

Electronic Supplementary Information

Photoelectrochemical-Voltaic Cells Consisting of Particulate $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ Photoanodes with Photovoltages Exceeding 1.23 V

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The $[\text{Ru}(\text{bpy})_3]^{3+}$ complex was prepared by the electrochemical oxidation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ at a Pt mesh electrode with applying a constant potential, 0.89 V vs. Fc/Fc^+ , such that the total concentration of Ru complexes was 2 mM with $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^{3+}$ ratio of one (Fig. S1).¹ The photoelectrochemical (PEC) measurements in the nonaqueous electrolyte were conducted by the typical three-electrode configuration with Ag/Ag^+ and Pt black-coated Pt wire as the reference and counter electrodes, respectively (Fig. S1(b)). Simulated sunlight adjusted to AM 1.5G was used as the light source.

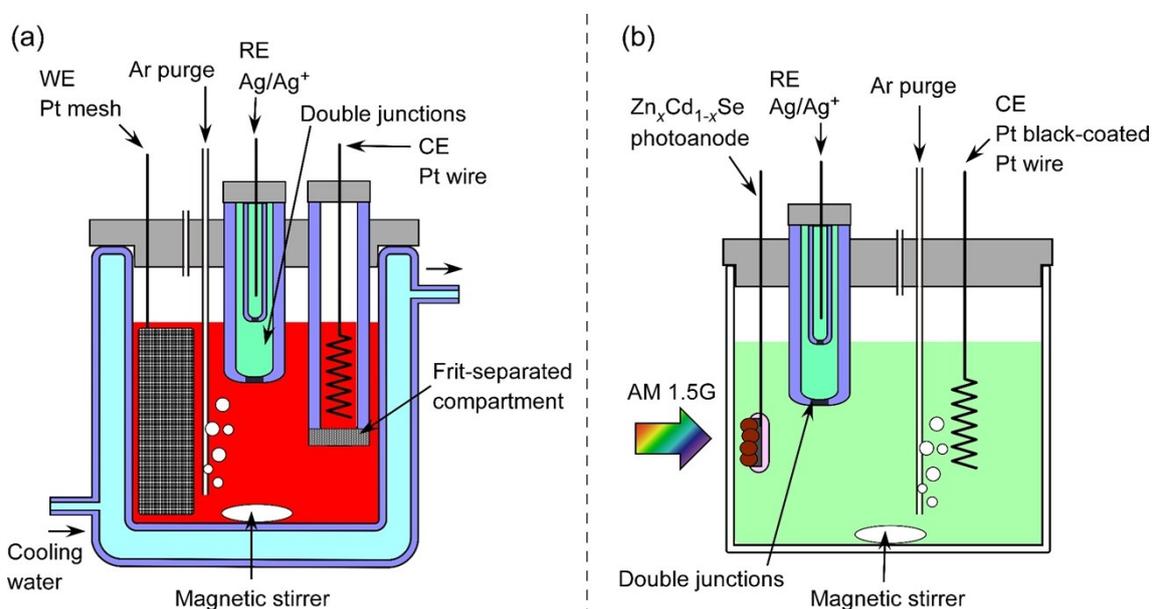


Fig. S1 Schematic drawings of the experimental setups for (a) the bulk electrolysis oxidizing $[\text{Ru}(\text{bpy})_3]^{2+}$ into $[\text{Ru}(\text{bpy})_3]^{3+}$, and the PEC measurements in the nonaqueous electrolyte.

Electronic Supplementary Information

The time course for the electrochemical oxidation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ with a constant potential is shown in Fig. S2(a). Anodic current gradually decreased and reached almost zero after several hours.

During the electrochemical trial shown in Fig. S2a, 20 ml of acetonitrile electrolyte containing 2 mM of the Ru complex and 0.1 M of TBAPF_6 was utilized. The passed current during the electrochemical oxidation was equivalent to 2.1×10^{-5} mol of electrons, which is almost consistent to one-half of the Ru complexes in the electrolyte, 2.0×10^{-5} mol. Therefore, it was certainly confirmed that $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^{3+} = 1$ in the acetonitrile electrolyte after the bulk electrolysis. The acetonitrile electrolyte containing only $[\text{Ru}(\text{bpy})_3]^{2+}$ (before the bulk electrolysis) shows light red color as shown in Fig. S2(b), whereas the electrolyte after the bulk electrolysis shows dark green color (Fig. S2(c)).

