Material nucleation/growth competition tuning towards highly reproducible planar perovskite solar cells with efficiency exceeding 20% †

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Text part:

In fact, when the high pressure air (0.1 MPa) expands into low pressure environment, the temperature will decrease. Therefore we need to investigate the influence of the temperature decrease of air in the sample chamber on the temperature of the sample.

In this work, the gas expansion process can be regarded as adiabatic degassing process. In order to facilitate the estimation of the final temperature of the air in the sample chamber, the following model can be established [1].

As shown in Figure S1, there is a rigid container filled with high pressure gas. And the gas status parameters can be assumed as p_1, T_1. Assume that there is a piston dividing the gas in two parts. The gas in the right is exhausted out and the gas in the left will fill the whole container, gas status parameter assumed as p_2, T_2.The pressure of the gas in the right p_1 changes to p_2 immediately after opening the valve. The volume of the gas in the left is V_1 and V_2 for before and after the valve opened.

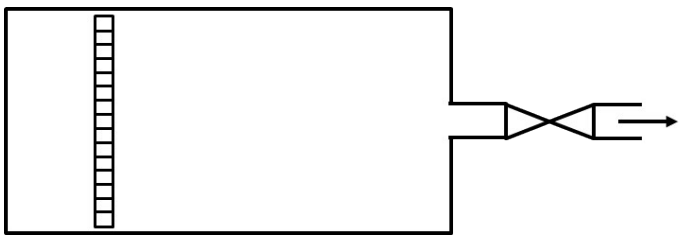

Figure S1. The adiabatic degassing process.

The gas in the left of the piston is doing work to the external invironment with pressure of p_2. Then, the amount of work of 1 Kg gas doing is w, the transferred heat of the system is Q. The internal energy increment of the system is Δu.

Then,

$\Delta u = -w + Q$, $Q = 0$, $w = p_2(V_2 - V_1)$;

Assume that the air is ideal gas, then,

$\Delta u = C_V(T_2 - T_1)$, $pV = nRT$;

Then, we can obtain that,

$$T_2 = T_1(\frac{1}{k} + \frac{(k-1)p_2}{k \quad p_1})$$

where C_V, k, n, R is the specific heat capacity at constant volume, heat capacity ratio, the amount of substance of the gas and the ideal gas constant, respectively. The heat capacity ratio is about a constant in this work according to the handbook[2]. Then,
k=1.4, p_1=100000 Pa, p_2=500 Pa, T_1=293 K,
Thus,
T_2=210 K.

According to the above analysis, the final temperature of the air in the sample chamber is -63°C, 83°C less than the initial temperature of 20°C. However, there are few air molecules at the pressure of 500 Pa. It can hardly influence the temperature of the sample for the sample is big enough even in a few seconds. Finally, the influence on the sample temperature can be ignored due to the temperature decrease of the air.

