Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Defect Engineering of Solution-Processed ZnO:Li Window Layer Towards High-Efficiency and Low-Cost Kesterite Photovoltaics

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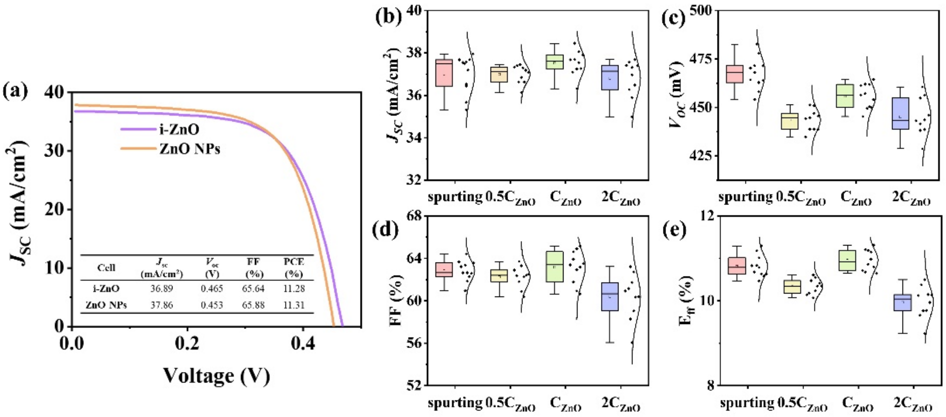

Figure S1 Statistical box diagrams of *J-V* curves, J_{sc}, V_{oc}, FF and PCE for CZTSSe solar cells with different ZnO NPs solution concentration.

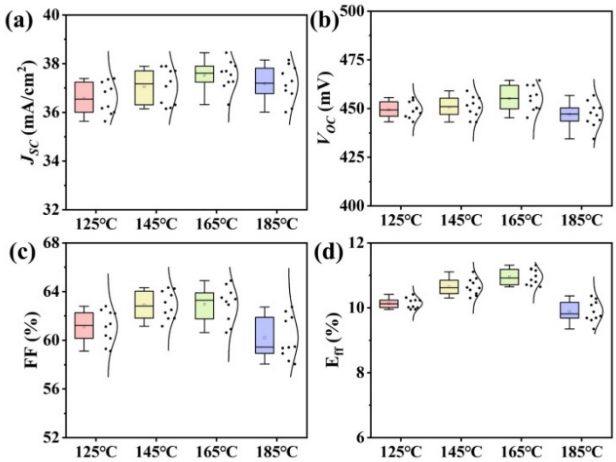

Figure S2 Statistical box diagrams of J_{sc}, V_{oc}, FF and PCE for CZTSSe solar cells at different ZnO NPs window layer annealing temperature.

