Electronic Supplementary Information

Fabrication of $CuInS_2$ Photocathodes on Carbon Microfiber Felt by Arc Plasma Deposition for Efficient Water Splitting Under Visible Light

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Photoelectrochemical measurements.

The potential of the working electrode was controlled by a potentiostat (VersaSTAT 3, Princeton Applied Research Co., Ltd.). A 0.5 M aqueous solution of Na_2SO_4 (pH adjusted to 4.0 by H_2SO_4 addition), a 0.1 M aqueous solution of Na_2HPO_4 (pH adjusted to 4.0, 9.0, 11.0, or 13.0 by H_3PO_4, NaH_2PO_4, or NaOH addition), or a 0.05 M aqueous solution of $Eu(NO_3)_3$ (pH adjusted to 4.0 by HNO_3 addition) was used as the electrolyte. For the current-potential curve measurements, the scan rate was fixed to 5 mV s^{-1} in the cathodic direction by means of a potentiostat. Before irradiation, the solution was thoroughly purged with Ar gas (99.999%) for more than 30 min to remove dissolved air. The prepared electrode was irradiated with a Xe lamp (300 W, Cermax, LX–300F) fitted with a cut-off filter ($\lambda > 400$ nm, L-42), or with AM 1.5 G simulated sunlight at 100 mW cm^{-2} (300 W, HAL–320, Asahi Spectra Co., Ltd.).

For the incident photon-to-current conversion efficiency (IPCE) measurements, a Xe lamp (300 W, MAX–302, Asahi Spectra Co., Ltd.) equipped with bandpass filters (full width at half maximum of 10–12 nm) was used as a source of monochromatic irradiation.

For PEC water splitting, a two-component cell separated by a porous glass filter was used. Both cells were filled with 140 mL of 0.1 M Na_2HPO_4 (pH adjusted to 11.0 with NaOH), leaving *ca*. 70 mM of head spaces for gas sampling in each cell. One cell was placed by the prepared photocathodes and a Ag/AgCl reference electrode, the other was placed by a Pt counter electrode. The PEC cell was immersed in a water bath to maintain the reaction temperature at *ca.* 23 °C, and light irradiation was performed by means of AM 1.5 G simulated sunlight at 100 mW cm^{-2} (300 W, HAL–320, Asahi Spectra Co., Ltd.) at -0.66 $V_{Ag/AgCl}$. The evolved gases were analyzed by means of an online gas chromatographer (3000 MicroGC, Inficon) fitted with a thermal conductivity detector and a 5A molecular sieve column at 70 °C with Ar as the carrier gas.

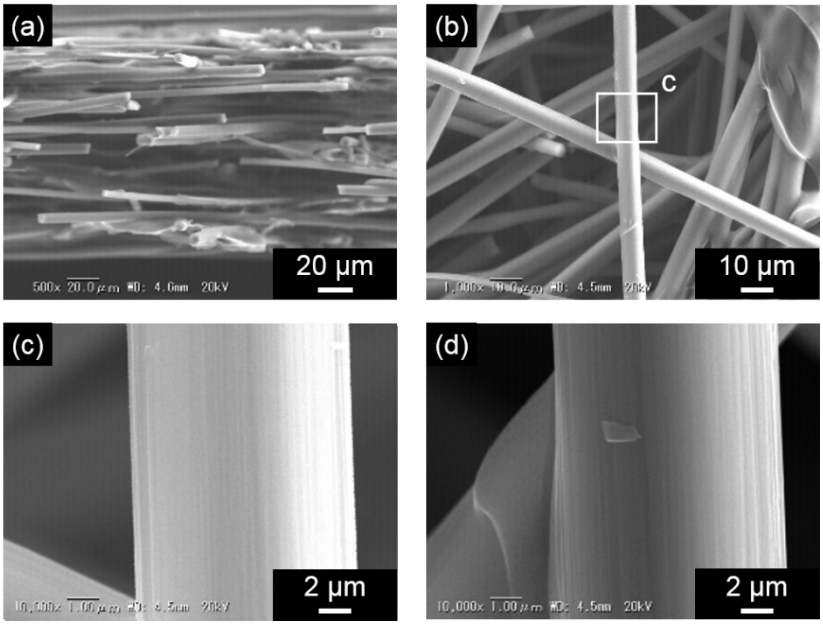

Figure S1. SEM images of (a)-(c) as-provided CMF and (d) CMF calcined at 500 ºC for 30 min in air ((a) cross-section and (b)-(d) top-view).

