Supporting Information

Heterojunction Lithiation Engineering and Diffusion-Induced Defects Passivation for Highly Efficient $Sb_2(S,Se)_3$ Solar Cells

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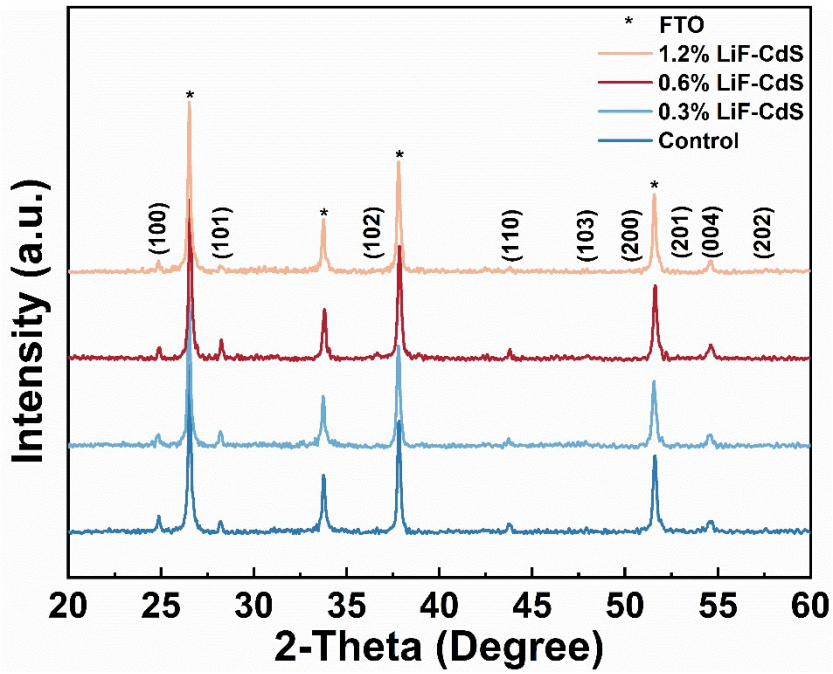

Fig. S1 XRD patterns of control, 0.3% LiF-CdS, 0.6% LiF-CdS and 1.2% LiF-CdS films.

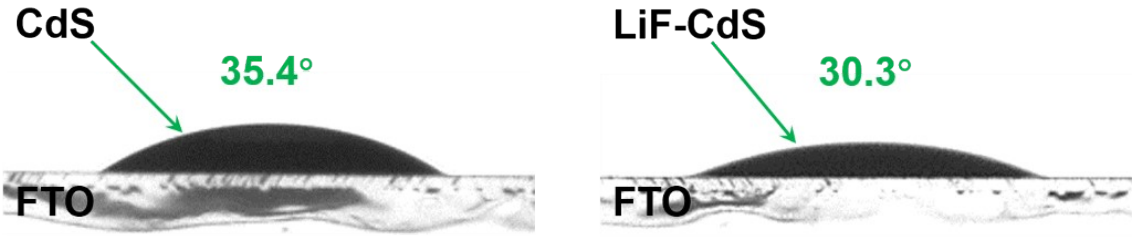

Fig. S2 Contact angle measurements of FTO substrates with pure CdS and LiF-CdS solutions.

