

Supporting Information

N-type Ag₂S modified CZTSSe solar cell with lowest $V_{oc,def}$

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Experimental section

Materials: Copper(I) chloride (CuCl, 99.95%), zinc acetate (Zn(CH₃COO)₂·2H₂O, 99.99%), tin(IV) chloride pentahydrate (SnCl₄·5H₂O, 99.995%), silver chloride (AgCl, 99.5%), and cadmium sulfate octahydrate (CdSO₄·8/3H₂O, 99%) powders were procured from Aladdin Reagent (Shanghai) Co., Ltd. Thiourea (SC(NH₂)₂, 99%) powder was sourced from Alpha Aesar (China) Chemicals Co., Ltd. 2-Methoxyethanol was acquired from Shanghai McLean Biochemical Technology Co., Ltd. Selenium

granules (99.999%) were obtained from Zhongnuo Advanced Materials Technology Co., Ltd. Ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%) was provided by Luoyang Haohua Chemical Reagent Co., Ltd. All chemical reagents and pharmaceuticals were used directly without further purification.

Preparation of CZTSSe absorber layer films: Preparation of CZTSSe precursor solution: First, 3.000 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 2.550 mmol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 19.950 mmol of $\text{SC}(\text{NH}_2)_2$, 4.032 mmol of CuCl , and 0.08 mmol of NaCl were placed into a clean 20 mL sample bottle. Next, 10.0 mL of 2-Methoxyethanol solvent was added to the bottle using a pipetting gun. The mixture was stirred at 60°C and 1000 r/min for 1 hour until completely dissolved, forming a light yellow solution. The resulting solution had $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn ratios of 0.73 and 1.20, respectively.

Preparation of CZTSSe absorber layer films: First, a Ta-doped MoSe_2 thin film was prepared on a Mo surface, following the specific preparation process described in our previous work.¹ The CZTSSe solution was centrifuged for 10 minutes to remove any impurities. The purified CZTSSe precursor solution was then coated onto a Mo substrate using a needle tube in an air atmosphere and spin-coated at 3000 rpm for 28 seconds. The coated substrate was heated at 280°C for 2 minutes on a hot plate to remove the organic solvent. The spin-coating and annealing steps were repeated 12 times to obtain a CZTS precursor film with a thickness of 1.8 to 2.0 μm . The CZTSSe precursor film was then placed into a square graphite box containing 0.8 g of selenium particles. The graphite box was inserted into a rapid thermal processor (RTP) furnace under a nitrogen atmosphere for high-temperature selenization treatment at 550°C for 15 minutes, resulting in a dense and large grain size CZTSSe absorber layer film.

In situ deposition of n-type Ag_2S on the surface of CZTSSe absorber layer: First, 4 mmol $\text{SC}(\text{NH}_2)_2$ and 1 mmol AgCl were successively added into a sample bottle containing 5 mL of 2-Methoxyethanol solvent. The mixture was stirred at 60°C and 1000 r/min for 30 minutes until completely dissolved, resulting in a clear, transparent, and colorless Ag_2S solution. A solution-based deposition followed by annealing was employed to in-situ prepare a thin layer of n-type Ag_2S on the surface of the CZTSSe absorber layer. The surface of the selenized CZTSSe film was coated with the Ag_2S precursor solution

using a syringe needle in an inert atmosphere glovebox. The coated film was then spin-coated at 3000 r/min for 28 seconds and treated at 260°C for 2 minutes on a hot plate to remove the organic solvent.

Fabrication of CZTSSe thin-film solar cell: The device structure of the CZTSSe solar cells prepared in this study consists of soda-lime glass (SLG)/Mo/CZTSSe/CdS/i-ZnO/ITO/Ag/MgF₂. A CdS buffer layer, approximately 50 nm thick, was deposited on the surface of both CZTSSe and Ag₂S/CZTSSe thin films using chemical bath deposition (CBD). Following this, a zinc oxide (ZnO) layer with a thickness of 50 nm and a tin oxide (ITO) layer with a thickness of 200 nm were deposited on top of the CdS buffer layer by magnetron sputtering. A vacuum evaporation apparatus was then used to deposit a 200 nm thick Ag layer as the top electrode. Finally, an 80 nm thick MgF₂ layer was deposited on the top of the device using a vacuum evaporation instrument as the anti-reflection layer. The sample was divided into 9 CZTSSe devices by mechanical scribing, each with a total device area of 0.23 cm² and an effective area of 0.21 cm².