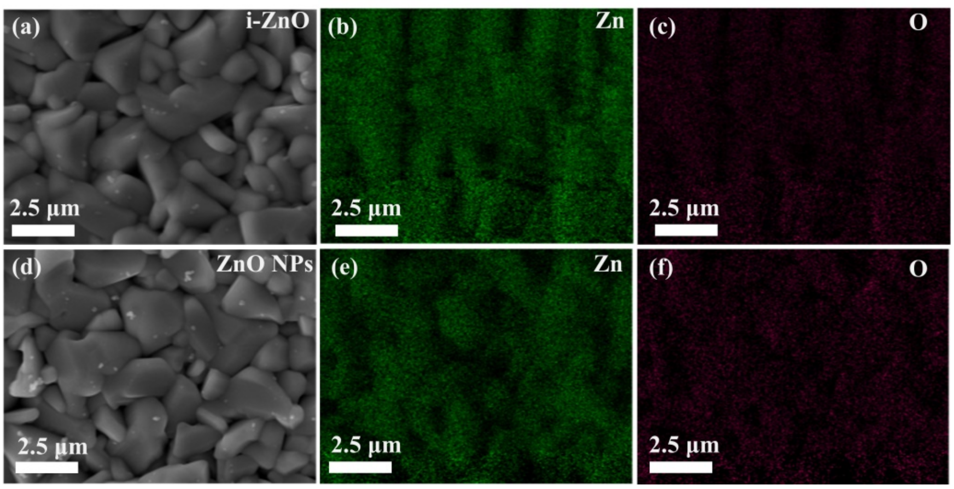

Figure S3. The SEM top-view images of the (a) sputtered i-ZnO/CdS/CZTSSe stack and (d) ZnO NPs/CdS/CZTSSe stack. The surface EDS element mapping of (b) Zn and (c) O for i-ZnO and (e) Zn and (f) O for ZnO NPs.

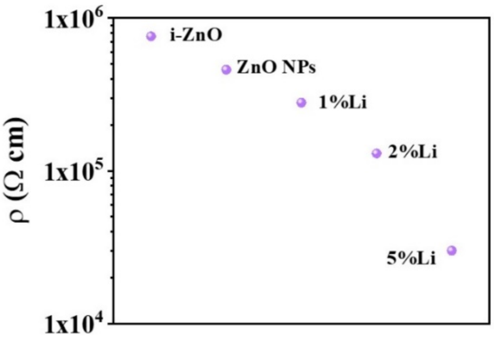

Figure S4 The resistivity ρ of sputtered i-ZnO and ZnO:Li NPs films with different Li content on soda-lime glass.

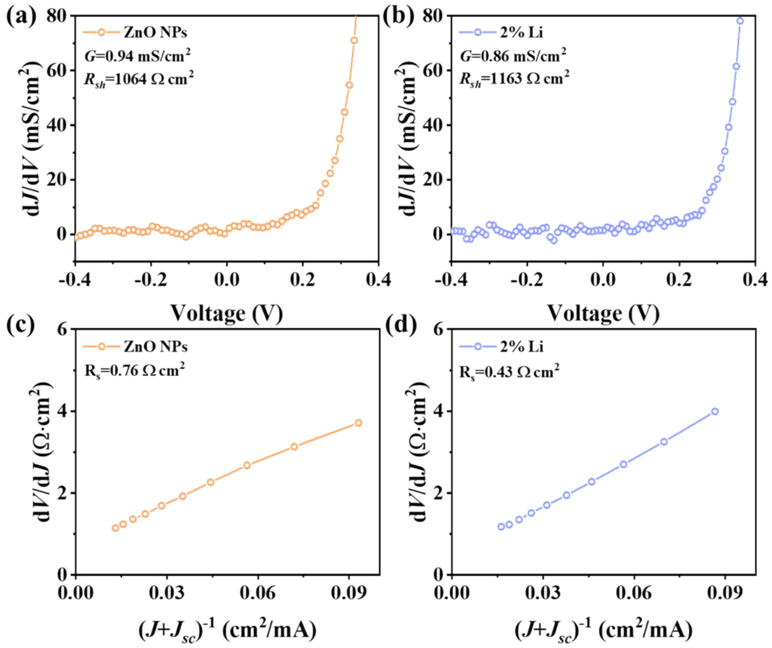

Figure S5 (a)-(b) are the shunt resistance and (c)-(d) are the series resistance of CZTSSe solar cells using ZnO NPs and ZnO:Li NPs window layer, respectively.

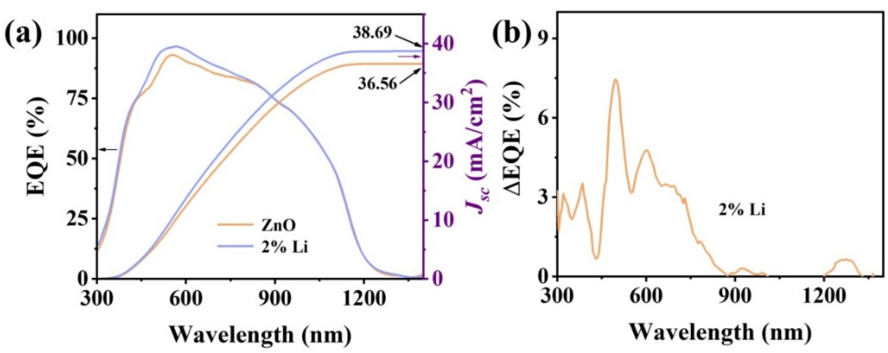

Figure S6. (a) EQE curves of CZTSSe solar cells using ZnO NPs and ZnO:Li NPs window layer. (b) The EQE difference (ΔEQE) of the CZTSSe solar cells before and after 2% Li doping.

