Supplementary Information (SI) for Sustainable Energy & Fuels.
This journal is © The Royal Society of Chemistry 2025

Supplementary Information

Yuxin Zhang ,[a] Cong Geng ,[a] Chunyang Zheng ,[a] Huiren Zheng ,[a] Xin Zhao ,[a] Mingwei Zhu ,[a] Yong Peng ,[*a] Yi-Bing Cheng [a]

a.State Key Lab of Advanced Technologies for Materials Synthesis and Processing,Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, Hubei Province,China.

Experimental methods

1.Materials

Tin chloride dihydrate ($SnCl_2$•$2H_2O$) was purchased from Aladdin. Urea was purchased from Alfa. Formamidnium iodide (FAI) and Formamidnium bromine (FABr) were purchased from Advanced Electron Technology Co., Ltd. PbI_2 (99.99%) , CsBr (99.99%), Butylamine Iodine(BAI), Butylamine Bromide(BABr) and Butylamine Chloride (BACl), were purchased from Xi'an Yuri Solar Co., Ltd. Isopropanol (IPA, 99.5%) was purchased from Aladdin. Spiro-OMeTAD (99.5%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd.

2.Device fabrication

Firstly, The FTO glass that has been etched by femtosecond laser is washed with detergent, pure water, and ethanol using ultrasonic waves for 15 minutes, then dry with dry air.

The SnO_2 layer was prepared by chemical bath deposition method. 5 g of urea was dissolved in 400 mL of deionized water, and then 100 μL of mercaptoacetic acid, 5 mL of HCl (37 wt%), and 1.096 g of $SnCl_2$ • $2H_2O$ were sequentially added to the solution during magnetic stirring. The solution was stored in a fridge before use. Before depositing the SnO_2 layer, the FTO substrate must first undergo a 15-minute UVO cleaning treatment. Then put the FTO glass into 0.002 M $SnCl_2 \cdot 2H_2O$ solution at 90℃ for 180 min. Finally, it will be annealed at 170℃ for 60 min.

Prior to thermal evaporation, the substrate covered with SnO_2 is cleaned with UVO for 15 minutes. Evaporation is carried out under a pressure of 8×10^{-6} mPa, depositing 35 nm of CsBr (at a rate of 0.5 Å/s) followed by 350 nm of PbI_2 (at a rate of 5 Å/s). Next, the FAI/FABr/BAX (X=I, Br, Cl) solution is sprayed onto the CsBr/PbI_2 film using an ultrasonic spray. The solution for the spray is prepared by dissolving 95.7 mg of FAI, 104.3 mg of FABr, and varying concentrations of BAX (x=0, 0.5, 1, 1.5 mg/mL) in 10 mL of isopropanol (IPA). After obtaining the wet film, transfer it to a hot plate at 170°C for annealing for 1 hour as soon as possible (with an air humidity of about 40%).

Subsequently, 30 μL of Spiro-OMeTAD solution is spin-coated onto the perovskite film at a speed of 2000 rpm as the hole transport layer (HTL) of the device, with an acceleration of 2000 rpm/s and a duration of 30 seconds. To prepare the Spiro OMeTAD solution, take 91.4 mg of Spiro-OMeTAD, 21 μL of Li-TFSI solution (Li-TFSI dissolved in acetonitrile at a concentration of 520 mg/mL), 11.4 μL of FK209 solution (FK209 dissolved in acetonitrile at a concentration of 300 mg/mL), and 35.7 μL of 4-tert-butylpyridine, and mix them in 1 mL of chlorobenzene (CBZ). Finally, 80 nm of gold is thermally evaporated on top of the HTL as the electrode of the device.