Characterization: The grazing incidence X-ray diffraction (GIXRD) data were obtained through testing with the Japanese Rigaku Smartlab, scanning rate was 3 °/min, with testing angle range from 10° to 70° and grazing incidence angles ranging from 0.1° to 5°. The longitudinal elemental depth distribution data of the thin film samples were obtained by testing using secondary ion mass spectrometry (SIMS, ION TOF-SIMS 5) under conditions of 1 keV energy and 80 nA current. The UPS data was obtained by ultraviolet photoelectron spectroscopy (UPS, Thermo ESCALAB 250XI) to analyze the difference between the E_F and the valence band maximum. The current density-voltage (J - V) curves were obtained by testing under standard illumination conditions (AM 1.5G, 100 mW/cm²) using a solar simulator manufactured by Zolihan Light Corporation. The external quantum efficiency (EQE) curve data were obtained using a Zolix SCS100 QE system equipped with a 150 W xenon lamp source and lock-in amplifier. The temperature-dependent current density-voltage (J - V - T) curves and deep-level transient spectroscopy (DLTS) of the CZTSSe devices were obtained using an FT-1030 HERA DLTS system. The J - V - T data were collected over a temperature

range of 80 to 340 K with a step size of 10 K. The DLTS data were obtained under the following test conditions: pulse voltages of 0.2 V and reverse biases of -0.4 V, with a temperature range from 150 K to 350 K. The atomic force microscopy (AFM) and conductive atomic force microscopy (c-AFM) images were captured by an atomic force scanning probe microscope (Dimension Icon) at a bias voltage of 0.5 V, with scanning rate of 1 Hz and scanning area of $5 \times 5 \mu\text{m}^2$. The capacitance–voltage (C-V) characteristics and drive-level capacitance profiling (DLCP) analysis were conducted using the Keithley 4200A-SCS system along with the JANIS cryogenic platform. Transient surface photovoltage (TSPV) data analysis of the CZTSSe devices was conducted using a 500 MHz digital oscilloscope (TDS 3054C, Tektronix) and amplified by a DC voltage amplifier under excitation from a third harmonic Nd:YAG laser (Quantel Brilliant Eazy: BRILEZ/IR-10).

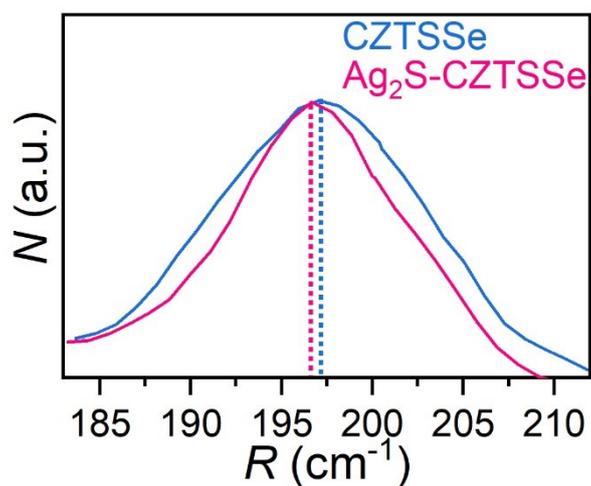


Fig. S1. The magnified Raman spectra of CZTSSe and Ag₂S-CZTSSe thin film samples.

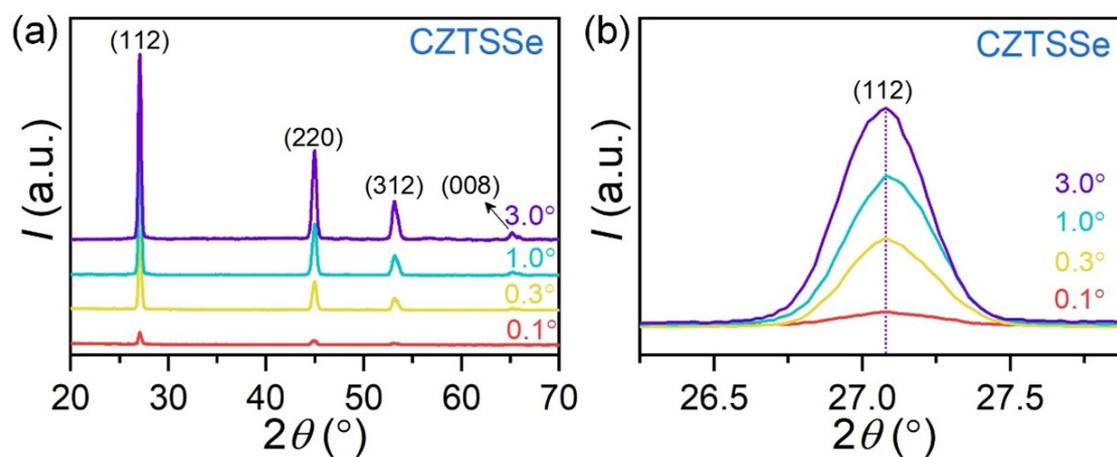


Fig. S2. (a) GIXRD spectra of CZTSSe thin film samples at different grazing incidence angles; and (b) the magnified spectra of the (112) diffraction peak.

