Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Engineering of Interface Band Bending and Defects Elimination via Ag-graded active layer for efficient $(Cu,Ag)_2ZnSn(S,Se)_4$ Solar Cells

Ya-Fang Qi, Dong-Xing Kou*, Wen-Hui Zhou, Zheng-Ji Zhou, Qing-Wen Tian, Yue-Na Meng, Xin-Sheng Liu, Zu-Liang Du and Si-Xin Wu*

The Key Laboratory for Special Functional Materials of MOE, Collaborative Innovation Center of Nano Functional Materials and Applications, Henan University, Kaifeng, Henan 475004, China. E-mail: koudongxing@henu.edu.cn; wusixin@henu.edu.cn.

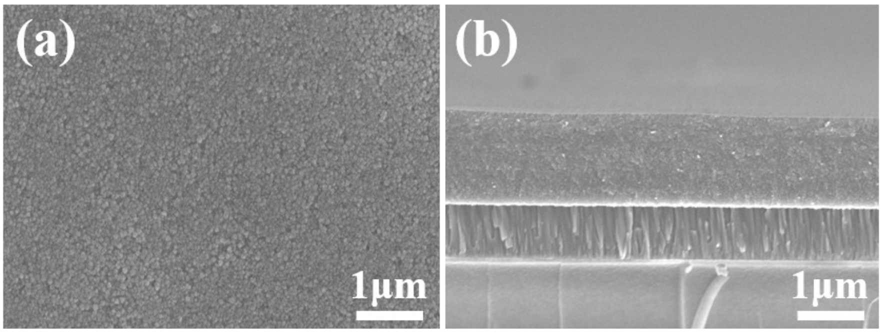

Fig. S1 (a) Top-view and (b) cross-section SEM images of the as-prepared $(Cu_{1-x}Ag_x)_2ZnSn(S,Se)_4$ thin films.