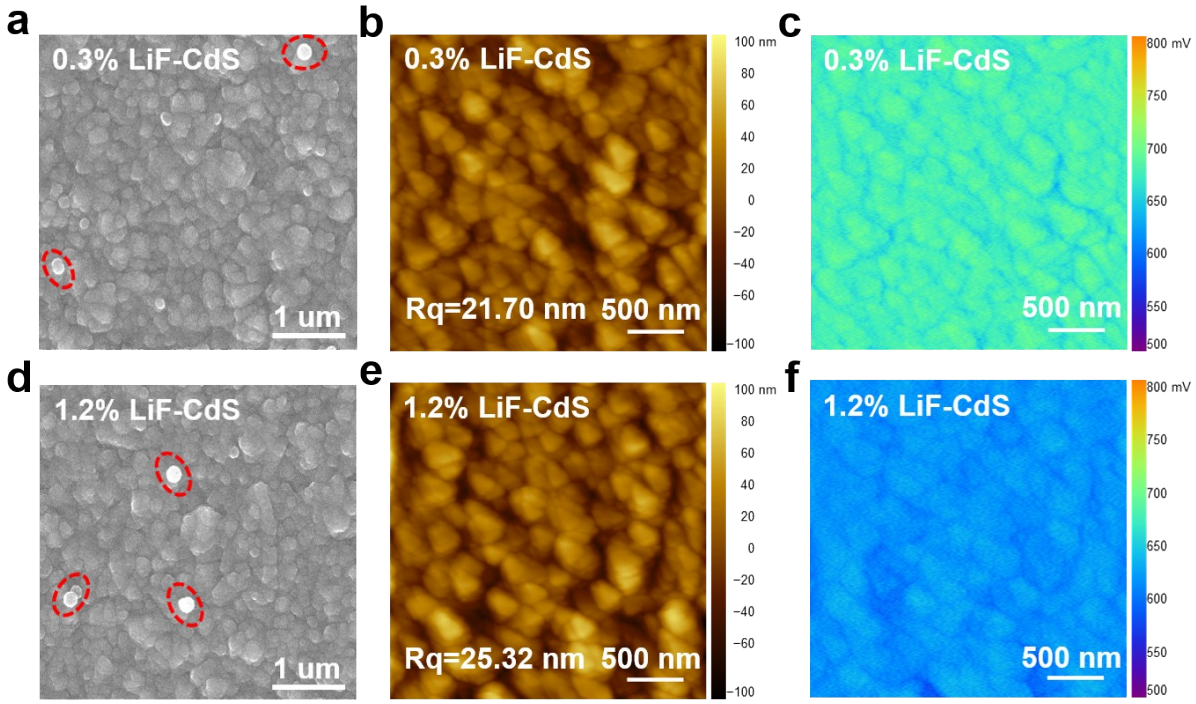

Fig. S3 Surface morphology and potential characterization of CdS films. (a, d) SEM, (b, e) AFM, (c, f) KPFM of the 0.3% LiF-CdS and 1.2% LiF-CdS films, respectively.

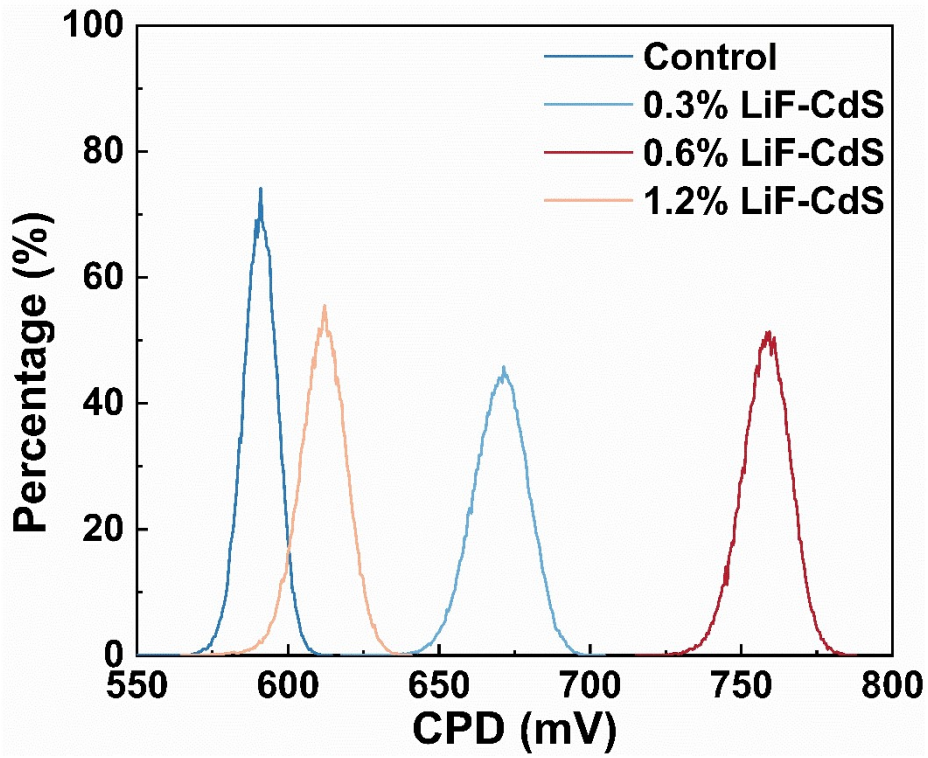

Fig. S4 Surface contact potential difference of control, 0.3% LiF-CdS, 0.6% LiF-CdS and 1.2% LiF-CdS films.