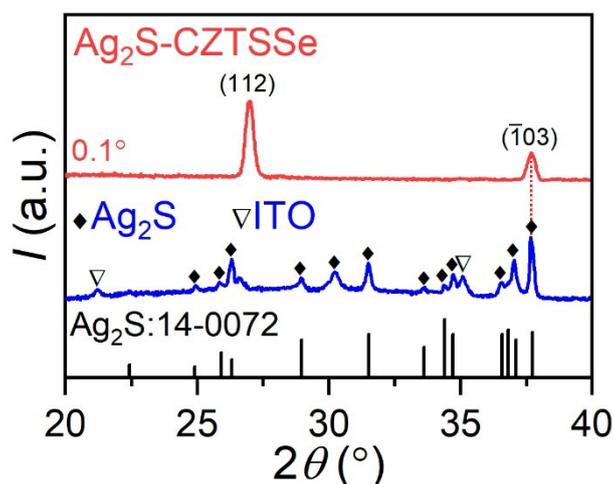


Fig. S3. The XRD spectra of the Ag_2S film and Ag_2S -CZTSSe film samples prepared by the solution method, where the result shows that $(\bar{1}03)$ crystal plane index is the preferred growth direction of the Ag_2S thin film.

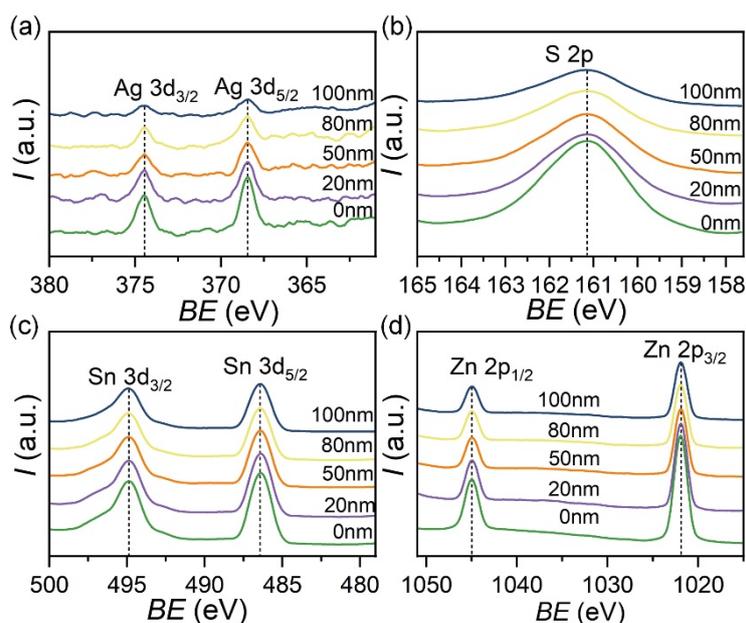


Fig. S4. XPS spectra of (a) Ag 3d, (b) S 2p, (c) Sn 3d and (d) Zn 2p of Ag_2S -modified CZTSSe samples at different depths (Sputtered depths of 0 nm, 20 nm, 50 nm, 80 nm, and 100 nm).

The binding energy differences of Ag 3d ($3d_{3/2}$ at 374.4 eV and $3d_{5/2}$ at 368.4 eV), Sn 3d ($3d_{3/2}$ at 494.8 eV and $3d_{5/2}$ at 486.4 eV) and Zn 2p ($2p_{1/2}$ at 1044.9 eV and $2p_{3/2}$ at 1021.9 eV) peaks are 6.0 eV, 8.4 eV, and 23.0 eV, which are indicative of the presence of Ag^+ , Sn^{4+} and Zn^{2+} .

