Electronic Supplementary Information

In-situ fast oxidation of spiro-OMeTAD hole transport layers under ambient indoor lighting compatible with air-processed perovskite solar cells

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Experimental Section

Reagents and materials: The SnO_2 solution was purchased from Xi'an Yuri Solar Co., Ltd (tin(IV) oxide, 12 wt% in H_2O). DMF, DMSO, chlorobenzene, acetonitrile, PbI_2 and FAI were purchased from Advanced Election Technology Co., Ltd. Other materials were purchased from Xi'an Yuri Solar Co., Ltd. All reagents and materials were used directly without further purification.

Fabrication of SnO_2 films: The SnO_2 solution was diluted in deionized water (1:3, v/v), denoted as SnO_2 precursor. After that, the SnO_2 precursor was ultrasonic treated for 40 min at 20°C, and filtered by a 0.45 mm PVDF syringe filter before used. FTO substrate was sequentially cleaned with deionized water, ethanol, isopropanol, and acetone before undergoing UV-ozone treatment for 15 min. Then the precursors were spin-coated on the clean FTO substrate at 3000 rpm for 30 s and annealed at 150°C for 60 min in atmospheric environment. Finally, the SnO_2 films were acquired.

Device fabrication: To prepare the perovskite precursor, 742.2 mg PbI_2, 224.4 mg FAI, 16.2 mg MABr, 19.8 mg CsI, and 20.3 mg MACl were dissolved into 1 mL of the DMF/DMSO (4 :1 volume ratio) solvent. The perovskite layer was deposited using an anti-solvent method, with ethyl acetate (EA) as the anti-solvent. The perovskite precursor was spin-coated onto the ETL at 500 rpm for 5 s and 4000 rpm for 30 s. EA was dropped on the substrate at 25 s of the spin-coating procedure. Next, the substrates were thermally annealed in air atmosphere at 150°C for 20 min. The HTL precursor was composed of 72.3 mg of Spiro-OMeTAD, 28.5 μL of 4-*tert*-butylpyridine, 17.5 μL of Li-TFSI (520 mg mL^{-1} in acetonitrile) and 1.0 mL of chlorobenzene. The HTL precursor was spin-coated at 3000 rpm for 40 s and undergo different oxidation processes. Finally, an Au electrode of about 50 nm thickness was deposited on the substrate in an evaporator. The 0.09 cm^2 device active area was determined by a metal mask. All processes of fabrication, storage, and measurement of the devices were carried out under atmospheric conditions (≈ 35% RH, 22°C).

HTL oxidation processes: The same batch of indoor light oxidized half-devices was placed under identical ambient air conditions for the same total duration, with varying light exposure times controlled by adjusting the shading. The indoor light intensity used in the experiment was approximately 3.9 W m^{-2} (FSL, LED T8 16W 6500K). For the dark oxidation, the half-devices were stored in air with a relative humidity of approximately 8% for 12 h.

Characterization and Measurement: ESR spectra were acquired using an EPR200 spectrometer from CIQTEK Co., Ltd. KPFM tests were carried out on a Bruker Dimension Fastscan. Photoluminescence (PL, FLS980, Ediburgh Instruments) spectra can track optical properties such as fluorescence intensity. In-situ PL and TRPL were recorded on a FLS1000 fluorescence spectrometer (Edinburgh Instruments). The devices were illuminated under AM1.5G sunlight (100 mW cm^{-2}) simulated by XES-100S1 (Class AAA, San-EI Electric Co., Ltd.). The light intensity of the solar simulator was calibrated by a standard Si solar cell (1218, Newport, USA). SCLC curves were obtained with an electrochemical workstation (VersaSTAT 3, Ametek, USA).