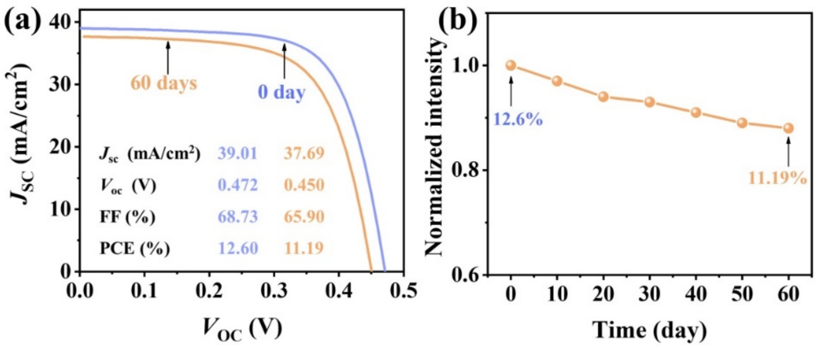

Figure S7 (a) The *J-V* curves of CZTSSe solar cells with 2% Li doping ZnO layer before and after 60 days storage. (b) The efficiency stability within 60 days for the champion CZTSSe device with 2% Li doping ZnO layer.

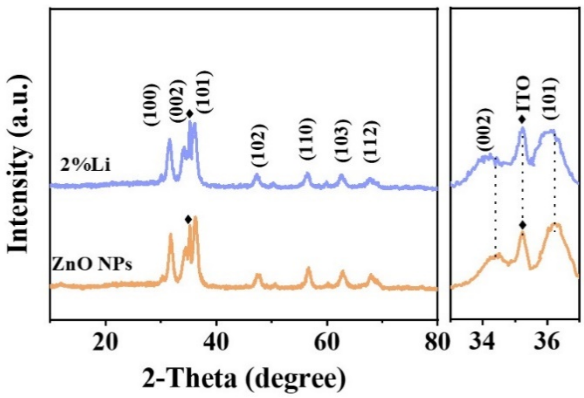

Figure S8 XRD of the pristine ZnO NPs and 2% ZnO:Li NPs films deposited on ITO glass.

$$q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda}$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

λ=1.5406 nm, a, b and c are cell parameters, (hkl) is the crystal face index, *d* is the interplanar spacing and 2*θ* is the diffraction angle. The unit cell parameters of ZnO wurtzite follow the principle that a=b≠c, α=β=90°, γ=120º. For the main peak (002) plane, the lattice parameters of pristine ZnO and ZnO:Li NPs are evaluated to be a=b=3.4216, c=5.4547 and a=b=3.4340, c=5.4830, respectively.

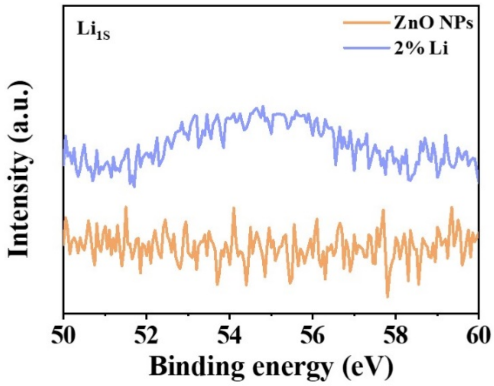

Figure S9 Li_{1S} of XPS for the pristine ZnO NPs and 2% ZnO:Li NPs films deposited on glass.