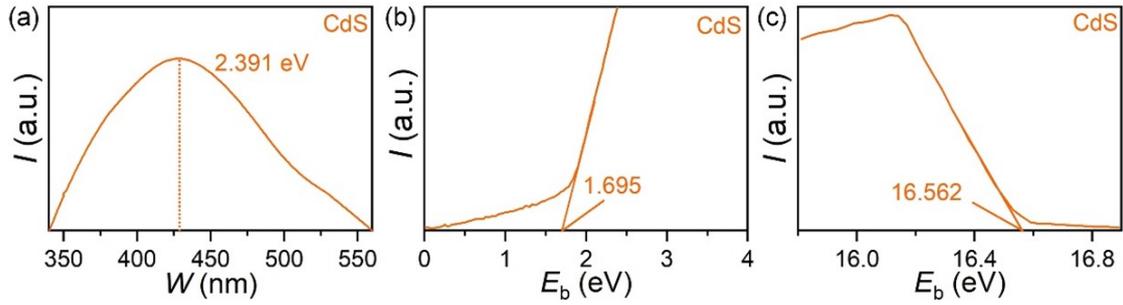


Fig. S5. (a) CdS thin film samples were analyzed by PL spectroscopy. The energy level positions of CdS thin film samples were analyzed by UPS: (b) UPS spectrum with magnified valence band edges; (c) UPS spectrum with magnified work function edges.

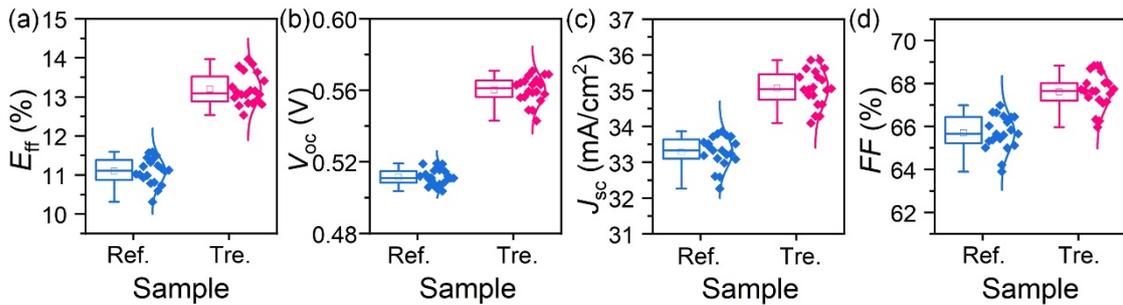


Fig. S6. Statistical box diagrams of performance parameters obtained from 20 CZTSSe (Reference) and Ag_2S -CZTSSe (Treated) devices with an area of 0.3 cm^2 . (a) PCE, (b) V_{oc} , (c) J_{sc} , and (d) FF.

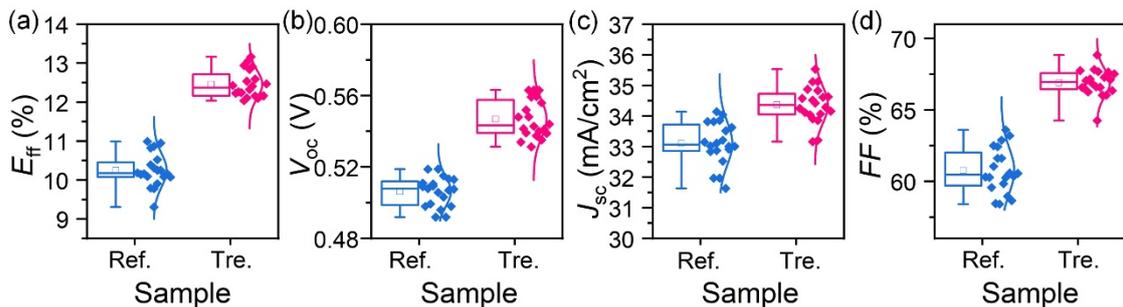


Fig. S7. Statistical box diagrams of performance parameters obtained from 20 CZTSSe (Reference) and Ag_2S -CZTSSe (Treated) devices with an area of 0.5 cm^2 . (a) PCE, (b) V_{oc} , (c) J_{sc} , and (d) FF.



福建省计量科学研究院
FUJIAN METROLOGY INSTITUTE
(国家光伏产业计量测试中心)
National PV Industry Measurement and Testing Center



检测报告

Test Report

报告编号: 24Q3-00019

Report No.

客户名称

Name of Customer

许昌学院 Xuchang University

联络信息

Contact Information

河南省许昌市魏都区八一路88号, No. 88, Bayi Road, Weidu District,
Xuchang City, Henan Province

物品名称

Name of Items

薄膜太阳能电池 Thin film solar cell (IV)

型号/规格

Type / Specification

CZTSSe 薄膜太阳能电池 CZTSSe thin film solar cell

物品编号

Items No

10-2

制造厂商

Manufacturer

许昌学院 Xuchang University

物品接收日期

Items Receipt Date

2024-01-04

检测日期

Test Date

2024-01-05



批准人

Approved by

黎健生

黎健生

核验员

Checked by

何翔

何翔

检测员

Test by

陈彩云

陈彩云

发布日期 2024 年 01 月 10 日

Date of Report

Year

month

Day



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1. 检测机构说明:

Testing institutions that

本院为国家法定计量检定机构, 国家光伏产业计量测试中心依托本院检测技术开展检测。本院/本中心质量管理体系符合 GB/T 27025 (ISO/IEC 17025, IDT) 标准要求。

The institute is a national legal metrological institution. National PV Industry Measurement and Testing Center carries out testing relying on the institute's testing technology. The Center's quality management system meets the requirements of GB/T 27025 (ISO/IEC 17025, IDT) standard.

