

Supporting Information

Promising GeSe nanosheet based thin film photocathode for efficient and stable overall solar water splitting

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Experimental detail:

Preparations of GeSe Films.

GeSe films were prepared via rapid thermal sublimation deposition method. GeSe powder (99.999%) and Mo substrate were putted inside of a graphic box, then the graphite box was loaded on top of AlN plate inside of a tube furnace (MTI cooperation, China). Molecular pump was assembled with this tube furnace to keep the deposition pressure at 3×10^{-2} pa.

The deposition process was first preheated the source and substrate at 350°C for 5 minutes, then quickly increased the source temperature up to 480-530°C within 10 seconds and then maintained this temperature for 90 seconds, after that we turned off the heating and allowed the film to cool down naturally.

Surface Modification with CdS Buffer Layer.

CdS layer was deposited by the chemical bath deposition method (CBD) under GeSe film in an

aqueous solution containing 12.5 mM CdSO₄, 0.22 mM SC(NH₂)₂, and 11 M NH₄OH at 60 °C for 13 min.

Surface Modification with TiO₂ Layer.

Surface modification of the yielded CdS-covered GeSe by TiO₂ layer was performed by LabNano 9100 atomic layer deposition (ALD) system. Titanium tetrakis(dimethylamide) and H₂O were used as titanium and oxygen source, respectively. Based on our empirical value (The deposition rate of the ALD of TiO₂ film was estimated by Spectroscopic ellipsometer measurement), the growth rate was estimated to be about 0.054 nm per cycle and the films were grown for 80nm at 120°C.

Surface Modification with Pt Catalyst.

Pt particles was deposited on the prepared TiO₂/CdS/GeSe films by Photoelectrodeposition. The deposition was performed by using a three-electrode system consisting of the TiO₂/CdS/GeSe sample as a working electrode, a Pt electrode as a counter electrode, and Ag/AgCl as a reference electrode. These electrodes were immersed in 0.1 M Na₂SO₄ solution containing 1 mM H₂PtCl₆, and the deposition was performed with a constant potential of -0.1 V for 30s. During the deposition, the TiO₂/CdS/GeSe working electrode was illuminated under simulated sunlight AM 1.5G from a 300W Xenon lamp solar simulator.

PEC Measurements.

An online gas chromatography system (Shimadazu GC-2014 gas analyzer equipped with a MS-5A column and a thermal conductivity detector) was used to detect H₂ and O₂ during the PEC water splitting. All the PEC measurements were operated in phosphate buffer solution (0.2 M Na₂HPO₄/NaH₂PO₄, pH 6.5) by using the above-mentioned solar simulator as a light source. The PEC cell was covered by a water jacket to maintain the temperature at 293 K. The same three electrode setup as that used for the Pt deposition (see above) was used for PEC measurements of the Pt-TiO₂/CdS/GeSe photocathode. Potentials referred to the Ag/AgCl electrode were converted to reversible hydrogen electrode (RHE) using the Nernst equation as follows equation S1:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.199 \quad \text{equation S1}$$

S1

HC-STH was determined from the current density-potential response of the photocathodes by using the following equation S2:

$$\text{HC-STH (\%)} = J \times (V - V_{\text{H}^+/\text{H}_2}) \times 100/P \quad \text{equation S2}$$

S2

Where J is the photocurrent density (mA cm^{-2}), V is the applied potential (V_{RHE}), and P is the intensity of simulated sunlight (100 mWcm^{-2}).

We always used the substrates with the size of $1\text{cm} \times 2\text{cm}$ for the deposition of GeSe. The illumination area was fixed by the mask in front of the samples. The light intensity at the position of our samples was measured and calibrated by a light intensity detector (Thorlabs PM100D with S401C detector).

Mott-Schottky analysis of GeSe, CdS/GeSe and $\text{TiO}_2/\text{CdS}/\text{GeSe}$ samples

The Mott-Schottky measurement (Solartron Modulab XM) and analysis were used to estimate the flat band potential (E_{FB}) and acceptor density (N_A) of the p-type GeSe, the flat band potential (E_{FB}) of n-type CdS above GeSe and n-type TiO_2 onto CdS/GeSe. The relation connecting the measured capacitance (C) and the applied potential V_{RHE} (against the reversible hydrogen electrode) at the electrode-electrolyte interface is given by the Mott-Schottky equation S3,

$$\frac{1}{C^2} = -\frac{2}{q\epsilon\epsilon_0N_A} \left(V_{\text{RHE}} - E_{\text{FB}} - \frac{kT}{q} \right) \quad \text{equation S3}$$

where the ϵ is the relative dielectric constant ($\epsilon = 15.3$, GeSe)^[1], while the q , ϵ_0 , k and T are the electron charge ($1.602 \times 10^{-19} \text{ C}$), vacuum permittivity ($8.85 \times 10^{-12} \text{ F m}^{-1}$), Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and absolute temperature, respectively. The kT/q value is negligible due to its small value (*i.e.*, *ca.* 25 mV at room temperature).

