text{CO})_2\text{Cl}_2]$ (RuCA1)

The complexes, $[\text{Ru}\{4,4'\text{-di}(1\text{-H-1-pyrrolylpropyl carbonate})\text{-}2,2'\text{-bipyridine}\}(\text{CO})_2\text{Cl}_2]$ (RuCE0) and $[\text{Ru}(4,4'\text{-diphosphate ethyl-}2,2'\text{-bipyridine})(\text{CO})_2\text{Cl}_2]$ (RuCA1) were synthesized according to previously reported method.^{1,2} $[\text{Ru}\{4,4'\text{-di}(1\text{H-pyrrolyl-}3\text{-propylcarbonate})\text{-}2,2'\text{-bipyridine}\}(\text{CO})(\text{MeCN})\text{Cl}_2]$ (RuCE1) was synthesized as follows. A MeCN solution (500 ml) containing 137.2 mg (0.2 mmol) of RuCE0 was irradiated using a white fluorescent light for 24 h at room temperature. After the solvent was evaporated under reduced pressure, the residual red solid was recrystallized with MeCN/ether. Yield: 89 %. $^1\text{H NMR}$ (δ , 400MHz, (acetone- d_6): 10.16 (d, 1H, $J = 5.6$ Hz, *bpy-6'*), 9.39 (d, 1H, $J = 5.6$ Hz, *bpy-6*), 9.06 (s, 1H, *bpy-3'*), 8.94 (s, 1H, *bpy-3*), 8.41 (d, 1H, $J = 5.6$ Hz, *bpy-5'*), 8.02 (d, 1H, $J = 5.6$ Hz, *bpy-5*), 6.78 (m, 2H, *pyrrol*), 6.02 (m, 2H, *pyrrol*), 4.45 (m, 2H, $-\text{CH}_2$), 4.21 (m, 2H, $-\text{CH}_2$), 2.32 (m, 2H, $-\text{CH}_2$), 2.25 (s, 3H, $\text{CH}_3\text{-CN}$). FT-IR (MeCN) $\nu_{\text{CO}} / \text{cm}^{-1} = 1976$. m/z (ESI-MS): 722.05 $[\text{M} + \text{Na}]^+$; 713.05 $[\text{M} - \text{MeCN} + \text{MeOH} + \text{Na}]^+$.

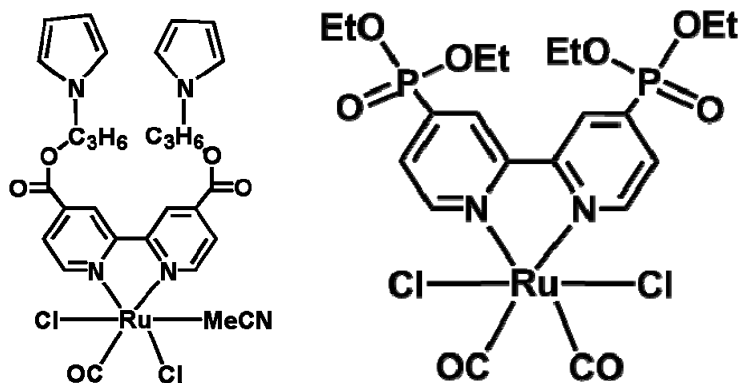


Fig. S1 The Structure of RuCE(Left) and RuCA (Right)

Preparation of Semiconductor/Metal-complex-electrocatalyst (SC/[MCE]) hybrid photocatalyst

To synthesize [RuCE] polymer, RuCE (0.026 mmol) was dissolved in MeCN and polymerized using chemical polymerization initiators. For [RuCE+RuCA] polymer, RuCE (0.013 mmol) and RuCA (0.013 mmol) dissolving in MeCN were polymerized using chemical polymerization initiators. The polymer solutions were dropped on the surface of semiconductor and dried out at 333K for five minutes. These coating procedures were repeated five times. The resulting SC/[MCE] hybrid photocathode put in the dark at room temperature over night. Finally, SC/[MCE] hybrid photocatalyst was rinsed with pure water. The total amount of MCE modified on SC was ca. 0.33 $\mu\text{mol}/\text{cm}^2$.