2. 本次检测所依据的检测方法(代号及名称):

Reference documents from the test (code, name)

IEC 60904-1-2020 光伏器件-第一部分: 光伏电流-电压特性的测量; SJ/T 11630-2016 太阳能电池用硅片几何尺寸测试方法

3. 本次检测所使用的主要测量仪器:

Measurement standards used in this test

仪器名称 Name	仪器编号 Number	测量范围 Measuring Range	不确定度/或准确度等级/或最大允许误差 Uncertainty or Accuracy Class or Maximum Permissible Error	溯源机构名称/证书编号 Name of traceability institution/Certificate No.	有效期限 Due date
源表	10807C008 78-2	电流: -10 μ A~1A; 电压: 20mV~20V	测量: DCV: $U_{rel}=0.05\%$, $k=2$; DCI: $U_{rel}=0.05\%$, $k=2$ 输出: DCV: $U_{rel}=0.05\%$, $k=2$; DCI: $U_{rel}=0.05\%$, $k=2$	福建计量院 23D2-02429	2024-04-16
太阳模拟器	2014-017	(300~1200) nm; (800~1200) W/m ²	光谱匹配度(300-360) nm: $U_{rel}=8.0\%$ ($k=2$); (360-1200) nm: $U_{rel}=6.2\%$ ($k=2$); 辐照度比(辐照度不均匀度、辐照度时间不稳定性): $U_{rel}=1.2\%$ ($k=2$)	福建计量院 23Q2-00526	2024-06-13
WPVS 单晶硅标准电池	015-2014	(300~1200) nm	$U_{rel}=1.3\%$ ($k=2$)	中国计量院 GXgf2023-01245	2025-03-29
自动影像测量仪	11656	X 轴: (0~195) mm; Y 轴: (0~195) mm	$U=2 \mu$ m ($k=2$)	福建计量院 23A2-11241	2024-07-13
/	/	/	/	/	/

4. 检测地点及环境条件:

Location and environmental condition for the test

地点: 本院闽侯基地 4 号楼 108Room 108, Building 4, Minhou Scientific Research Base

Location

温度: 25.4 $^{\circ}$ C
Temperature

相对湿度: 36 %
Relative Humidity

其它: /
Others

5. 备注: /

Note

本报告提供的结果仅对本次被检的物品有效。

The data are valid only for the instrument(s) under testing.

检测报告续页专用

Continued page of test report



检测结果/说明:

Results of Test and Additional Explanation.

1 标准测试条件 STC Standard Test Condition (STC):

总辐照度 Total Irradiance: 1000 W/m²

被测电池温度 Temperature: 25.0 °C

光谱分布 Spectral Distribution: AM1.5G

2 STC 条件下测量数据

Measurement Data under STC

正扫 Forward Scan

I_{sc} (mA)	V_{oc} (V)	I_{MPP} (mA)	V_{MPP} (V)	P_{MPP} (mW)	FF (%)	η (%)	A (cm ²)
7.426	0.5701	6.506	0.4374	2.846	67.22	13.06	0.2180

反扫 Reverse Scan

I_{sc} (mA)	V_{oc} (V)	I_{MPP} (mA)	V_{MPP} (V)	P_{MPP} (mW)	FF (%)	η (%)	A (cm ²)
7.432	0.5743	6.482	0.4374	2.835	66.42	13.00	0.2180