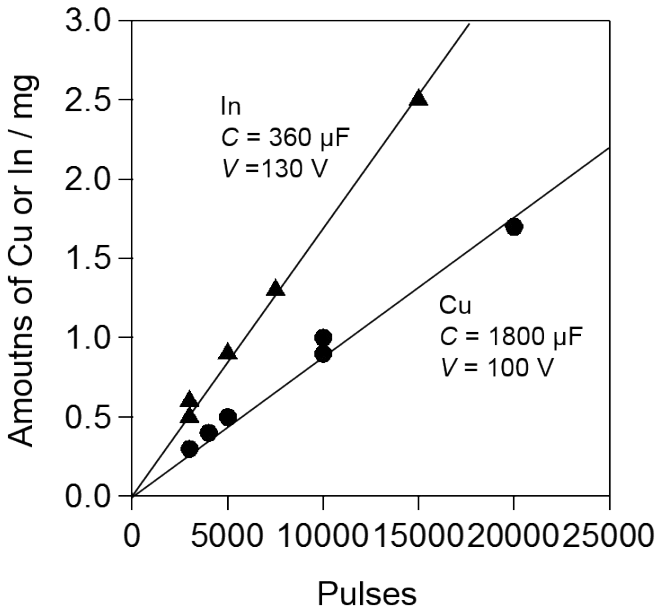

Figure S2. Correlations between the number of arc discharge and the amounts of Cu or In on CMF (*C*; capacitance of condenser (μF), *V*; voltage for arc discharge (V), Substrate area; 3.0 cm^2).

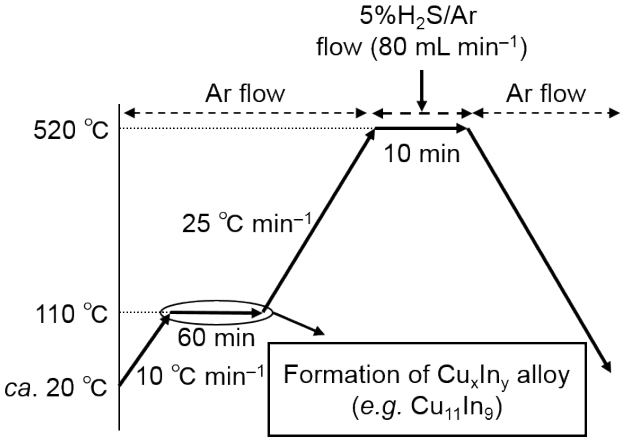

Figure S3. Time profile of heat treatment for sulfurization of In/Cu/CMF and In/Cu/Mo samples.

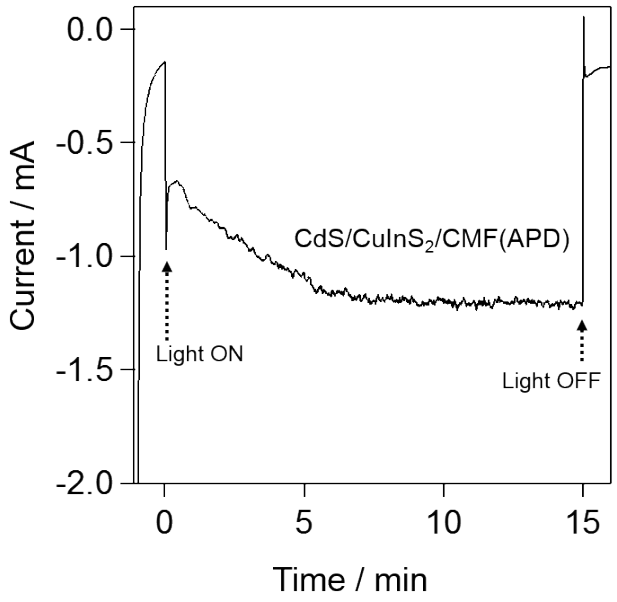

Figure S4. Time course of the photocurrent during photoelectrochemical Pt deposition at -0.1 V (*vs*. Ag/AgCl) under light irradiation ($\lambda > 300$ nm) (Substrate area; 3.0 cm^2).

