

## Supporting Information

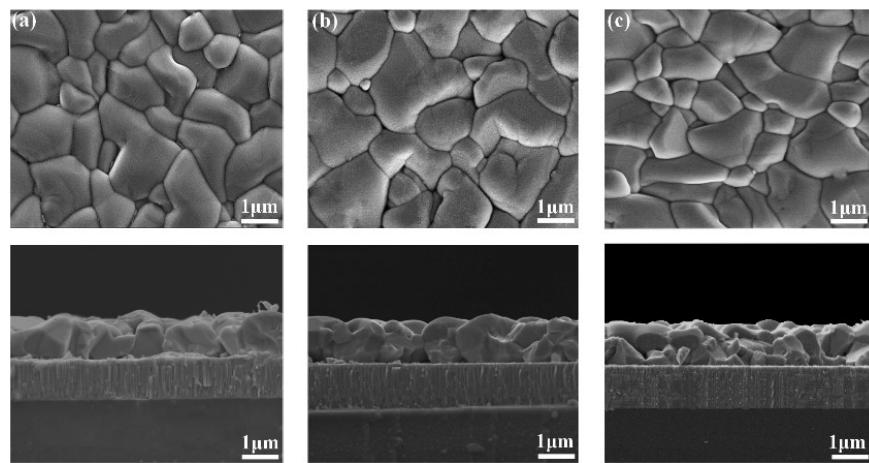
# Regulating Charge Carrier Recombination in Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> Solar Cells via Cesium Treatment: Bulk and Interface Effects

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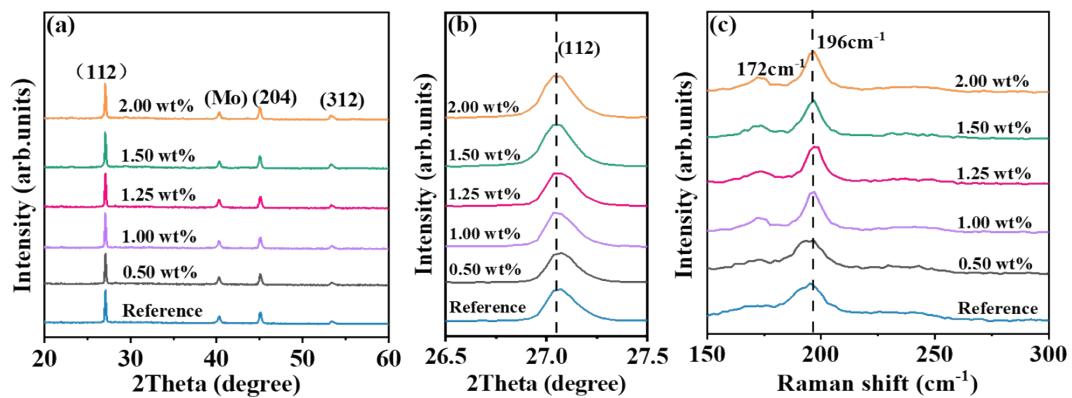
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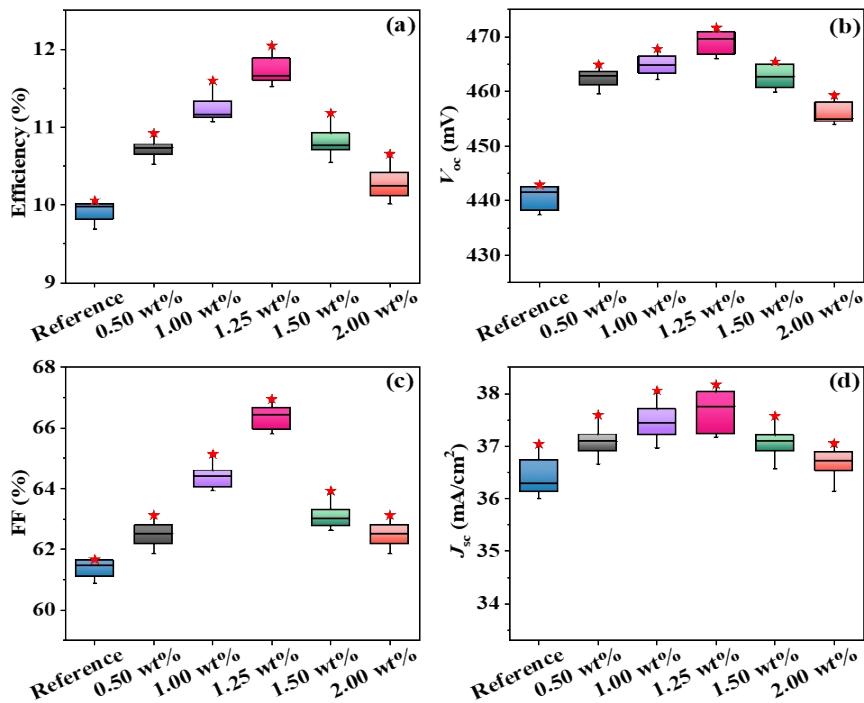
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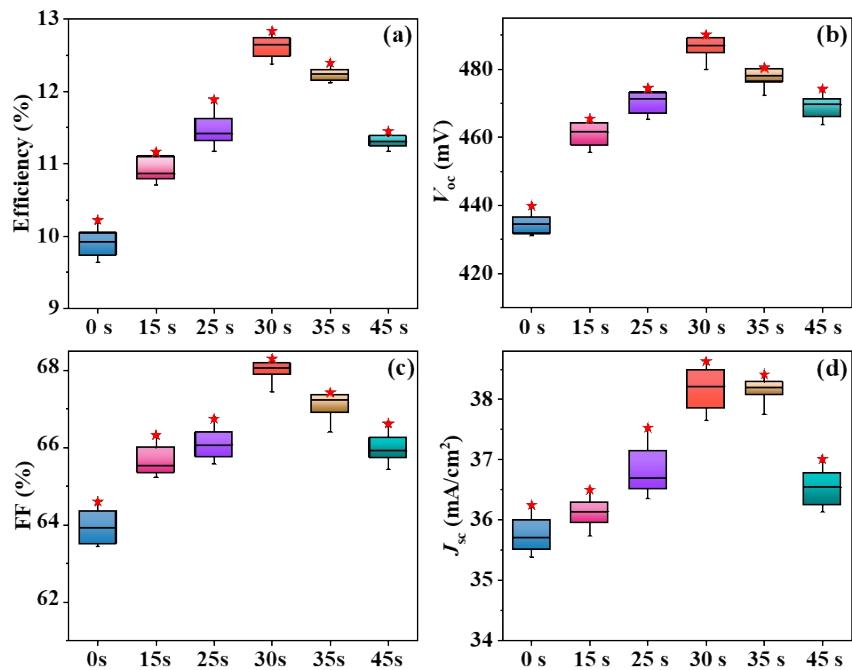
**Fig. S1** SEM top-view and cross-sectional images of the CZTSSe thin films treated with different concentrations of CsCl hot solution: (a) Reference, (b) 1.25 wt%, and (c) 2.00 wt%.