失配因子 Mismatch Factor: 1.014

STC 下电流-电压特性曲线和功率-电压特性曲线

I-V & P-V Characteristic Curves under STC

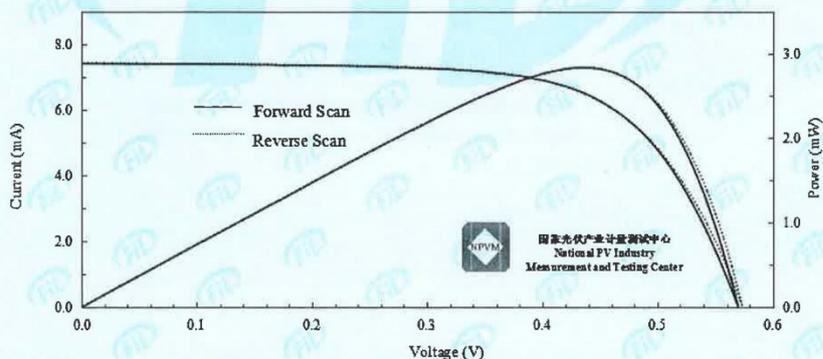


图 1 STC 下电流-电压特性曲线和功率-电压特性曲线

Figure 1. I-V and P-V characteristic curves of the measured sample under STC

Fig. S8. The certification report of the third-party test (National Photovoltaic Industry Measurement and Testing Center).

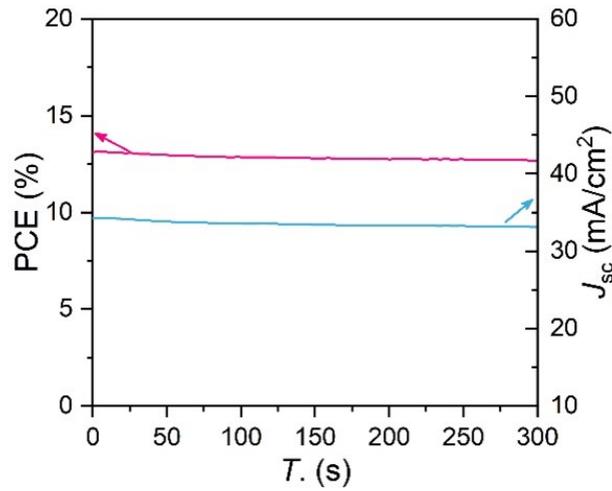


Fig. S9. Stabilized power output at maximum power point tracking of the cell for 300s.

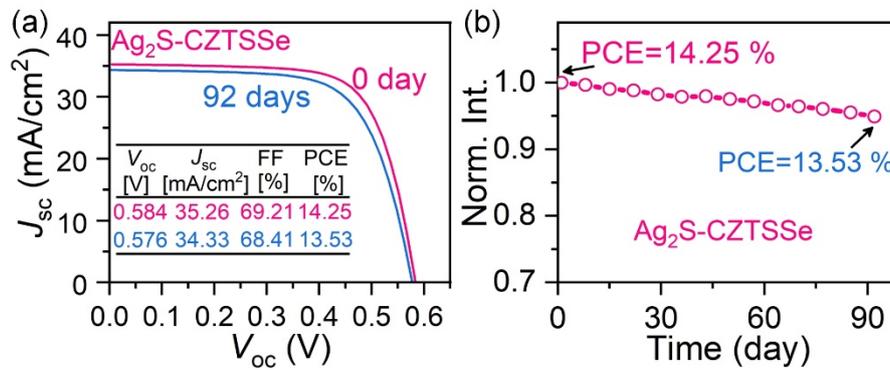


Fig. S10. (a) The J - V curves of n- Ag_2S -modified CZTSSe solar cells before and after being stored in ambient air for 92 days. (b) The efficiency stability within 92 days for the champion Ag_2S -modified CZTSSe device. The Ag_2S -modified CZTSSe devices are stored in a clean room and the efficiencies are tested 14 times within 92 days.

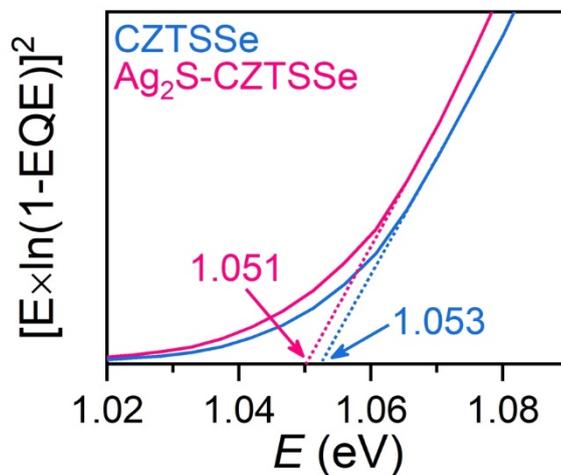


Fig. S11. Band gap diagram of the absorber layer derived from Fig. 5h.