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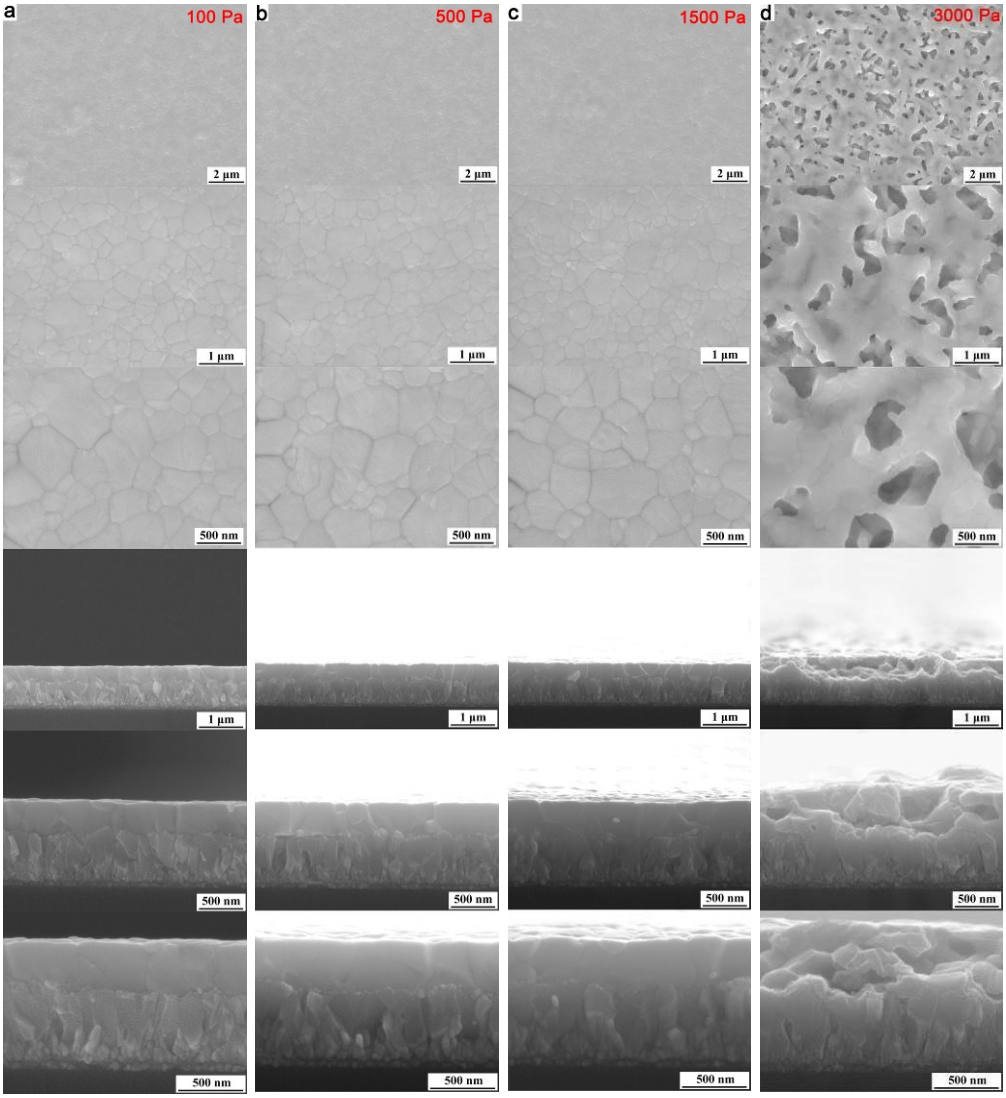

Figure S2. Different magnification of the surface and cross-sectional view morphologies for the perovskite films obtained by the GGPM at the pressure of (**a**) 100 Pa, (**b**) 500 Pa, (**c**) 1500 Pa and (**d**) 3000 Pa.