3.Characterizations

The surface morphology of the perovskite films was observed using a scanning electron microscope (Hitachi SU8010). Characterization of perovskite films were carried out using an X-ray diffractometer (Bruker D8 Advance).The perovskite films were also characterized by UV–vis spectrometer (lambda 750 S, PerkinElmer). Characterization of the surface chemical state of perovskite films by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB Xi+).The steady-state PL and time-resolved PL attenuation spectra were measured using a fluorescence spectrometer (FLS 980) using a 470 nm laser (EPL-510, Edinburgh Instruments

Ltd).The electrical impedance spectroscopy (EIS) was carried out under dark condition at 0.9 V bias voltage by an EC-lab (SP300).The J-V curves of the devices were measured under AM 1.5 G sunlight (100 mW/cm^2), using a solar simulator (Oriel 94023A, 300 W) and a Keithley 2400 source meter in the cleanroom. All devices were tested using a black metal mask with an aperture area of 0.148 cm^2.

Supplementary Figures and Tables

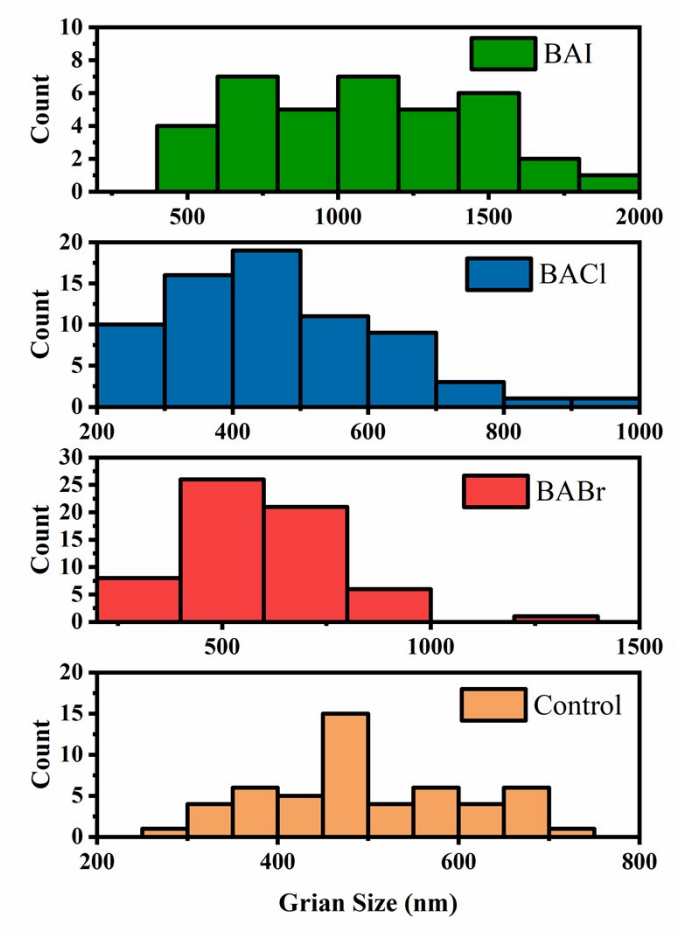

Fig.S1 BAI,BACl,BABr and Control perovskite film grain sizes statistic.

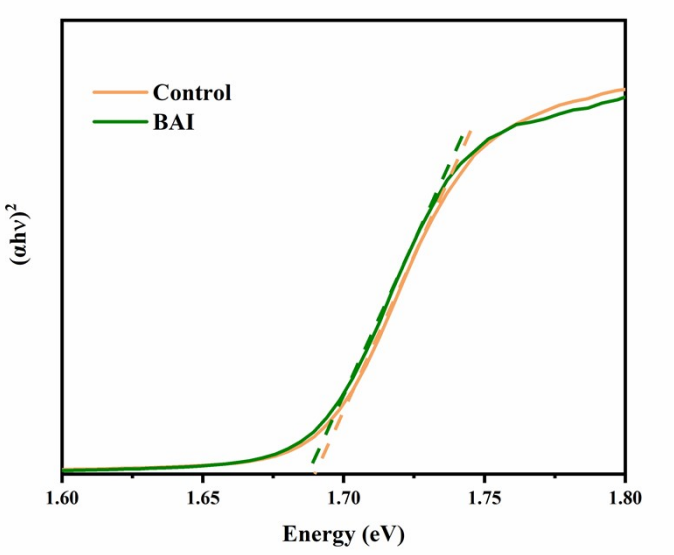

Fig.S2 Tauc plots of the corresponding perovskite films.