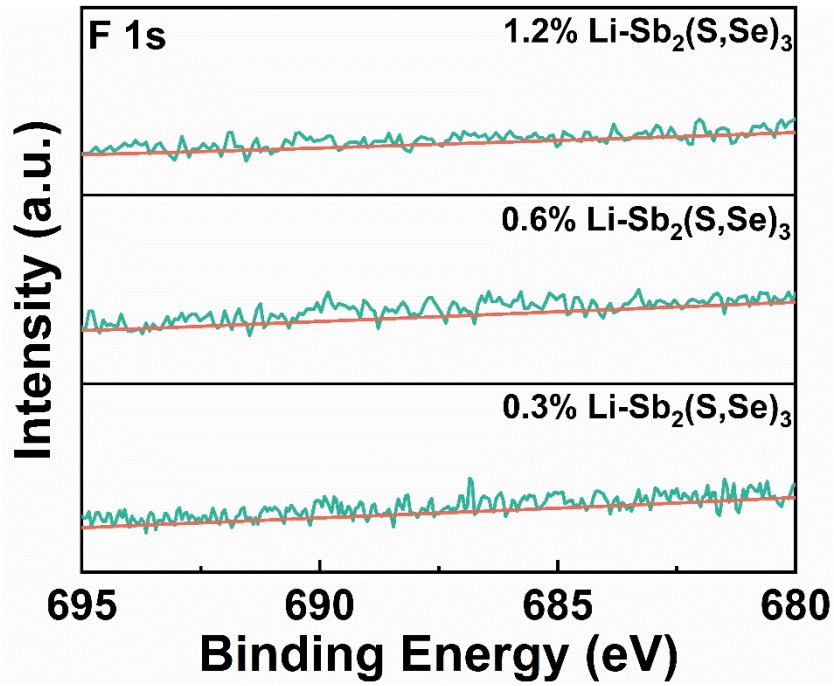

Fig. S5 F 1s XPS spectra of 0.3%, 0.6% and 1.2% Li-$Sb_2(S,Se)_3$ films.

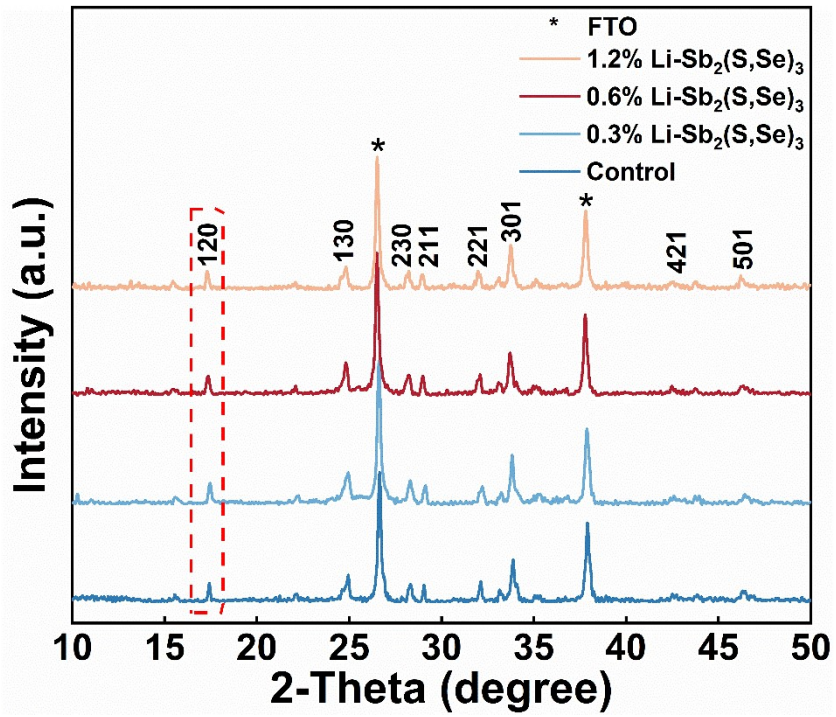

Fig. S6 XRD patterns of the control, 0.3%, 0.6% and 1.2% Li-$Sb_2(S,Se)_3$ films.