The C as a function V_{RHE} was calculated from the Mott-Schottky measurements based on the imaginary part of the impedance (Z_{im}) using equation S4,

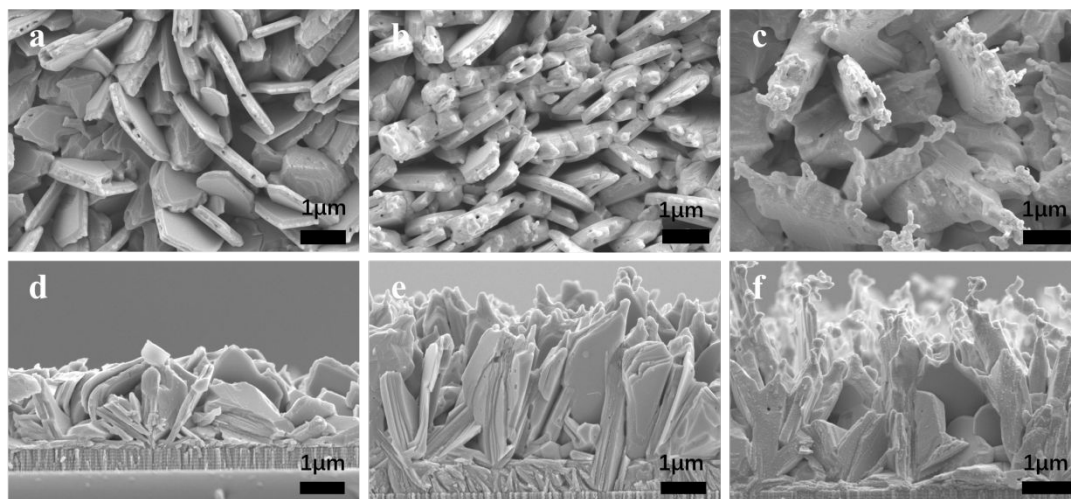
$$C = -\frac{i}{2\pi f Z_{im}} \quad \text{equation S4}$$

where the i , f is the imaginary unit and applied frequency (1000Hz), respectively. By plotting $1/C_2$ as a function of V_{RHE} , the E_{FB} can be estimated from the intercept *via* extrapolating the linear part of the curve to the potential axis, while the N_A can also be calculated from the corresponding slope of the linear part using equation S5,

$$N_A = \frac{2}{q\epsilon\epsilon_0} \left(\frac{d\left(\frac{1}{C^2}\right)}{dV_{RHE}} \right)^{-1} \quad \text{equation S5}$$

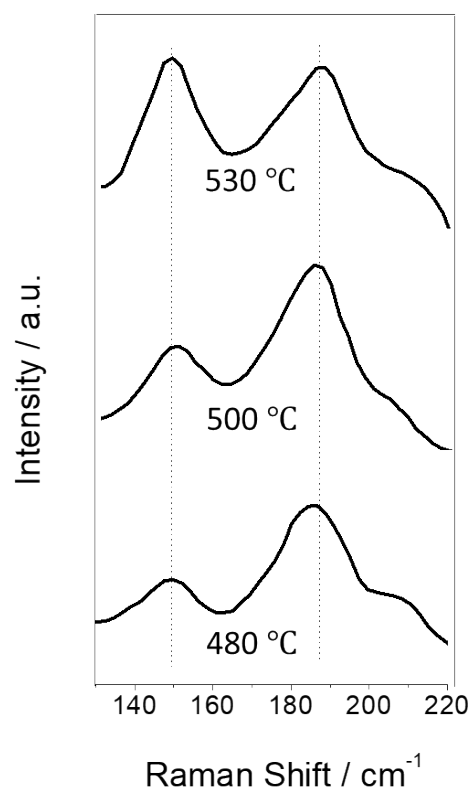
Structural Characterization.

Crystalline structures of the films were determined by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE X-ray diffractometer with Cu K α radiation ($\lambda=1.54056\text{\AA}$). Raman spectroscopy using a Rigaku Mini Flex X-ray diffractometer and a Jasco NRC 3100 laser Raman spectrophotometer respectively. Surface and cross section morphology was observed by scanning electron microscope (SEM) using Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images, High Resolution TEM (HRTEM) images, and selected area electron diffraction (SAED) patterns were recorded on a JEM-2100HR microscope operating at 200 kV. Samples were prepared by dropping a diluted nanosheet solution onto copper grids. The optical transmittance of GeSe film was recorded by UV-vis-near IR spectrophotometer (UH4150, HITACHI). Surface and bulk chemical structures of the samples were examined by X-ray photoelectron spectroscopy (XPS) using a Shimadzu AXIS ULTRA X-ray photo-electron spectrometer.



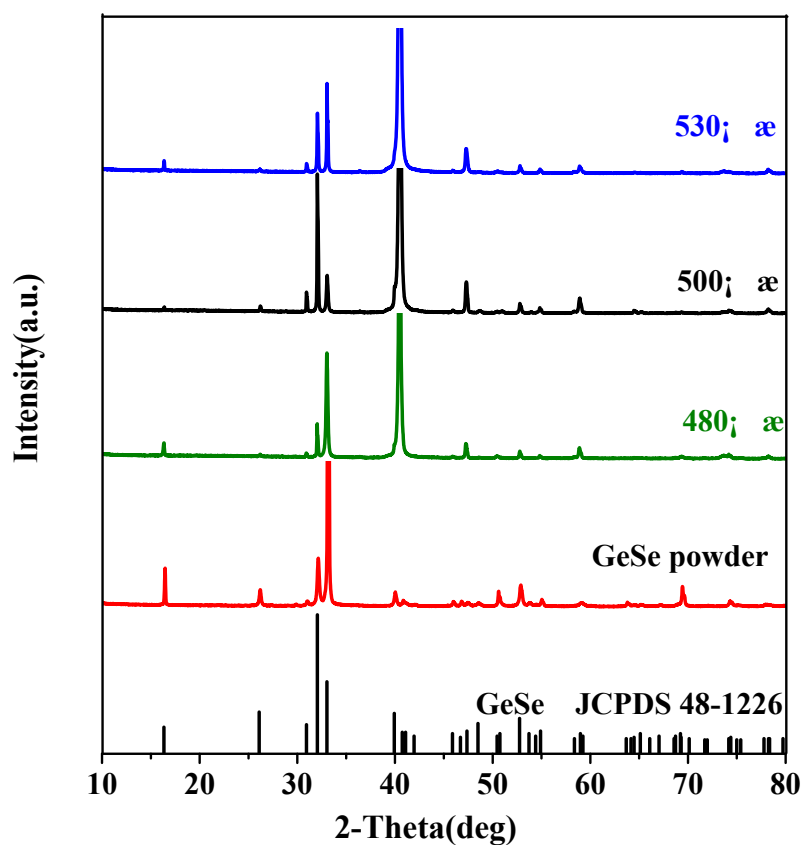
FigureS1: Surface and cross-sectional morphology of the GeSe film prepared under 480°C (a, d), 500 °C (b, e) and 530°C (c, f), respectively.