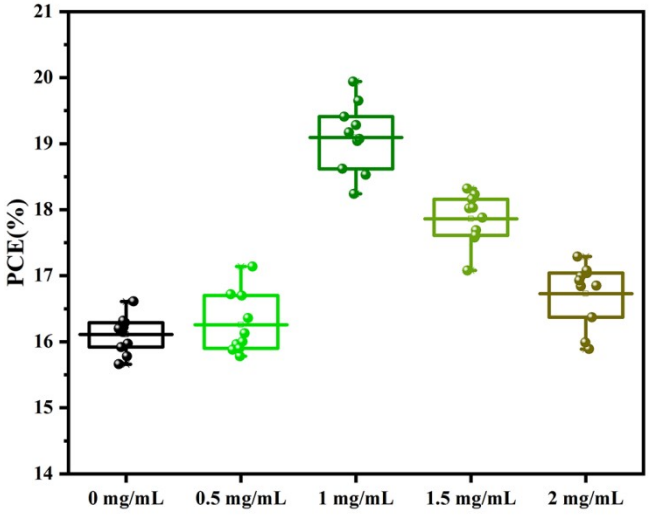

Fig.S3 Statistic PCE of PSCs with varied concentrations of BAI.

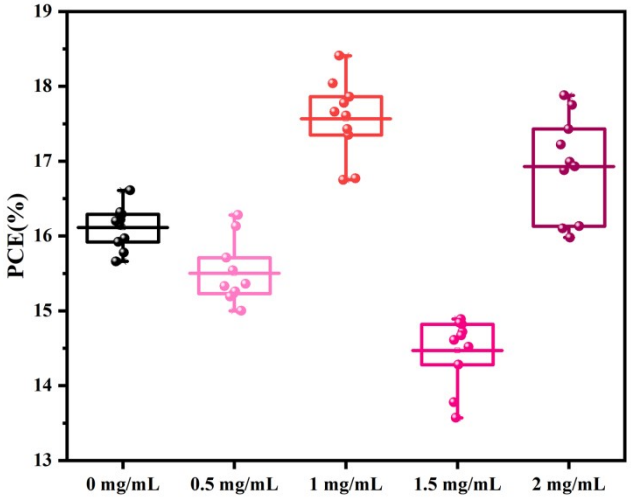

Fig.S4 Statistic PCE of PSCs with varied concentrations of BABr.

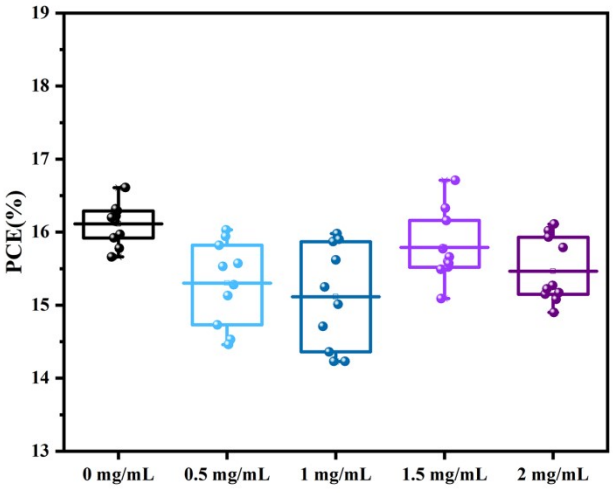

Fig.S5 Statistic PCE of PSCs with varied concentrations of BACl.

Table.S1 The fitted parameters of Control, BAI, BABr and BACl perovskite deposited on glass substrates from TRPL spectra.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
Control	0.6	18.11	0.38	87.89	70.76
BAI	0.30	51.74	0.56	383.42	361.06
BABr	0.35	15.87	0.54	204.85	195.81
BACl	0.54	28.55	0.44	75.74	60.81

Table.S2 Summary of photovoltaic parameters of the 15 Control cells.

