Enhanced photoelectrochemical performance from particulate (ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_{2})_{0.15} photocathodes during solar hydrogen production via particle size control

Fumiaki Takagi, a Yosuke Kageshima, *ab Katsuya Teshima, ab Kazunari Domen bc and Hiromasa Nishikiori* ab

a Department of Materials Chemistry, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan. E-mail: kage_ysk@shinshu-u.ac.jp; nishiki@shinshu-u.ac.jp
b Research Initiative for Supra-Materials (RISM), Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan.
c Office of University Professors, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

A schematic illustration of the particle classification procedure is provided in Fig. S1. In this process, the as-synthesized (ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_{2})_{0.15} (ZnSe:CIGS) particles are roughly sorted by ultrasonication in isopropanol (IPA) in conjunction with a membrane filter having a 5 μm pore size. The particles remaining above the membrane are regarded as “large” (Fig. S1a). The relatively small particles that pass through the membrane are further classified based on settling within the IPA suspension over a time span of 30 min (Fig. S1b). The particles that precipitate during this time are denoted as “middle,” whereas those that remain suspended in the IPA are referred to as “small.”

**Fig. S1** Schematic illustrations of the classification process consisting of (a) ultrasonication with a 5 μm pore size membrane filter in IPA followed by (b) precipitation from an IPA suspension.
The detailed procedure of the PT method is illustrated in Fig. S2. The ZnSe:CIGS particles dispersed in isopropanol (IPA) were drop casted on the glass substrate and dried (Fig. S2 (1)). The thin Mo and C, and subsequent thick Ti layers were deposited on the ZnSe:CIGS particles as the backside metal layers by radio frequency (RF)-magnetron sputtering (Fig. S2 (2) and (3)). The composite of ZnSe:CIGS particles and the metal layer was then peeled from the primary glass substrate by using secondary glass substrate with carbon tape (Fig. S2 (4)). The excess particles that were not contacted with backside metal layer were removed by ultrasonication.

**Fig. S2** Schematic illustrations of the PT method.
Fig. S3 shows the SEM images of the particulate ZnSe:CIGS electrodes composed of large, middle and small particles coated with different thickness of Au layer by vacuum evaporation. The backside metal layer of these particulate electrodes consisted of Ti layer (Au/ZnSe:CIGS/Ti). For the Au stripping voltammetry, the surface of the particulate electrodes were coated with appropriate thickness of Au (400 nm, 200 nm and 30 nm for large, middle and small ZnSe:CIGS particles), which represent Au400/Large/Ti, Au200/Middle/Ti and Au30/Small/Ti, respectively, as shown in Fig. S3 (a), (b) and (c). The thickness of Au layer on the ZnSe:CIGS particles with different sizes was optimized so as to cover the entire surface of each semiconductor particles with maintaining the morphology of particles. Fig. S3 (d), (e) and (f) show the ZnSe:CIGS electrodes composed of large, middle and small particles coated with overly thick Au layer, 600 nm, 500 nm and 100 nm, respectively. The excess amount of Au on the electrode surface certainly affected the morphology and evidently infilled the voids between the particles, possibly resulted in the decreased roughness of surface.

Fig. S3  Top-view SEM images of the particulate ZnSe:CIGS electrodes covered with different thickness of Au layer. (a—c) The ZnSe:CIGS electrodes consisting of (a) large, (b) middle and (c) small particles modified with appropriate thickness of Au. (d—f) The ZnSe:CIGS electrodes consisting of (d) large, (e) middle and (f) small particles coated with the overly thick Au layer.
Fig. S4  SEM images of (a) large, (b) middle and (c) small particles after classification with same magnifications.
**Fig. S5**  Average particle sizes of large, middle and small ZnSe:CuInGaSe₂ (CIGS) particles determined from several SEM images accompanied with the corresponding error bars.
The elemental ratios of Cu, Zn, In and Ga at the surface of the classified ZnSe:CIGS particles were further evaluated by XPS as shown in Fig. S6. The variation of elemental ratios with the particle sizes determined by XPS showed almost similar tendency to the results of ICP-OES (see Fig. 2 in the main manuscript), that is, the atomic ratios of Ga and Cu gradually decreased as the particle size increased, while the In ratios increased. However, the ratio of In/(In+Ga) slightly increased at the surface (determined by XPS) compared to the bulk (determined by ICP-OES), whereas the content of Zn at the surface were slightly lower than that of bulk. The decreased amount of Zn at the surface can be attributed to the volatility of Zn. Nevertheless, the hydrogen evolution should proceed at the surface of Pt cocatalysts, the ECSA of Pt (as discussed in Fig. 8 in the main manuscript) should be more critical than the minimal variation of atomic composition at the surface.

**Fig. S6** (a) Elemental ratios of Cu, Zn, In and Ga at the surface of the classified ZnSe:CIGS particles as determined by XPS spectra. (b) XPS spectra of the classified ZnSe:CIGS particles. (c)-(e) The enlarged XPS signals assigned to Cu 2p, Zn 2p, In 3d and Ga 2p in the XPS spectra obtained from the classified ZnSe:CIGS particles.
The valence band maximum (VBM) energy levels for the classified ZnSe:CIGS particles were determined using photoelectron spectroscopy in air (PESA), with the results shown in Fig. S7, using the work function of Au (5.1 eV) as a reference. During these trials, each ZnSe:CIGS sample was fixed on Ti foil in the same manner as when preparing ZnSe:CIGS/Ti electrodes via the particle transfer method, to avoid charging of the semiconductor particles.

