

## Supplementary Materials

### Improving the crystallization and properties of CZTSSe film by adding NaTFSI in the precursor solution

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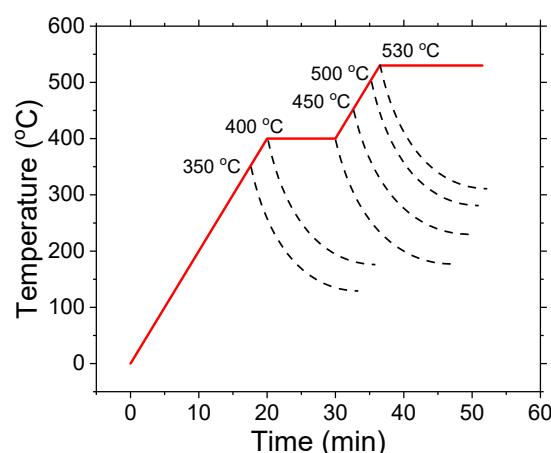
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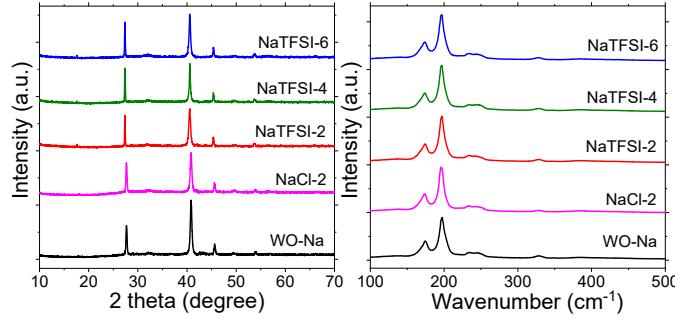
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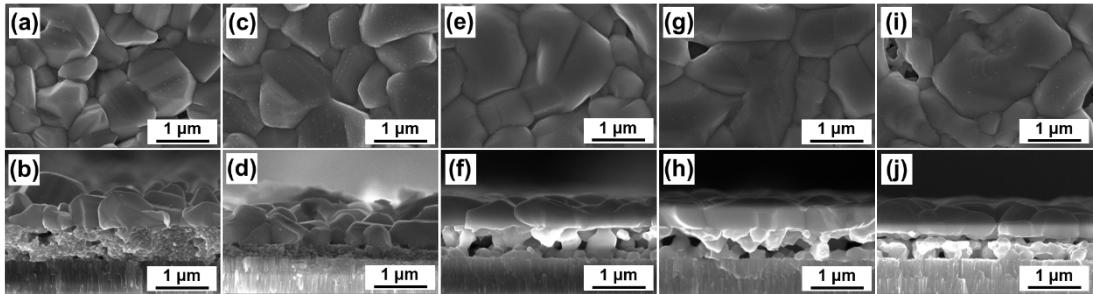
**Figure S1.** Temperature profile used for the selenization process

**Table S1.** EDS results for the WO-Na and NaTFSI films

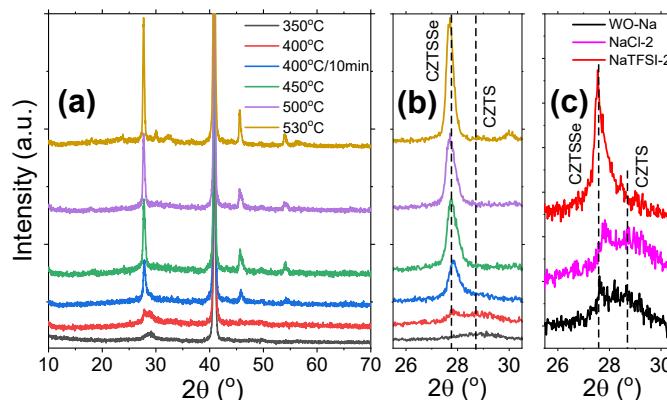
Sample	Cu (%at)	Zn (%at)	Sn (%at)	Se (%at)	S (%at)	S/(S+Se)
WO-Na	25.9	16.0	13.3	37.9	6.9	15.4
NaTFSI-2	28.4	18.0	14.2	36.8	2.6	6.6
NaCl-2	24.5	17.7	13.9	37.2	6.7	10.8



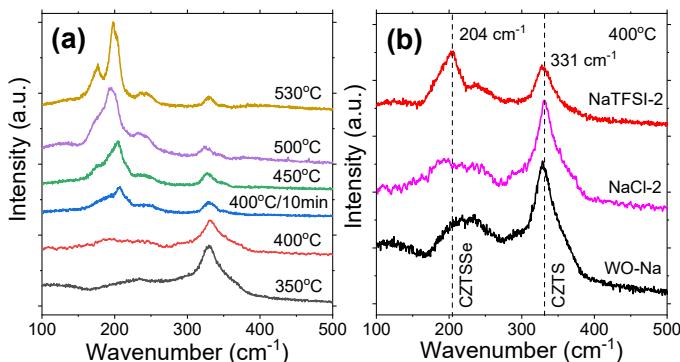
**Figure S2.** XRD patterns and Raman spectra for CZTSSe films without Na and with different Na salts