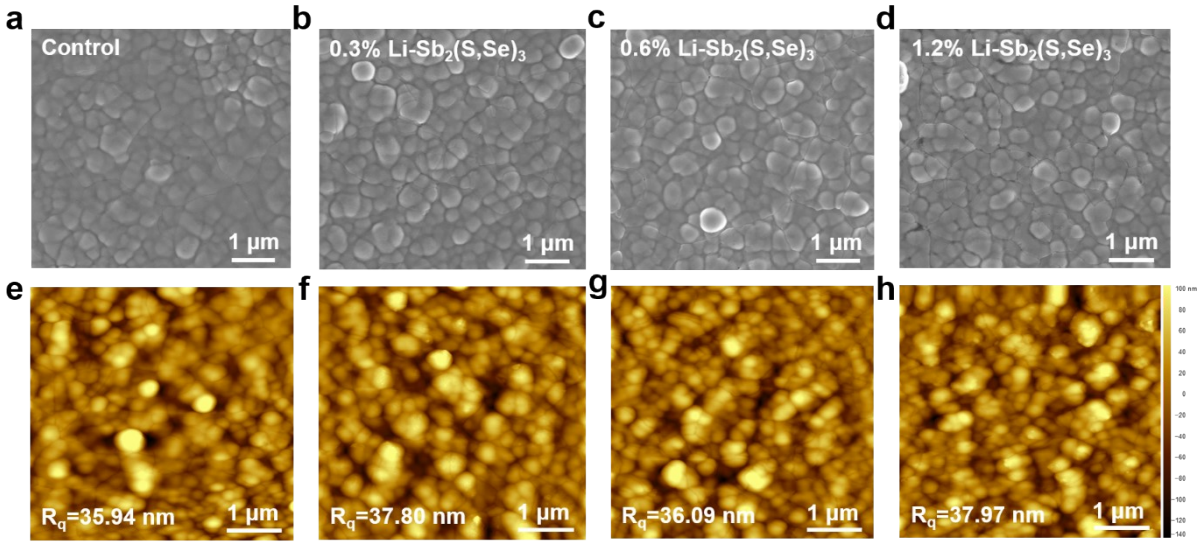

Fig. S7 Surface morphology and AFM images of $Sb_2(S,Se)_3$ films. (a-d) SEM and (e-h) AFM of the control, 0.3%, 0.6% and 1.2% Li-$Sb_2(S,Se)_3$ films, respectively.

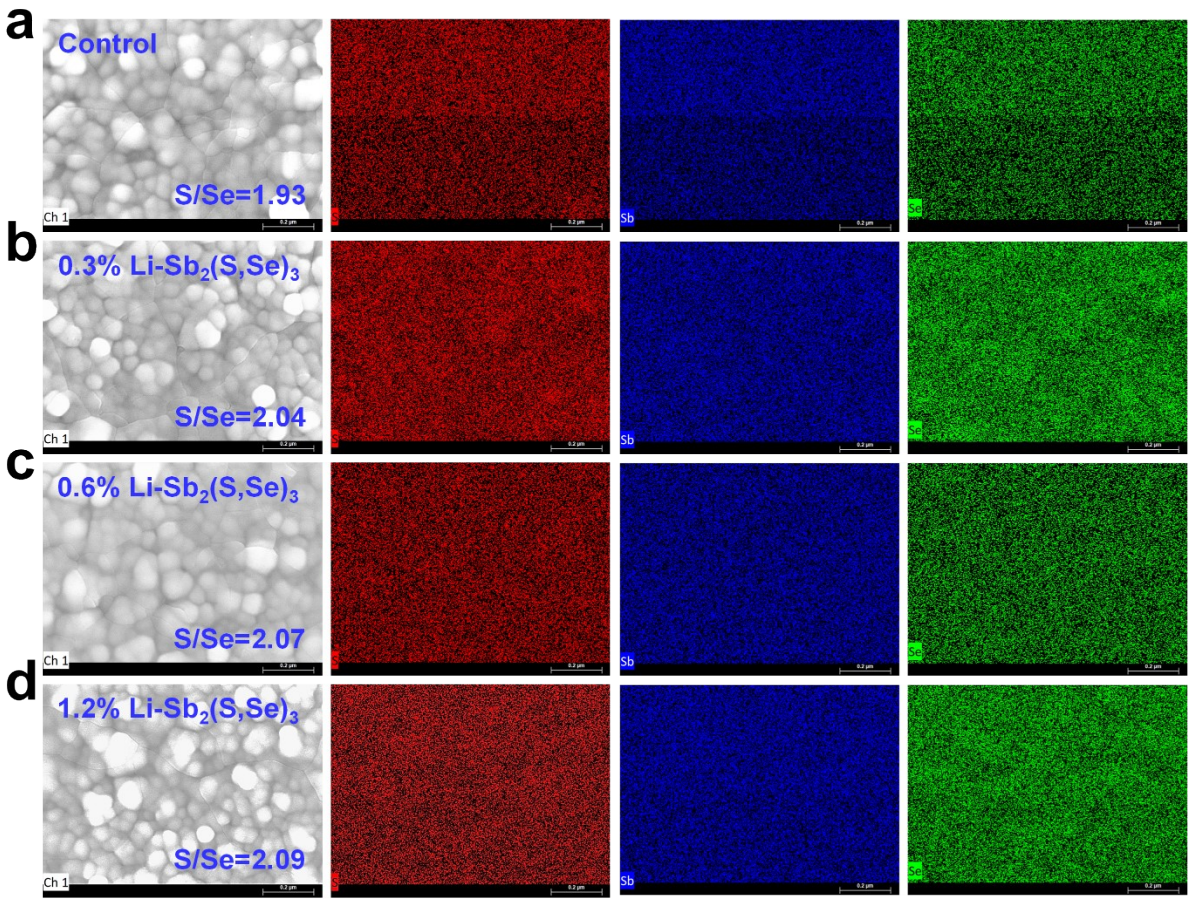

Fig. S8 SEM-EDS analysis of the different $Sb_2(S,Se)_3$ films.