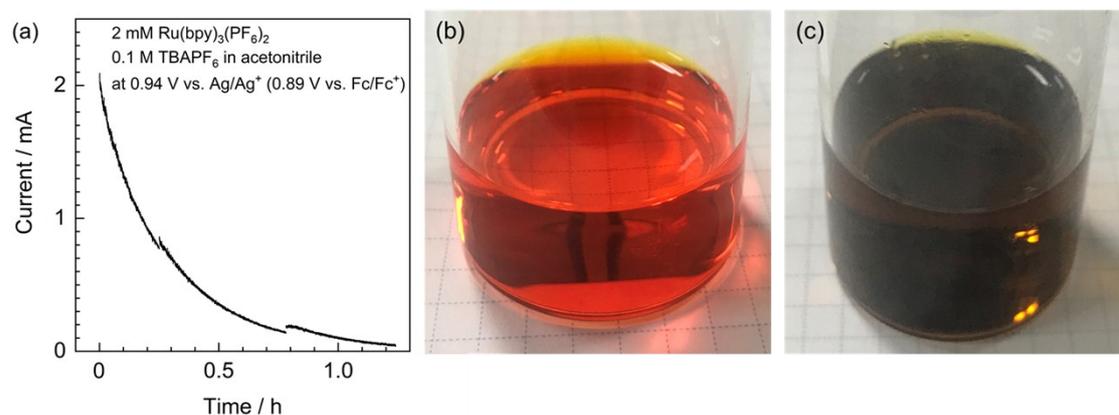


Fig. S2 (a) Time course for the bulk electrolysis oxidizing $[\text{Ru}(\text{bpy})_3]^{2+}$ into $[\text{Ru}(\text{bpy})_3]^{3+}$, and photographs of the acetonitrile electrolyte (b) before and (c) after the bulk electrolysis.

Electronic Supplementary Information

X-ray diffraction (XRD) patterns and diffuse reflectance (DR) spectra of the $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ synthesized at various temperatures are shown in Fig. S3. The specimen synthesized at 500°C showed a phase separation into the alloy and the precursor, while almost single-phase alloys were successfully synthesized at higher temperatures. The higher synthesis temperature resulted in a better crystallinity (Fig. S3(a) and S3(b)). On the other hand, the synthesis temperature hardly affected the optical properties of the obtained particles (Fig. S3(c)).