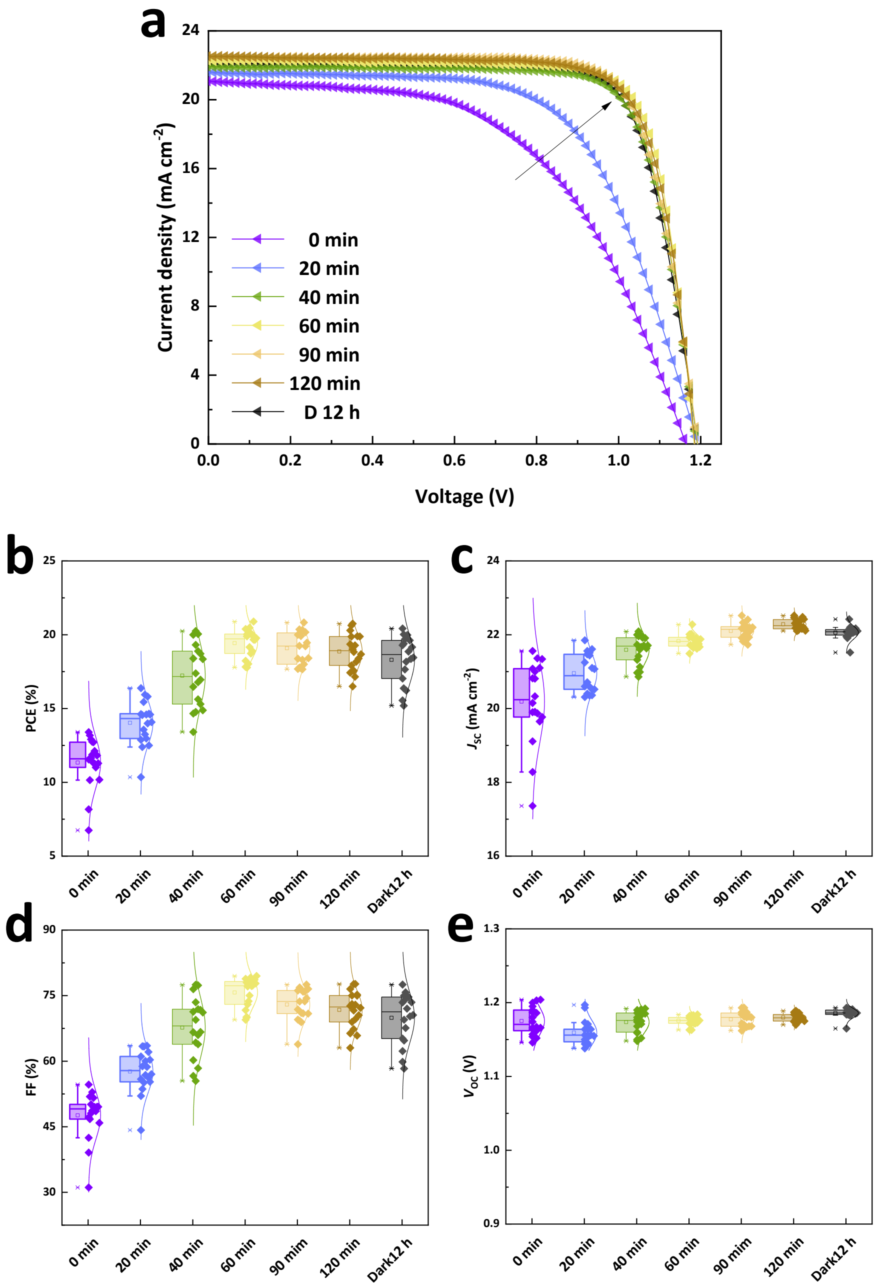

Fig. S1. J–V curves of the champion PSCs fabricated based on various indoor light exposure times and dark oxidation conditions. Statistical distribution of PCEs, V_{OC}s, J_{SC}s and FFs of the PSCs.