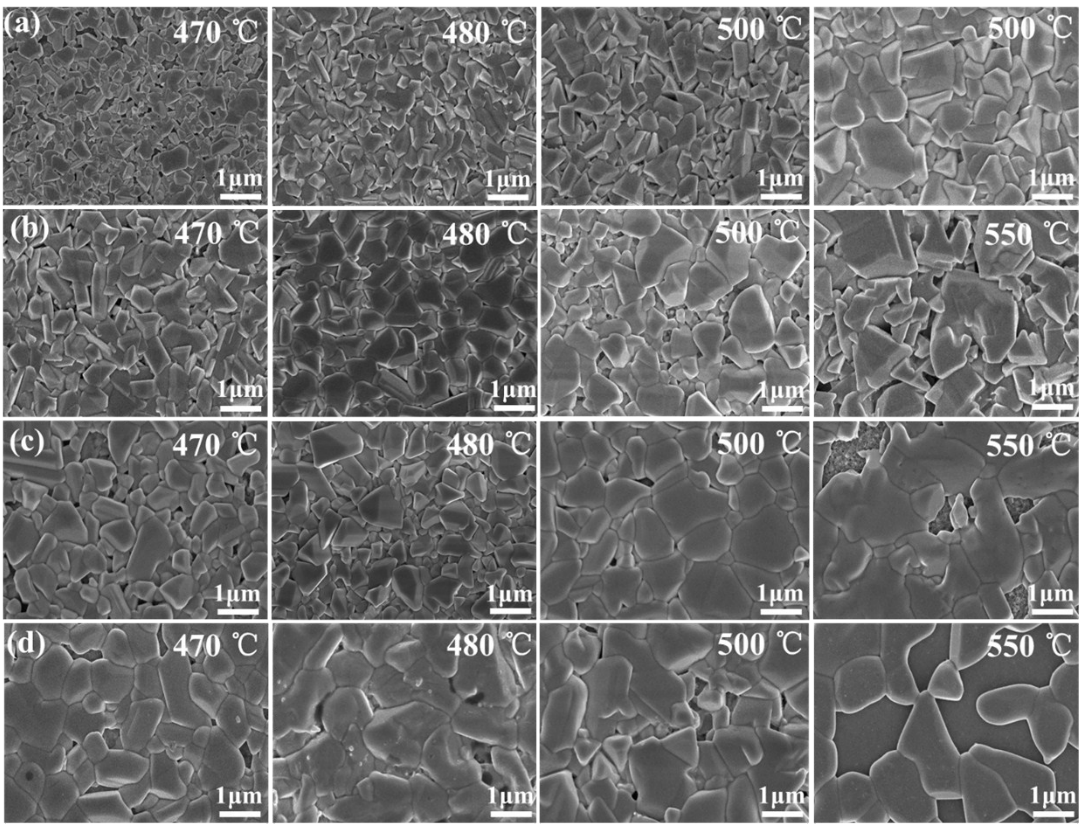

Fig. S2 The top-view SEM images for CAZTSSe thin films with Ag/(Ag+Cu) ratio of (a) 0%, (b) 5%, (c) 20%, (d) 40% prepared at different selenization temperatures. The selenization time was 15 min.

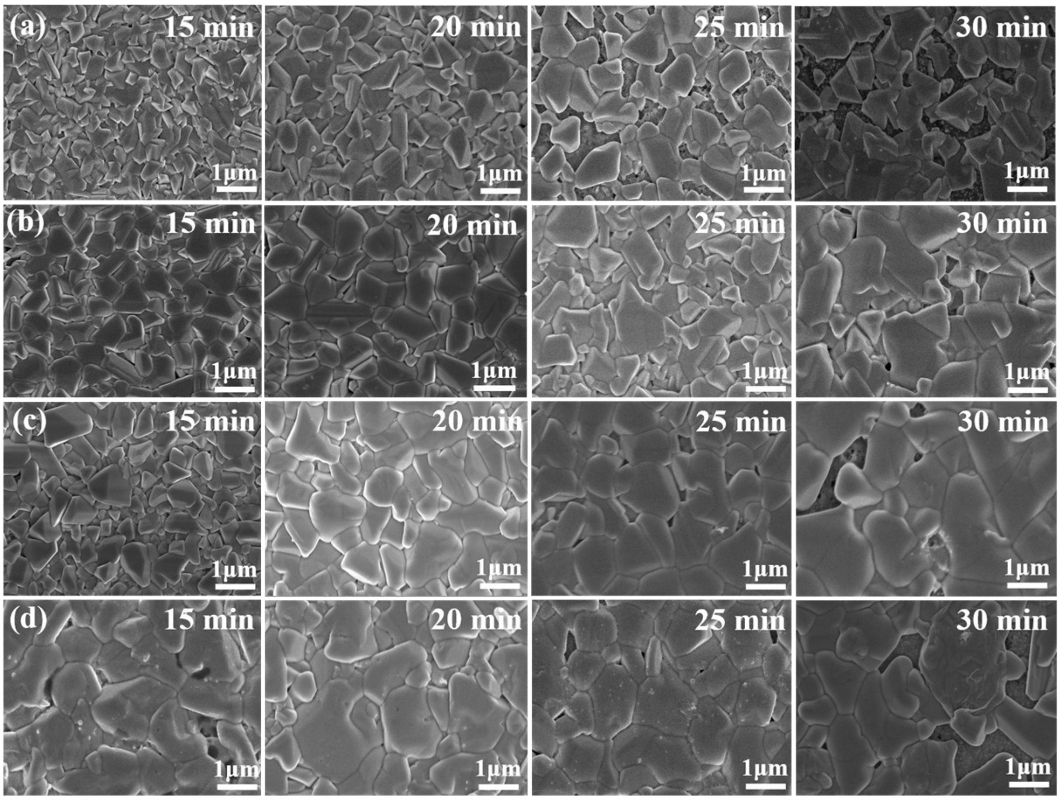

Fig. S3 The top-view SEM images for CAZTSSe thin films with Ag/(Ag+Cu) ratio of (a) 0%, (b) 5%, (c) 20%, (d) 40% prepared at different selenization time under 480 °C.

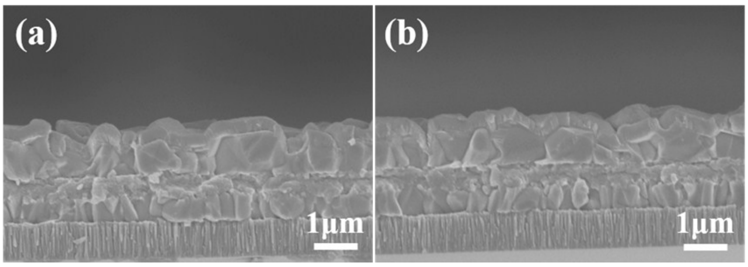

Fig. S4 The cross-section SEM image of the CAZTSSe samples with 5% and 30%/5%/30% Ag profiles.

