# Multifunctional additive strategy to stabilize precursor solution and passivate film defects for MA-free perovskite solar cells with an efficiency of 22.75%

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#### Materials

99.9%), Formamidine hydroiodide 99.9%), Lead (II) bromide  $(PbBr_2,$ (FAI, bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI, 99%), 2,2',7,7'-Tetrakis[N,N-di(4methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD, 99.86%) and 4-tert-butyl pyridine (tBP, 99%) were purchased from Advanced Election Technology CO., Ltd. Lead (II) iodide (PbI<sub>2</sub>, 99.99%), Methylammonium bromide (MABr, 99.9%), lead (II) chloride (PbCl<sub>2</sub>, 99.99%) and methylamine hydrochloride (MACl, 99.5%) were purchased from Xi'an Polymer Light Technology Corp. TiCl<sub>4</sub> (99.99%), Cesium iodide (CsI, 99.99%) and Rubidium iodide (RbI) were obtained from Aladdin. Acetonitrile (ACN, 99.8%) were got from Macklin. Benzoylhydrazine (BH, >98.0%) purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Chlorobenzene (CB, >99.9% purity), N, N-dimethylformamide (DMF, 99.8%) and dimethyl sulfoxide (DMSO, 99.8%) were purchased from Sigma-Aldrich. All the chemicals were used without further purification.

### **Device Fabrication:**

Laser patterned FTO glasses (purchased from Jiangsu Yanchang Sunlaite New Energy Co., Ltd.) were ultrasonically cleaned with detergent water and ethanol for 20 min in sequence. After being blown dry by nitrogen (99.99%), the FTO was treated with ultraviolet ozone (UV-O<sub>3</sub>) for 30 min. Then, the electronic transport layer (TiO<sub>2</sub>) was deposited on the FTO. Among them, TiO<sub>2</sub> was prepared using cryogenic assisted techniques, and 4.5 ml TiCl<sub>4</sub> was dissolved in 200 ml distilled water. Then, soak FTO in the TiCl<sub>4</sub> solution and place it in a constant temperature drying oven (70 °C) for 40 minutes. After that, FTO was annealed at 200 °C for 30 min. After cooling down to room temperature and then treated with UV-O<sub>3</sub> for 20 min. Then, all substrates were transferred to an argon-filled glovebox for perovskite deposition. The 1.55 M perovskite (Rb<sub>0.02</sub>(FA<sub>0.95</sub>Cs<sub>0.05</sub>)<sub>0.98</sub>PbI<sub>2.91</sub>Br<sub>0.03</sub>Cl<sub>0.06</sub>) precursor solution was prepared by dissolving FAI of 248.16 mg, CsI of 19.73 mg, RbI of 6.58 mg, PbI<sub>2</sub> of 682.73 mg, PbBr<sub>2</sub> of 8.53 mg, PbCl<sub>2</sub> of 12.74 mg, and MACl of 35 mg in the mixed solvents of DMF and DMSO (*V*<sub>DMF</sub>: *V*<sub>DMSO</sub> = 4: 1). The as-prepared perovskite precursor solution was filtered by the 0.22 µm PTFE filter before use. The perovskite film was deposited by the consecutively spin-coating process at 4000 rpm for the 30s where 80 µL CB antisolvent was dripped on perovskite

films at 16 s before ending the program, and the film was then annealed at 130 °C for 30 min (argon atmosphere). For BH treatment, different mass concentrations of BH were dissolved in the perovskite precursor solution. The Spiro-OMeTAD solution was prepared by mixing 72.3 mg Spiro-OMeTAD, 28.8  $\mu$ L of 4-*tert*-butyl pyridine (*t*BP) and 17.5  $\mu$ L of lithium bis(trifluoromethane sulfonyl)imide (Li-TFSI) stock solution (520 mg Li-TSFI in 1 mL acetonitrile) in 1 mL CB. Subsequently, 20  $\mu$ L Spiro-OMeTAD solution was spin-coated onto the perovskite films at 4000 rpm for 30 s to form the hole transport layer. Finally, about 100 nm metal counter electrode was thermally evaporated on the top of Spiro-OMeTAD film under a vacuum of 3 × 10<sup>-3</sup> Pa through using a shadow mask.