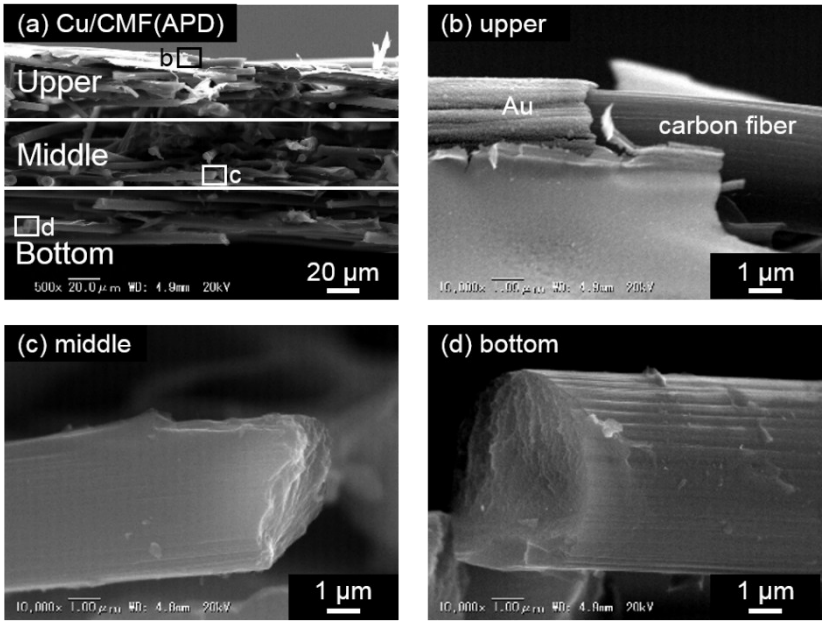

Figure S5. Cross-sectional SEM images of Au particles deposited CMF sample by means of conventional sputtering.

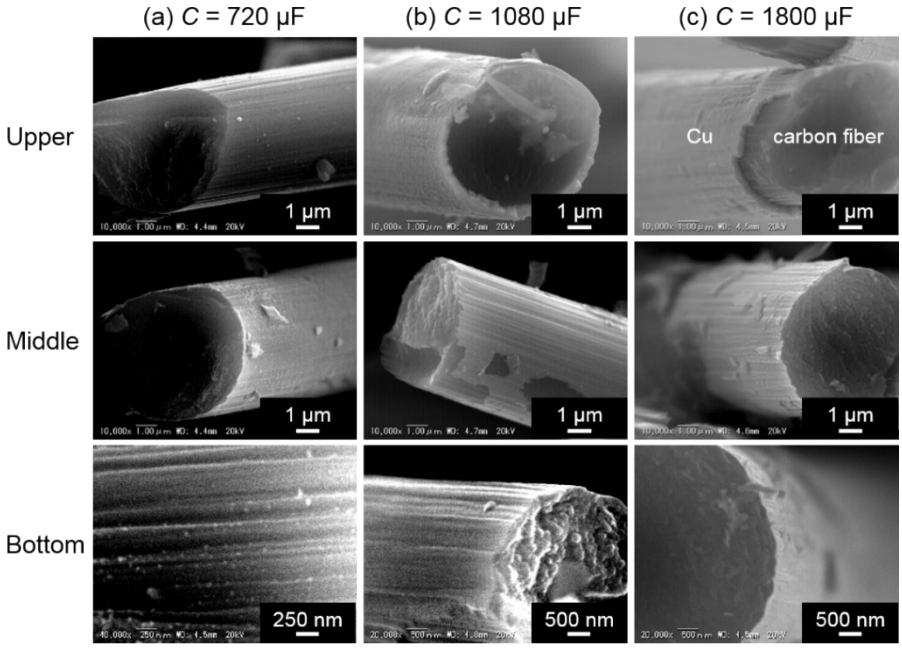

Figure S6. Cross-sectional SEM images of Cu/CMF(APD) samples prepared at different capacitance of the condenser (100 V); (a) C = 720 μF, (b) C = 1080 μF, (c) C = 1800 μF. (c) Enlarged SEM images of Cu/CMF(APD) samples shown in Figure 2 (b)-(d).

