

Supporting information

8.0% Efficient Sub-Micron CuIn(S,Se)₂ Solar Cells on Sn:In₂O₃

Back Contact via a Facile Solution Process

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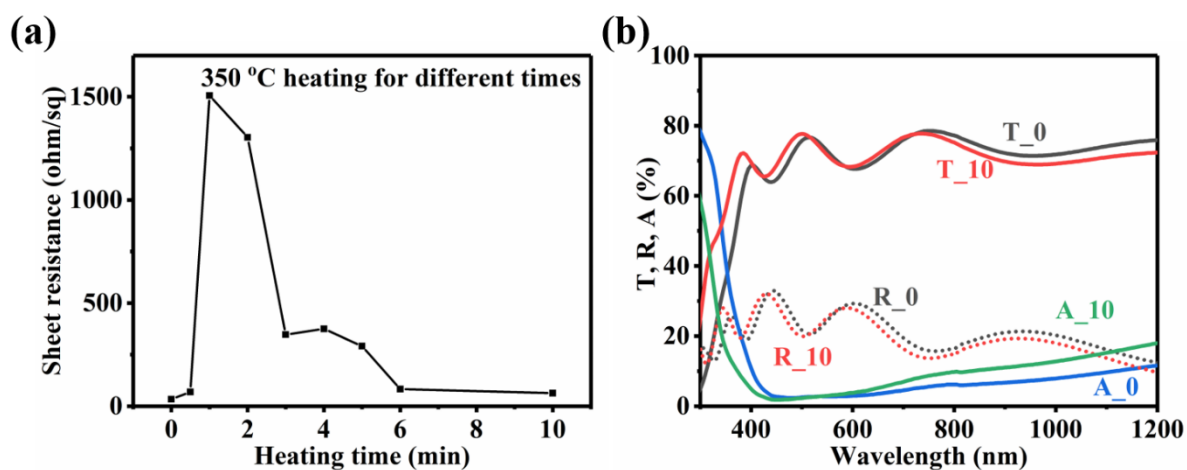


Figure S1 (a) Sheet resistance of 400 nm ITO films heated for different times at 350 °C under atmospheric conditions; (b) transmission, reflection, and absorption properties of 400 nm ITO without heating (T₀, R₀, and A₀) and with 10 min heating (T₁₀, R₁₀, and A₁₀).

Table S1 Composition of ultra-thin absorbers obtained under different selenization temperatures measured by XRF.

	Cu (at%)	In (at%)	Se (at%)	S (at%)	Cu/In	S/(S+Se)
500 °C	21.63	28.52	47.36	2.12	0.76	0.04
520 °C	19.50	25.32	35.23	19.62	0.77	0.36
540 °C	20.60	26.08	39.74	13.19	0.79	0.25
560 °C	18.04	23.83	25.86	31.92	0.76	0.55

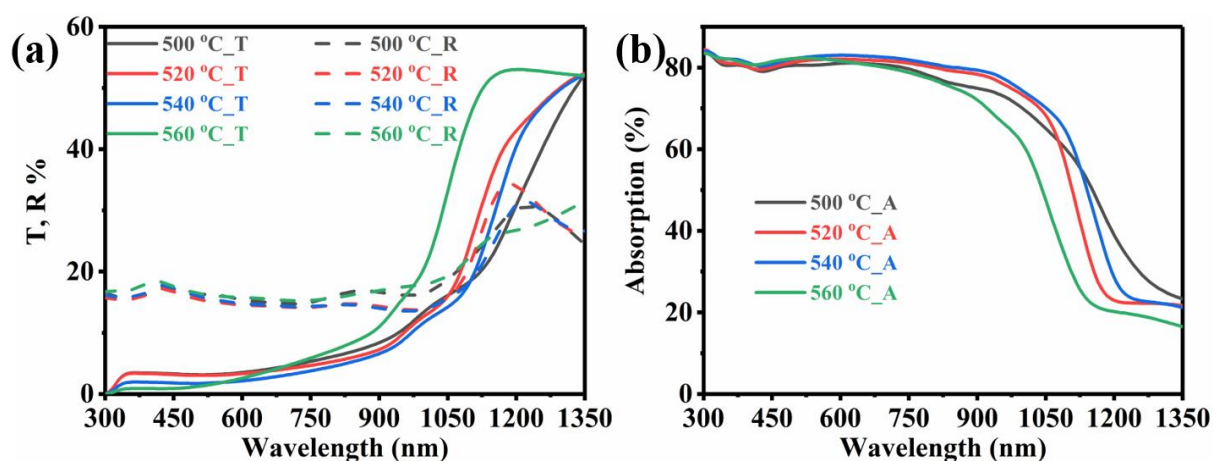


Figure S2 (a) transmission (solid line) and reflection (dashed line), (b) absorption of CISSe absorbers deposited on soda lime glass with various selenization temperatures.