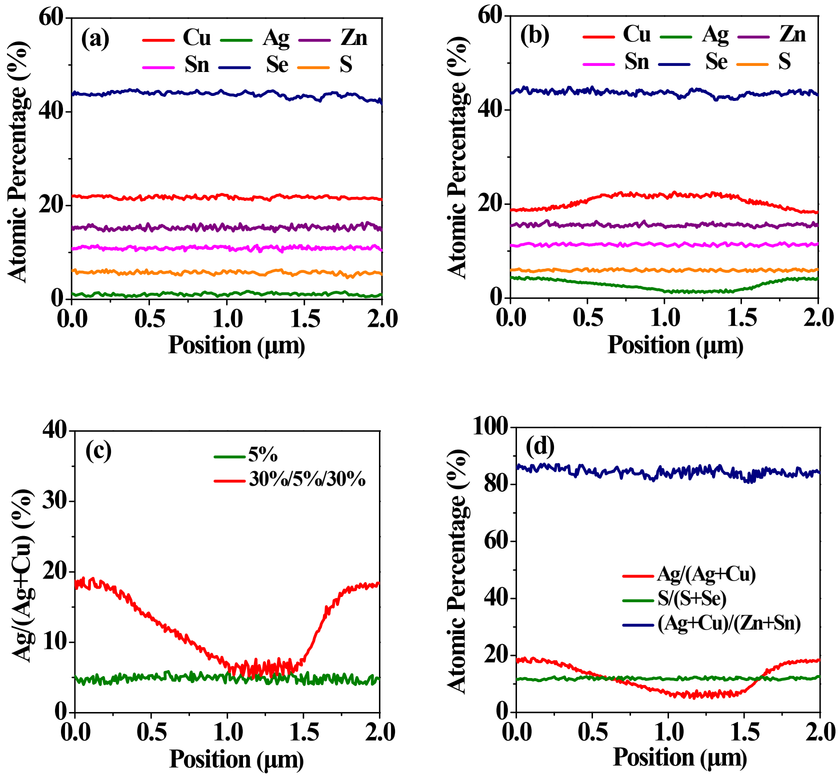

Fig. S5 Compositional distributions of the CAZTSSe samples with 5% (a) and 30%/5%/30% (b) Ag depth profile measurements; (c) is the Ag/(Ag+Cu) ratios evaluated from Fig. S5a and S5b; and (d) is the detailed Ag/(Ag+Cu), S/(S+Se) and (Ag+Cu)/(Zn+Sn) ratios evaluated from Fig. S5b.

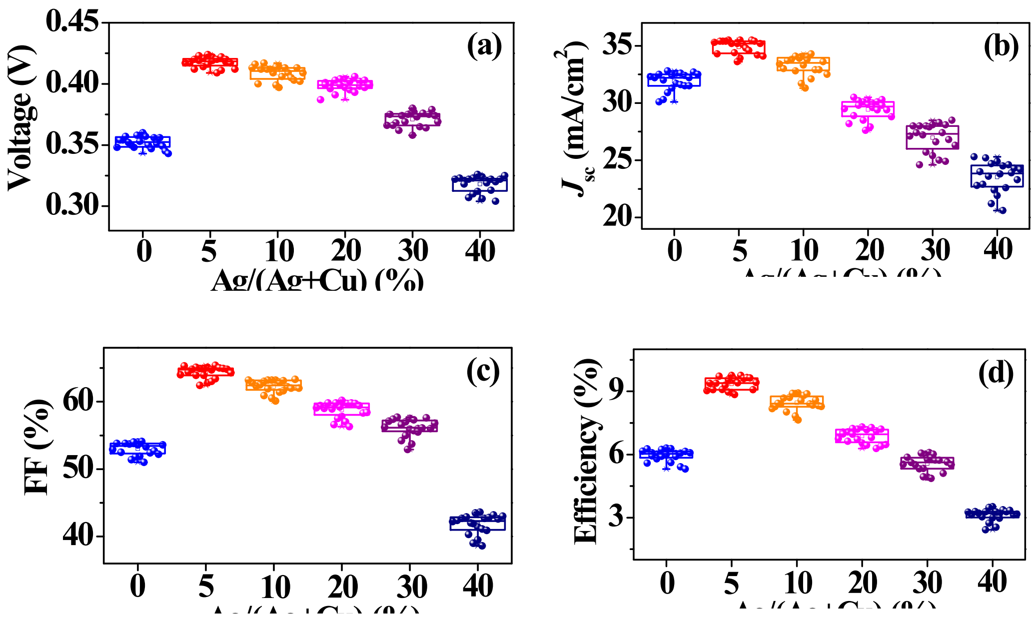

Fig. S6 Statistical distribution of (a) V_{oc}, (b) J_{sc}, (c) FF, (d) PCE for CAZTSSe solar cells with different Ag content. The data are derived from 20 devices.