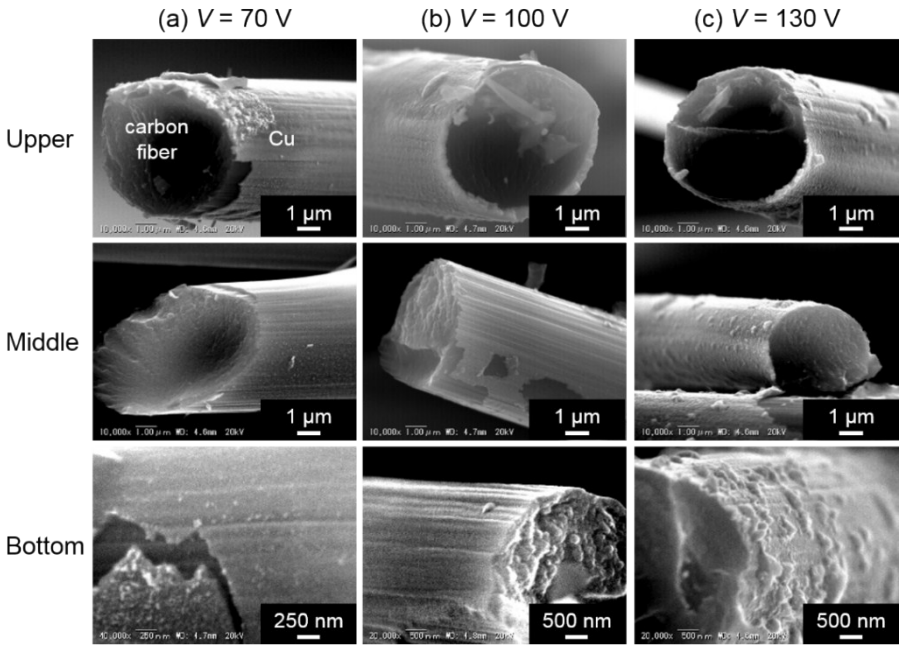

Figure S7. Cross-sectional SEM images of Cu/CMF(APD) samples prepared at different voltage (1080 μF); (a) V = 70 V, (b) V = 100 V, (c) V = 130 V.