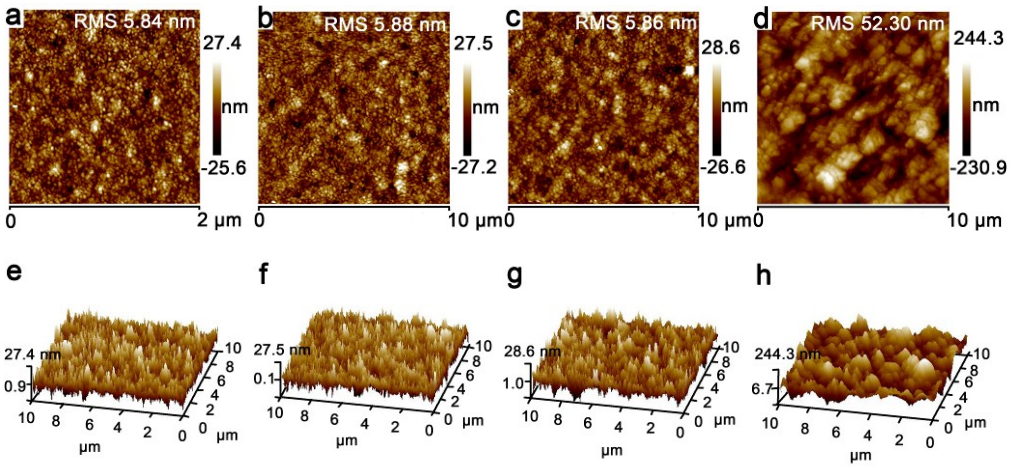

Figure S3. Two and Three-dimensional AFM images of perovskite films fabricated at the pressure of (**a** and **e**) 100 Pa, (**b** and **f**) 500 Pa, (**c** and **g**) 1500 Pa and (**d** and **h**) 3000 Pa with area of 10 × 10 μm.

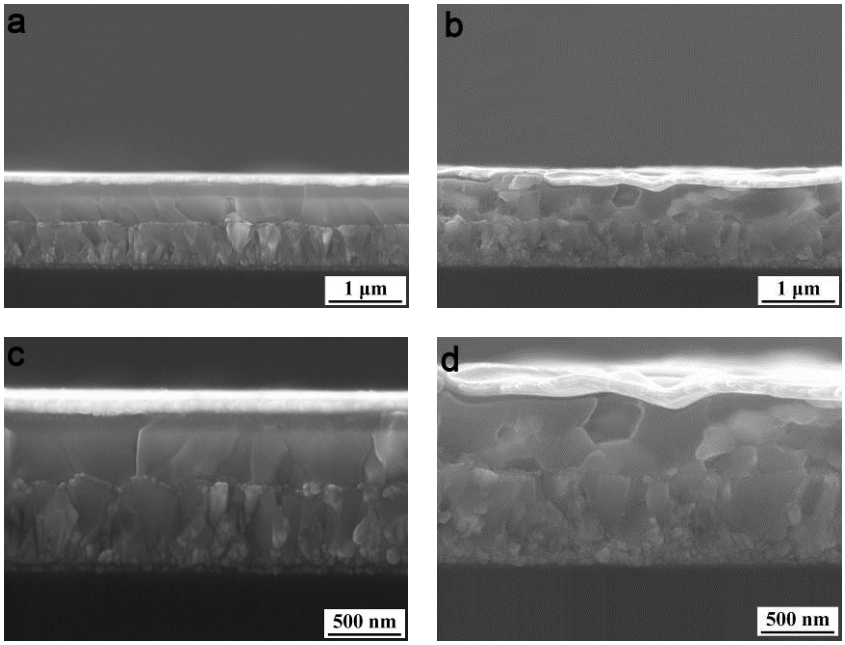

Figure S4. Cross-sectional view SEM image of the typical normal planar perovskite solar cells using the perovskite films fabricated by the GGPM at the pressure of 1500 Pa with (**a**) low magnification and (**c**) high magnification; 3000 Pa with (**b**) low magnification and (**d**) high magnification.

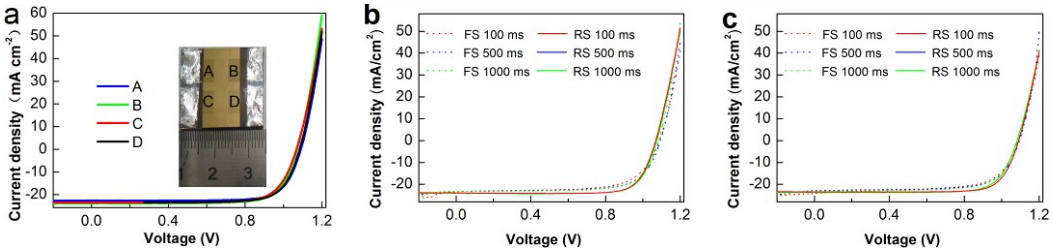

Figure S5. (**a**) The *J-V* curves of four devices at the pressure of 1500 Pa on a 2.5×2.5 cm substrate. The *J-V* curves obtained by reverse and forward scans at a scan step of 23.7 mV and delay time of 100 ms, 500 ms and 1000 ms under a simulated AM 1.5G solar illumination of 100 mW/cm^2 respectively for the champion cells fabricated at the pressure of (**b**) 500 Pa and (**c**) 1500 Pa.

