Supporting information

Experimental procedure

Lead iodide (PbI_2), ammonium methyl iodide (MAI), carbon pulp, poly (3-hexylthiophene-2,5-diyl) (P3HT) and chlorobenzene were purchased from Advanced Election Technology Co., Ltd. Tin chloride pentahydrate ($SnCl_4•5H_2O$) was provided by Tianjin Optimization Technology Co., Ltd. N,N-Dimethylformamide amine (DMF) and dimethyl sulfoxide (DMSO) were supplied by Sigma Aldrich, Shanghai, China. Bis(3,3-2 aminopyridine) sulfide (BSL) was purchased from Jinan Henghua Technology Co., Ltd. All materials have been directly used without further purification.

Device fabrication

The ITO glass is scrubbed with ethanol and then ultrasonicated for 30 minutes. 0.1753 g of $SnCl_4•5H_2O$ was dissolved in 10 mL of isopropanol and stirred at 500 rpm for 30 min to obtain an electron layer solution. 0.25, 0.5, 1.0 or 1.5 mg of BSL was dissolved in 1 mL of DMSO. 0.461 g PbI_2 and 0.159 g MAI were weighed in a mixed solvent of DMF and DMSO (DMF: DMSO=9:1) to offer a perovskite solution. After 200 μL electron layer solution was spin-coated in the ITO substrates, and successively annealled at 100 ^oC for 10 min and then at 180 ^oC for 1 h, the electron layer was prepared. 100 μL BSL solution was spin-coated in the ITO with electron layer, and then annealed at 100 ^oC for 10 min, giving buried interface. 100 μL of the perovskite solution was spin-coated with 300 μL of ethyl acetate antisolvent for 25 s, and annealed at 100 ^oC for 10 min. Finally, carbon pastes were scraped from the obtained perovskite phase to acquire a complete device.

Characterization

The morphology and roughness of the films were observed by scanning electron microscopy (SEM, JSM-7610 F, JEOL) and atomic force microscopy (AFM, Bruker Dimension® Icon™, United States). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermofisher Escalab 250xi spectrometer. The crystallinity determination of perovskite films by X-ray diffraction (XRD) was conducted on an X-ray powder diffractometer (XRD, DX-2700, Haoyuan Instrument Co., Ltd.). UV-vis absorption spectroscopy analysis was carried out on a Lambda 950 UV-Vis NIR tester. Photoluminescence spectroscopy (PL) and transient luminescence spectroscopy (TRPL, Varian Cary 500) were determined by micro-microscopic confocal Raman spectroscopy using Ar^+ excitation light source. The excitation light wavelength is 532 nm. Photocurrent-voltage (J-V) curves of PSCs were acquired by using a Kethely 2400 light source meter with AM 1.5 G and 100 mW/cm^2. Electrochemical impedance spectroscopy (EIS) was measured at an electrochemical workstation (Zahner, Germany).

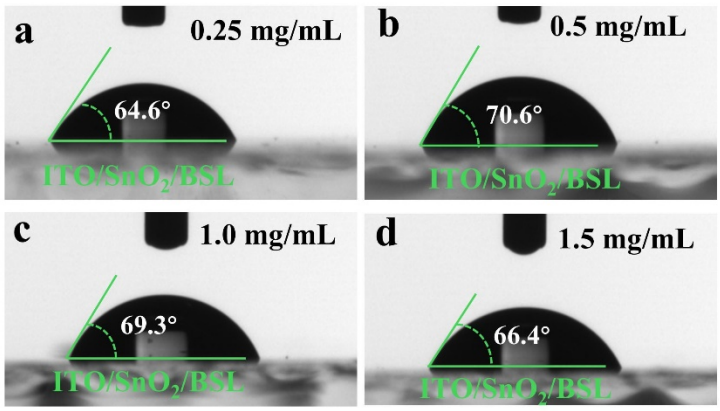

Fig. S1 Contact angles of electron shells: (a-d) 0.25, 0.5, 1.0 and 1.5 mg/mL ITO/SnO_2/BSL.