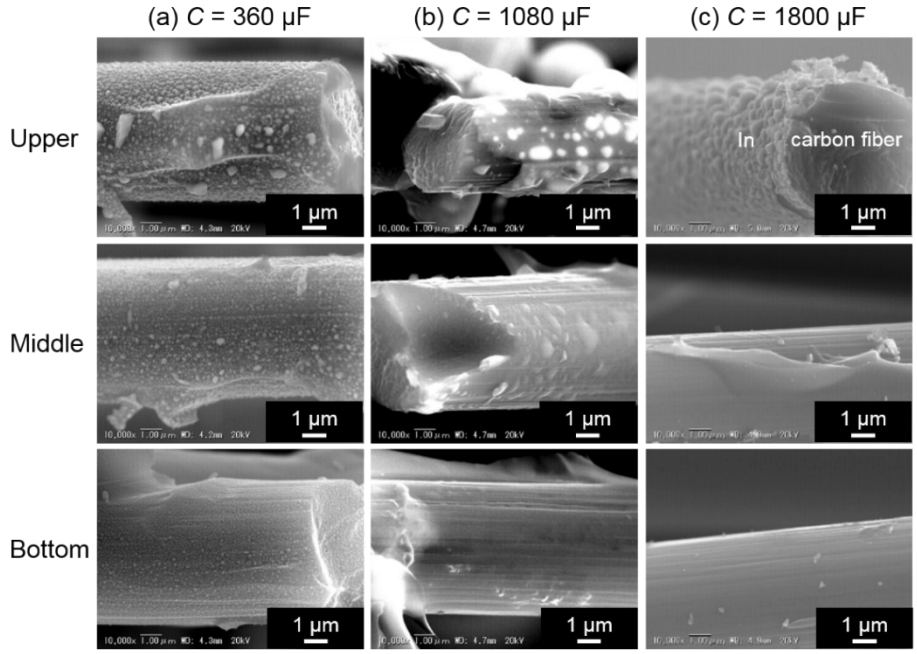

Figure S8. Cross-sectional SEM images of In/CMF(APD) samples prepared at different capacitance of condenser (100 V); (a) C = 360 μF, (b) C = 1080 μF, (c) C = 1800 μF.

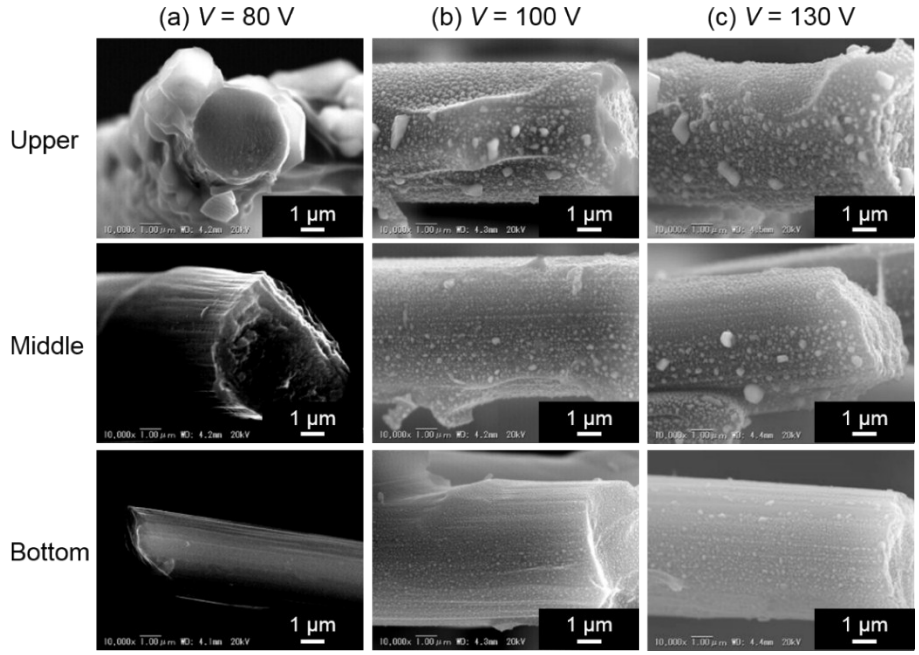

Figure S9. Cross-sectional SEM images of In/CMF(APD) samples prepared at different voltage (360 μF); (a) V = 80 V, (b) V = 100 V, (c) V = 130 V. (c) Enlarged SEM images of In/CMF(APD) samples shown in Figure 3 (a)-(c).

