Supporting Information

Hydrogen evolution from water using Ag$_x$Cu$_{1-x}$GaSe$_2$ photocathodes under visible light

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Solar simulator used in PEC measurements

**Fig. S1** Spectra of used solar simulator in PEC experiments. The commercially-supplied solar simulator (XES-301S, San-ei Electric) was used. The spectrum of the solar simulator in the PEC cell was calibrated to AM1.5 Global (AM1.5G).
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Anodic photocurrent responses of ACGSe electrodes

**Fig. S2**  *I-E* curves of ACGSe electrodes at potential of >0.8 $V_{\text{RHE}}$. 0.1 M Na$_2$SO$_4$ aqueous solution (pH 9.5) was used as an electrolyte. An applied potential was swept for positive direction with 5 mV s$^{-1}$ under an intermittent irradiation of simulated sunlight with period of 6 s.
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Photoelectron spectroscopy in air (PESA) of ACGSe films

**Fig. S3**  PESA spectra of ACGSe films. The VBM potential gradually increases with increase of Ag substitution amount.
XPS spectra of ACGSe (Ag 5.9%) before and after PEC measurements

**Fig. S4** XPS spectra of ACGSe (Ag 5.9%) before and after Pt deposition and the PEC measurements: (a) wide scan, (b) high-resolution narrow scan of Ag 3d.
Characterization of optical band gap energies of the ACGSe films

Band gap energies of the ACGSe films were determined by Tauc method. The absorption coefficient ($\alpha$) around an absorption edge can be expressed as a function of photon energy ($h\nu$) as follow:

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^{1/n}$$  \hspace{1cm} (S1)

Here, $n = 2$ for direct transition semiconductors, $A$, $h$, $\nu$ and $E_g$, are the absorption constant, Planck constant, frequency and band gap energy, respectively. $\alpha$ can be determined from transmittance ($T$) and reflectance ($R$) spectra according to Lambert’s law which can be written as:

$$\alpha = \frac{1}{d} \ln \left( \frac{1 - R}{T} \right)^2$$  \hspace{1cm} (S2)

where $d$ is the film thickness. As an example, the transmittance and reflectance spectra of ACGSe with Ag/(Cu+Ag) = 5.9% deposited on FTO substrate are shown in Fig. S3 and its Tauc plot is shown in Fig. S4. By extrapolating the linear part of curve to energy axis, the $E_g$ of ACGSe (Ag 5.9%) was found to be 1.65 eV.
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Fig. S5  UV-vis transmittance ($T$) and reflectance ($R$) spectra of the ACGSe with Ag/(Cu+Ag) = 5.9% deposited on FTO substrate.

Fig. S6  Tauc plot of the ACGSe with Ag/(Cu+Ag) = 5.9% deposited on FTO substrate.

Structural characterization of ACGSe films by XRD

**Fig. S7** XRD patterns of ACGSe films. A reference pattern of CGSe (PDF No. 31–456) is shown as CGSe-ref.
Table S1  FWHM of (112) XRD peak for ACGSe films

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGSe</td>
<td>0.156</td>
</tr>
<tr>
<td>ACGSe (Ag 2.4%)</td>
<td>0.143</td>
</tr>
<tr>
<td>ACGSe (Ag 5.9%)</td>
<td>0.117</td>
</tr>
<tr>
<td>ACGSe (Ag 10.0%)</td>
<td>0.106</td>
</tr>
<tr>
<td>ACGSe (Ag 19.4%)</td>
<td>0.097</td>
</tr>
<tr>
<td>ACGSe (Ag 78.3%)</td>
<td>0.128</td>
</tr>
<tr>
<td>AGSe</td>
<td>0.113</td>
</tr>
</tbody>
</table>

The FWHM of (112) diffraction peak decreased with increasing amount of Ag except for Ag ≥78.3%. The increase of FWHM is due to the difference of preferable deposition temperature. The substrate temperature of 550°C during the film deposition is too high to prepare AGSe-based films with high qualities.
SEM images of AGSe film

**Fig. S8** Top and cross-sectional SEM images of AGSe film.
Applied bias potential efficiencies (ABPEs) of Pt/CdS/ACGSe

**Fig. S9** ABPEs of Pt/CdS/ACGSe (Ag 5.9%), two-step deposited Pt/CdS/ACGSe and Pt/CdS/CGSe prepared under optimized conditions. Electrolyte, and light source were 0.1 M Na$_2$SO$_4$ (pH = 9.5), and solar simulator, respectively.
Results of gas product analysis

**Fig. S10**  Current-time curve of Pt/CdS/ACGSe (Ag 5.9%) electrode (a), and amount of evolved H₂ during the measurement (b). 2-electrode system was employed in the measurement using Pt mesh as a counter electrode. 0.1 M Na₂SO₄ aqueous solution (pH = 9.5), and 300 W Xe lamp equipped with filters were used as an electrolyte, and light source, respectively. Amount of evolved H₂ from Pt/CdS/ACGSe (Ag 5.9%) was examined by μGC. The faradaic efficiency was found to be ca. 85%.
SEM images and XPS spectra of CdS/ACGSe (Ag 5.9%) before and after Pt deposition and stability test

**Fig. S11** SEM images of CdS/ACGSe (Ag 5.9%) electrode before (a) and after Pt deposition and stability test (b). The sample after stability test showed branched structure on its surface, indicating partial and preferential dissolution of CdS during the durability test.

**Fig. S12** XPS spectra of CdS/ACGSe (Ag 5.9%) before and after Pt deposition and durability test. Signals of Cd and S were found, while signals from Ag, Cu, Ga and Se were not detected, indicating that after stability test, the electrode surface was still fully covered by CdS.
Stability of Pt/CdS/ACGSe (Ag 5.9%) electrode without annealing

**Fig. S13** Time course of the photocurrent for Pt/CdS/ACGSe (Ag 5.9%) electrode without annealing, tested at 0 V\textsubscript{RHE} under simulated sunlight. The electrolyte used was a 0.1 M Na\textsubscript{2}HPO\textsubscript{4} solution (pH = 10 by NaOH addition).