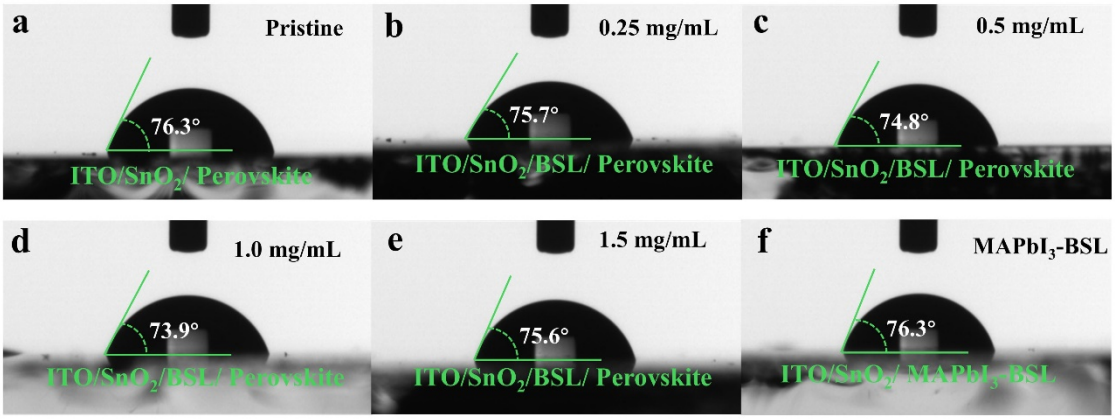

Fig. S2 Contact angles of perovskite films: (a) the pristine, (b-e) ITO/SnO_2/BSL/$MAPbI_3$ of 0.25, 0.5, 1.0 and 1.5 mg/mL, and (f) ITO/SnO_2/$MAPbI_3$-BSL.

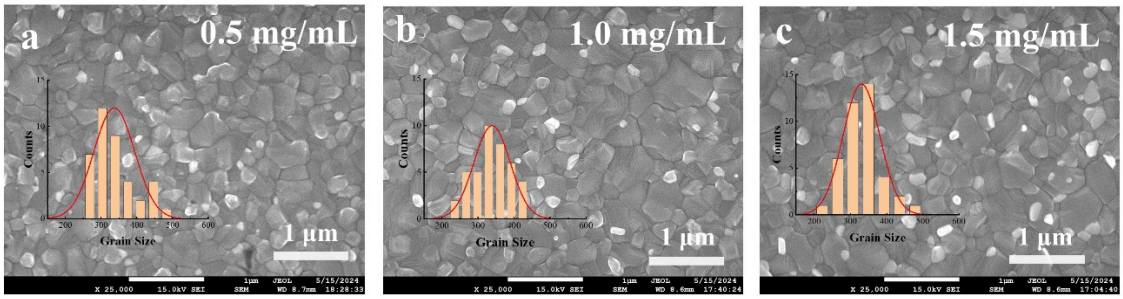

Fig. S3 SEM images of (a-c) 0.5, 1.0 and 1.5 mg/mL of ITO/SnO_2/BSL/$MAPbI_3$.

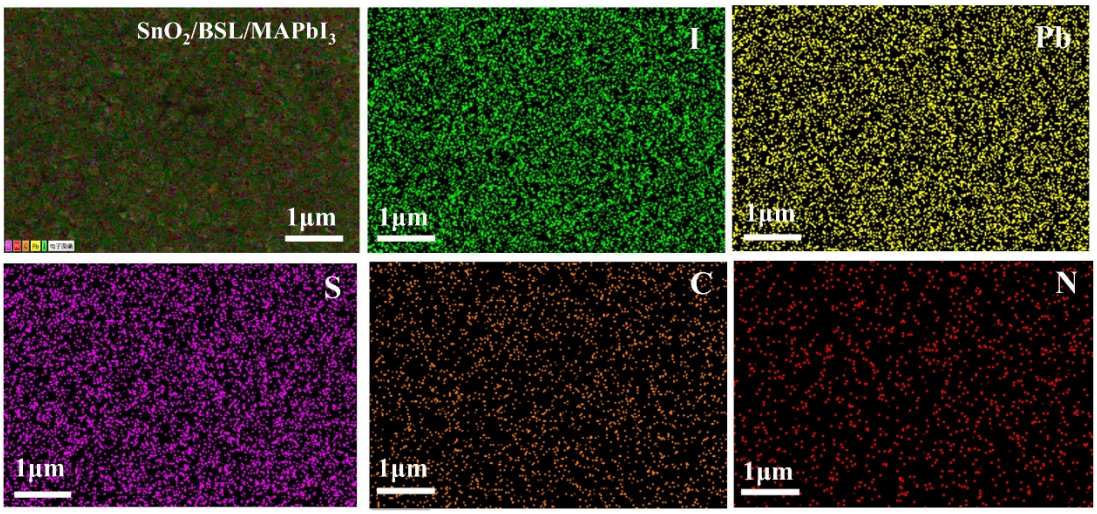

Fig. S4 SEM-EDS elemental maps of ITO/SnO_2/BSL/$MAPbI_3$.