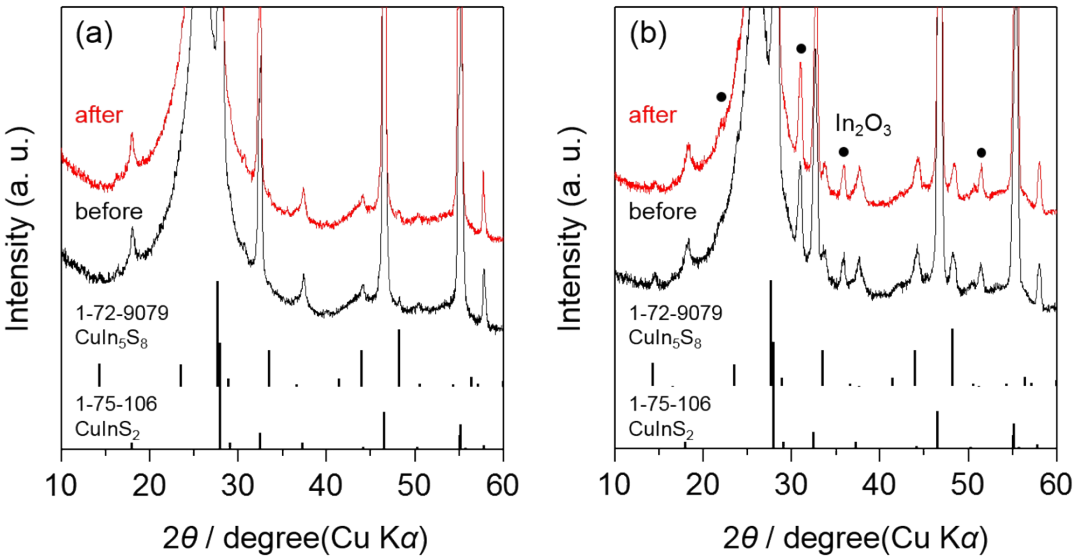

Figure S10. XRD patterns of $CuInS_2$/CMF samples prepared by (a) cathodic arc-plasma deposition (APD) and (b) electrodeposition (ED) before and after the KCN etching.

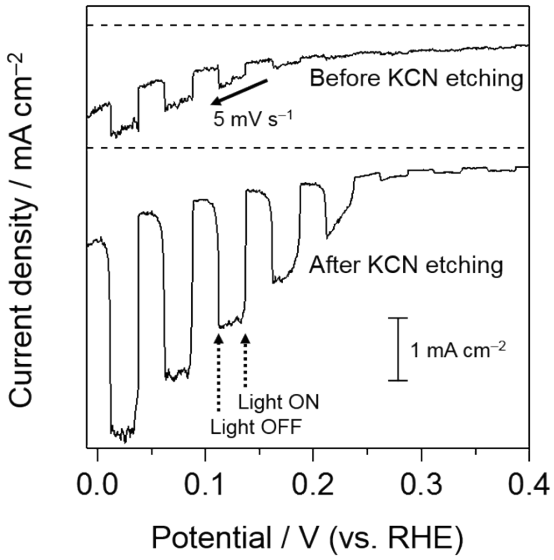

Figure S11. Influence of the KCN etching on the current density for $CuInS_2$/CMF(APD) samples in 0.05 M $Eu(NO_3)_3$ aq. (pH adjusted to 4.0 by HNO_3 addition) under chopped visible light irradiation ($\lambda > 400$ nm).

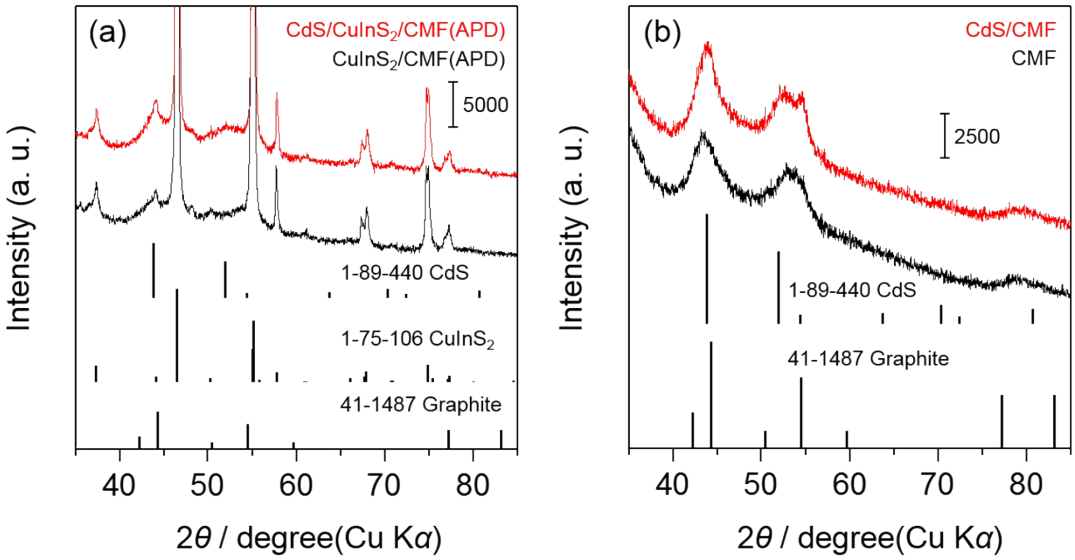

Figure S12. XRD patterns of (a) $CdS/CuInS_2/CMF(APD)$ and (b) CdS/CMF samples prepared by chemical bath deposition.

