Electronic Supplementary Information

Realizing Highly Luminescent Perovskite Thin Film by Controlling Grain Size and Crystallinity through Solvent Vapour Annealing

Sang-Hyun Chin,^{‡a,c} Jin Woo Choi,^{‡a} Hee Chul Woo,^a Jong H. Kim,^b Hong Seok Lee^{*c} and Chang-Lyoul Lee^{*a}

^{a.} Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology (GIST), Gwangju, 61005, Republic of Korea.

^{b.} Department of Molecular Science and Technology, Ajou University, Suwon, 16499, Republic of Korea.

^{c.} Department of Physics, Research Institute of Physics and Chemistry, Chonbuk National University, Jeonju, 54896, Republic of Korea.

EXPERIMENTAL METHODS

Perovskite thin film fabrication: Glass substrates were cleaned with detergent and sonicated in acetone, isopropyl alcohol (IPA), deionized water (DI water) for 15 minutes sequentially and washed with boiling isopropyl alcohol. After UV ozone treatment for 15 minutes, poly(3,4ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was spun-coat on substrates at 3000 rpm for 40 s and thermally annealed on hot-plate at 150 °C for 20 min. 0.3 M of lead bromide (PbBr₂, Sigma-Aldrich >98%) was dissolved in N,N-Dimethylformamide (DMF) and spun-coat on substrate at 3000 rpm for 20 s. Vapour-Assisted Solution Process (VASP) was carried out after PbBr₂ coating. 10 g of methylammonium bromide (CH₃NH₃Br, Aldrich) was sublimated at 125 °C for 1.5 hours in closed glass petri dish (radius 45 mm, height 20 mm). The solvent vapour annealing (SVA) process is demonstrated in the movie clip (Supporting Information). 100 μ l of polar solvent (N,N-Dimethylformamide; Sigma-Aldrich >99.8%, Dimethyl sulfoxide; Sigma >99.5%, DI water and Ethanol; Sigma-Aldrich >99.8%) was dropped on petri dish using 8 points and immediately the dish was sealed.

Characterizations of perovskite thin films: The X-ray diffraction (XRD) measurements were performed using a Rigaku D/max-2500 diffractometer with Cu–K α radiation (λ = 1.54 Å) at 40 kV and 100 mA. Steady-state photoluminescence (PL) spectra of CH₃NH₃PbBr₃ films were measured using monochromator (SP-2150i, Acton) equipped with photomultiplier tube (PMT, Acton PD-471) and ps-laser (LDH–P-C-405, PicoQuant) as an excitation source. The absolute photoluminescence quantum yield (PLQY) measurements of perovskite films were performed using a Hamamatsu C9920-02. The PL decay profiles of CH₃NH₃PbBr₃ films were investigated using the time-correlated single photon counting (TCSPC) measurement. A pulsed diode-laser head (LDH-P-C-405, PicoQuant) coupled with a laser-diode driver (PDL 800-B, PicoQuant) was used as the excitation source with a repetition rate of 5 MHz. The excitation

wavelength was 400 nm. The PL emissions were spectrally resolved using collection optics and a monochromator (SP-2150i, Acton). The time-resolved signals were measured by a TCSPC module (PicoHarp 300, PicoQuant) with a MCP-PMT (R3809U-50, Hamamatsu). The total instrument response function (IRF) was less than 140 ps, and temporal resolution was 16 ps. The deconvolution of PL decay curve, which separates the instrument response function (IRF) and actual PL decay signal, was performed using fitting software (FluoFit, PicoQuant) to deduce the time constant associated with each exponential decay curve.

DFT Simulation for interaction distance calculation: The DMol³ program in the Materials Studio 4.4 package, which is the quantum mechanical code, was used for this calculation.



Fig. S1. CH₃NH₃PbBr₃ films under UV light treated with various polar solvents.



Fig. S2. PL decay curves of perovskite films treated with various polar solvents.



Fig. S3. PL spectra of pristine and isopropyl alcohol treated CH₃NH₃PbBr₃ films.



Fig. S4. SEM images of perovskite films treated with (a) EtOH (b) DMF and (c) DMSO.



Fig. S5. Atomic portion of (a) top-side of pristine film, (b) bottom-side of pristine film,(c) top-side of SVA-treated film and (d) bottom-side of SVA-treated film.

The presented atomic ratio (At %) of Br/Pb explains the precursor-converting behaviour of SVA. Before the SVA, the unreacted PbBr₂ was remaining in the bottom side of the film as mentioned in the manuscript. For this reason, the bottom side shows lower atomic portion of Br/Pb (3) than the upper side (3.54). In contrast, we obtained similar value of Br/Pb portion (Bottom: 3.30 and Upper: 3.22) on the both sides of SVA treated film. This indicates that solvent vapour soaked into the grain and induced substantial reaction. As we mentioned in the manuscript, SVA process promotes blending of unreacted PbBr₂ and CH₃NH₃Br and convert into CH₃NH₃PbBr₃ perovskite. Finally, PL intensity of SVA treated film was increased by limiting exciton quenching through the trap state of Pb atoms.



Fig. S6. XRD pattern of CH₃NH₃PbBr₃ film treated by DMF.



Fig. S7. Deconvolution of PL spectrum of CH₃NH₃PbBr₃ film at SVA I stage.



Fig. S8. Cross sectional TEM image of perovskite film. (Inset: Small grains in bottom-side of film).



Fig. S9. Temperature-dependent photoluminescence characteristics of perovskite films with different grain size.



Fig. S10. XRD spectra of (a) pristine film, (b) SVA I film, (c) SVA II film and (d) SVA III film.



Fig. S11. PL images of CH₃NH₃PbBr₃ films with different SVA time.



Figure S12. Interaction distance between polar solvent molecules and CH₃NH₃⁺.

	τ_1 [ns] (f_1)	τ_2 [ns] (f_2)	χ^2
EtOH	8.27 (0.18)	0.13 (0.82)	1.201
H ₂ O	35.30 (0.88)	1.95 (0.12)	1.709
DMF	19.68 (0.57)	3.94 (0.43)	1.873
DMSO	16.53 (0.43)	2.42 (0.57)	2.372

Table S1. PL decay profiles of perovskite films treated with various polar solvents.

Monitored wavelength was 530 nm. The PL decay curves were fitted by a bi-exponential function to investigate exciton dynamics of perovskite.

	Ethanol	Water	DMF	DMSO
Chemical formula	CH ₃ CH ₂ OH	H ₂ O	(CH ₃) ₂ NCOH	(CH ₃) ₂ SO
Interaction distance (Å)	2.29	1.18	3.24	2.95
Polarity index	5.2	9.0	6.4	7.2
Vapour pressure (mmHg) at 20°C	44.6	17.7	2.7	0.42

Table S2. Interaction distance between polar solvent molecules and $CH_3NH_3^+$.