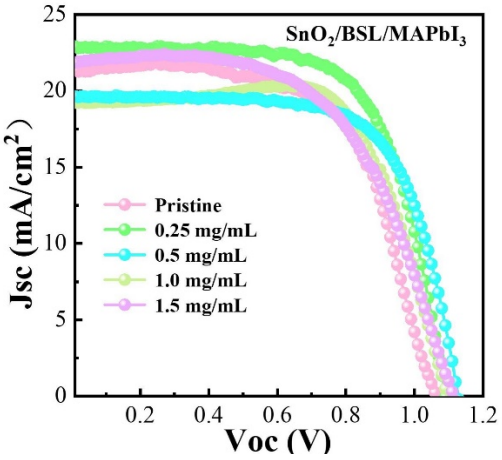

Fig. S5 J-V curves of an optimal ITO/SnO_2/BSL/$MAPbI_3$/P3HT/carbon device based on different concentration gradients.

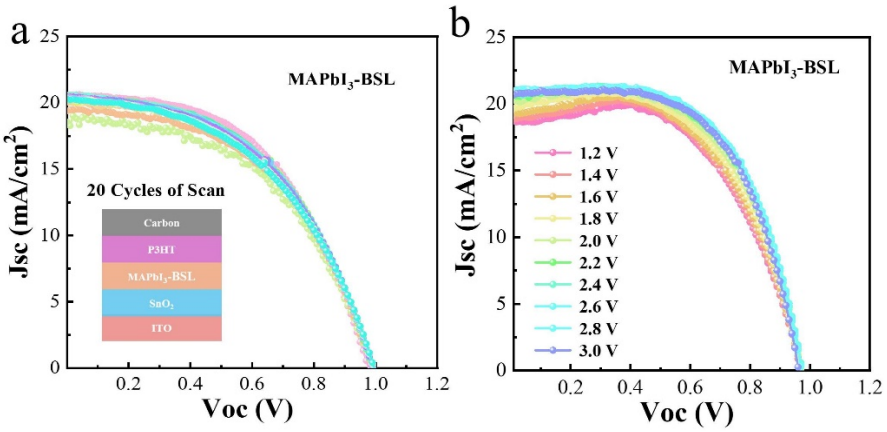

Fig. S6 (a) 20 scan cycles, and (b) differential voltage sweeps in a range from 1.2 to 3.0 V of a typical ITO/SnO_2/$MAPbI_3$-BSL/P3HT/carbon device.

Table S1

Photovoltaic data of the ITO/SnO_2/BSL/$MAPbI_3$/P3HT/carbon devices with different concentrations.

Sample	Voc (V）	Jsc (mA/cm^2)	FF (%)	Eta (%)
Control	1.06	21.28	63.36	14.29
0.25 mg/mL	1.10	22.24	69.14	16.91
0.5 mg/mL	1.12	19.65	68.17	15.00
1.0 mg/mL	1.07	20.94	64.43	14.44
1.5 mg/mL	1.11	21.83	58.46	14.17

Table S2

(a) Multiple scans of the pristine PSC devices.

Pristine	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1	1.10	18.46	69.51	14.11
2	1.10	20.56	68.53	15.50
3	1.09	20.51	66.94	14.97
4	1.09	20.43	65.38	14.56
5	1.08	20.29	63.57	13.93
6	1.07	20.21	62.39	13.49
7	1.07	20.02	61.12	13.09
8	1.07	19.83	60.16	12.76
9	1.06	19.61	58.91	12.25
10	1.06	19.40	58.62	12.05
11	1.05	19.14	57.78	11.61
12	1.05	18.86	57.31	11.35
13	1.04	18.63	56.36	10.92

14	1.04	18.20	54.37	10.29
15	1.03	17.86	53.47	9.84
16	1.03	17.47	52.07	9.37
17	1.03	17.00	51.30	8.98
18	1.02	16.53	49.94	8.42
19	1.02	16.10	48.71	8.00
20	1.01	15.68	47.78	7.57

(b) Multiple scans of the ITO/SnO_2/BSL/$MAPbI_3$/P3HT/carbon devices.