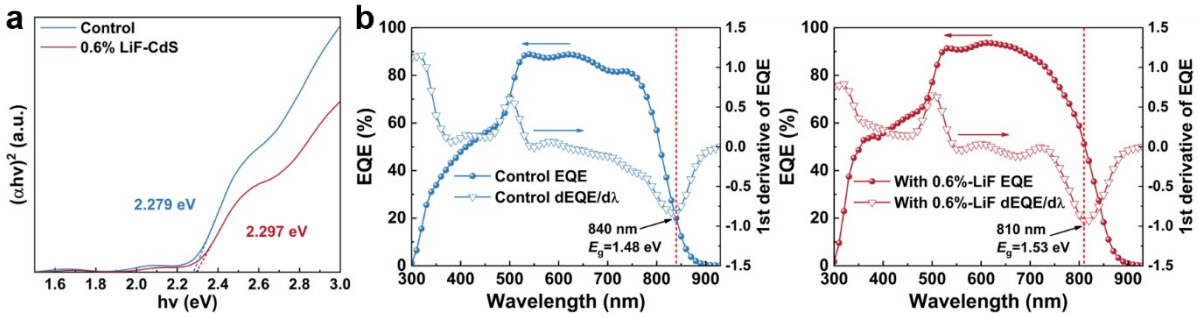

Fig. S9 Band gap characterization of CdS and $Sb_2(S,Se)_3$. (a) Tauc plots of the control and 0.6% LiF-CdS films. (b) EQE spectra and the first derivatives of dEQE/dλ for the control and 0.6% LiF incorporated devices.

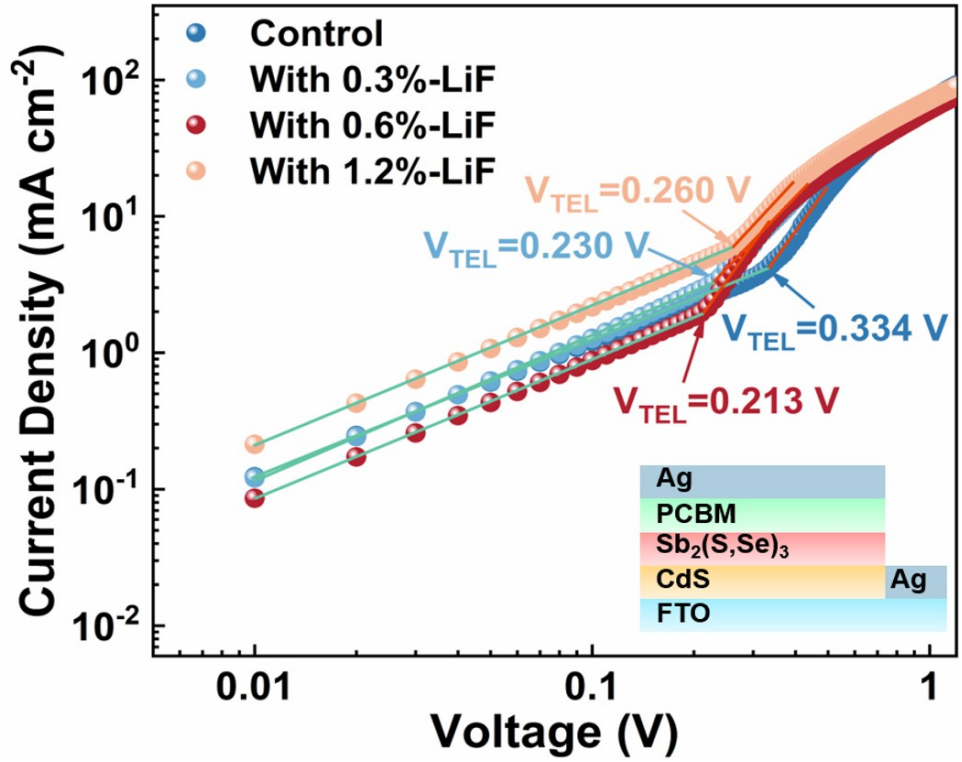

Fig. S10 *J-V* curves plotted using the space charge limited current (SCLC) model for the control and LiF incorporated devices.

Fig. S11 Certification reports of our champion cell were received from the South China National Center of Metrology (SCM).