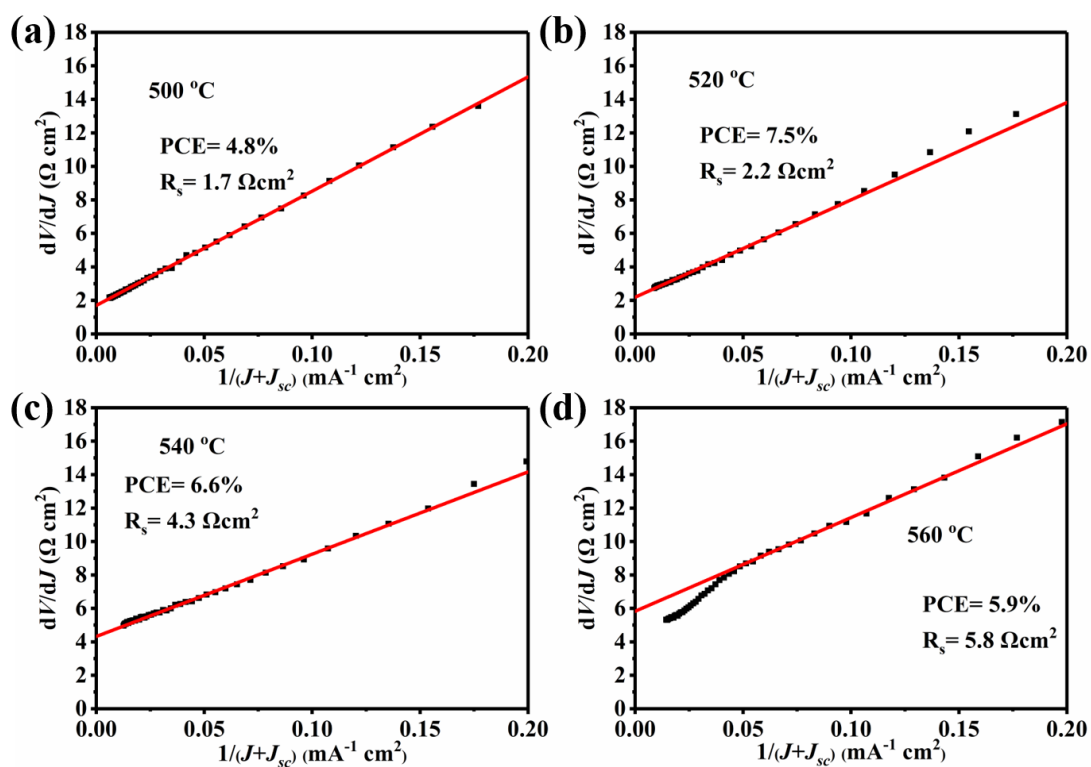


Figure S3 Determination of series resistance (R_s) for ultra-thin absorbers deposited on ITO back contact and selenized at different temperatures.

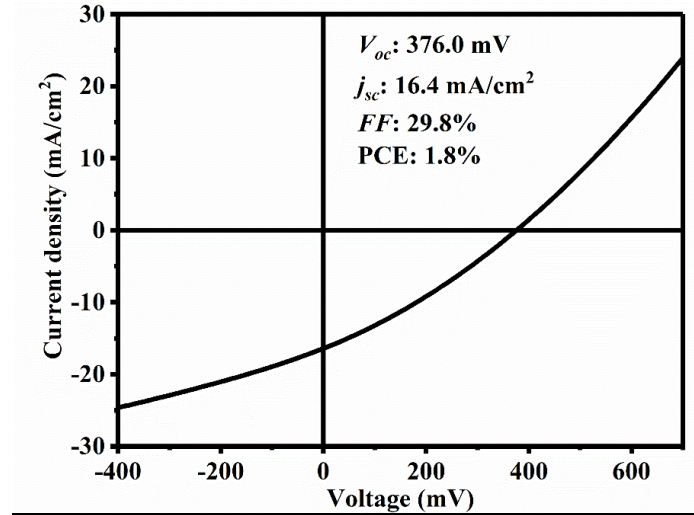


Figure S4 J - V curve of CISSe device with micron absorber thickness (1440 nm).