![PESA spectra](image)

**Fig. S7** PESA spectra obtained from the (a) large, (b) middle and (c) small ZnSe:CIGS particles.
Based on the VBM levels determined using PESA (Fig. S7) and the optical band gap energy values calculated from Tauc plots (Fig. 4b in the main manuscript), the band edge potentials of the classified ZnSe:CIGS particles vs. a standard hydrogen electrode (SHE) were determined and are plotted in Fig. S8. Here, the energy level of the VBM is seen to be almost independent of particle size, while the conduction band minimum (CBM) gradually shifts to more positive potentials with increases in the particle size, possibly due to movement of the cation ratios away from the stoichiometric values. Even so, the CBM values of all specimens were located at sufficiently negative potentials (that is approximately 0.6-0.7 V more negative than the hydrogen evolution potential), indicating the possibility of using the present ZnSe:CIGS particles to drive photoelectrochemical (PEC) hydrogen evolution. In addition, the VBMs of the present ZnSe:CIGS particles were located at approximately 0.9 V vs. SHE ($V_{SHE}$), which is more positive than the values reported for the VBM of CIGS (approximately 0.8 $V_{SHE}$). The more positive VBMs of these ZnSe:CIGS specimens compared to that of pure CIGS (without ZnSe) would be expected to contribute to the relatively positive onset potential of the ZnSe:CIGS photocathode, which is in agreement with the results of previous studies.

**Fig. S8** A schematic diagram showing the band edge potentials for the classified ZnSe:CIGS particles vs. SHE.
The amount of H\textsubscript{2} gas produced by the particulate ZnSe:CIGS photocathode composed of the middle particles were further measured using micro gas chromatograph under irradiation with AM 1.5G simulate sunlight at 0 V\textsubscript{RHE} in neutral phosphate buffer solution as shown in Fig. S9. The cathodic photocurrent was observed only under light irradiation. The amount of evolved H\textsubscript{2} was consistent to the simultaneously recorded current, supporting almost 100% of Faradaic efficiency for hydrogen evolution.

**Fig. S9** (a) Current-time curves for Pt/CdS/ZnSe:CIGS/Mo/C/Ti under intermittent irradiation with AM 1.5G. The photocathode was fabricated from the middle particles. Geometric area: 0.363 cm\textsuperscript{2}. (b) Time course of the evolved H\textsubscript{2} during the PEC water reduction in (a). The dashed line indicates the expected amount of H\textsubscript{2} calculated from the simultaneously recorded current (\(\text{e}^-/2\)), whereas the plots indicate the observed amount of H\textsubscript{2} by gas chromatograph. Electrolyte: 1.0 M KPi (adjusted to pH 7).
The current-potential curve for the ZnSe:CIGS/Ti (without surface modification by the vacuum-evaporated Au) was also acquired in the same measurement conditions to the Au oxide stripping voltammetry as described in the main manuscript. As shown in Fig. S9, anodic dark current around 1.1 \( V_{\text{RHE}} \) and more positive potential can be assigned to the oxidation of ZnSe:CIGS itself and Ti backside electrode as well as Au, respectively. Since no cathodic peak can be observed without Au, the cathodic peak around 1.1 \( V_{\text{RHE}} \) in Fig. 6a in the main manuscript should be assigned to the reduction of Au oxide.

**Fig. S10** The CV data acquired from a photocathode made from the middle ZnSe:CIGS particles anchored on a Ti backside electrode without surface Au layer (ZnSe:CIGS/Ti) under dark condition. Electrolyte: 1.0 M KPi (adjusted to pH 7).
The specific surface areas of the particulate electrodes were also estimated from the cross-sectional SEM images as shown in Fig. S10. The specific surface area of the photoelectrodes consisting of the large, middle and small ZnSe:CIGS particles roughly assessed by the cross-sectional SEM images were 6.85, 5.12 and 2.86 cm$^2$ cm$^{-2}$, respectively. These were determined by the following equation.

Specific surface area = $(L_2/L_1)^2$ (cm$^2$ cm$^{-2}$)

**Fig. S11** Cross-sectional SEM images of particulate ZnSe:CIGS photocathodes consisting of (a) large, (b) middle and (c) small particles. (d) The specific surface areas of particulate ZnSe:CIGS photocathodes determined by the cross-sectional SEM images. L1 shown in the SEM images indicate the geometric length of electrodes. L2 indicate the actual length of roughness determined by tracing the surfaces of each particulate electrode.
**Fig. S12** Typical current-time curves for CdS/ZnSe:CIGS photocathodes made from the large and middle particles during photoelectrodeposition of Pt. Electrolyte: 10 µM H$_2$PtCl$_6$, 100 µM NaOH and 0.1 M Na$_2$SO$_4$ aq. Light sources: simulated sunlight (AM 1.5G).
Fig. S13  Typical EIS results obtained from ZnSe:CIGS photocathodes composed of particles having different sizes at (a, b) 0 and (c, d) 0.3 V vs. a reversible hydrogen electrode (V_RHE). (a, c) Nyquist and (b, d) Bode plots. Symbols and lines indicate the experimental data and the fittings, respectively.
Fig. S14 Current-potential curves for particulate photocathodes comprised of middle size of ZnSe:CIGS particles with or without CdS modification.