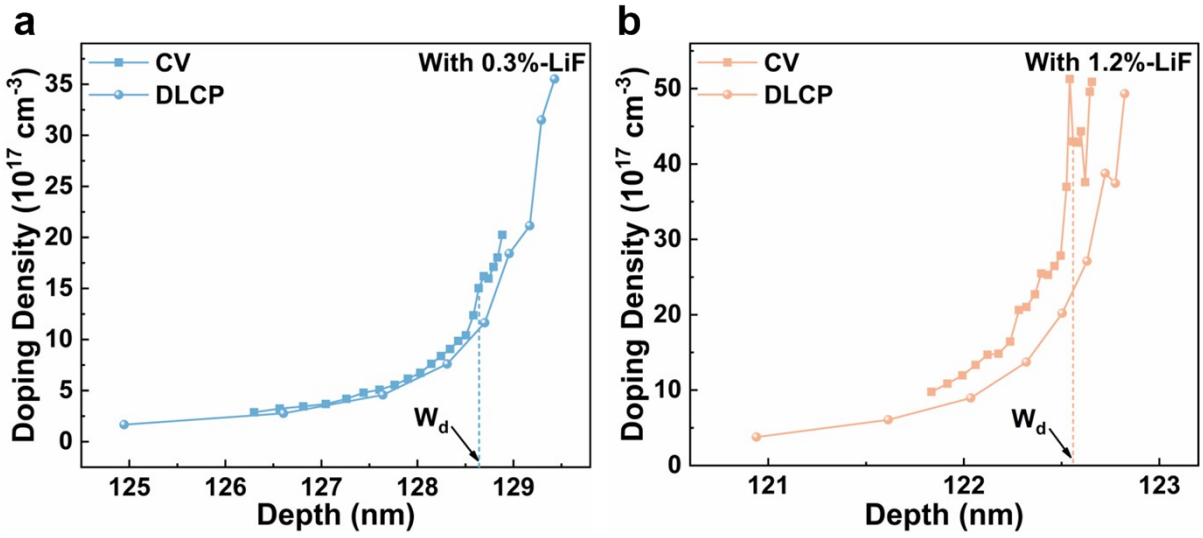

Fig. S12 (a, b) C-V and DLCP profiling for the 0.3% and 1.2% LiF incorporated devices, respectively.