Characterization of CZTS and CZTSSe

Crystal phase of CZTS and CZTSSe was determined by X-ray diffraction (XRD, RINT2200, Rigaku Corporation). The composition ratio of CZTS and CZTSSe was determined by X-ray fluorescence analysis (XRF, XRF-1500, Shimadzu Corporation). Depth profile of CZTSSe was measured by secondary ion mass spectrometer (SIMS, IMS-6f, Cameca). Photoemission yield spectroscopy in air (PESA, AC-2, RIKEN KEIKI, Co., Ltd.) was measured to estimate the valence band maximum (E_{VBM}) of semiconductor electrodes.

Determination of products

The amount of HCOO^- was determined using an ion chromatograph (ICS-2000, Dionex Corporation) with IonPacAS15 and IonPacAG15 columns. The column temperature was maintained at 308 K. A 3 mM KOH solution was used as the first eluent for 10 minutes, and then the eluent was gradually changed to a 10 mM KOH solution for the next 5 minutes, after which the eluent was gradually changed to a 30 mM KOH solution for the next 5 minutes.

To identify the main product, an ion chromatograph, interfaced with a time-of-flight mass spectroscopy system (IC-TOFMS, JEOL JMS-T100LP), was used with MeOH added as the mobile phase.

Photoelectrochemical measurement

Photoelectrochemical measurements were performed using an electrochemical analyzer (ALS2323, ALS Co., Ltd.). Ag/AgCl and glassy carbon were used as reference and counter electrode, respectively. All potentials reported in this paper are relative to Ag/AgCl. Purified water was used as the electrolyte. A Pyrex glass cell was used as a reactor, and a Xenon light source (MAX-302, Asahi Spectra Co., Ltd.) equipped with an optical filter (LUX422, Asahi Spectra Co., Ltd., $\lambda > 400$ nm) and a cold mirror was used to irradiate visible light. The light was irradiated through a quartz glass fiber (Φ 6mm, ca. 0.28cm^2) and the light intensity ($400 < \lambda < 800$ nm) was adjusted ca. 70 times of AM 1.5. The applied potential was scanned from positive to negative potential as scanning speed 50 mV/s.

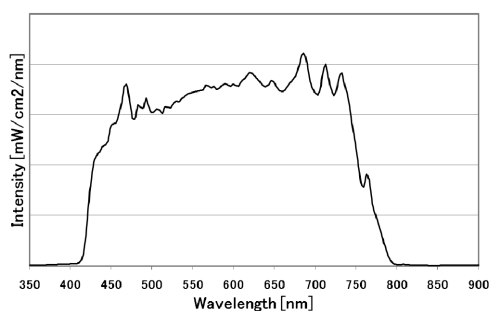


Fig. S2 The spectrum of the Xenon light source equipped with an optical filter and a cold mirror.

XRD patterns of CZTS and CZTSSe photocathode

The observed patterns of both CZTS and CZTSSe were correspond to the pattern of $\text{Cu}_2\text{ZnSnS}_4$ (PDF#00-026-0575), which has kesterite structure. The bulk structure of CZTS was not changed after chronoamperometry measurement for 3 hours.

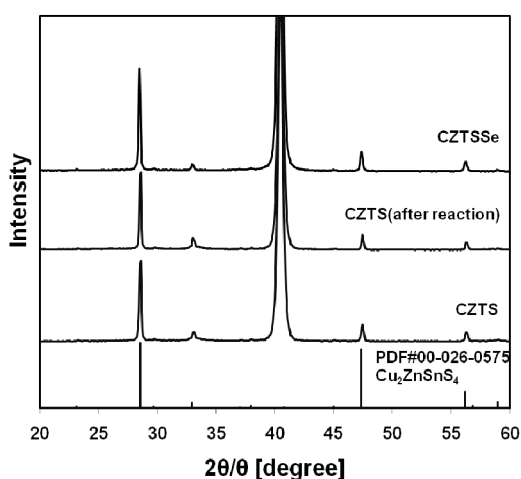


Fig. S3 XRD patterns of CZTS and CZTSSe photocathode

Cu-K-alpha radiation (40 kV, 30 mA), divergence slit: 1° , scattering slit: 1° , receiving slit: 0.3 mm

The results of XRF analysis for CZTS and CZTSSe photocathode

Both CZTS and CZTSSe photocathodes showed copper poor composition in XRF analysis.