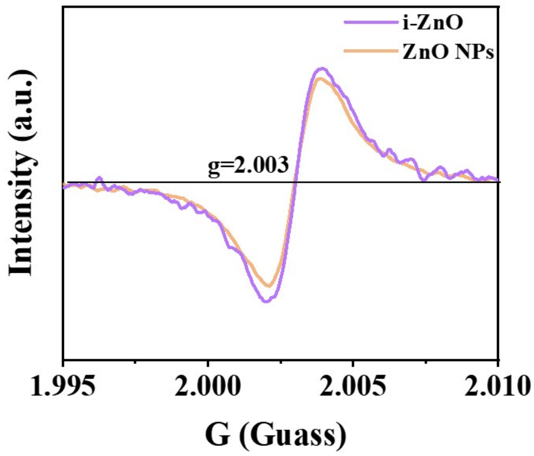

Figure S10. EPR of sputtered i-ZnO and solution-processed ZnO NPs films.

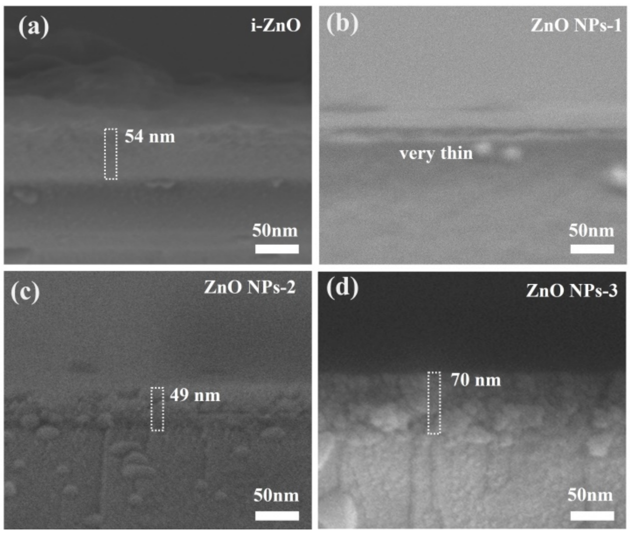

Figure S11 SEM cross-section morphologies of the (a) i-ZnO, (b) one layer of ZnO NPs films, (c) two layers of ZnO NPs films and (d) three layers of ZnO NPs films deposited on soda-lime glass.

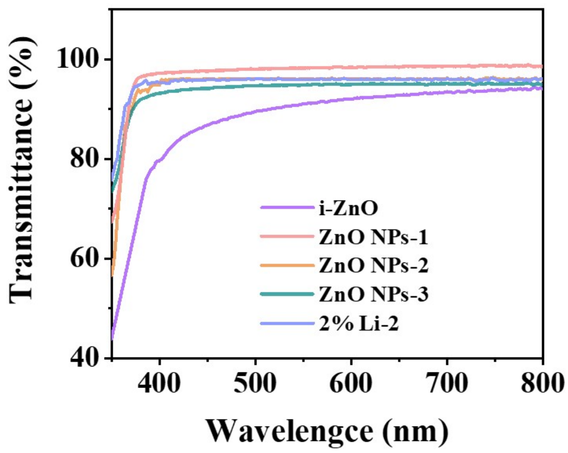

Figure S12 Transmittance spectrum of the sputtered ZnO, pristine ZnO NPs (1, 2, 3 layers) and ZnO:Li NPs (2 layers) films deposited on soda-lime glass.

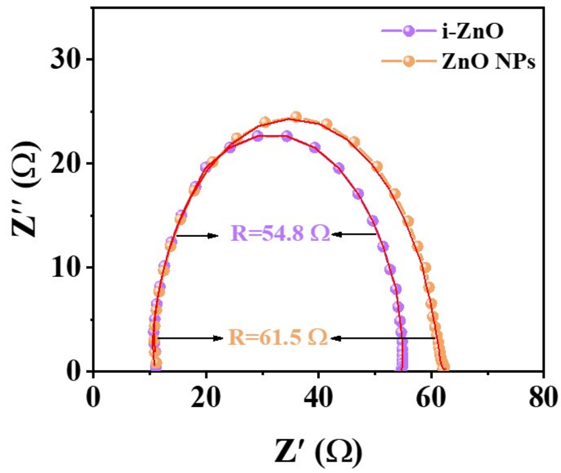

Figure S13 EIS Nyquist diagrams for the CZTSSe solar cells with i-ZnO and ZnO NPs window layers measured under -0.45 V.