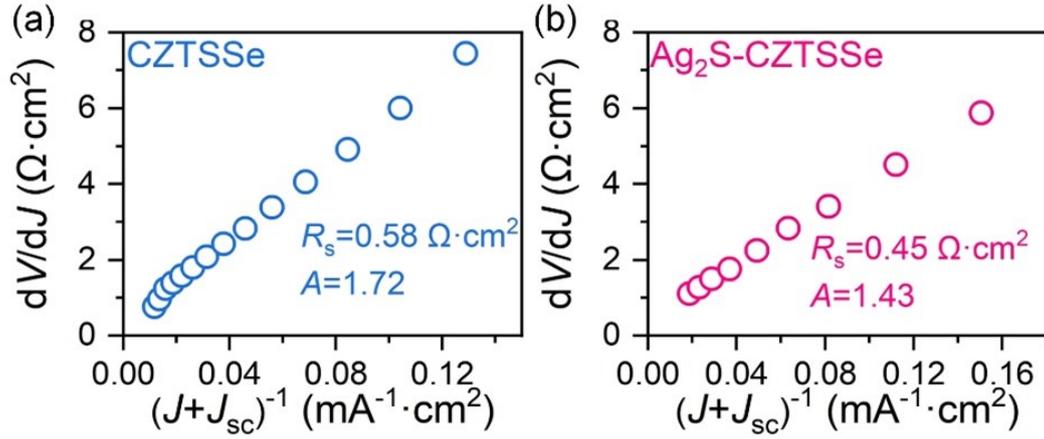


Fig. S12. dV/dJ vs $(J+J_{sc})^{-1}$ curves for (a) CZTSSe and (b) Ag_2S -CZTSSe. R_s is obtained from the intercept of linear region, and the slope is equal to AkT/q , where $q/kT=38.7$.

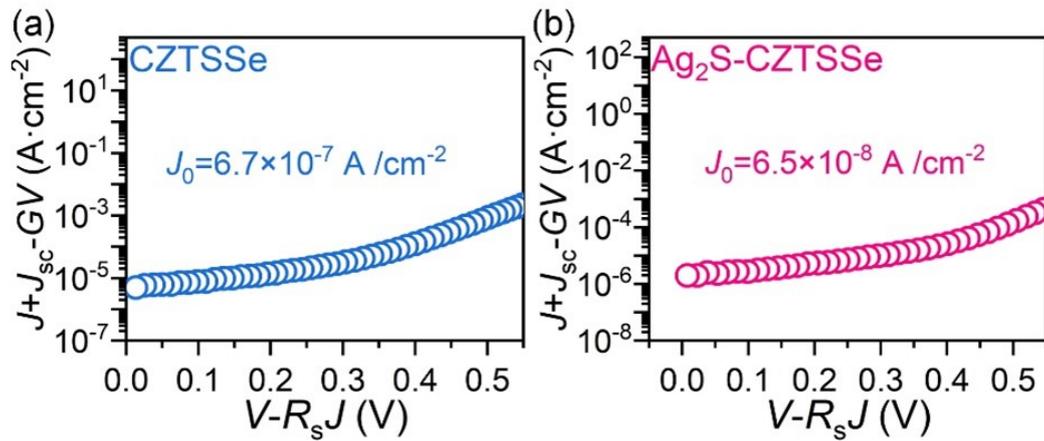


Fig. S13. Semi-logarithmic plots of $J+J_{sc}-GV$ vs $V-R_sJ$ for (a) CZTSSe and (b) Ag_2S -CZTSSe devices. J_0 is obtained from the intercept of linear region.

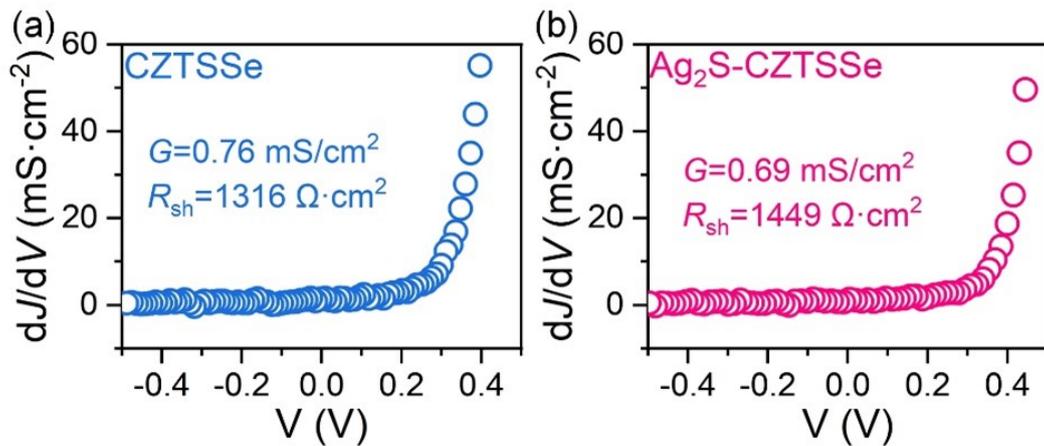


Fig. S14. dJ/dV vs V curves for (a) CZTSSe and (b) Ag_2S -CZTSSe devices. G is

evaluated from the average value of plateau range (-0.2~0.2 V), and its reciprocal represents R_{sh} .