Table S1 The results of XRF analysis for CZTS and CZTSSe photocathode

Sample	Ratio of Composition			
	Cu/(Zn+Sn)	Zn/Sn	Cu/Zn	Cu/Sn
CZTS	0.86	0.85	1.87	1.59
CZTSSe	0.87	1.10	1.66	1.82

The results of photoemission yield spectroscopy in air (PESA) for CZTS and CZTSSe photocathode

The results of photoemission yield spectroscopy are shown in Fig. S4. Photoemission threshold energy were determined to be 4.84 and 5.09 eV for CZTS and CZTSSe, respectively. The potential of valence band maximum E_{VBM} were calculated by subtracting ΔE_{NHE} and $\Delta E_{Ag/AgCl}$ from photoemission threshold energy. ΔE_{NHE} , which is the energy difference between vacuum level and normal hydrogen electrode, is about 4.44 eV. $\Delta E_{Ag/AgCl}$, which is the redox potential of Ag/AgCl reference electrode, is about 0.22 eV. As the results, the E_{VBM} for CZTS and CZTSSe were estimated to be 0.18 and 0.42 eV, respectively.

Photoemission threshold energy measured by PESA indicates the reduction of oxygen in air by photoexcited electron of sample. Therefore, the estimated E_{VBM} would have some error by comparing the E_{VBM} estimated by photoelectrochemical measurement in aqueous solution.

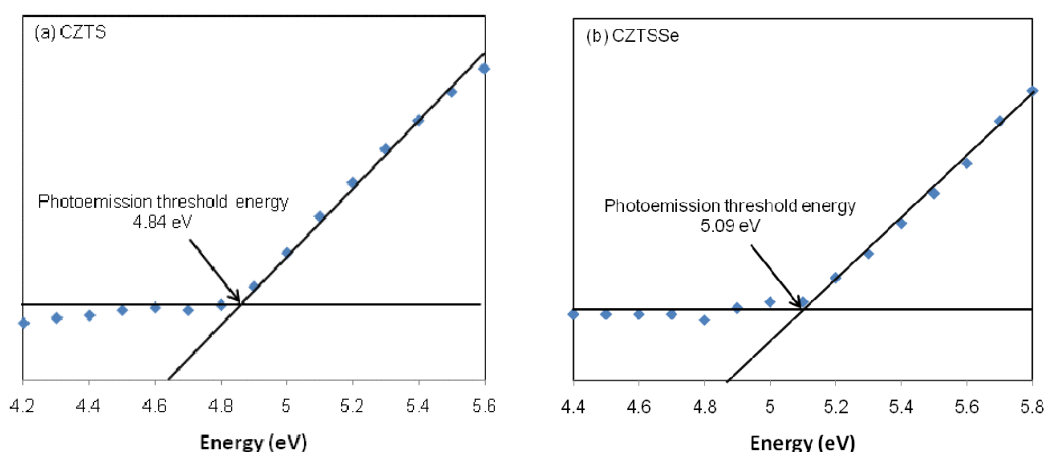


Fig. S4 The results of PESA measurement for (a) CZTS and (b) CZTSSe photocathode
Light intensity was adjusted at 50 and 150 nW for CZTS and CZTSSe, respectively.

The estimation of E_{VBM} for CZTS and CZTSSe by photoelectrochemical measurement

The potential of valence band maximum E_{VBM} for CZTS and CZTSSe were estimated by photoelectrochemical measurement. The current-potential properties were measured by three electrode configuration. Ag/AgCl and platinum wire were used as reference and counter electrode, respectively. 0.2M K_2SO_4 solution was used as the electrolyte. The applied potential was scanned from positive to negative potential as scanning speed 50 mV/s. The changes of photocurrent from cathodic to anodic current were observed around 0.3 V (vs Ag/AgCl) for both CZTS and CZTSSe photocathode. Therefore, the E_{VBM} for both CZTS and CZTSSe were estimated to be 0.3 eV (vs Ag/AgCl).