The structure of GeSe films prepared under 480 °C and 500°C are almost the same: sheet liked grains were well grown under the substrate. However, the size of the sheet GeSe grains prepared under 500°C are larger than that was prepared under 480°C (Figure S1a, b), while the thickness of the GeSe film prepared under 500°C was observed to be obviously higher than that was prepared under 480 °C (Figure S1d, e). When we further increased the preparation temperature to 530°C, the obtained GeSe film was observed to has a surface re-evaporation liked structure failure (Figure S1c, f). Thus, from the microstructure viewpoint, the GeSe film prepared under 500°C is suitable to fabricate photoelectrochemical devices.



FigureS2: Raman spectrum of the GeSe film prepared under 480°C, 500°C and 530°C.

There is no difference in the locations of Raman peaks of the GeSe films prepared under 480°C, 500°C and 530°C. The observed Raman peaks at 150cm⁻¹ and 188cm⁻¹ were well matched to the reported typical data from GeSe.^[1,2]



FigureS3: XRD patterns of the GeSe films prepared under 480°C, 500°C and 530°C.

There has no obvious difference in XRD results between the GeSe film prepared under 480°C, 500°C and 530°C, all the observed peaks are well matched to the standard data from GeSe (PDF card No. JCPDS48-1226), indicating the GeSe films we prepared in this work were grown well with no obvious impurity phases.

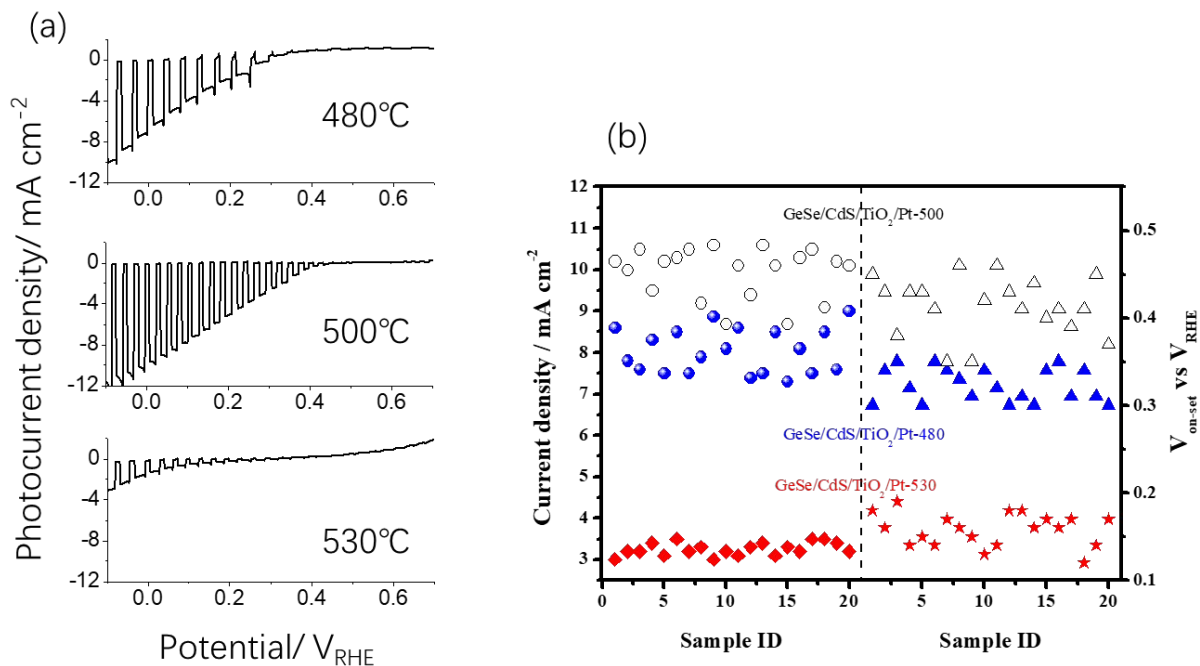
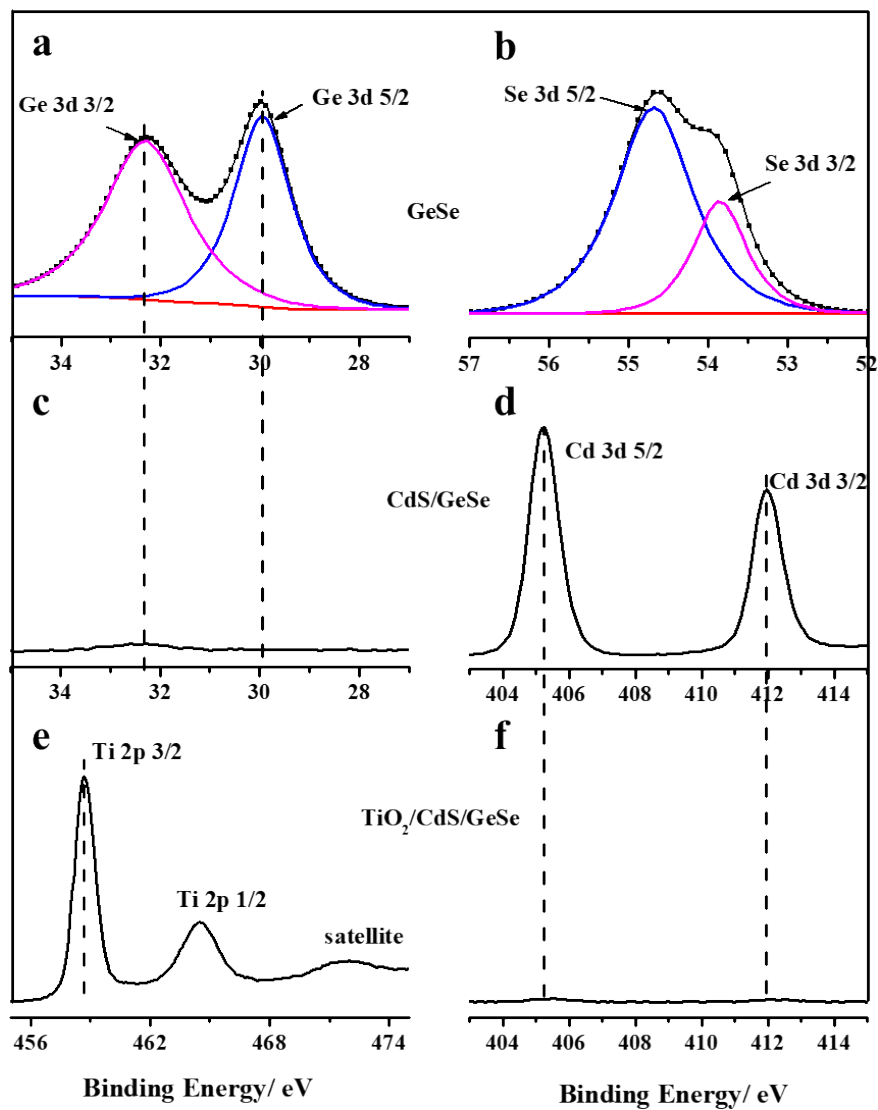