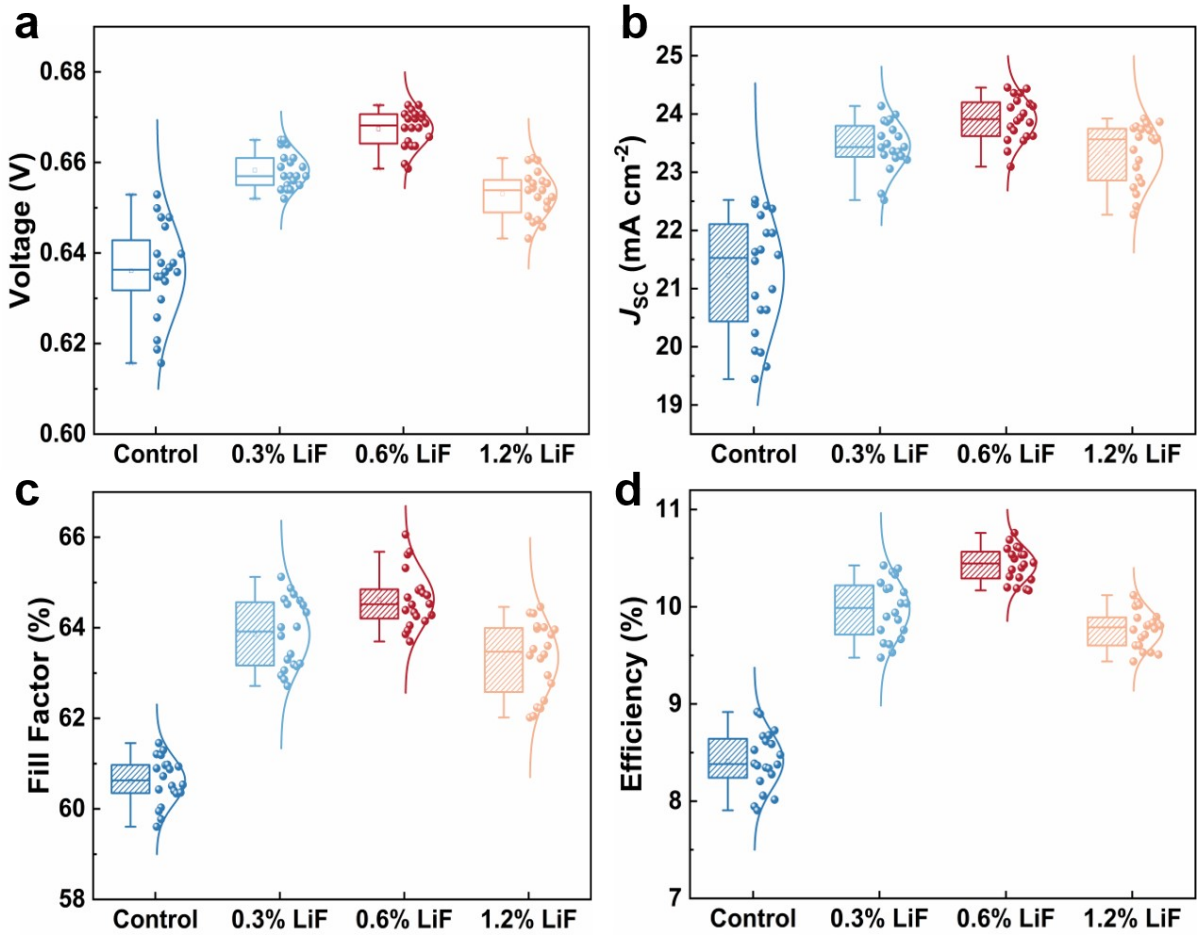

Fig. S13 Photovoltaic parameters statistics. Statistical box plots of (a) V_{OC}, (b) J_{SC}, (c) Fill Factor and (d) Efficiency for the control, 0.3%, 0.6% and 1.2% LiF incorporated devices, respectively.

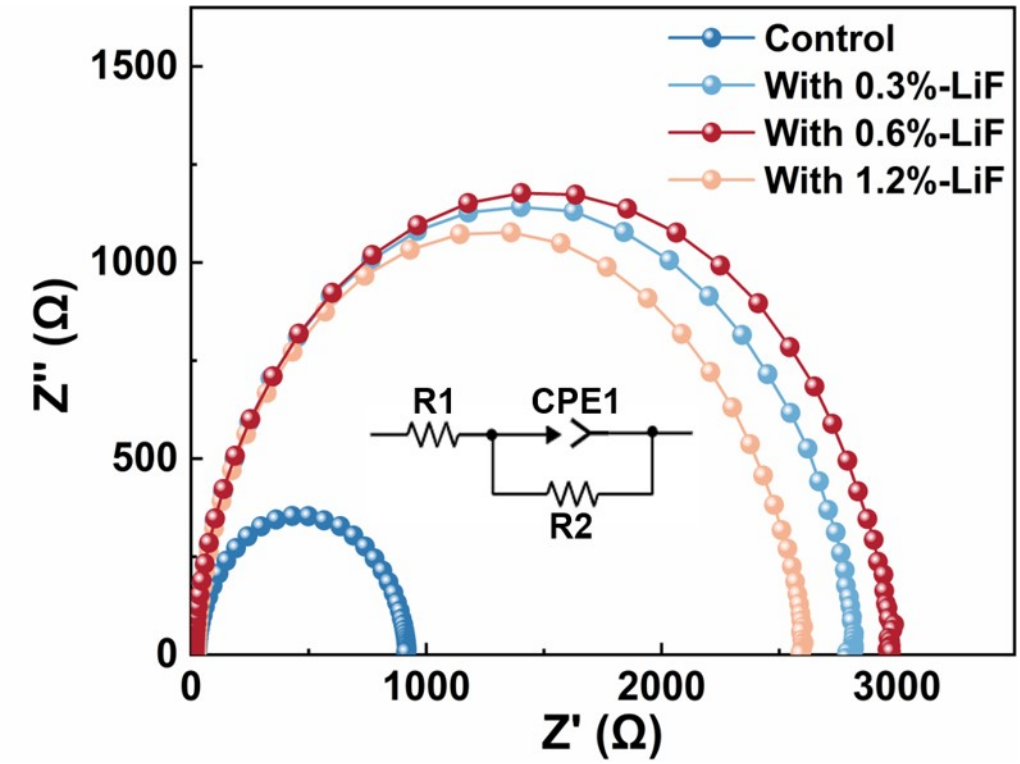

Fig. S14 Electrical impedance spectra (EIS) for the control and LiF incorporated devices.

