Supporting Information

Solution-processed $CuIn(S,Se)_2$ solar cells on transparent electrode offering 9.4% efficiency

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Experimental Section

Preparation of the molecular precursor solutions: The precursor solution was prepared according to our previous reports.[1,2] Briefly, 2.4358 g thiourea (Tu) was added into 10 mL DMF under stirring to form a clear solution, then 0.6316 g CuCl (99.999%, Aldrich) was added into the clear solution and stirred intensely. After CuCl completely dissolved, 1.8708 g $InCl_3 \cdot 4H_2O$ (99.99%, Aladdin) was added and stirred until completely dissolved (The molar ratio of Cu: In: S in the solution was 1:1:5).

Preparation of CISSe absorber films: CISSe absorber films were prepared by a simple spin-coating and subsequent selenization. The precursor films were fabricated on fluorine-doped tin oxide (FTO) substrates in a glovebox with O_2 and H_2O levels below 10 ppm. The FTO substrates (sheet resistance 7 Ω/sq, purchased from Shenzhen South China Xiangcheng Technology Co., Ltd.) were cleaned by subsequent sonication in ultrapure water, acetone and isopropanol, each for 15 min, and then dried by a nitrogen flow. The precursor solution was filtered with 0.8 μm PTFE filter and spin-coated on FTO substrates at 4000 rpm for 60 s. The films were immediately annealed on a hot plate at 300 ℃ for 1min and cooled down naturally.

The coating-annealing-cooling cycle was repeated 10 times. Then, the films were put into a graphite box with Se tablets (0.35~0.38 g) and placed in a tube furnace for selenization. The selenization was performed in a 0.16 Mpa Ar_2 atmosphere for 20 min and the selenization temperature was set at 600 ℃.

Fabrication of CISSe solar cells: After selenization, the absorber film was first etched in 14% $(NH_4)_2S$ solution for 15 min and then 50 nm CdS buffer layer was deposited on the top of the absorber by chemical bath deposition (CBD). CBD was performed by loading the sample into a 65 ℃ water bath beaker containing 22 mL 18.46 mmol/L $CdSO_4$ (99%, Sinopharm Chemical Reagent Co., Ltd.) aqueous solution, 28 mL NH_4OH (25~28%, Sinopharm Chemical Reagent Co., Ltd.) and 150 mL ultrapure water under stirring. After stirred for 1 min, 22 mL 0.75 mol/L aqueous solution of Tu (99%, Aladdin, recrystallized twice) was poured into the bath beaker and the solution was kept stirred for 15 min. A window layer containing 50 nm i-ZnO and 250 nm ITO were deposited on top of CdS by RF sputtering followed by thermal deposition of top contacts of nickel and aluminum through a shadow mask. The solar cell area was defined by mechanical scribing for approximately 0.10 cm^2.

Film and device characterizations: The *J-V* curves were measured using Keithley 2400 Source Meter under simulated AM 1.5 sunlight at 100 mW/cm^2 irradiance generated by an AAA sun simulator (CROWNTECH, Inc.) with the intensity calibrated by an NREL calibrated Si reference cell. The *J-V* measurement was performed in air at a temperature of 300 K and a humidity of 40%. The scanning speed was 0.2 V/s without dwell. The EQE of the solar cells were measured on Enlitech QE-R3018 using calibrated Si and Ge diodes (Enli technology Co., Ltd.) as references. The film morphology was measured on Hitachi S4800 SEM using 5 kV power. XRD patterns (2θ scan) were collected by a Siemens D5005 X-ray powder diffraction system using Cu K (λ = 1.5406 Å) X-ray as the source at a scan rate of 6°/min.