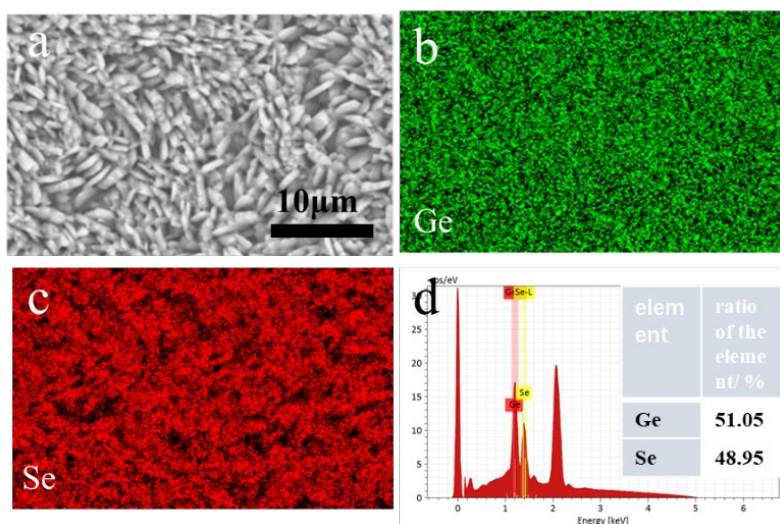
Figure S4: (a) typical LSV performances of Pt-TiO₂/CdS/GeSe photocathode based on the GeSe film prepared under 480°C, 500°C and 530°C under chopped AM 1.5G sunlight irradiation; (b) statistic results of onset potential (V_{oc}) and photocurrent density at 0V_{RHE} of the GeSe based photocathode with different preparation temperatures of 480°C, 500°C and 530°C.

Figure S4a shows the typical LSV curves of the Pt-TiO₂/CdS/GeSe photocathode based on the GeSe film prepared under 480°C, 500°C and 530°C under chopped AM 1.5G sunlight irradiation. It was found that the 500°C prepared GeSe based Pt-TiO₂/CdS/GeSe photocathode showed significant better PEC performance than that of the cathode based on the GeSe films prepared under 480°C and 530°C, while 530°C prepared GeSe based photocathode presented the lowest PEC properties. Figure S4b shows the statistic results of onset potential (V_{oc}) and photocurrent density at 0V_{RHE} of the GeSe based photocathode with different preparation temperatures of 480°C, 500°C and 530°C. The trend as a function of the preparation temperatures is very clear: the Pt-TiO₂/CdS/GeSe photocathodes based on the 500°C prepared GeSe photoabsorbers has higher onset potentials and photocurrent densities (at 0V_{RHE}) than that of the photocathode based on 480°C prepared GeSe