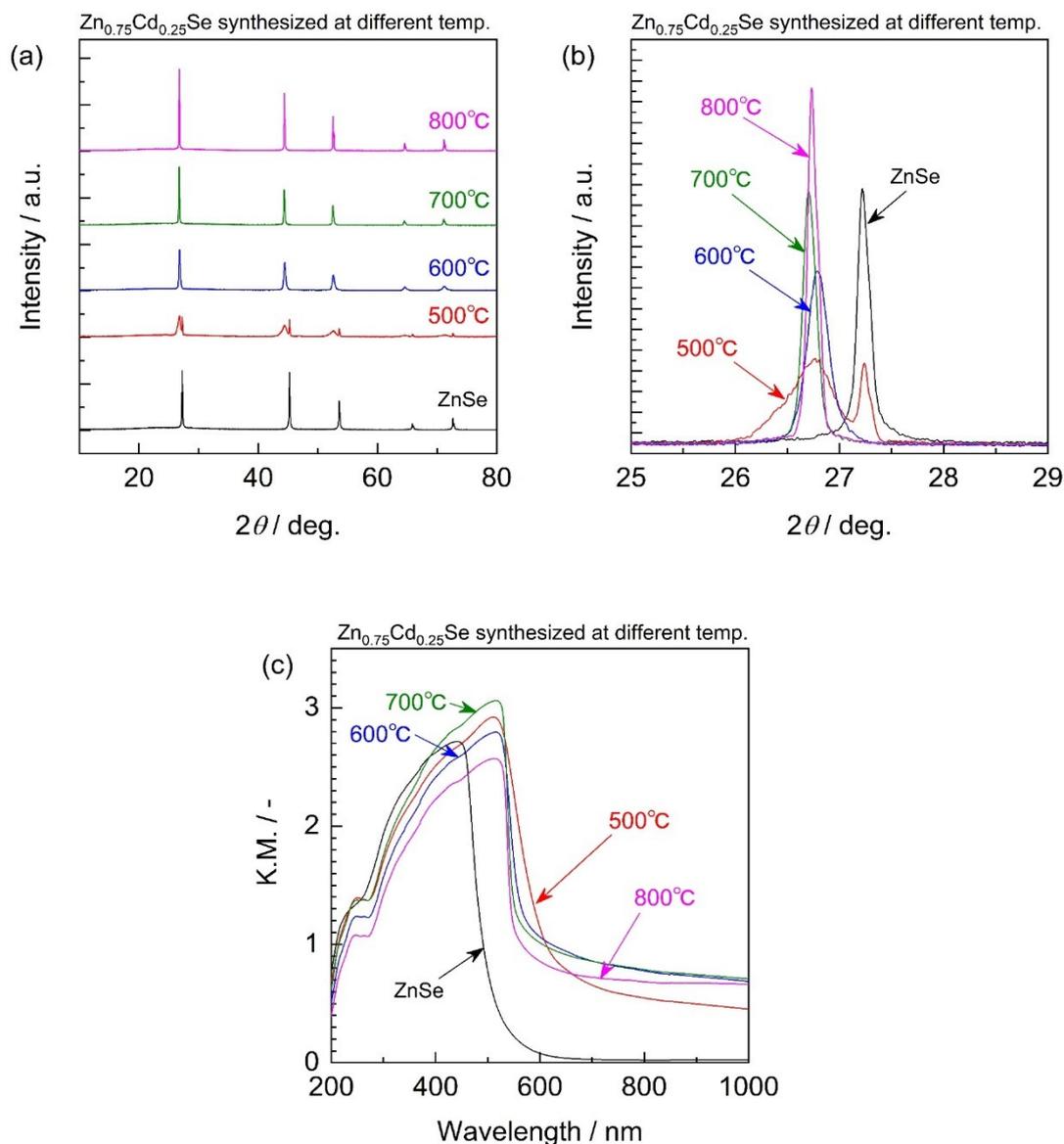


Fig. S3 (a and b) XRD patterns and (c) DR spectra for the $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ particles synthesized at various temperatures. Main peaks in (a) are enlarged in (b).

The $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ particles synthesized at various temperatures were fabricated into the shape of the photoanode by the particle transfer (PT) method.² The PEC performances of the photoanodes were acquired in an aqueous electrolyte containing a sacrificial reagent under illumination of simulated sunlight (Fig. S4). The $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ photoanode fabricated from the alloy synthesized at 600°C showed the highest photocurrent among the present alloys prepared at different temperatures. Thus, $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ particles with another Zn/Cd ratio were further evaluated with 600°C of synthesis temperature in the main manuscript.