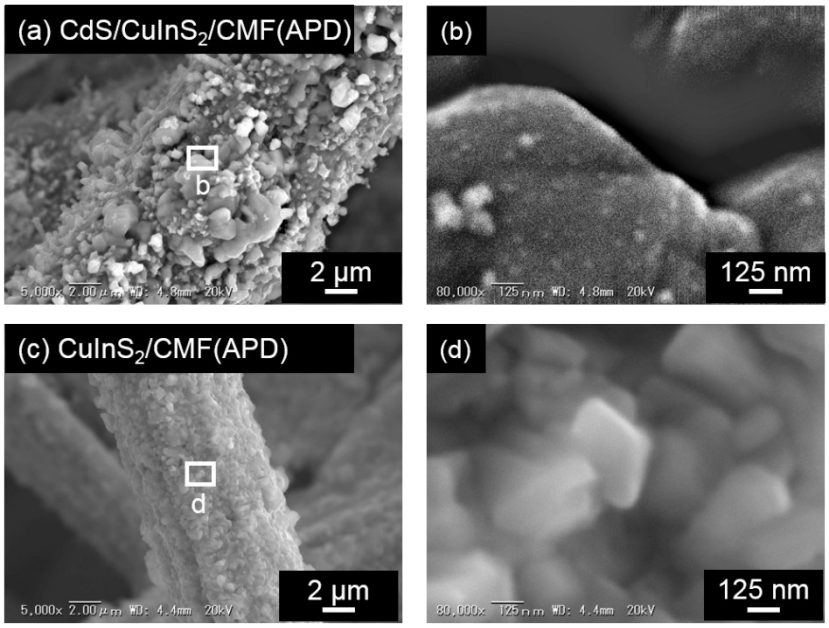

Figure S13. SEM images of (a)-(b) $CdS/CuInS_2/CMF(APD)$ and (c)-(d) $CuInS_2/CMF(APD)$ samples.

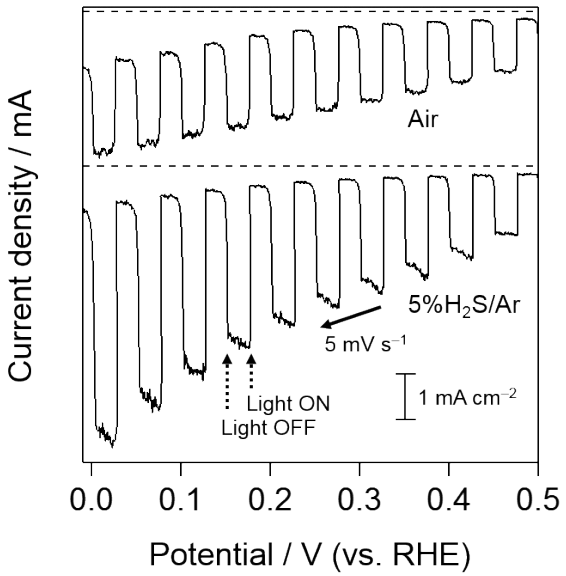

Figure S14. Influence of the post calcination ambience (70 °C, 30 sec) after CdS deposition on the current density for Pt-CdS/$CuInS_2$/CMF(APD) photocathodes in 0.5 M Na_2SO_4 aq. (pH adjusted to 4.0 by H_2SO_4 addition) under chopped visible light irradiation ($\lambda > 400$ nm).