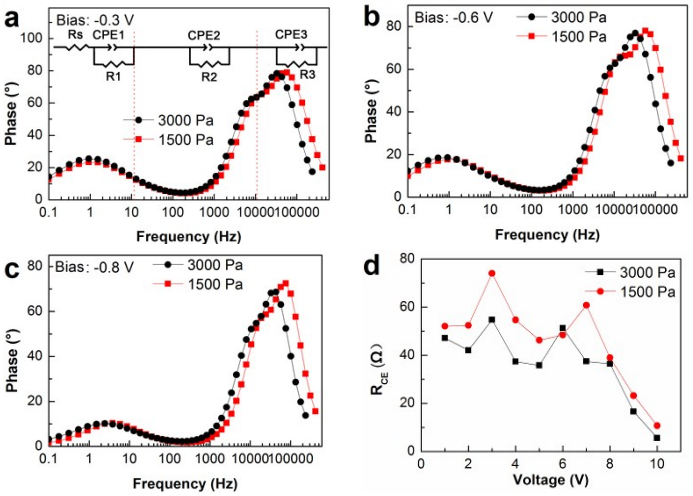

Figure S6. Electronic impedance spectroscopy characteristics of the PSCs under illumination. Bode phase plots of devices based on perovskite films fabricated at the pressure of 1500 Pa and 3000 Pa under illumination with a bias at (**a**) -0.8 V, (**b**) -0.6 V and (**c**) -0.3 V. (**d**) The charge transfer resistance of devices at different biases.

Table S1. Photovoltaic parameters of 28 devices fabricated by the GGPM at the pressure of 100 Pa measured with a 0.1 cm^2 mark under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
1	23.65	1.10	72.87	18.90
2	22.28	1.05	78.74	18.45
3	22.31	1.10	74.88	18.38
4	21.87	1.07	78.91	18.40
5	23.33	1.06	75.85	18.73
6	21.67	1.09	79.39	18.76
7	23.03	1.08	75.60	18.80
8	24.00	1.08	72.69	18.82
9	23.69	1.06	74.99	18.83
10	24.09	1.07	75.59	19.40
11	23.71	1.07	74.90	19.03
12	23.13	1.08	78.48	19.53
13	23.13	1.07	77.77	19.17
14	23.19	1.08	76.70	19.25
15	22.26	1.09	79.43	19.26
16	22.88	1.09	77.14	19.26
17	22.63	1.07	79.62	19.27
18	23.00	1.09	77.49	19.46
19	22.56	1.09	79.32	19.46
20	23.63	1.06	77.49	19.45
21	23.22	1.09	77.35	19.53
22	22.69	1.09	78.88	19.59
23	23.09	1.07	79.23	19.61
24	22.65	1.09	79.57	19.64
25	23.39	1.07	78.79	19.77
26	23.52	1.08	79.14	20.01
27	23.43	1.09	79.97	20.44
28	23.22	1.08	79.07	19.86
Average	23.04 ± 0.61	1.08 ± 0.01	77.50 ± 2.08	19.25 ± 0.50

Table S2. Photovoltaic parameters of 28 devices fabricated by the GGPM at the pressure of 500 Pa measured with a 0.1 cm^2 mark under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
1	21.70	1.07	78.85	18.24
2	21.68	1.11	79.96	19.22
3	22.60	1.10	74.51	18.46
4	23.09	1.06	75.62	18.54
5	23.42	1.09	73.08	18.65
6	21.79	1.09	79.03	18.77
7	22.22	1.11	76.19	18.78
8	21.81	1.08	79.88	18.81
9	22.98	1.08	76.22	18.86
10	23.82	1.09	73.17	18.97
11	23.24	1.08	75.74	19.01
12	22.73	1.07	78.82	19.11
13	23.05	1.09	76.65	19.21
14	22.66	1.10	77.10	19.24
15	22.09	1.09	79.73	19.13
16	22.85	1.05	79.63	19.15
17	24.25	1.04	76.06	19.22
18	23.06	1.05	79.54	19.22
19	23.67	1.06	76.58	19.23
20	22.54	1.09	78.86	19.30
21	22.86	1.09	77.32	19.30
22	22.96	1.06	78.97	19.31
23	22.42	1.09	79.78	19.51
24	23.35	1.07	78.67	19.72
25	23.47	1.07	78.85	19.72
26	22.66	1.10	79.09	19.76
27	23.10	1.09	79.46	20.03
28	24.04	1.07	78.67	20.30
Average	22.86 ± 0.68	1.08 ± 0.02	77.71 ± 2.03	19.17 ± 0.46