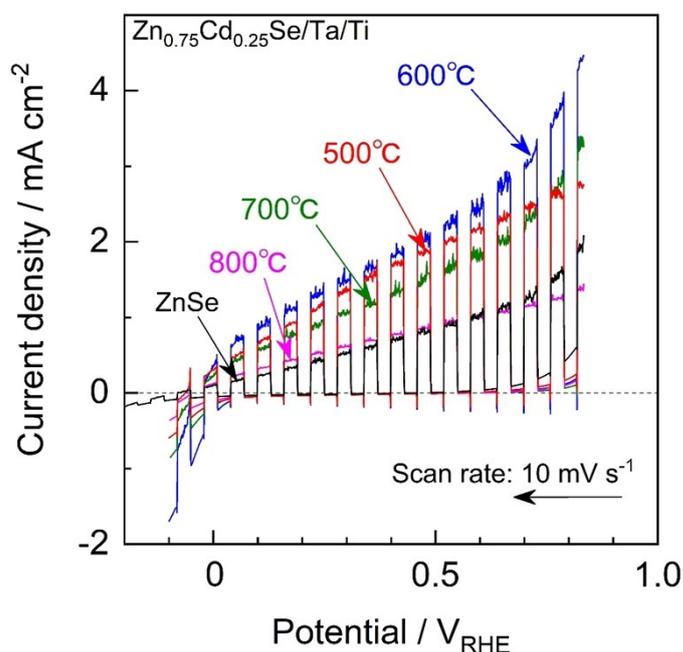


Fig. S4 Current-potential curves for $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ photoanodes in an aqueous electrolyte containing a sacrificial reagent, 1 M Na_2SO_3 . The $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{Se}$ particles were synthesized at various temperatures, and fabricated into the shape of the photoanode by the PT method with using a Ta contact layer and Ti conductor layer. Simulated sunlight (AM 1.5G) was used as the light source.

Electronic Supplementary Information

The equilibrium potential for ferrocene at Pt electrode in the acetonitrile electrolyte was estimated to be approximately 0.05 V vs. Ag/Ag⁺ from the middle point between the oxidation and reduction peaks (Fig. S5). The peak separation was 77 mV regardless of the scan rate, indicating a nearly ideal reversible one-electron reaction. The diffusion coefficient of ferrocene was approximately $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The potential in the nonaqueous electrolyte is described in the unit of V vs. the equilibrium potential for ferrocene and ferrocenium ion (V vs. Fc/Fc⁺) in the main manuscript.

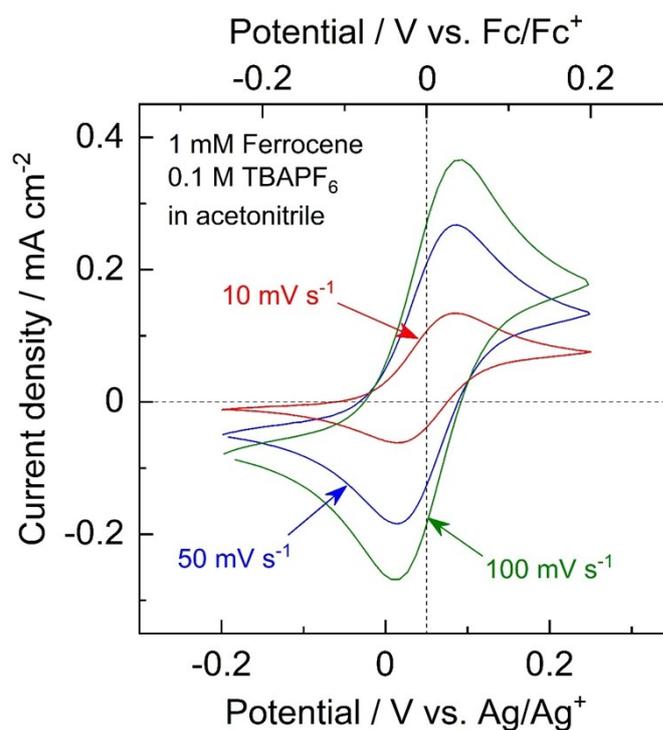


Fig. S5 Current-potential curves for a Pt electrode in an acetonitrile electrolyte containing 1 mM ferrocene and 0.1 M TBAPF₆.

Electronic Supplementary Information

The energy levels of the valence band maximum (VBM) of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ were measured by the photoelectron spectroscopy in air (PESA) as shown in Fig. S6, with using the work function of gold as a reference. The $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ particles were fixed on Ti foil by the PT method.