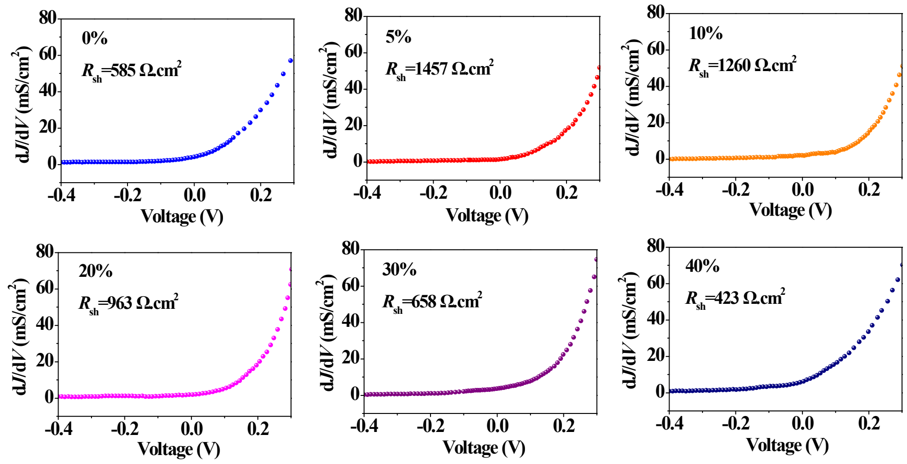

Fig. S7 dJ/dV vs. V curves, where the shunt resistance of CAZTSSe devices with different Ag content is the reciprocal of shunt conductance (G_{sh}) evaluated from the plateau value ranging from -0.3−0 V.

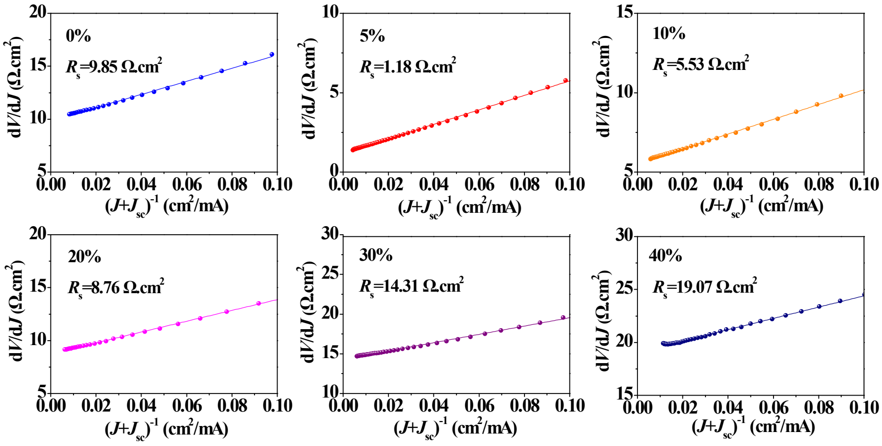

Fig. S8 dV/dJ vs. $(J+J_{sc})^{-1}$ plots, where the series resistance (R_s) of CAZTSSe devices with different Ag content is extracted from the y-intercept.

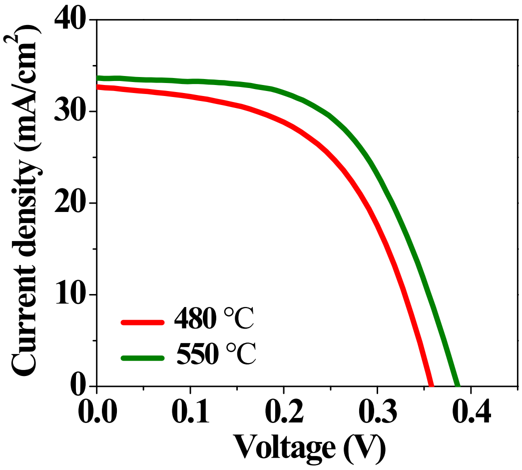

Fig. S9 The J-V curves of unsubstituted CZTSSe solar cells with different selenization temperature.