Table S3. Photovoltaic parameters of 28 devices fabricated by the GGPM at the pressure of 1500 Pa measured with a 0.1 cm^2 mark under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
1	23.28	1.09	71.19	18.09
2	22.64	1.09	73.22	18.12
3	22.31	1.06	79.30	18.77
4	22.18	1.10	75.77	18.49
5	23.33	1.07	73.68	18.33
6	23.06	1.07	74.90	18.42
7	23.09	1.07	74.64	18.42
8	22.98	1.07	75.37	18.44
9	23.77	1.09	72.04	18.72
10	22.33	1.06	79.06	18.75
11	23.10	1.08	75.16	18.81
12	22.87	1.06	76.94	18.73
13	23.65	1.08	74.00	18.94
14	22.68	1.10	75.79	18.98
15	23.20	1.04	78.47	18.98
16	23.25	1.04	78.38	19.00
17	23.36	1.08	77.08	19.52
18	23.35	1.08	77.85	19.57
19	24.23	1.08	75.37	19.74
20	22.74	1.07	78.47	19.10
21	23.63	1.07	75.33	19.11
22	22.62	1.07	78.65	19.12
23	23.47	1.09	74.81	19.16
24	23.18	1.05	79.46	19.35
25	23.73	1.10	74.41	19.44
26	23.19	1.07	79.23	19.60
27	23.23	1.08	78.55	19.78
28	23.45	1.09	78.12	19.97
Average	23.14 ± 0.47	1.08 ± 0.02	76.26 ± 2.33	18.98 ± 0.51

Table S4. Photovoltaic parameters of 28 devices fabricated by the GGPM at the pressure of 100 Pa measured with a 0.1 cm^2 mark under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
1	12.21	1.02	55.06	6.88
2	14.75	0.96	50.73	7.15
3	15.30	0.92	56.81	8.04
4	15.49	0.86	62.35	8.27
5	15.71	0.85	65.23	8.73
6	14.95	0.80	74.27	8.85
7	21.95	0.86	47.15	8.89
8	17.69	0.75	69.23	9.24
9	17.77	0.88	59.37	9.26
10	20.63	0.93	50.20	9.66
11	15.45	0.95	64.69	9.50
12	16.24	0.95	65.49	10.10
13	15.53	0.96	68.41	10.15
14	16.28	0.92	72.48	10.87
15	21.97	0.95	52.41	10.92
16	17.85	0.90	68.24	10.96
17	18.94	1.01	57.32	10.97
18	18.97	0.90	64.78	11.00
19	17.64	0.87	72.40	11.15
20	18.56	0.93	64.61	11.16
21	17.82	1.01	63.59	11.41
22	17.06	0.99	69.15	11.63
23	19.61	1.03	58.76	11.86
24	16.07	1.02	72.80	11.96
25	19.73	0.98	66.52	12.81
26	20.36	1.00	64.29	13.04
27	22.55	0.87	71.41	13.98
28	22.29	1.00	64.29	14.28
Average	17.84 ± 2.62	0.93 ± 0.07	63.29 ± 7.41	10.46 ± 1.88