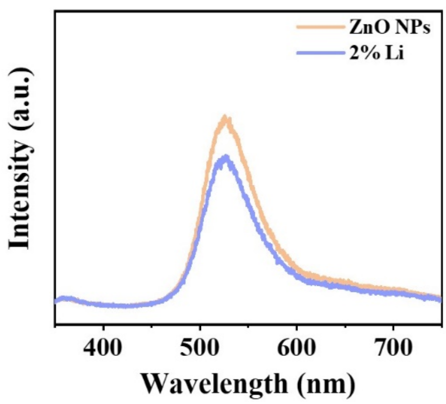

Figure S14 PL of pristine ZnO NPs and 2% ZnO:Li NPs films.

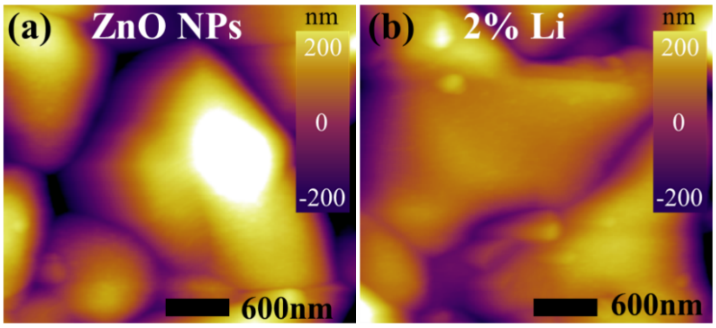

Figure S15 Two dimensional atomic force microscopy images of ZnO NPs/CdS /CZTSSe stack and ZnO:Li NPs/CdS/CZTSSe stack.

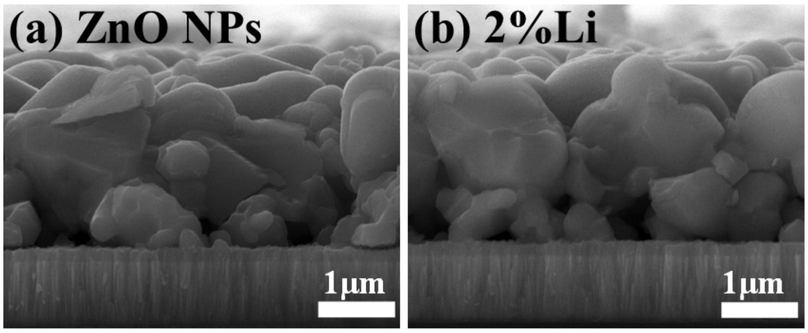

Figure S16 Cross-section scanning morphology of EBIC for the CZTSSe solar cells using ZnO NPs and ZnO:Li NPs window layer.

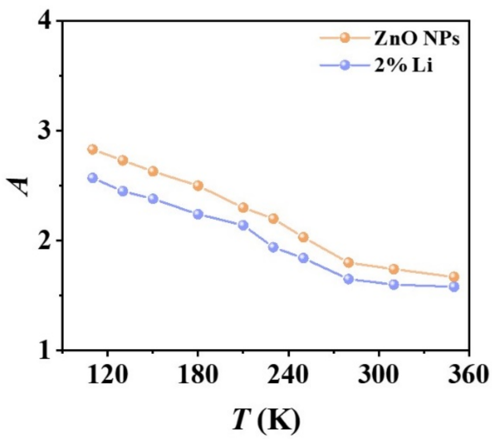

Figure S17 (a) The temperature-dependent ideal factor *A* of CZTSSe solar cells with ZnO NPs and 2% Li doping ZnO layers with the range of 350-100 K under dark condition.