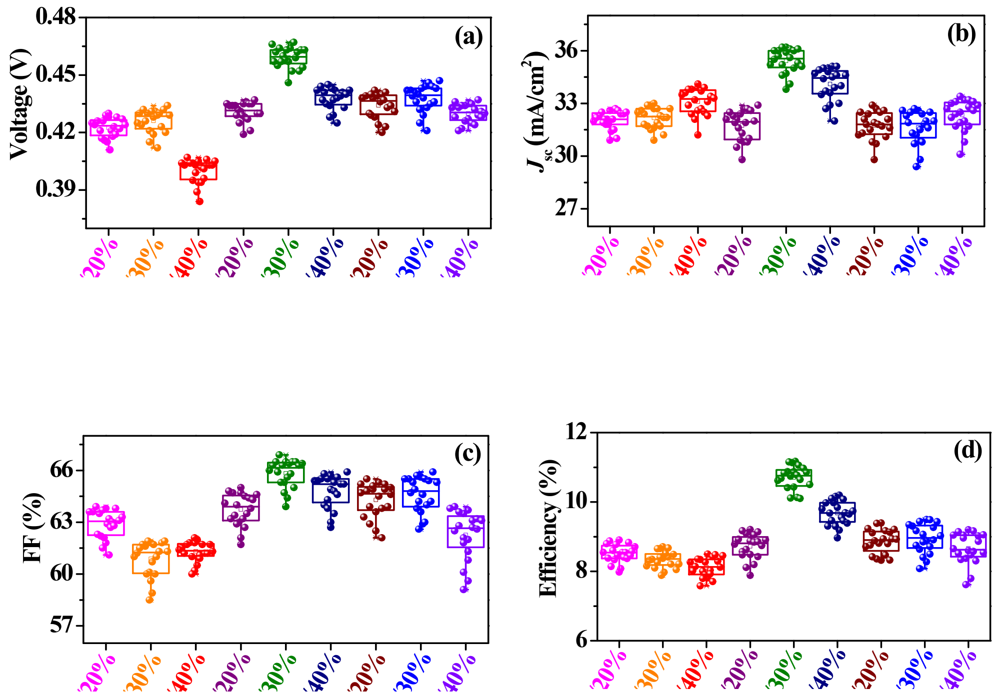

Fig. S10 Statistical distribution of (a) V_{oc}, (b) J_{sc}, (c) FF, (d) PCE for CAZTSSe solar cells with different Ag composition gradient from CdS interface to Mo substrate. The data are derived from 20 devices.

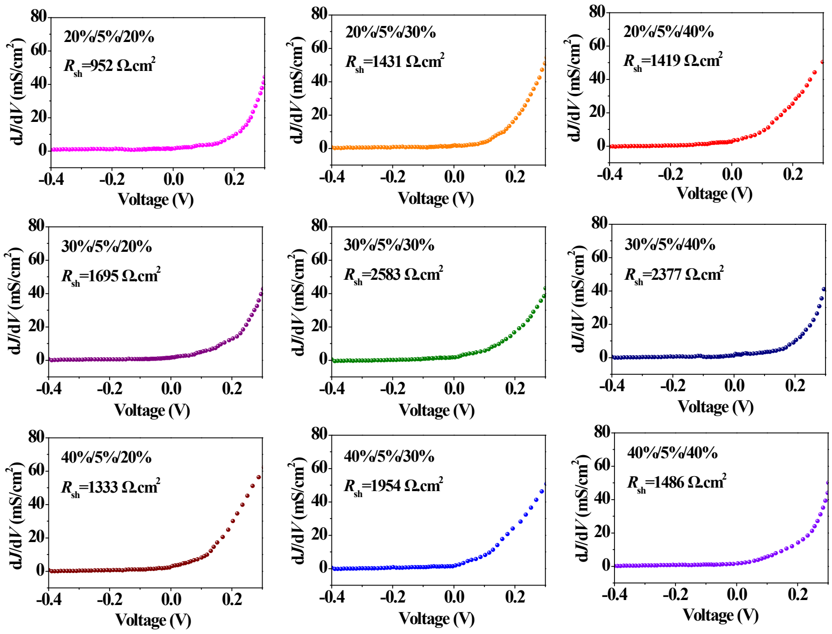

Fig. S11 dJ/dV vs. V curves, where the shunt resistance of CAZTSSe devices with different Ag composition gradient is the reciprocal of shunt conductance (G_{sh}) evaluated from the plateau value ranging from -0.3−0 V.