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1	1.064	18.68	0.79	15.78
2	1.103	19.48	0.74	15.97
3	1.117	19.73	0.73	16.15
4	1.063	19.80	0.77	16.22
5	1.104	19.20	0.75	15.92
6	1.074	20.25	0.75	16.29
7	1.071	20.84	0.70	15.66
8	1.043	19.77	0.79	16.32
9	1.074	20.51	0.74	16.20
10	1.077	20.73	0.74	16.61
11	1.103	19.42	0.78	16.61
12	1.075	19.50	0.76	15.97
13	1.119	20.05	0.72	16.04
14	1.077	19.86	0.73	15.58
15	1.081	18.61	0.76	15.21
Average	**1.083**	**19.76**	**0.75**	**16.03**

Table.S3 Summary of photovoltaic parameters of the 15 BAI cells.

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1	1.152	22.04	0.77	19.65
2	1.198	19.20	0.79	18.24
3	1.106	21.75	0.79	18.83
4	1.108	21.99	0.80	19.37
5	1.181	21.58	0.76	19.28
6	1.098	22.06	0.79	19.04

7	1.116	21.76	0.79	19.07
8	1.112	21.28	0.79	18.62
9	1.122	21.35	0.80	19.17
10	1.188	21.47	0.78	19.83
11	1.085	21.32	0.80	18.53
12	1.150	21.16	0.80	19.41
13	1.073	21.52	0.79	18.16
14	1.126	21.84	0.81	19.91
15	1.113	22.10	0.79	19.40
Average	**1.128**	**21.49**	**0.79**	**19.10**

Table.S4 Summary of photovoltaic parameters of the 15 BABr cells.

	V_{OC} (V)	**J_{SC} (mA/cm²)**	**FF**	**PCE (%)**
1	1.065	21.88	0.78	18.17
2	1.045	21.66	0.78	17.66
3	1.054	21.10	0.79	17.57
4	1.042	21.59	0.77	17.38
5	1.031	21.78	0.78	17.53
6	1.064	20.48	0.80	17.43
7	1.075	20.97	0.77	17.35
8	1.082	20.75	0.79	17.78
9	1.100	19.89	0.77	16.75
10	1.081	20.91	0.78	17.61
11	1.092	20.37	0.78	17.43
12	1.067	20.8	0.80	17.86
13	1.110	20.45	0.79	18.04
14	1.092	19.42	0.79	16.77
15	1.114	20.38	0.81	18.41
Average	**1.074**	**20.83**	**0.79**	**17.58**

Table.S5 Summary of photovoltaic parameters of the 15 BACl cells.

	V_{OC} (V)	**J_{SC} (mA/cm²)**	**FF**	**PCE (%)**
1	1.132	19.02	0.75	16.11
2	1.121	19.23	0.74	15.87
3	1.122	20.19	0.71	16.16
4	1.066	20.86	0.70	15.49
5	1.083	20.44	0.70	15.60

6	1.043	19.57	0.74	15.01
7	1.068	19.31	0.76	15.66
8	1.060	19.51	0.71	14.67
9	1.091	19.26	0.74	15.52
10	1.058	20.56	0.72	15.77
11	1.053	18.45	0.77	15.00
12	1.052	20.31	0.71	15.09
13	1.069	20.25	0.77	16.71
14	1.075	19.81	0.77	16.33
15	1.073	18.67	0.78	15.57
Average	**1.078**	**19.70**	**0.74**	**15.64**

Table.S6 Photovoltaic parameters of optimal PSC fabricated under different additives.

	Scan direction	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF**	**PCE (%)**	**HI**
Control	Reverse	1.103	19.42	0.78	16.61	0.28
	Forward	1.077	19.35	0.57	11.88	
BAI	Reverse	1.126	21.84	0.81	19.91	0.04
	Forward	1.124	21.80	0.78	19.04	
BABr	Reverse	1.114	20.38	0.81	18.41	0.18
	Forward	1.083	20.38	0.68	15.08	
BACl	Reverse	1.069	20.25	0.77	16.71	0.19
	Forward	1.053	20.24	0.63	13.50	

H-index (HI): HI = ($PCE_{reverse}$ - $PCE_{forward}$)/$PCE_{reverse}$.