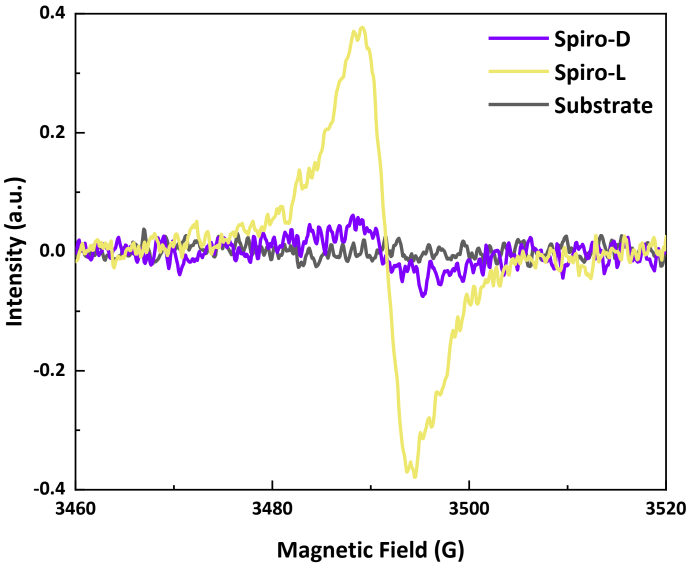

Fig. S2. ESR spectra of the samples.

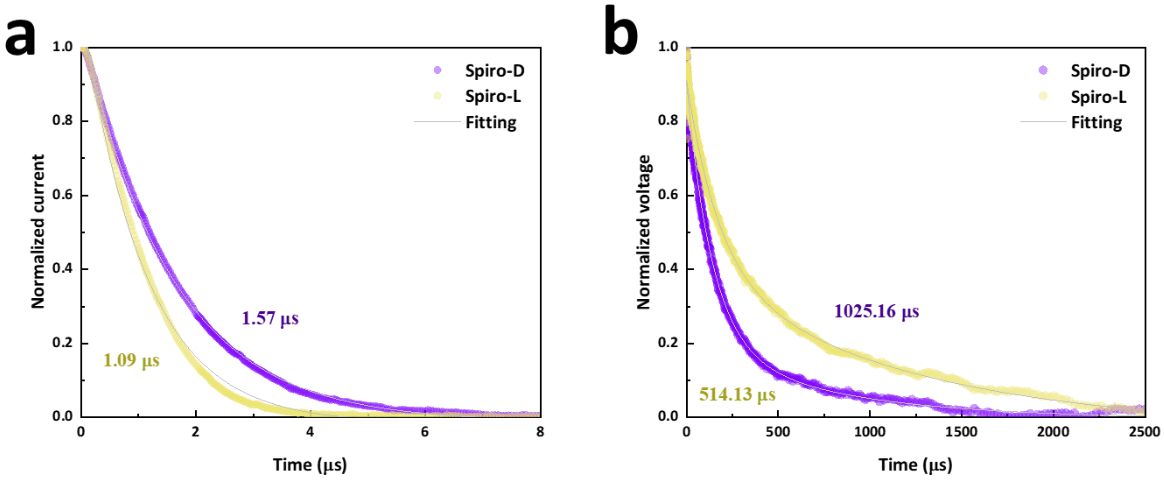

Fig. S3. (a) TPC curves and (b) TPV curves of the PSCs based on the Spiro-D and Spiro-L HTLs.