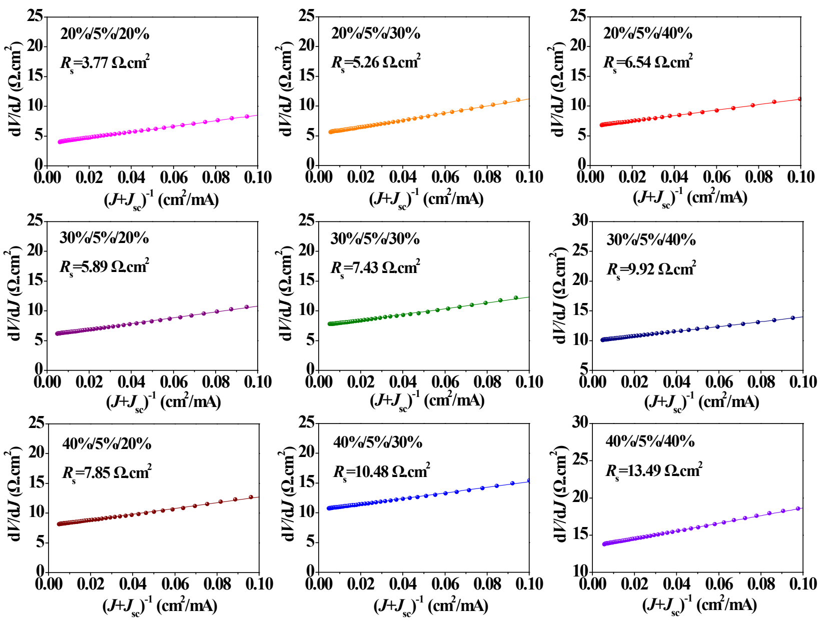

Fig. S12 dV/dJ vs. $(J+J_{sc})^{-1}$ plots, where the series resistance (R_s) of CAZTSSe devices with different Ag composition gradient is extracted from the y-intercept.

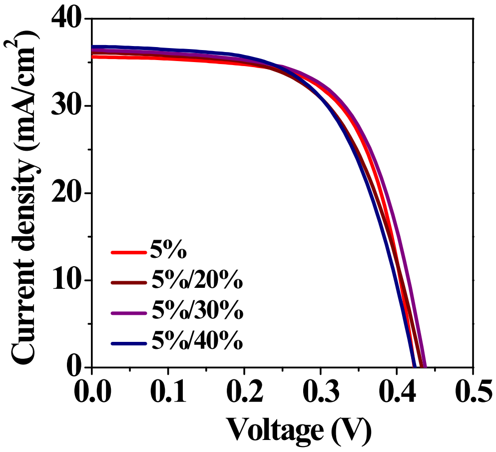

Fig. S13 The *J-V* curves of CAZTSSe solar cells with only backside grading near the CAZTSSe/Mo interface.