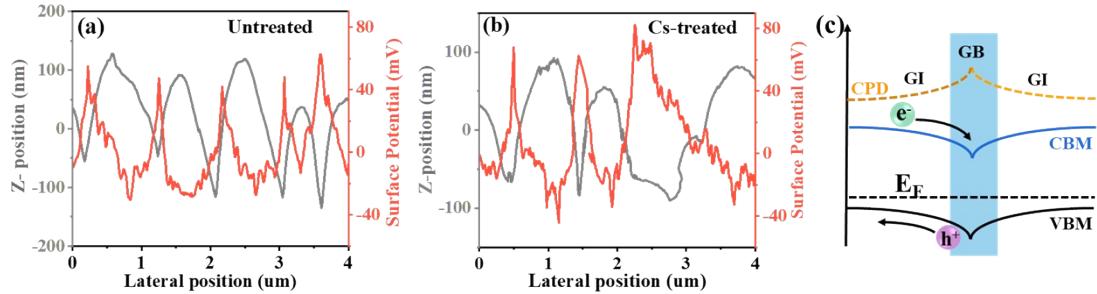
**Fig. S2** (a) X-ray diffraction (XRD) spectra, (b) the enlarged view of the (112) lattice plane, and (c) Raman spectra for the CZTSSe-based samples treated with different concentration of CsCl hot solution.



**Fig. S3** Statistical boxplots of (a) PCE, (b)  $V_{oc}$ , (c) FF, and (d)  $J_{sc}$  for the CZTSSe solar cells with the absorber films treated by different concentration of CsCl hot solution.



**Fig. S4** Statistical boxplots of (a) PCE, (b)  $V_{oc}$ , (c) FF, and (d)  $J_{sc}$  for the CZTSSe solar cells with the soaking time of CZTSSe absorber films varied in the range of 0–45 s.



**Fig. S5** Plots of the surface topography and surface potential line profiles for the (a) untreated sample and (b) Cs-treated sample. (c) Schematic of the band diagrams across the grain boundaries (GBs).

**Table S1** Summary of the photovoltaic parameters for CZTSSe solar cells with the absorber films treated by different concentration of CsCl hot solution (0-2.00 wt%).

The data are the average values calculated from 18 devices with standard deviation.

Sample	PCE (%)	V <sub>oc</sub> (mV)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)
Reference	9.92±0.12	440.58±2.06	36.42±0.35	61.49±0.18
0.50 wt%	10.71±0.10	462.46±1.55	37.06±0.26	62.52±0.36
1.00 wt%	11.22±0.14	464.80±1.80	37.49±0.32	64.39±0.35
1.25 wt%	11.73±0.16	469.01±1.95	37.69±0.36	66.35±0.38
1.50 wt%	10.82±0.17	462.69±1.97	37.07±0.22	63.10±0.42
2.00 wt%	10.27±0.18	456.09±1.97	36.62±0.32	61.84±0.37

**Table S2** Summary of the photovoltaic parameters for CZTSSe solar cells with the soaking time of CZTSSe absorber films varied in the range of 0–45 s. The data are the average values calculated from 18 devices with standard deviation.

Sample	PCE (%)	V <sub>oc</sub> (mV)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)
Reference	9.90±0.17	433.19±3.47	35.76±0.27	63.96±0.40
15s	10.92±0.15	460.48±3.25	36.13±0.23	65.66±0.37
25s	11.44±0.19	470.43±2.91	36.81±0.35	66.08±0.36
30s	12.63±0.13	486.57±3.21	38.17±0.16	68.01±0.25
35s	12.24±0.08	477.64±2.37	38.16±0.30	67.11±0.29
45s	11.30±0.08	469.07±2.98	36.53±0.27	65.97±0.34