Supporting Information *for*

Controlled Growth of Organic-Inorganic Hybrid CH₃NH₃Pbl₃

Perovskite Thin Films from Phase-Controlled Crystalline

Powders

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Preliminary results on powder phase formation depending on solvents

Fig. S1. XRD patterns and photographs of the powders synthesized with different solvents of GBL and DMF for the MAPbI₃ solution synthesis. The powders were synthesized with the input ratio of PbI_2 :MAI = 1:1. From the preliminary experiments, we found that the powder synthesized with GBL exhibited a single perovskite phase regardless of input ratio, as shown in the blue pattern of the figure, whereas the powder synthesized with DMF showed phases

that were changed depending on the input ratio. The phase changes with input ratio are clearly shown in Fig. 3.

Formation process of precipitates during step II



Fig. S2. Sequence of photographs showing typical formation of precipitates inside DCM.

Phase identification from XRD patterns

Powder with input ratio of 1:1.0		Powder with input ratio of 1:2.2	
Observed peaks (°)	Identified phases (Δ^a)	Observed peaks (°)	Identified phases (Δ^a)
13.001	PbI ₂ -MAI-DMF (0.005)	10.222	PbI ₂ -MAI-DMF (0.043)
13.883	Perovskite (0.084)	11.579	PbI ₂ -MAI-DMF (-0.049)
14.951	PbI ₂ -MAI-DMF (-0.098)	12.956	PbI ₂ -MAI-DMF (0.050)
15.354	PbI ₂ -DMF (-0.060)	14.053	Perovskite (0.086)
19.564	PbI ₂ -DMF (0.004)	14.790	PbI ₂ -MAI-DMF (0.063)
20.889	PbI ₂ -DMF (-0.001)	15.282	PbI ₂ -MAI-DMF (0.056)
22.593	PbI ₂ -MAI-DMF (0.072)	15.862	PbI ₂ -MAI-DMF (0.125)
23.393	Perovskite (0.077)	16.177	PbI ₂ -MAI-DMF (-0.084)
24.877	PbI ₂ -DMF (-0.042)	18.251	PbI ₂ -MAI-DMF (0.053)
25.083	PbI ₂ -DMF (-0.053)	19.160	PbI ₂ -MAI-DMF (0.151)
25.518	PbI ₂ -MAI-DMF (-0.096)	20.850	PbI ₂ -MAI-DMF (0.090)
26.244	PbI ₂ -MAI-DMF (-0.061)	22.017	PbI ₂ -MAI-DMF (0.070)
	1	1	

Table S1. Classification of different phases from XRD patterns of two typical powders.

27.960	PbI ₂ -MAI-DMF (-0.101)	22.926	PbI ₂ -MAI-DMF (0.022)
28.683	PbI ₂ -MAI-DMF (-0.032)	23.400	Perovskite (0.070)
28.946	PbI ₂ -DMF (-0.075)	24.491	MAI (0.044)
29.568	PbI ₂ -DMF (-0.095)	25.678	PbI ₂ -MAI-DMF (0.087)
30.142	PbI ₂ -MAI-DMF (-0.028)	26.209	PbI ₂ -MAI-DMF (0.027)
30.876	PbI ₂ -DMF (0.001)	27.061	PbI ₂ -MAI-DMF (0.016)
31.231	PbI ₂ -DMF (0.034)	28.143	Perovskite (0.004)
32.394	PbI ₂ -MAI-DMF (0.026)	28.690	PbI ₂ -MAI-DMF (-0.039)
32.747	PbI ₂ -MAI-DMF (0.024)	29.746	MAI (0.064)
34.716	PbI ₂ -DMF (-0.0021)	30.266	PbI ₂ -MAI-DMF (-0.152)
36.248	PbI ₂ -MAI-DMF (-0.056)	31.387	PbI ₂ -MAI-DMF (0.003)
37.011	PbI ₂ -MAI-DMF (-0.028)	31.838	Perovskite (0.024)
37.287	PbI ₂ -DMF (0.072)	32.586	PbI ₂ -MAI-DMF (-0.166)
38.562	PbI ₂ -MAI-DMF (0.092)	33.462	PbI ₂ -MAI-DMF (-0.062)
39.399	PbI ₂ -DMF (0.024)	33.804	PbI ₂ -MAI-DMF (0.028)
39.797	PbI ₂ -DMF (-0.060)	34.509	PbI ₂ -MAI-DMF (0.051)
40.992	PbI ₂ -DMF (0.003)	35.080	PbI ₂ -MAI-DMF (0.047)
42.981	Perovskite (0.044)	36.110	PbI ₂ -MAI-DMF (0.082)
43.606	PbI ₂ -MAI-DMF (0.059)	36.485	MAI (-0.078)
44.694	PbI ₂ -DMF (0.001) ^b	37.272	Perovskite (-0.090)
45.261	Perovskite (0.008)	37.791	PbI ₂ -MAI-DMF (0.059)
46.871	PbI ₂ -DMF (-0.038) ^b	38.424	PbI ₂ -MAI-DMF (0.107)
		39.702	PbI ₂ -MAI-DMF (0.089)
		40.007	PbI ₂ -MAI-DMF (0.021)
		41.247	PbI ₂ -MAI-DMF (0.077)
		42.684	Perovskite (-0.114)
		1	