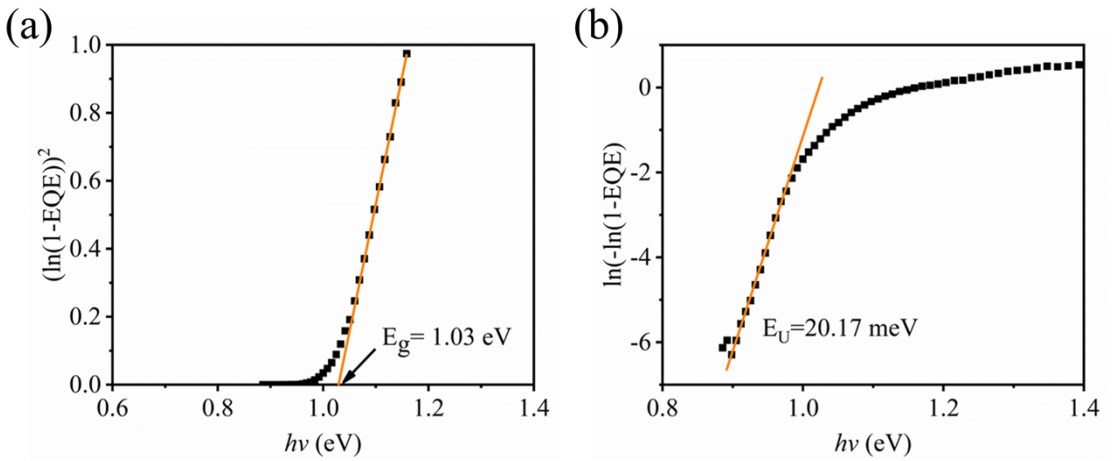

Fig. S1. (a) Band gap of the champion CISSe solar cell on FTO substrate. (b) Urbach energy of the champion CISSe solar cell on FTO substrate.

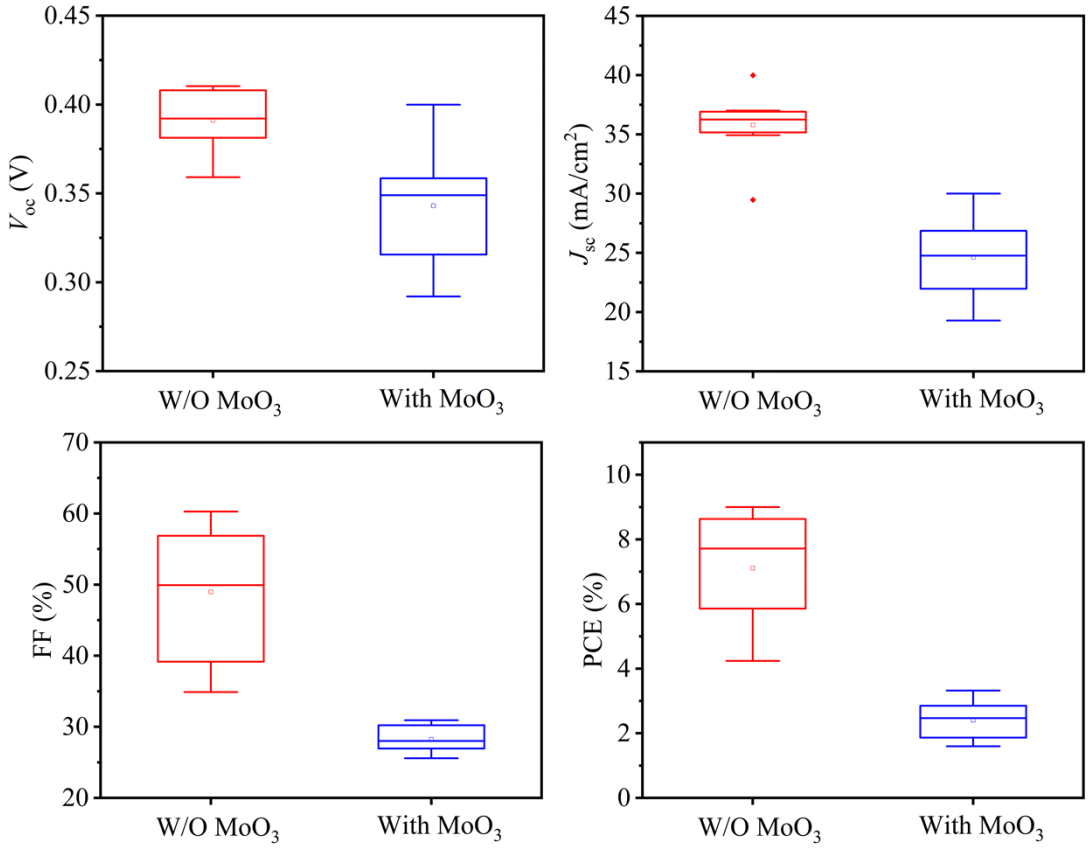

Fig. S2. The box-plots of the statistical device photovoltaic parameters of CISSe solar cells on FTO substrate without and with MoO_3.

Table S1. The resistance (Ω/square) of bare FTO substrates and FTO selenized at

different temperatures of 560 ℃, 580 ℃ and 600 ℃ (named FTO-560 ℃, FTO-580 ℃ and FTO-600 ℃).

Samples	Average resistance (Ω/square)
Bare FTO	7.58
FTO-560 ℃	9.16
FTO-580 ℃	9.70
FTO-600 ℃	10.84

References

[1] Jiang J, Yu S, Gong Y, et al. 10.3% Efficient $CuIn(S,Se)_2$ solar cells from DMF molecular solution with the absorber selenized under high argon pressure. Sol. RRL 2018, 2, 1800044.

[2] Jiang J, Giridharagopal R, Jedlicka E, et al. Highly efficient copper-rich chalcopyrite solar cells from DMF molecular solution. Nano Energy, 2020, 69, 104438.