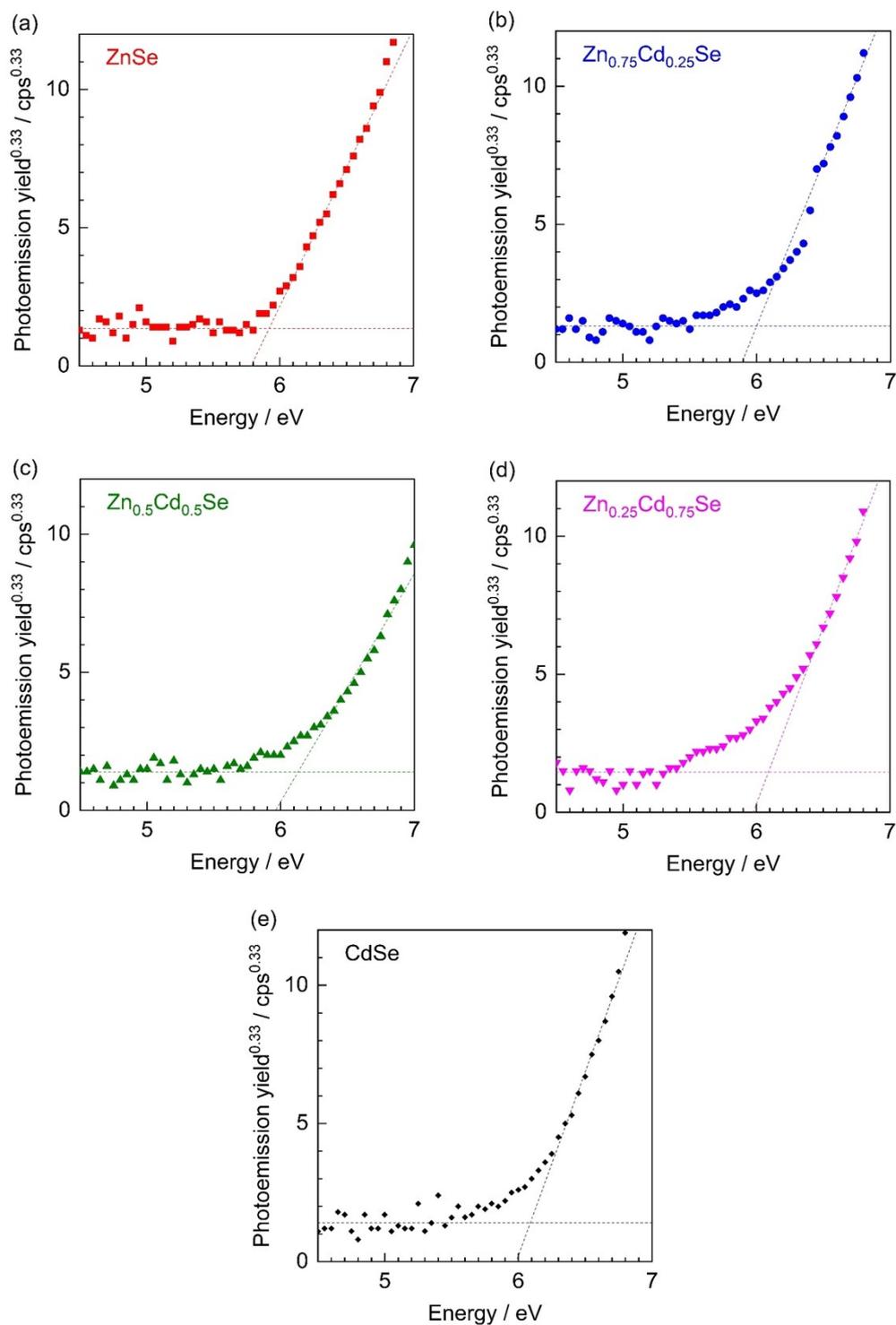


Fig. S6 PESA spectra for $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ particles.

The onset potential for the present particulate $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ photoanodes gradually shifted to negative potential according to the increased light intensity as shown in Fig. S7. The results are summarized in Fig. 3(b) in the main manuscript.