SnO_2/BSL/$MAPbI_3$	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1	1.08	23.58	64.65	16.46
2	1.10	22.08	65.32	15.86
3	1.11	23.27	57.99	14.98
4	1.11	23.48	58.84	15.34
5	1.10	21.67	64.13	15.29
6	1.10	21.64	64.27	15.30
7	1.10	21.64	63.87	15.20
8	1.11	21.61	63.57	15.25
9	1.11	21.57	62.93	15.07
10	1.11	21.53	62.68	14.98
11	1.11	21.43	62.49	14.86
12	1.11	21.41	61.80	14.69
13	1.11	21.42	61.13	14.53
14	1.11	21.30	60.96	14.41
15	1.11	21.25	60.48	14.27
16	1.11	21.17	60.28	14.17
17	1.11	21.09	59.70	13.98
18	1.11	21.05	59.07	13.80

19	1.11	20.82	58.91	13.61
20	1.11	20.58	58.31	13.32

(c) Multiple scans of the ITO/SnO_2/$MAPbI_3$-BSL/P3HT/carbon devices.

$MAPbI_3$-BSL	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1	0.98	20.58	51.86	10.46
2	0.99	18.57	50.56	9.30
3	0.99	19.39	51.43	9.87
4	0.99	20.03	51.29	10.17
5	0.99	20.35	51.20	10.32
6	0.99	20.49	50.98	10.34
7	0.99	20.54	50.20	10.21
8	0.99	20.56	50.57	10.29
9	0.99	20.57	50.51	10.29
10	0.99	20.41	50.47	10.20
11	0.99	20.46	50.35	10.20
12	0.99	20.36	50.56	10.19
13	0.99	20.35	50.23	10.12
14	0.99	20.46	49.59	10.04
15	0.99	20.39	49.35	9.96
16	0.99	20.39	49.17	9.93
17	0.99	20.33	49.04	9.87
18	0.99	20.31	49.30	9.91
19	0.99	20.23	49.58	9.93
20	0.99	20.26	49.19	9.87

Table S3

(a) Different voltage sweeps result of pristine device in a range from1.2 to 3.0 V.

Voltage (V)	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1.2	1.06	18.50	49.05	9.62
1.4	1.06	18.41	49.08	9.58
1.6	1.06	18.31	49.84	9.67
1.8	1.05	18.42	50.49	9.77
2.0	1.05	18.21	51.56	9.86
2.2	1.05	18.12	52.45	9.98
2.4	1.05	18.09	53.22	10.11
2.6	1.04	17.87	53.32	9.91
2.8	1.03	17.35	51.42	9.19
3.0	1.02	16.46	46.32	7.78

(b) Different voltage sweeps result of ITO/SnO_2/BSL/$MAPbI_3$/P3HT/carbon device in a range from 1.2 to 3.0 V.

Voltage (V)	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1.2	0.97	18.69	59.62	10.81
1.4	0.97	18.89	59.38	10.88
1.6	0.97	19.32	59.24	11.10
1.8	0.97	19.72	59.37	11.36
2.0	0.97	20.34	59.70	11.78
2.2	0.97	20.54	60.25	12.00
2.4	0.97	20.80	60.07	12.12
2.6	0.97	20.95	60.43	12.28
2.8	0.97	20.92	60.31	12.24
3.0	0.96	20.69	60.82	12.08

(c) Different voltage sweeps result of ITO/SnO_2/$MAPbI_3$-BSL/P3HT/carbon device in a range from 1.2 to 3.0 V.

Voltage (V)	Voc (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
1.2 V	1.10	21.18	61.77	14.39
1.4 V	1.10	21.13	61.96	14.40
1.6 V	1.09	21.07	61.75	14.18
1.8 V	1.09	21.05	61.57	14.13
2.0 V	1.09	21.05	61.35	14.08
2.2 V	1.09	20.94	61.71	14.09
2.4 V	1.09	20.96	61.60	14.07
2.6 V	1.09	20.94	61.81	14.11
2.8 V	1.09	20.92	61.58	14.04
3.0 V	1.09	20.83	61.27	13.91

Table S4

(a) Photovoltaic parameters of 30 pristine devices.