#### **Characterization:**

*J–V* curves were obtained using a solar simulator equipped and a Keithley 2400 source meter, and the black metal mask was employed to define the effective active area of the device to be 0.09 cm<sup>2</sup>. The PCE of the PSCs was tested under air conditions. Fourier transformed infrared (FTIR) spectra were obtained on an FTIR spectrometer (Tensor27, BRUKER, Germany). TR-UV-vis spectra were measured on an Agilent 8453 UV-vis G1103A spectrometer. Steady-state photoluminescence (PL) and PL-Mapping were recorded by a Confocal Raman system (iHR 550 HORIBA) with a laser of 532 nm. XPS spectra were collected from a Physical Electronics Model 5700 XPS instrument. SEM observations were performed on SEM (FESEM, JEOL-JSM-6701F) in ADD mode. Time-resolved photoluminescence (TRPL) was measured by using a self-built scanning confocal system based on an inverted microscope (Nikon, TE2000-U) with a 450 nm laser in the State Key Laboratory of Quantum Optics and Quantum Optics Devices of Shanxi University. Electrochemical impedance spectroscopy was performed by an electrochemical workstation (CHI 660e).



Figure S1. The full XPS spectra of (a) PVSK, (b) BH, and (c) PVSK+BH. (d) I 3*d* XPS spectra of the perovskite films with or without BH treated.



Figure S2. Grain size statistics of the film (a) without and (b) with BH additive.



Figure S3. 2D TR-UV-vis spectroscopy of the film (e) without and (f) with BH modification.



Figure S4. Schematic diagram of the reduction of  $I_2$  by BH.



Figure S5. Statistics of (a) $V_{OC}$ , (b)  $J_{SC}$ , and (c) FF of PSCs modified by different concentrations of BH.



Figure S6. The J-V curves of the PSCs by using the precursor solution which was placed for 72 h.



Figure S7. (a) Normalized  $J_{SC}$ , (b) Normalized  $V_{OC}$ , and (c) Normalized FF as a function of time for the unencapsulated devices without and with BH modification exposed to the humidity of 5-15 RH% at room temperature in the dark.



Figure S8. (a) Normalized  $J_{SC}$ , (b) Normalized  $V_{OC}$ , and (c) Normalized FF as a function of time for the unencapsulated devices without and with BH modification aged at 40-50% relative humidity at room temperature.



Figure S9. (a) Normalized  $J_{SC}$ , (b) Normalized  $V_{OC}$ , (c) Normalized FF, and (d) Normalized PCE as a function of time for the unencapsulated devices without and with BH modification aged at 65 °C with 15-25% RH at air condition.



Figure S10. PCE evolution of the devices with or without BH modification aged under one sun illumination at room temperature where the devices were located in the glovebox filled with nitrogen.

	Glass/PVSK	Glass/PVSK+BH
$\tau_1$ (ns)	13.68	23.98
%	40.4	46.3
$\tau_2$ (ns)	71.12	122.41
%	59.6	53.7
$\tau_{\rm ave} ({\rm ns})$	64.49	108.20

Table S1 Fitted results of TRPL dynamics of the devices with the structure of glass/perovskite and glass/perovskite+BH.

BH (mg/mL)		$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
0	Champion	1.08	24.82	78.75	21.11
	Average	$1.081 \pm 0.0065$	24.68±0.0013	78.63±0.3335	20.99±0.1527
0.05	Champion	1.095	24.81	80.36	21.83
	Average	$1.089 \pm 0.0056$	24.87±0.0014	$80.40 \pm 0.3784$	21.72±0.1072
0.25	Champion	1.11	25.22	81.26	22.75
	Average	$1.103 \pm 0.0048$	25.16±0.0009	81.3±0.2096	22.62±0.0909
0.5	Champion	1.09	25.27	80.39	22.14
	Average	$1.086 \pm 0.0037$	25.18±0.0010	80.12±0.2906	21.95±0.1918

Table S2. Champion, average, and standard deviation photovoltaic parameters of the PSCs modified different concentrations of BH.

Devices		$J_{\rm SC}({\rm mA/cm^2})$	Voc	FF	PCE (%)
Control	FS	21.35	1.017	74.59	16.19
Control	RS	21.24	1.023	75.04	16.31
Target	FS	25.02	1.101	80.43	22.16
	RS	25.10	1.103	80.92	22.40

Table S3 Photovoltaic parameters of the champion PSCs without and with BH after precursor solution aging 72h.