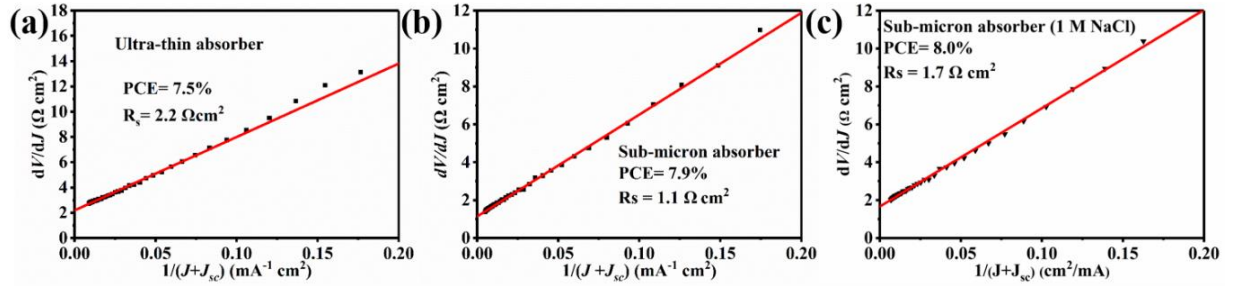


Figure S5 Determination of series resistance (R_s) for (a) ultra-thin absorber, (b) sub-micron absorber, and (c) sub-micron absorber with NaCl treatment deposited on ITO back contact and selenized at 520 °C.

Table S2 Averaged (over six devices) and best CISSe photovoltaic device parameters without and with various concentrations of NaCl treatment. The absorber thickness is 740 nm.

	V_{oc} (mV)	j_{sc} (mA/cm ²)	FF (%)	η (%)
no additional NaCl	448.5±2.6	29.1±0.6	56.3±3.2	7.3±0.4
	445.6	29.7	59.8	7.9
0.4 M NaCl	449.3±3.9	29.2±0.6	57.2±1.3	7.5±0.1
	450.0	29.2	58.8	7.7
0.8 M NaCl	432.6±9.9	28.3±1.2	53.4±3.3	6.5±0.6
	439.9	27.6	59.0	7.2
1 M NaCl	463.9±5.9	28.2±0.6	58.0±2.0	7.6±0.3
	466.0	28.7	59.6	8.0