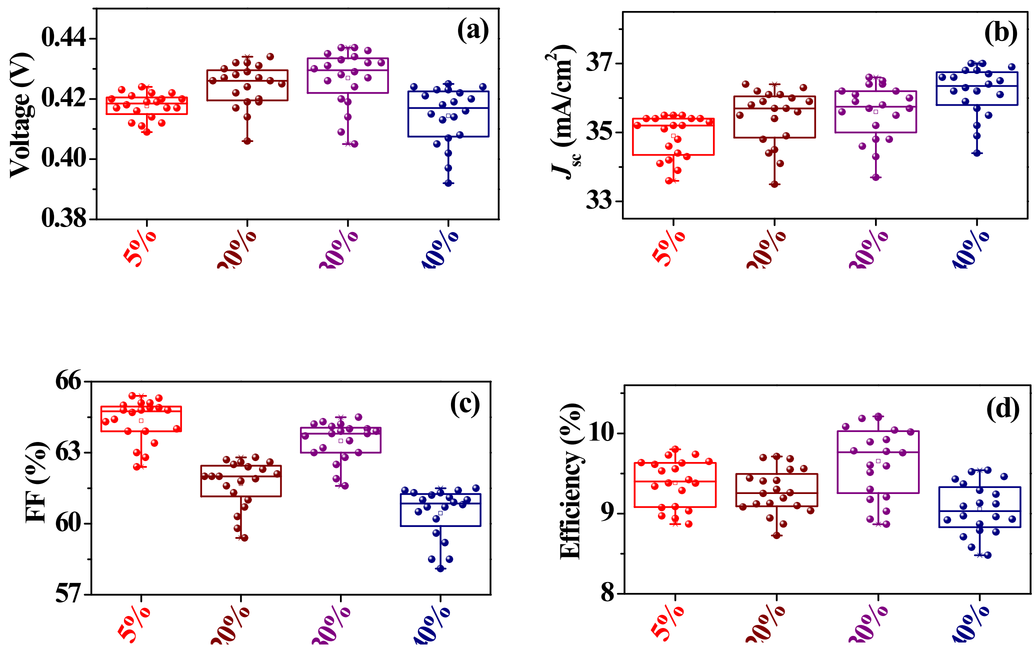

Fig. S14 Statistical distribution of the photovoltaic parameters extracted from 20 solar cells for CAZTSSe solar cells with only backside grading near the CAZTSSe/Mo interface. (a) V_{oc}, (b) J_{sc}, (c) FF, (d) PCE.

Table S1 Summary of the photovoltaic parameters for CAZTSSe solar cells with different Ag content. The data are the average values calculated from 20 devices with standard deviation.

Ag/(Ag+Cu)	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
X = 0%	352.3±4.7	31.90±0.78	53.02±0.96	5.95±0.28
X = 5%	417.6±4.2	34.90±0.61	64.34±0.86	9.38±0.29
X = 10%	408.7±5.9	33.26±0.85	62.26±0.95	8.46±0.35
X = 20%	398.8±4.7	29.43±0.84	58.79±1.17	6.90±0.34
X = 30%	371.0±6.1	26.96±1.24	56.11±1.33	5.61±0.36
X = 40%	318.0±6.7	23.53±1.30	41.81±1.48	3.13±0.28

Table S2 The typical resistivity of the selenized CAZTSSe thin films with different Ag/(Ag+Cu) ratio.

Ag/ (Ag+Cu)	0%	5%	10%	20%	30%	40%	5%/ 20%	5%/ 30%	5%/ 40%	20%/ 5%/ 20%	30%/ 5%/ 30%	40%/ 5%/ 40%
ρ (Ω·cm)	2.6	5.7	17.9	45.8	103.4	191.8	8.7	14.6	29.8	15.3	31.2	58.5

Table S3 The detailed photovoltaic parameter of unsubstituted CZTSSe solar cells with different selenization temperature.

	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
480 ^oC	358	32.6	54.0	6.3
550 ^oC	386	33.6	57.3	7.4

Table S4 Summary of the photovoltaic parameter for CAZTSSe solar cells with different Ag composition gradient from CdS interface to Mo substrate. The data are the average values calculated from 20 devices with standard deviation.

CdS/CAZTSSe/Mo	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
20%/5%/20%	422.5±5.1	32.04±0.51	62.89±0.82	8.51±0.26
20%/5%/30%	426.1±6.0	32.17±0.60	60.87±1.02	8.34±0.24
20%/5%/40%	400.0±6.1	33.10±0.75	61.31±0.58	8.12±0.27
30%/5%/20%	430.8±4.9	31.74±0.86	63.73±0.93	8.72±0.36
30%/5%/30%	459.0±5.4	35.41±0.70	65.82±0.81	10.71±0.34
30%/5%/40%	437.7±5.5	34.10±0.91	64.80±0.95	9.67±0.35
40%/5%/20%	434.1±6.5	31.75±0.78	64.28±0.98	8.86±0.34
40%/5%/30%	437.8±7.0	32.62±0.93	64.61±1.02	8.94±0.42
40%/5%/40%	430.0±4.7	32.33±0.87	62.26±1.42	8.66±0.44

Table S5 The detailed photovoltaic parameter of CAZTSSe solar cells with only backside grading near the CAZTSSe/Mo interface.

CdS/CAZTSSe/Mo	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
5%	422	35.5	65.1	9.8
5%/20%	432	36.1	62.6	9.7
5%/30%	437	36.4	64.2	10.2
5%/40%	423	36.8	61.3	9.5