Pristine	Voc (V)	Jsc (mA/cm^2)	FF (%)	Eta (%)
1	1.06	21.02	60.22	13.42
2	1.06	20.70	60.68	13.31
3	1.06	22.30	56.78	13.42
4	1.07	20.82	61.05	13.60
5	1.05	19.53	64.86	13.30
6	1.07	18.81	65.58	13.20
7	1.10	18.81	59.43	12.30
8	1.07	18.47	63.02	12.45
9	1.05	18.36	62.58	12.06
10	1.04	22.76	54.62	12.93
11	1.06	21.45	56.04	12.74
12	1.07	18.72	61.43	12.30
13	1.05	22.01	52.44	12.12

14	1.07	18.56	62.67	12.45
15	1.04	20.91	56.62	12.31
16	1.05	18.61	63.00	12.31
17	1.06	20.19	59.99	12.84
18	1.05	18.74	63.43	12.48
19	1.07	22.36	58.05	13.89
20	1.08	18.44	64.59	12.86
21	1.08	18.12	64.01	12.53
22	1.08	20.63	54.49	12.14
23	1.08	18.81	66.37	13.48
24	1.09	20.65	61.44	13.83
25	1.05	19.08	64.03	12.83
26	1.05	21.32	59.42	13.30
27	1.05	18.32	68.29	13.14
28	1.08	19.58	56.44	11.94
29	1.07	20.05	55.54	11.92
30	1.06	21.28	63.36	14.29

(b) Photovoltaic parameters of 30 ITO/SnO_2/BSL/$MAPbI_3$/P3HT/carbon devices.

SnO_2/BSL/$MAPbI_3$	Voc (V)	Jsc (mA/cm^2)	FF (%)	Eta (%)
1	1.11	22.31	54.32	13.45
2	1.10	22.31	64.14	15.74
3	1.08	20.99	63.05	14.29
4	1.08	22.60	63.34	15.46
5	1.07	20.65	65.70	14.52
6	1.09	21.76	63.23	15.00
7	1.10	21.40	60.98	14.35
8	1.09	21.04	67.46	15.47

9	1.09	22.95	66.86	16.73
10	1.10	22.24	69.14	16.91
11	1.08	21.29	67.41	15.50
12	1.09	21.60	64.86	15.27
13	1.08	21.47	62.47	14.49
14	1.07	22.02	67.45	15.89
15	1.08	22.84	67.33	16.61
16	1.10	21.75	57.46	13.75
17	1.09	22.72	63.06	15.62
18	1.08	22.55	63.21	15.39
19	1.08	20.73	65.83	14.74
20	1.10	20.49	64.26	14.48
21	1.10	21.79	55.98	13.42
22	1.08	22.75	54.42	13.37
23	1.07	20.52	65.05	14.28
24	1.08	21.69	67.79	15.88
25	1.09	20.11	59.39	13.02
26	1.10	21.65	60.52	14.41
27	1.08	21.98	60.47	14.35
28	1.08	21.54	61.53	14.31
29	1.07	22.91	68.84	16.88
30	1.07	21.87	59.57	13.94

(c) Photovoltaic parameters of 30 ITO/SnO_2/$MAPbI_3$-BSL/P3HT/carbon devices.

$MAPbI_3$-BSL	Voc (V)	Jsc (mA/cm^2)	FF (%)	PCE (%)
1	0.98	20.58	51.86	10.46
2	0.97	21.72	49.90	10.51
3	1.01	20.80	56.04	11.77

4	1.01	20.07	55.36	11.22
5	1.03	18.12	54.87	10.24
6	1.03	21.41	49.23	10.86
7	0.99	20.91	52.47	10.86
8	1.00	20.47	52.21	10.69
9	0.99	21.24	58.04	12.20
10	0.99	22.39	59.87	13.27
11	0.99	22.64	60.79	13.63
12	0.98	21.37	59.87	12.54
13	0.97	18.56	60.32	10.86
14	0.99	20.78	62.08	12.77
15	0.98	19.72	59.71	11.54
16	1.01	19.62	51.85	10.27
17	0.98	18.06	56.63	10.02
18	0.98	21.22	55.83	11.61
19	0.98	20.83	54.66	11.16
20	0.99	20.59	53.34	10.87
21	1.01	19.40	57.77	11.32
22	0.99	19.70	55.15	10.76
23	1.03	21.26	56.56	12.39
24	1.03	19.42	55.57	11.12
25	1.01	20.08	54.46	11.04
26	1.03	19.96	54.69	11.24
27	1.03	20.47	58.70	12.38
28	1.03	19.89	56.75	11.63
29	1.00	18.72	52.05	9.74
30	1.00	18.68	53.31	9.96