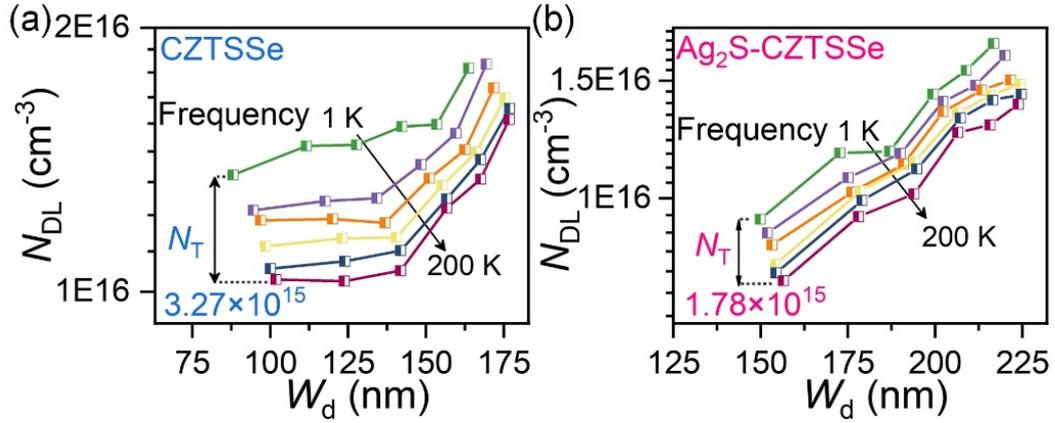


Fig. S15. DLCP measured across frequencies range from 1 kHz to 200 kHz for (a) the CZTSSe and (b) the Ag_2S -modified CZTSSe solar cells.

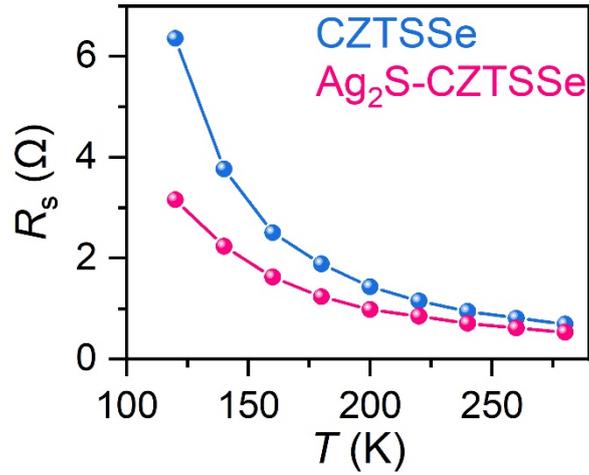


Fig. S16. Temperature-dependence of series resistance (R_s) vs. T curves of the CZTSSe and $\text{Ag}_2\text{S-CZTSSe}$ devices.

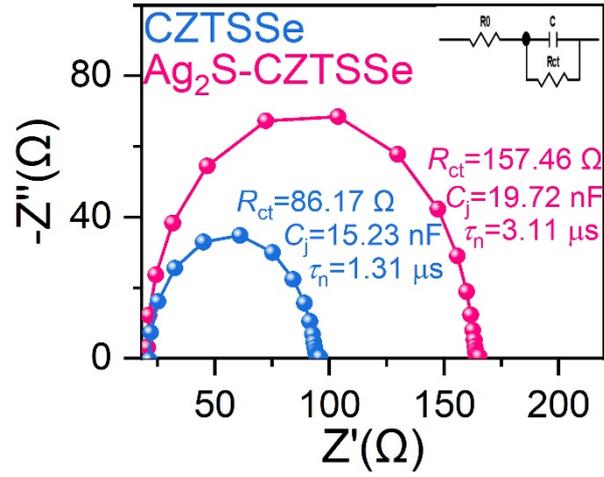


Fig. S17. Nyquist diagram and equivalent circuit diagram of CZTSSe and Ag₂S-CZTSSe devices under -0.4V test conditions.

1. J. Fu, A. Zhang, D. Kou, Z. Xiao, W. Zhou, Z. Zhou, S. Yuan, Y. Qi, Z. Zheng and S. Wu, *Chem. Eng. J.*, 2023, **457**, 141348.