Table S5. Photovoltaic parameters of the champion cell fabricated by the GGPM at the pressure of 100 Pa measured at a scan step of 23.7 mV and delay time of 100 ms, 500 ms and 1000 ms under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
RS-100 ms	23.70	1.09	78.97	20.35
FS-100 ms	23.36	1.09	61.47	15.60
RS-500 ms	23.74	1.08	79.65	20.43
FS-500 ms	23.42	1.07	72.68	18.25
RS-1000 ms	23.43	1.09	79.97	20.44
FS-1000 ms	23.06	1.09	73.78	18.51

Table S6. Photovoltaic parameters of the champion cell fabricated by the GGPM at the pressure of 500 Pa measured at a scan step of 23.7 mV and delay time of 100 ms, 500 ms and 1000 ms under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
RS-100 ms	24.04	1.07	78.67	20.30
FS-100 ms	23.43	1.09	68.18	17.39
RS-500 ms	23.95	1.07	79.04	20.23
FS-500 ms	23.28	1.09	71.73	18.25
RS-1000 ms	23.74	1.06	79.89	20.19
FS-1000 ms	23.35	1.08	72.77	18.42

Table S7. Photovoltaic parameters of the champion cell fabricated by the GGPM at the pressure of 1500 Pa measured at a scan step of 23.7 mV and delay time of 100 ms, 500 ms and 1000 ms under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
RS-100 ms	23.77	1.08	76.12	19.58
FS-100 ms	24.17	1.09	66.29	17.44
RS-500 ms	23.60	1.08	77.76	19.88
FS-500 ms	22.95	1.09	71.24	17.90
RS-1000 ms	23.45	1.09	78.12	19.97
FS-1000 ms	23.24	1.09	71.56	18.09

Table S8. PV parameters for 30 devices with size of 20.5 × 5.5 mm fabricated by the GGPM at the pressure of 1500 Pa measured under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
1	20.95	1.10	62.50	14.35
2	24.40	1.10	55.83	14.92
3	22.80	1.09	58.11	14.39
4	23.61	1.08	57.71	14.68
5	24.08	1.09	56.77	14.85
6	22.80	1.07	59.11	14.49
7	24.64	1.11	54.56	14.91
8	22.44	1.11	60.41	15.00
9	24.30	1.04	59.20	15.02
10	21.03	1.09	66.36	15.20
11	23.52	1.07	61.23	15.40
12	22.89	1.11	61.67	15.61
13	22.88	1.11	60.41	15.30
14	21.91	1.08	65.43	15.44
15	22.40	1.09	63.22	15.48
16	21.36	1.07	66.97	15.24
17	22.05	1.09	64.27	15.50
18	23.68	1.09	61.31	15.88
19	23.15	1.07	61.59	15.29
20	23.39	1.09	62.78	16.05
21	22.25	1.11	68.41	16.90
22	23.44	1.09	64.56	16.45
23	23.73	1.08	64.74	16.63
24	22.34	1.13	66.67	16.80
25	22.96	1.07	66.12	16.19
26	23.65	1.09	63.07	16.32
27	23.86	1.08	63.96	16.52
28	23.09	1.10	65.95	16.73
29	22.56	1.12	67.78	17.05
30	23.97	1.12	60.47	16.19
Average	23.00 ± 0.96	1.09 ± 0.02	62.37 ± 3.65	15.63 ± 0.80

Table S9. PV parameters for 30 devices with size of 20.5 × 5.5 mm fabricated by the GGPM at the pressure of 1500 Pa measured under a simulated AM 1.5G solar illumination of 100 mW/cm^2.

Cell No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
A-FS	23.10	1.10	60.21	15.29
A-RS	23.09	1.10	65.95	16.73
B-FS	22.56	1.11	63.39	15.92
B-RS	22.56	1.11	67.78	17.05

References

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2. J. R. Zhang, T. Y. Zhao, Thermal Physical Properties Manual of Commonly Used Material in Engineering, the New Era of Press, Beijing, 1987, p. 203. (张家荣, 赵廷元, 工程常用物质的热物理性质手册, 新时代出版社, 1987, p. 203.)