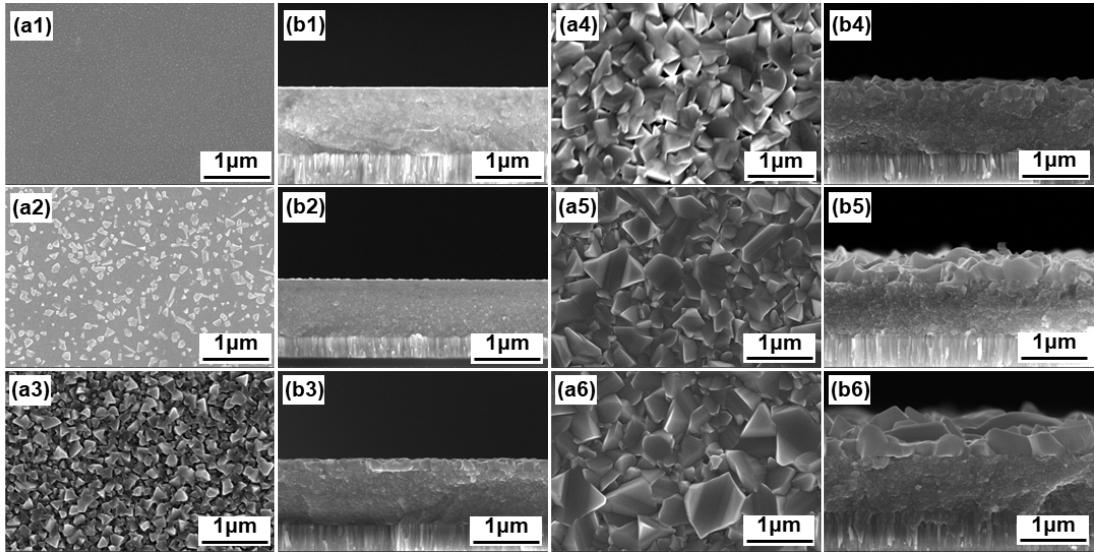
**Figure S3.** SEM images for the CZTSSe films without Na (a,b), with NaCl (c,d) and with different concentration of NaTFSI (e,f NaTFSI-2; g,h NaTFSI-4; i,j NaTFSI-6).



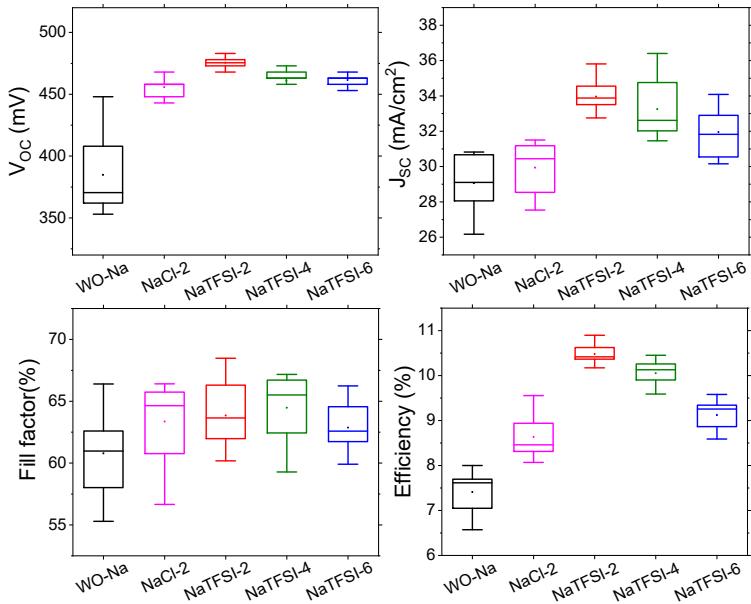
**Figure S4.** XRD patterns of the half-selenized NaCl-2 films (a,b); comparison of the XRD patterns for the half-selenized films at 400 °C (c).



**Figure S5.** Raman spectra of the half-selenized NaCl-2 films (a); comparison of the Raman spectra for the half-selenized films at 400 °C (b).



**Figure S6.** SEM images for the half-selenized NaCl-2 films (a1,b1, 350°C; a2,b2, 400°C; a3,b3, 400 °C/10min; a4,b4, 450°C; a5,b5, 500°C; a6,b6, 530°C).



**Figure S7.** Statistics of the parameters for solar cells based on different CZTSSe films.