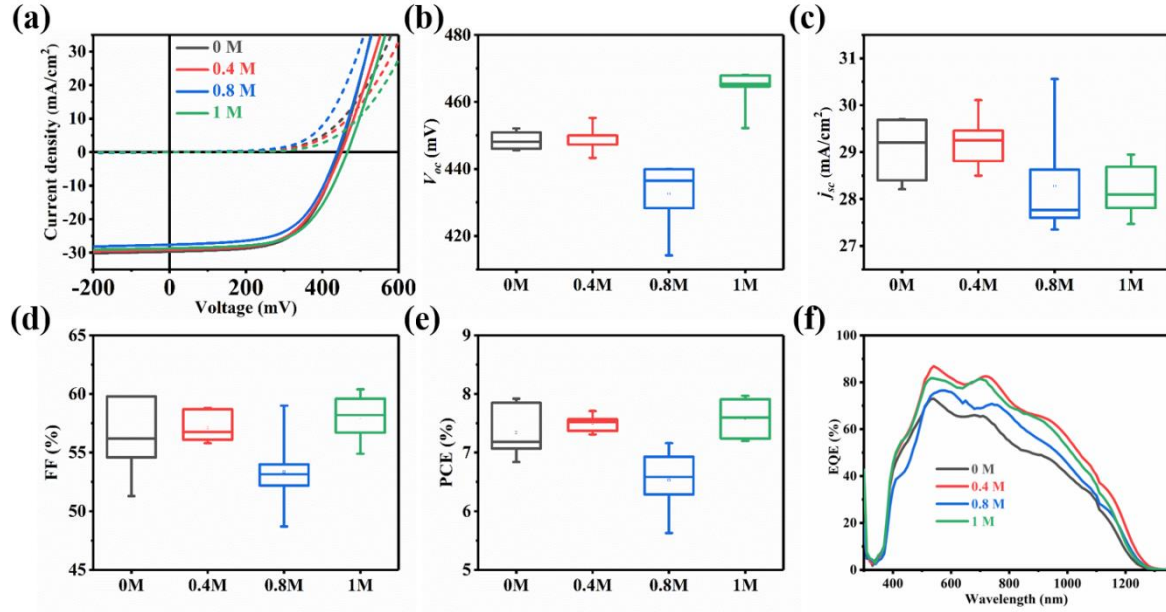


Figure S6 (a) J - V curves and (f) EQE spectra of the best sub-micron CISSe devices without and with different concentrations of NaCl for preselenization treatment. The distribution of (b) V_{oc} , (c) j_{sc} , (d) FF , and (e) PCE.

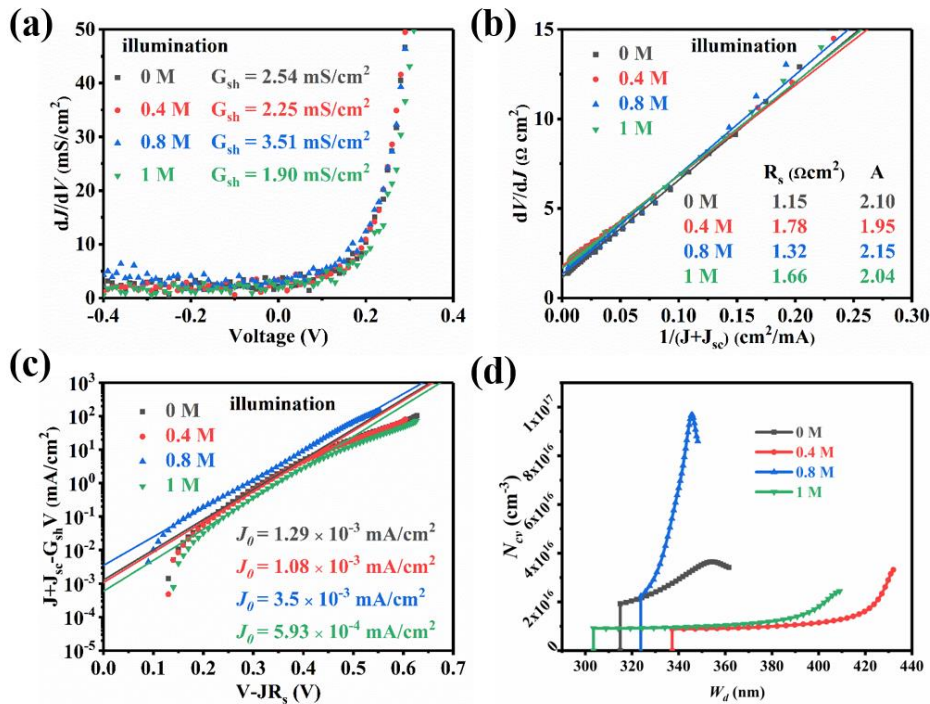


Figure S7 Plots of (a) dJ/dV vs. V for extraction of G_{sh} , (b) dV/dJ vs. $1/(J+J_{sc})$ for derivation of R_s and A , and (c) semi-logarithmic plot of $J+J_{sc}-G_{sh}V$ vs. $V-JR_s$ to determine J_0 ; (d) space-charge density N_{cv} and depletion width W_d for CISSe solar cells with sub-micron absorber without NaCl and with various concentrations of NaCl for preselenization treatment.

Table S3 Summary of electrical parameters extracted from further J - V and C - V analysis of the best CISSe solar cells without and with various concentrations of NaCl treatment. The absorber thickness was 740 nm.