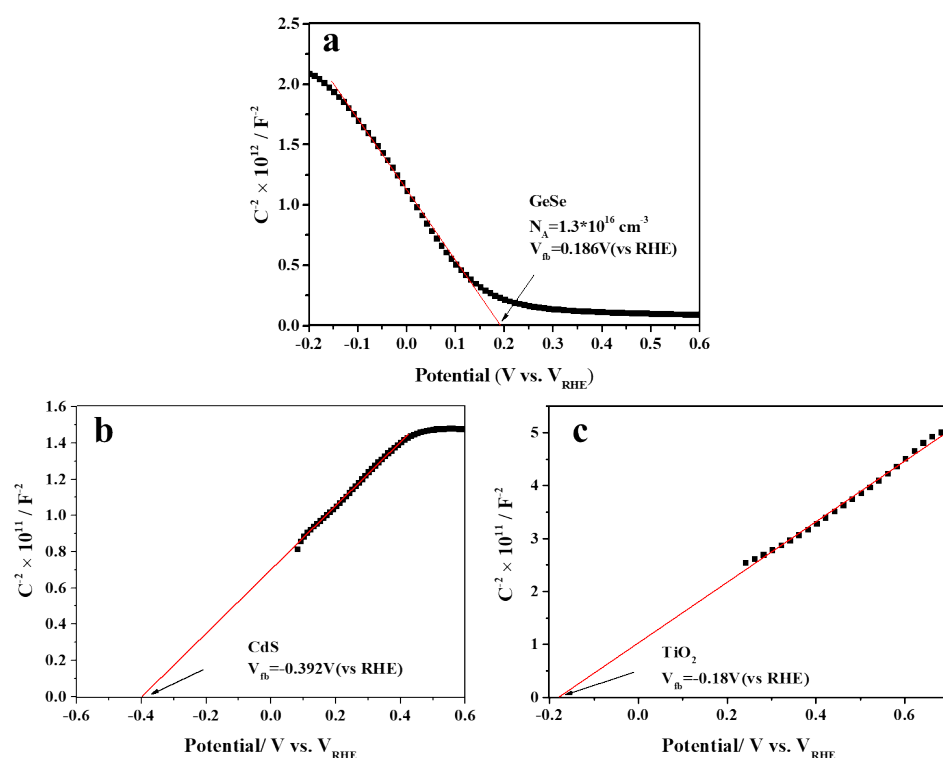
photoabsorbers, while the Pt-TiO₂/CdS/GeSe photocathodes based on the 530°C prepared GeSe photoabsorbers showed the lowest onset potentials and photocurrent densities.



FigureS5: XPS detection results of the GeSe film (a, b), CdS/GeSe (c, d) and TiO₂/CdS/GeSe (e, f), respectively.

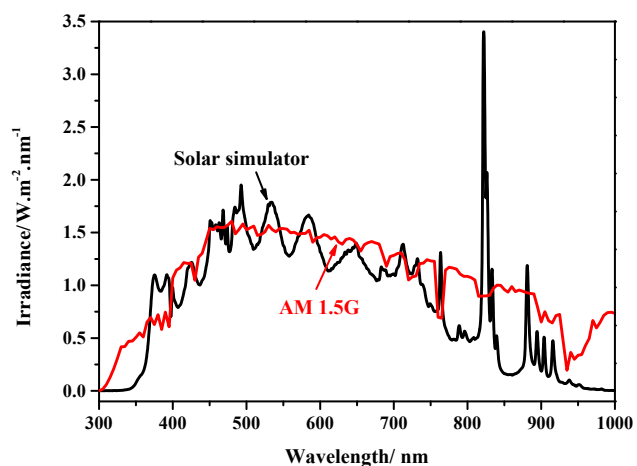


FigureS6: (a) Surface morphology of GeSe film, (b, c) elemental mapping of Ge and Se, (d) elemental ratios of Ge and Se detected from EDS.



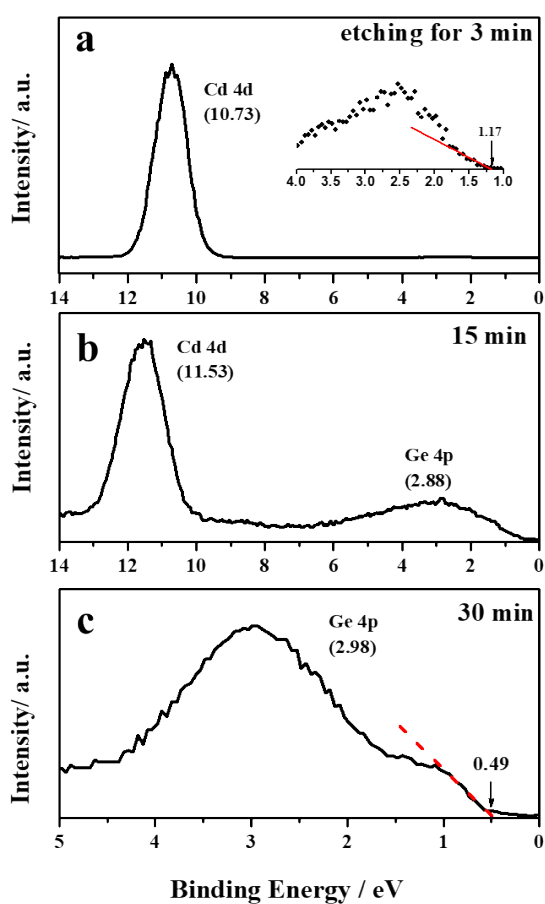
FigureS7: Mott-schottky curves of GeSe (a), CdS/GeSe (b) and TiO₂/CdS/GeSe (c), respectively. 0.2 mol dm⁻³ Na₂HPO₄/NaH₂PO₄ (pH 6.5) was used as an electrolyte.

We used the flat area of our samples because it is difficult to calculate the area of the rough surface, therefore the calculated doping density may be slightly more higher than that was calculated based on the rough surface area.