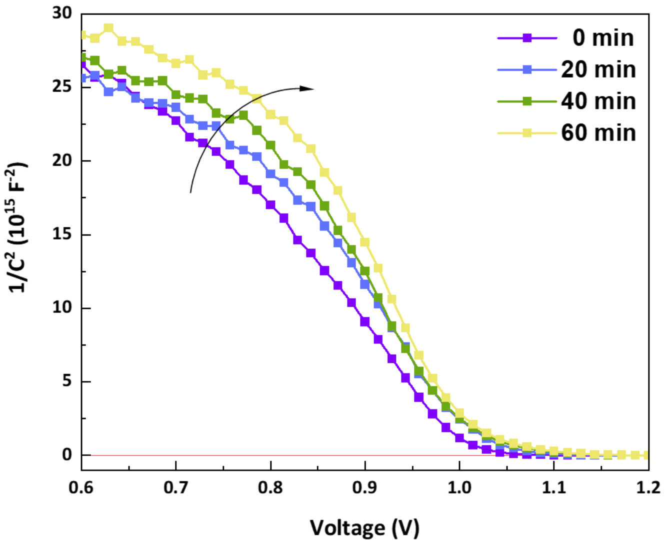

Fig. S4. Mott–Schottky plots of the PSCs based on Spiro HTLs with various indoor light exposure times.

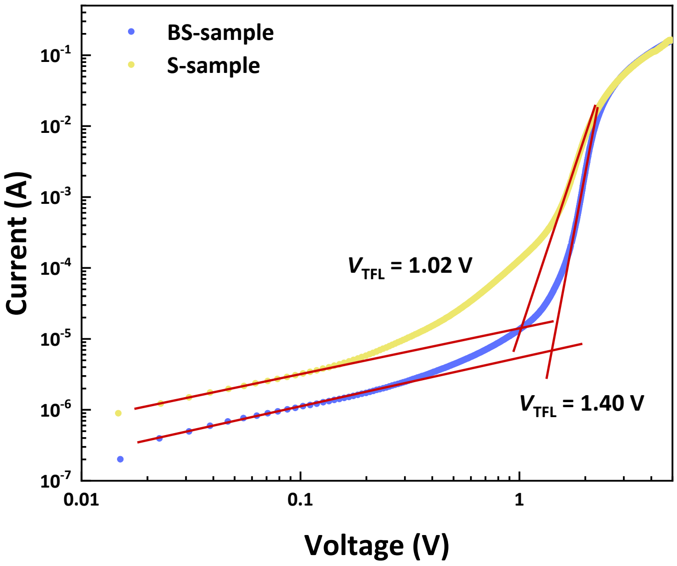

Fig. S5. Dark *I*–*V* curves of the electron-only devices based on BS- and S-sample. (FTO/SnO_2/perovskite/PCBM/Au)

Table S1. The J-V parameters for PSCs fabricated based on various indoor light exposure times and dark oxidation conditions.

Sample	VOC (V)	JSC (mA cm^{-2})	FF (%)	PCE (%)
0 min	1.164	21.08	54.62	13.40
20 min	1.193	21.61	63.54	16.38
40 min	1.192	21.92	77.49	20.25
60 min	1.184	22.28	79.50	20.98
90 min	1.193	22.52	77.53	20.83
120 min	1.186	22.52	77.67	20.75
Dark 12 h	1.193	22.08	77.53	20.42

Table S2. TRPL results fitted by bi-exponential function*.

Sample	A_1	A_1(%)	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
Spiro-L	0.7344	77.19	12.00	0.2171	34.58	22.38
Spiro-D	0.4341	50.44	26.83	0.4266	117.20	100.13

* Empirical bi-exponential equation (1):

$$y = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + y_0 \qquad (1)$$

* The average carrier lifetimes (τ_{ave}) was determined by the following equation (2):

$$\tau_{\text{ave}} = \frac{A_1\tau_1{}^2 + A_2\tau_2{}^2}{A_1\tau_1 + A_2\tau_2} \qquad (2)$$

Table S3. Time required for each step in the laboratory fabrication of PSCs (unit: h).

Sample	FTO Cleaning	SnO_2 Preparation	Perovskite Preparation	Spiro Deposition	Spiro Oxidation	Au Deposition
Light-oxidation	2.5	2.0	1.5	0.5	1.0	1.5
Dark-oxidation	2.5	2.0	1.5	0.5	12.0*	1.5

* The conventional dark oxidation process typically requires overnight storage (12 h) but often exceeds 12 h.