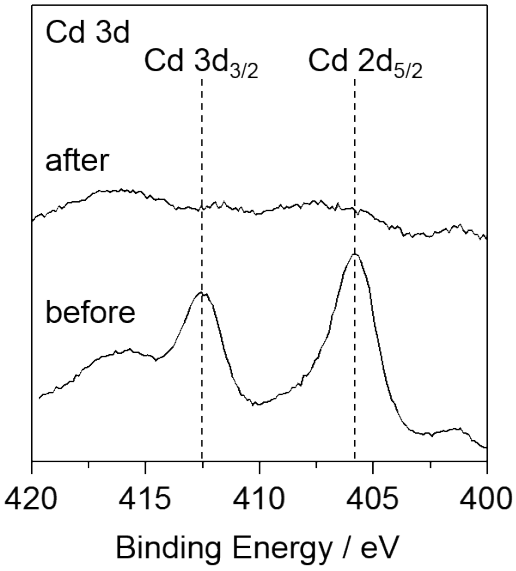

Figure S15. XPS of Pt-CdS/$CuInS_2$/CMF(APD) samples before and after PEC reaction.

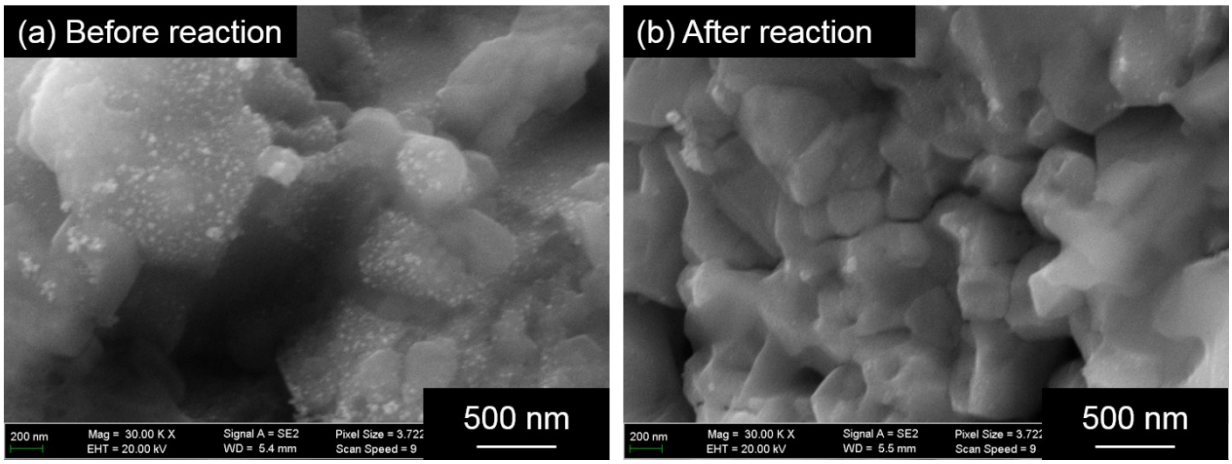

Figure S16. SEM images of Pt-CdS/$CuInS_2$/CMF(APD) samples before and after PEC reaction.

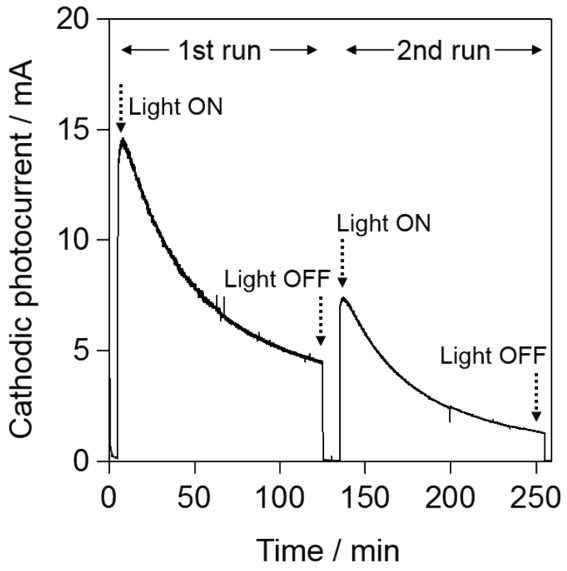

Figure S17. Time course of cathodic photocurrent using Pt-CdS/$CuInS_2$/CMF(APD) photoelectrode (Substrate area; 3.0 cm^2) during PEC water splitting under simulated solar light irradiation (AM 1.5 G, 100 mW cm^{-2}).