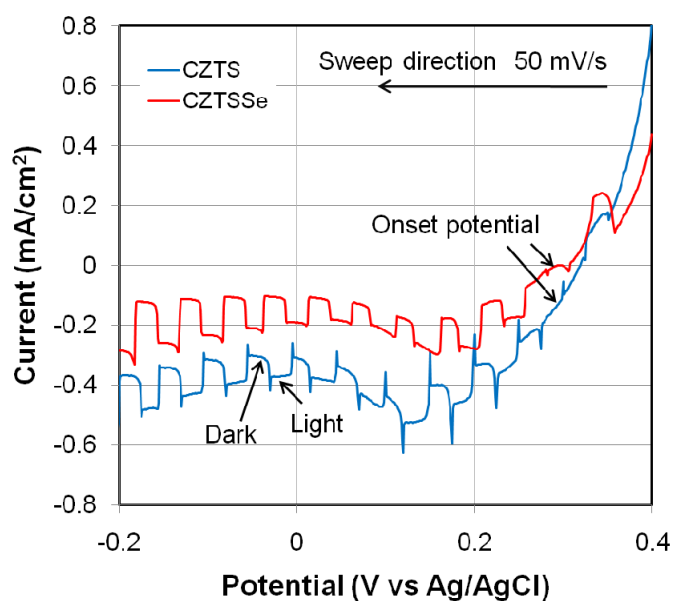
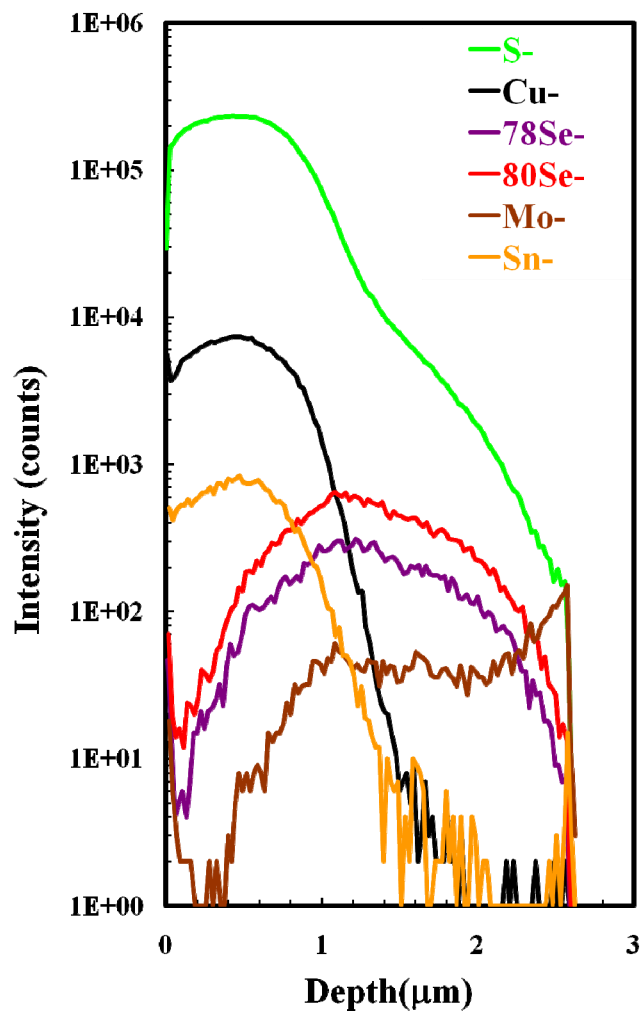


Fig. S5 Current-potential properties for CZTS and CZTSSe

The result of SIMS measurement for CZTSSe photocathode

Depth profiling obtained by SIMS measurement revealed that CZTSSe has a gradient composition. The thickness of CZTSSe layer is ca. 1 μ m.



SIMS depth profile for CZTSSe photocathode

Reference

- 1 P. A. Anderson, et al., *Inorg. Chem.* 1995, **34**, 6145.
- 2 S. Chardon-Noblat, A. Deronzier, R. Ziessel, D. Zsoldos, *J. Electrochem. Soc.* 1998, **444**, 253.