	G_{sh} (mS/cm ²)	R_{sh} ($\Omega \cdot \text{cm}^2$)	R_s ($\Omega \cdot \text{cm}^2$)	j_0 (mA/cm ²)	A	N_{cv} (cm ⁻³)	W_d (nm)
no additional NaCl	2.54	393.70	1.15	1.29×10^{-3}	2.10	1.9×10^{16}	315.0
0.4 M NaCl	2.25	444.44	1.78	1.08×10^{-3}	1.95	8.9×10^{15}	337.3
0.8 M NaCl	3.51	284.90	1.32	3.50×10^{-3}	2.15	2.2×10^{16}	323.8
1 M NaCl	1.90	526.32	1.66	5.93×10^{-4}	2.04	9.1×10^{15}	303.5

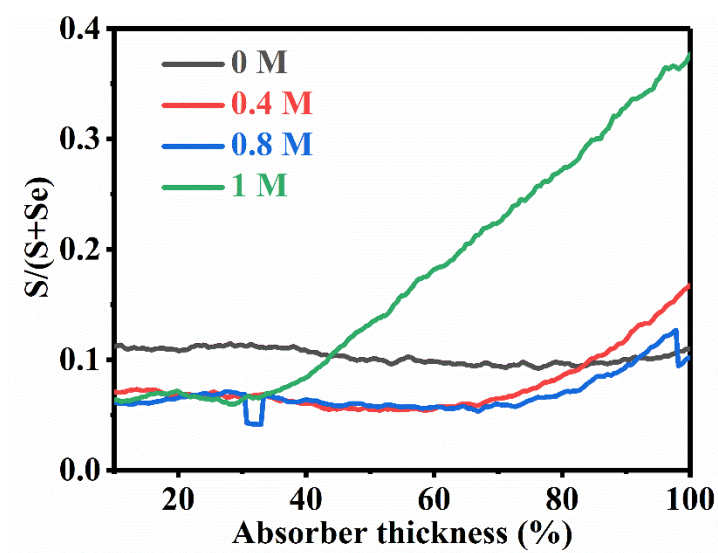


Figure S8 $S/(S+Se)$ ratios of sub-micron absorbers subject to different concentrations of NaCl solution for preselenization treatment.

Table S4 Overview on high-performance CIGSSe-based solar cells deposited on transparent conductive back contact via a solution process.

Precursor	Deposition	Device	Thickness	η	Reference
Cu and In oxide NPs and Ga oxide	Screen printing	FTO/Cu(In,Ga)Se ₂ /CdS/i-ZnO/ZnO:Al	1.3 μm	6.1%	[S1]
CuIn _x Ga _{1-x} S ₂ nanoparticles	doctor blading	FTO/Cu(In,Ga)Se ₂ /CdS/i-ZnO/ZnO:Al	2 μm	6.5%	[S2]
Cu(NO ₃) ₂ , In(NO ₃) ₃ and Ga(NO ₃) ₃	spin-coating	ITO/Cu(In,Ga)S ₂ /CdS/i-ZnO/ZnO:Al	800 nm	5.7%	[S3]
			1.1 μm	6.6%	[S4]
CuCl, InCl ₃ and Thiourea	spin-coating	ITO/CuIn(S,Se) ₂ /CdS/i-ZnO/ZnO:Al	550 nm	7.5%	Our work
			740 nm	8.0%	

References

- [S1] Sousa, V.; Goncalves, B. F.; Rosen, Y. S.; Virtuoso, J.; Anacleto, P.; Cerqueira, M. F.; Modin, E.; Alpuim, P.; Lebedev, O. I.; Magdassi, S.; Sadewasser, S.; Kolen'ko, Y. V. Over 6% Efficient Cu(In,Ga)Se₂ Solar Cell Screen-Printed from Oxides on Fluorine-Doped Tin Oxide. *ACS Appl. Energy Mater.* 2020, 3, 3120-3126.
- [S2] Park, S. J.; Cho, J. W.; Park, G. S.; Jeong, J. S.; Kim, J.; Ko, D.-H.; Hwang, Y. J.; Min, B. K. A Comparative Study of Nanoparticle-Ink-Based CIGSSe Thin Film Solar Cells on Different Back Contact Substrates. *Bull. Kor. Chem. Soc.* 2016, 37, 361-365.
- [S3] Barange, N.; Chu, V. B.; Nam, M.; Ahn, I. H.; Kim, Y. D.; Han, I. K.; Min, B. K.; Ko, D. H. Ordered Nanoscale Heterojunction Architecture for Enhanced Solution-Based CuInGaS₂ Thin Film Solar Cell Performance. *Adv. Energy Mater.* 2016, 6, 1601114.
- [S4] Chu, V. B.; Park, S. J.; Park, G. S.; Jeon, H. S.; Hwang, Y. J.; Min, B. K. Semi-transparent Thin Film Solar Cells by a Solution Process. *Korean J. Chem. Eng.* 2016, 33, 880-884.