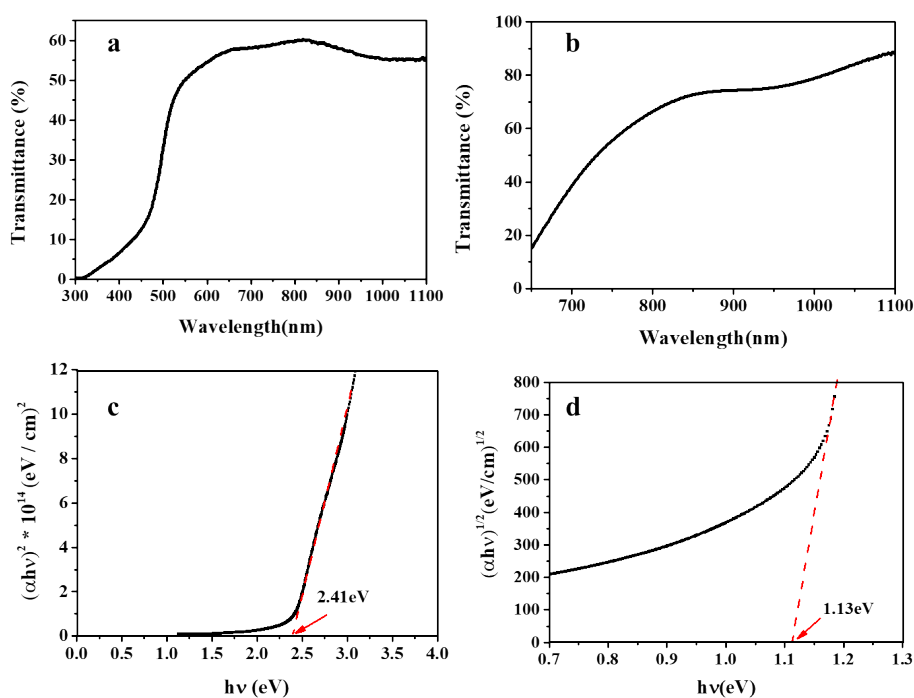


FigureS8: Comparison of the used solar simulator with the standard AM 1.5G solar spectra data.

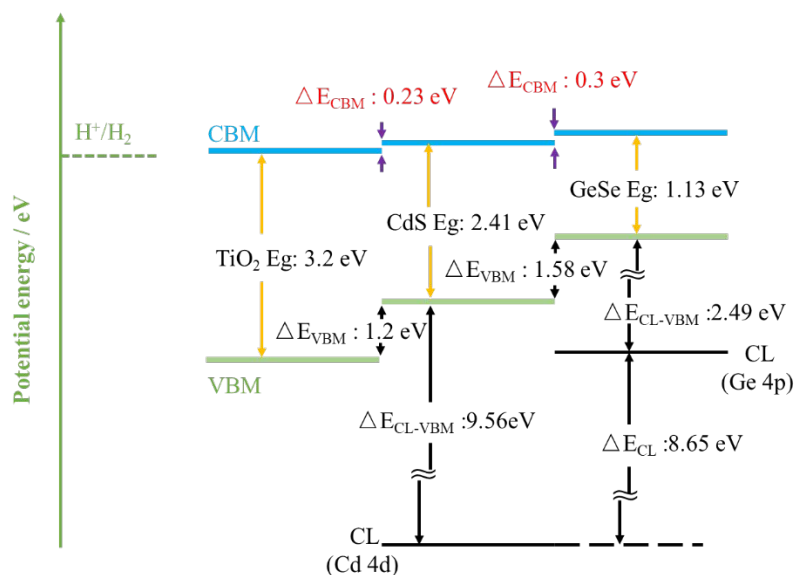
The spectral properties of solar simulator and AM 1.5G matches relatively well.



FigureS9: XP spectra of CdS/GeSe in valence and shallow regions obtained after Ar⁺ ion etching for 3, 15, and 30 min.

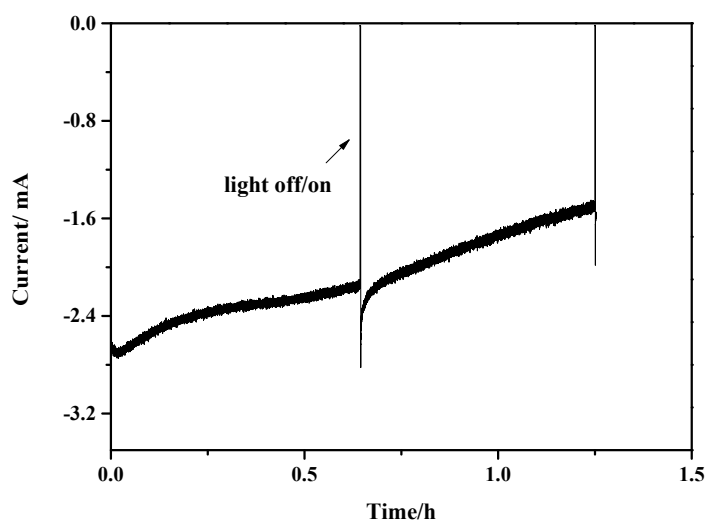


FigureS10: Transmittance of CdS/glass (a) and GeSe/glass (b), Tauc curves of CdS/glass (c) and GeSe/glass (d) for the calculation of their band gap (Tauc plot ($n = 1/2$, indirect) for GeSe film.)



FigureS11: Energy diagram of TiO₂/CdS/GeSe photocathode

The band positions between CdS/GeSe was estimated from XP spectroscopy and optical data from FigureS10. And the band alignment between TiO₂ and CdS was constructed by reference to the previous reported band positions of TiO₂ and CdS.^[3]



FigS12: Photocurrent Vs. time of Pt-CdS/GeSe detected under $0V_{\text{RHE}}$ as a function of illumination time, the active area is about 0.69cm^2 .