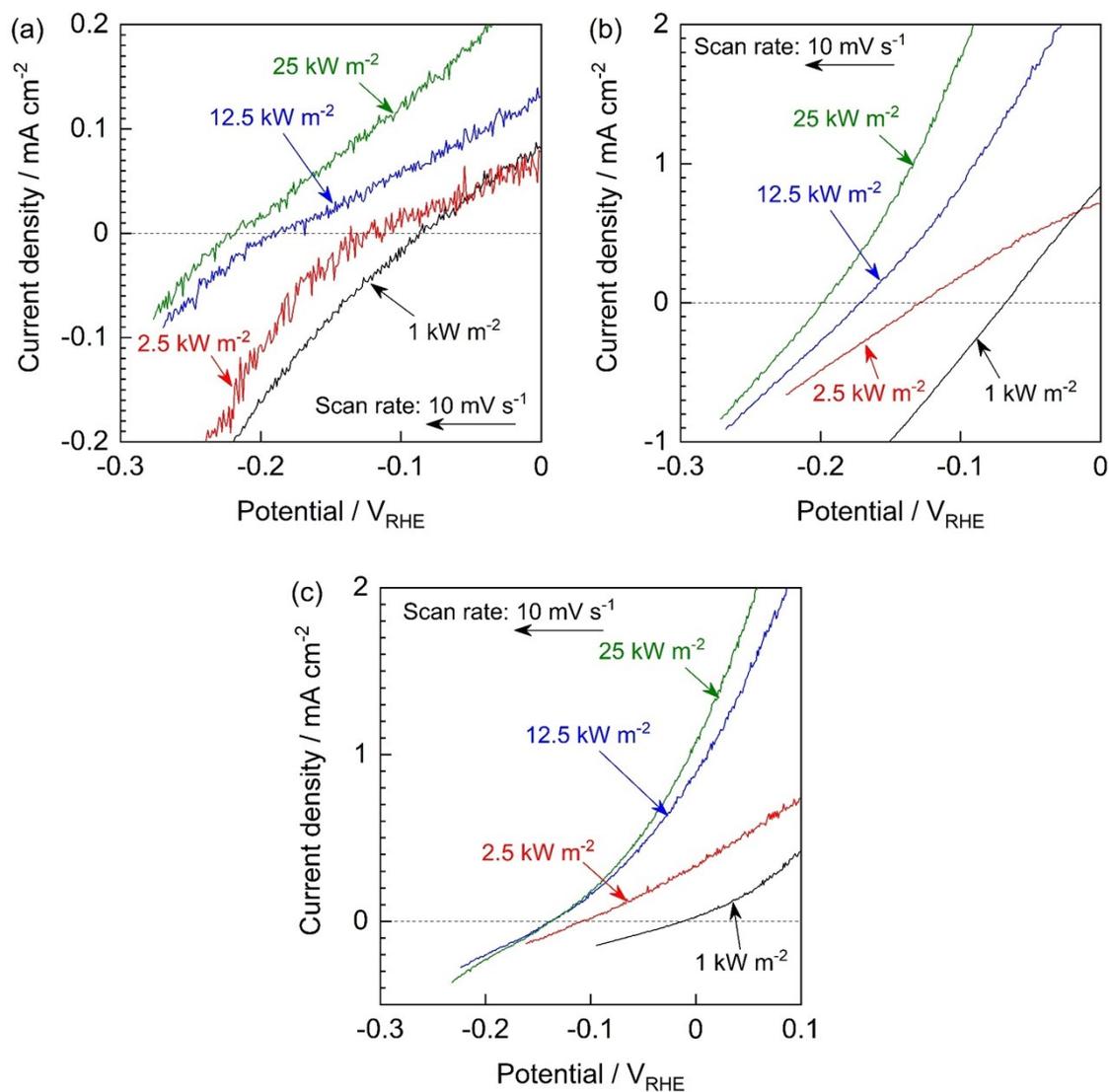


Fig. S7 Current-potential curves for (a) ZnSe, (b) Zn_{0.5}Cd_{0.5}Se, and (c) CdSe photoanodes under the continuous irradiation of various intensity of light. An aqueous solution containing a 0.5 M potassium phosphate and a sacrificial reagent, 1 M Na₂SO₃, was used as the electrolyte. The photoanodes were prepared by the PT method with using a Ta contact layer and Ti conductor layer. A 300 W Xe lamp equipped with the appropriate neutral density filters was used as the light source.

Electronic Supplementary Information

References

1. Y. Kageshima, H. Kumagai, T. Minegishi, J. Kubota, K. Domen, *Angew. Chem. Int. Ed.*, 2015, **54**, 7877.
2. T. Minegishi, N. Nishimura, J. Kubota, K. Domen, *Chem. Sci.*, 2013, **4**, 1120.