	42.980	Perovskite (-0.045)
	43.795	PbI ₂ -MAI-DMF (-0.130)
	43.824	MAI (-0.014)
	44.356	MAI (-0.052)
	44.947	PbI ₂ -MAI-DMF (-0.107)
	45.445	PbI ₂ -MAI-DMF (-0.119)
	46.154	PbI ₂ -MAI-DMF (-0.060)
	47.101	PbI ₂ -MAI-DMF (-0.153)
	48.467	PbI ₂ -MAI-DMF (-0.161)
	49.391	PbI ₂ -MAI-DMF (-0.084)
	50.055	Perovskite (0.105)

^a Δ : Difference between two peak positions of observed peaks and calculated peaks. The calculated peak positions were obtained from reference 24. / ^b These peak positions were calculated using X'Pert HighScore Plus 3.0 software based on the structural parameters of PbI₂-DMF described in ref. 24, because there is no information between 41 to 50°.



Low-magnification surface FESEM images of the MAPbl₃ thin films

Fig. S3. Low-magnification FESEM surface images of the MAPbI₃ films deposited on mp-TiO₂/TiO₂-BL/FTO.



Presence of pure MAI from high-MAI-excess powder

Fig. S4. (a) FT-IR spectra of the powder having 1:2.2 ratio and corresponding thin films fabricated by solution processing with the powder and subsequent air-annealing. (b) Enlarged spectra and pure MAI spectrum. The powder consists of two phases of MAPbI₃ and PbI₂-MAI-DMF phase, but the thin films exhibit pure MAPbI₃ phases. As shown in the enlarged spectrum of (b), a pure MAI phase, as denoted by blue dotted lines, is clearly observed in addition to the phase of PbI₂-MAI-DMF complex from the powder. However, this MAI phase with the PbI₂-MAI-DMF complex phase is completely absent from the thin film.



• Effects of purity of Pbl₂ and MAI on structure and device performance

Fig. S5. Effects of purity of two chemicals (PbI₂ and MAI) on structure and photovoltaic device performance. (a) XRD patterns of as-prepared powders and (b) photovoltaic device performance (inset photograph: as-prepared powders). Powder type 1: PbI₂ (99.9985%) and purified MAI; powder type 2: PbI₂ (99.0%) and purified MAI; powder type 3: PbI₂ (99.9985%) and unpurified MAI. The input ratio is fixed at 1:1.6. As clearly shown, the structures of the prepared powders and corresponding device performances are very similar regardless of the purity of the initial chemicals.





Fig. S6. Schematic for the synthesis of various hybrid perovskite powders and photographs of as-synthesized powders. We obtained various hybrid perovskite powders by simply choosing the initial chemical sources, as shown in the figure.



Preliminary results on the formation of different intermediate phases

Fig. S7. Fourier-transform infrared (FT-IR) spectra of the MAPbI₃ thin films using intermediate-phase-controlled powders. The samples of PbI₂-MAI-DMSO and PbI₂-MAI-DMF were fabricated by the powders obtained from different polar solvents of DMSO (dimethyl sulfoxide) and DMF, respectively. The films were studied prior to the annealing step to detect the intermediate phases within the samples because the material was completely transformed to the crystalline MAPbI₃ phase after annealing. In the sample of PbI₂-MAI-DMSO, the peak corresponding to the PbI₂-MAI-DMSO complex is clearly observed [S1], as denoted by a green circle, whereas no intermediate phase is observed from the MAI-PbI₂-DMF because of the weak interaction with DMF [S2].



Comparison with the previous method: Device performances

Fig. S8. Comparison of photovoltaic performances with the case fabricated by the previous method (or normal method). The procedures for the deposition of MAPbI₃ solution with spin coating and annealing are the same for both methods. To obtain the statistical data, we tested over 80 devices fabricated by each method. Device stability tests were performed over 10 days with a device showing 15% efficiency under relative humidity conditions of ~30% in air. As clearly shown in Fig. S8, the device fabricated with our method exhibited better device efficiency and stability than that with the previous method.

REFERENCES for Supporting Information

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