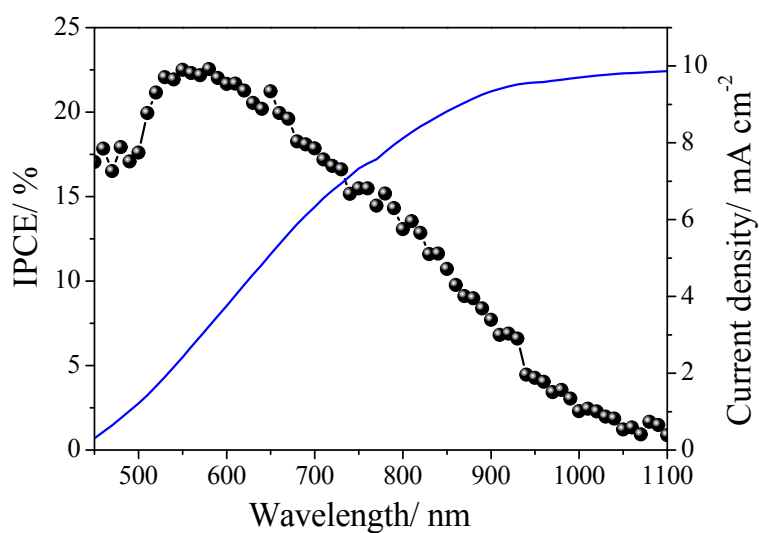


Figure S13. The incident photon conversion efficiency (IPCE) of Pt-TiO₂/CdS/GeSe photocathode at an applied potential of 0 V versus RHE under AM1.5G solar light soaking (filled circles). The blue curve is the integrated photocurrent density (reaches 9.88 mA/cm^2), which is consistent with the photocurrent density that was shown in Figure 3c.

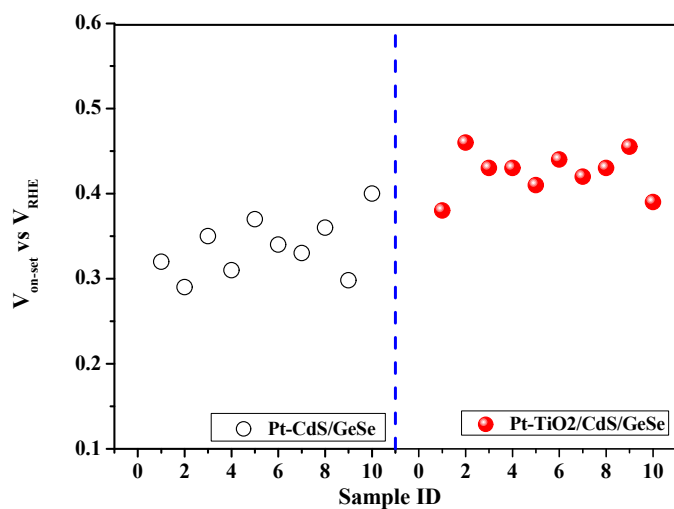


Figure S14: Comparison of the onset potentials of Pt-CdS/GeSe samples with Pt-TiO₂/CdS/GeSe samples detected under AM1.5G solar light soaking.