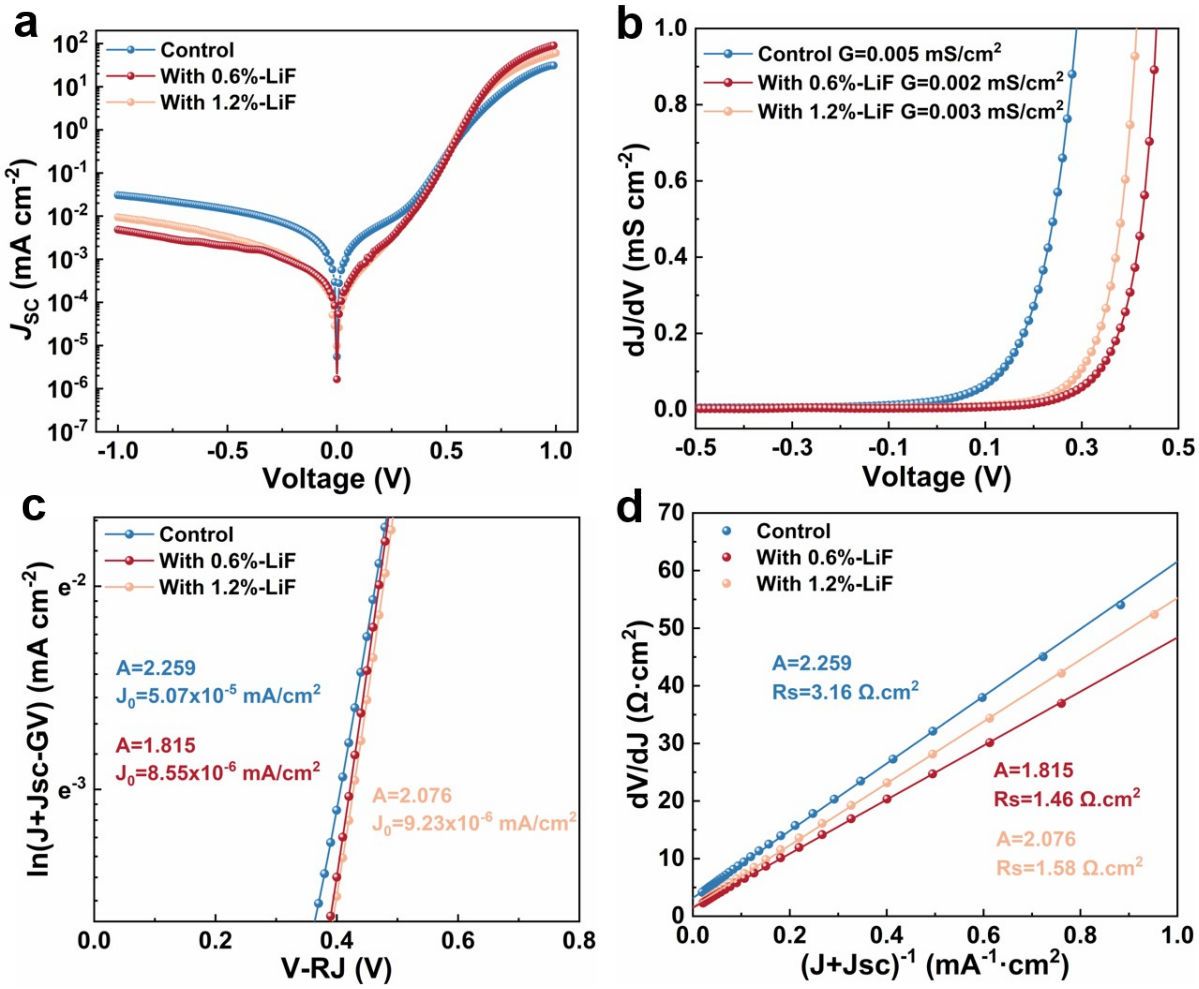

Fig. S15 Device Dark *J-V* Characteristics. (a) Dark *J-V* curves of the control and LiF-incorporated devices. (b) Characterization of shunt conductance G. (c) ln(J+J_{SC}−GV) with the fit used to determine A and J_0. (d) dV/dJ with the fit used to determine R_S and A.

Table S1. Hall tests of the control and LiF incorporated CdS films.

Sample	Resistivity (Ω cm)	Conductivity (1/Ω cm)	Mobility (cm^2/Vs)	Carrier Concentration ($1/cm^3$)	Hall Coefficient (cm^3/C)
Control	1.17×10^{4}	8.53×10^{-5}	1.96×10^{1}	-2.72×10^{13}	-2.30×10^{5}
With LiF	1.13×10^{4}	8.81×10^{-5}	8.73×10^{0}	-6.30×10^{13}	-9.91×10^{4}

Table S2. Biexponential fitting results of decay kinetics curves.

Sample	A_1 (%)	τ_1 (ps)	A_2 (%)	τ_2 (ps)	A_3 (%)	τ_3 (ps)	τ_{av} (ps)
Control	34.19	7.525	34.87	428.14	30.94	2955.51	2954.50
With LiF	23.16	9.056	32.79	435.58	44.05	3792.61	3524.12

Table S3. Interfacial defects of the control, 0.3%, 0.6% and 1.2% LiF incorporated devices, respectively.

Sample	N_{CV} (1/cm^3)	W_d(nm)	N_{DLCP} (1/cm^3)	N_{IT} (1/cm^3)
Control	6.34×10^{18}	116.36	3.55×10^{18}	2.79×10^{18}
With 0.3% LiF	1.50×10^{18}	128.64	1.16×10^{18}	3.39×10^{17}
With 0.6% LiF	1.33×10^{18}	145.09	1.09×10^{18}	2.40×10^{17}
With 1.2% LiF	4.30×10^{18}	122.56	2.02×10^{18}	2.28×10^{18}