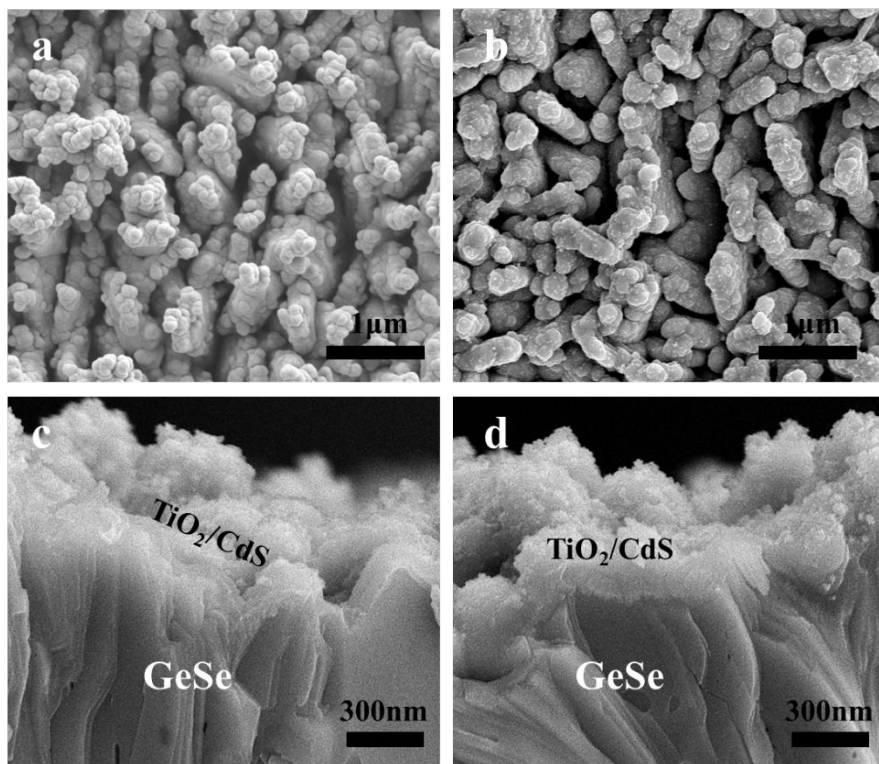
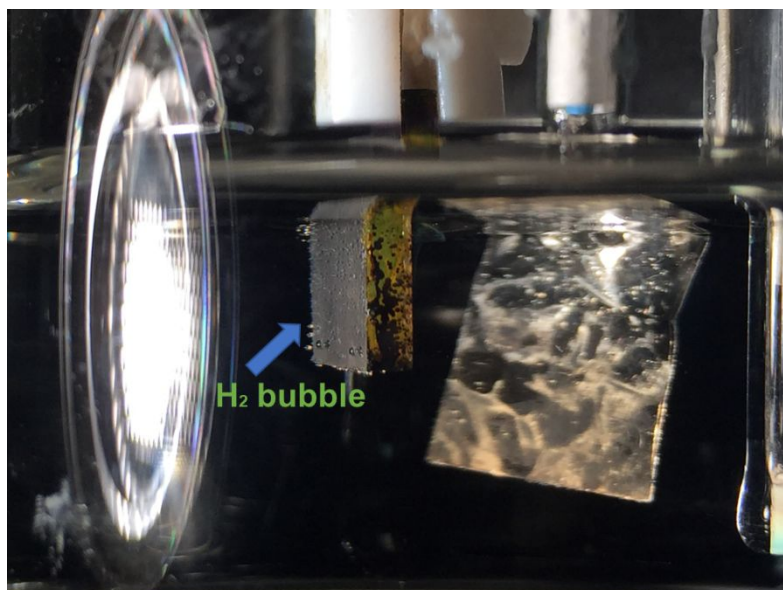
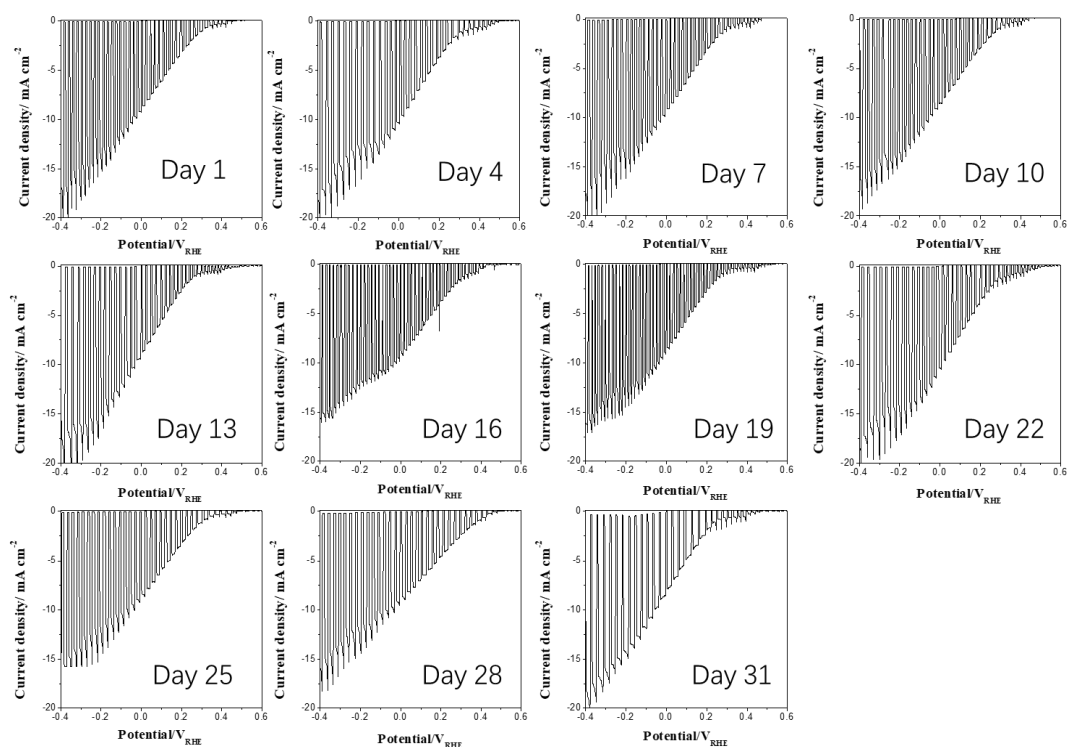


Figure S15: Surface and cross-sectional morphology of the TiO₂/CdS/GeSe photocathode before (a, c) and after (b, d) the 8 hours durability test.



FigureS16: typical photograph of the $\text{TiO}_2/\text{CdS}/\text{GeSe}$ photocathode under working.



FigureS17: Current–potential curves of $\text{Pt}/\text{TiO}_2/\text{CdS}/\text{GeSe}$ electrodes under chopped illumination by AM 1.5G simulated sunlight as detected during one month region.

The $\text{Pt}/\text{TiO}_2/\text{CdS}/\text{GeSe}$ sample was kept out of the electrolyte solution and let it sit in the air, and then measure it once a day to see if it has degraded.

Table S1: The comparison of record photovoltaic performances of the solar cell based on the related compound semiconductors

photoabsorbers	Eg	substrate	photocathodes	Test condition	Jsc (mA cm ⁻²)	Voc (V)	FF (%)	PEC(%)	Reference
GeSe	1.14	SLG/ITO	ITO/CdS/GeSe/Au	AM 1.5G	-14.48	0.24	42.6	1.48	Xue, 2017 ref. 5
CuSbS ₂	1.4	SLG/Mo	Mo/CuSbS ₂ /CdS/ZnO/Al	AM 1.5G	15.64	0.47	43.56	3.22	Baun, 2016 ref. 6
Cu ₂ BaSnSSe ₃	1.55	SLG/Mo	Mo/CBTS/CdS/CdS/i-ZnO/ITO	AM 1.5G	17.4	0.611	48.89	5.2	Shin, 2017 ref. 7
Sb ₂ Se ₃	1.17	SLG/ITO	ITO/CdS/Sb ₂ Se ₃ /Au	AM 1.5G	-29.9	0.42	60.4	7.6	Wen, 2018 ref. 8
Cu ₂ ZnSnS ₄	1.45	SLG/Mo	Mo/CZTS/CdS/ZnO/ITO/MgF ₂	AM 1.5G	21.744	0.7306	69.27	11.01	Yan, 2018 ref. 9
CuInS ₂	1.62	SLG/Mo	Mo/CIS/CdS/ZnO/Ni-Al/MgF ₂	AM 1.5G	21.83	0.729	71.7	11.4	Siemer, 2001 ref. 10

Reference:

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