## **Supporting information**

## Unveiling the relationship between the perovskite precursor solution and the resulting device performance

Jincheol Kim, Byung-wook Park, Jongho Baek, Jae Sung Yun, Hyoung-Woo Kwon, Jan Seidel, Hanul Min, Simao Coelho, Sean Lim, Shujuan Huang, Katharina Gaus, Martin A. Green, Tae Joo Shin, Anita W. Y. Ho-baillie, Min Gyu Kim, Sang Il Seok

## Methods

**Microscope imaging.** The perovskite solution was placed in an eight-well chamber (Ibidi 80841) and sealed to prevent degradation. Imaging was performed using a home-built TIRF microscope equipped with a 100× 1.49 NA objective lens (Figure S2). Images were acquired simultaneously with two electron-multiplying charge-coupled device (EMCCD) cameras (Andor iXon Ultra 888). Emission from the perovskite colloids was split using a long-pass dichroic filter (Semrock FF560-FDi01), and each filter-equipped EMCCD camera acquired high-channel (570–630 nm) and low-channel (500–550 nm) spectral signals simultaneously to record a time series. Every frame was exposed for 500 ms under excitation by 488 nm diode lasers (Vortran Stradus) for 6,000 frames. As stochastic binding to the surface occurs very sparsely, this allows super-resolution blinking analysis and single-molecule localisation microscopy.<sup>1,2</sup>

**Image analysis.** The images acquired were analyzed using single molecule analysis software.<sup>3</sup> Briefly, a  $13 \times 13$  pixel square was used to identify a single binding event. A Gaussian function was fitted to the diffraction-limited point-spread function to determine the centre of mass. A table was generated containing all the fitted centres and their parameters. The final super-resolved image is a rendering of all the overlaid points.

**Temperature dependence of nuclear growths for LHP precursors.** Pb L<sub>III</sub>-edge and I K-edge X-ray absorption spectra, X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS), were collected on the BL10C beam line (WEXAFS) at the Pohang Light Source (PLS-II) with top-up mode operation under a ring current of 400 mA at 3.0 GeV. From the high-intensity X-ray photons of the multipole wiggler source, monochromatic X-ray beams could be obtained using a liquid-nitrogen-cooled double-crystal monochromator (Bruker ASC) with Si(111) crystal pair. All X-ray absorption spectra were recorded with transmittance mode using N<sub>2</sub>/Ar mixed gas-filled ionization chambers (IC-SPEC, FMB Oxford) for the incident and transmitted X-ray photons. Higher-order harmonic contaminations were eliminated by detuning to reduce the incident X-ray intensity by ~30%. Energy calibration was simultaneously carried out for each measurement with reference Pb foil in front of the third ion chamber. Temperature-dependent XAFS experiments were performed using *in situ* spectroscopic

heating cell consisting of V-shape folded polyimide tube (Diameter: 0.075 in.). The solution tube was placed between two heating chuck plates and pressed to a thickness of about 150  $\mu$ m. During temperature-dependent *in-situ* XAFS measurements, the precursor solutions were precisely heated up to 100 °C with heating rate of 0.42 °C/min under temperature control (Model 336 Cryogenic Temperature Controller, Lakes Shore Cryotronics Inc., USA). Using UWXAFS package, Fourier-transformed (FT) radial distribution function (RDF) of  $k^3$ -weighted Pb L<sub>III</sub>-edge and I K-edge EXAFS spectra,  $k^3\chi(k)$ , have been obtained in the *k* range between 2.5 and 12.0 Å<sup>-1</sup> through standard data analysis process.

Time of flight secondary-ion mass spectrometry (ToF-SIMS) measurement. ToF-SIMS profiling, imaging, and 3D tomography were used to measure the lateral and depth distributions of the LHP layers and completed devices. The samples were analyzed using a TOF-SIMS V instrument (IONTOF GmbH) with high current bunced mode (2 cross-over of beam alignment in ion lens, 21 ns and 8 pA). The hybrid system has a basic configuration with a ToF-SIMS generation IV sputter gun and a detector. Primary beam set at 25 keV and 1 pA by Bi<sup>+</sup> and sputter beam set 0.5 KeV and 40 nA by Cs<sup>+</sup>. It set the pulse length (10.9 ns), repetition rate (10KHz), acceleration voltage of secondary ions (2000 V), extraction timing (0 sec.), flight length (2 m), voltage of ion mirror (20 V), acquisition time (1000 sec.), incident angle (45 degree), sputter size (200×200  $\mu$ m<sup>2</sup>), analysis area (50×50  $\mu$ m<sup>2</sup>) and area dosage of ions (PIDD: 2.04522e+14), respectively.

**KPFM (Kelvin Probe Force Microscopy) measurement.** KPFM was performed using an atomic force microscopy (AFM, AIST-NT SmartSPM<sup>TM</sup> 1000) in a flowing nitrogen atmosphere. A nitrogen gun was used to remove particles on the sample surfaces before the measurements. AFM and KPFM measurements were performed using diamond-coated conductive probes (DCP20, force constant, k=48 N/m) which possess a resonance frequency of 420 kHz for both measurements. The probe was in non-contact mode with an AC voltage of -1 to +1 V. Note that the measurement was performed in the dark, and the operating laser wavelength of the AFM was 1300 nm, which is outside the absorption range of the LHP film. For the CPD measurement in light, the sample was illuminated from the top by a light-emitting diode with an intensity of ~0.3 suns.

**Crystallography, size of colloid, imaging of film, and optical properties**. X-ray diffraction measurements were performed using a D/MAX2500V/PC instrument (Rigaku) with a Cu target at 40 kV and 200 mA. The obtained XRD curves at [110]tetragonal are fitted by Gaussian kernel for sorting the precise crystal components such as amorphous, disorder and order phases from three LHP samples. Basically, there are many sub-crystal components in a non-symmetrical XRD peak and they can be distinguished by the Gaussian curve fitting. Each fitted curve is attributed to various crystal strain modes such as no-strain, uniform-strain and non-uniform strain those are also corresponding to no-defect, defective and un-forming crystals. Those three crystal components are well investigated in previous report.<sup>4</sup> The UV–Vis–NIR optical properties were measured using a JASCO V-780 instrument with an integrating sphere. Dynamic light scattering (DLS) measurements were performed by Zetasizer Nano ZS. The measurement was done with a quartz cuvette using multi-size distribution (MSD) mode. The surface morphologies and local crystal properties were examined at the Central Research Facility of Ulsan National Institute of Science and Technology. The surface morphologies of the LHP thin films were captured at 80k and 5k magnification at a beam power of 5 kV by cold FE-SEM (SU-8220, Hitachi High-Technologies). To investigate the local crystal properties, most samples were prepared using a dual beam focused ion beam (FIB; FEI Nova Nanolab 200). The FIB milling and polishing process ensured that the samples had a smooth cross sectional surface, which was then then imaged using the SEM on the dual beam focus ion beam.

**Obtained optical properties of LHP samples**. To calculate the absorption coefficients and optical energy band gaps from Tauc plots, the prepared LHP samples were scanned by a V-780 UV–Vis–NIR spectrophotometer (Jasco. Co. Ltd.) equipped with an integrating sphere (ILN-902i, 150 mm diameter). The system consisted of a Czerny–Turner mount, a double monochromator, fully symmetrical double-beam-type lamps (deuterium, spectral range 190–350 nm and halogen, spectral range 330–1600 nm), and a photomultiplier tube with a Peltier-cooled InGaAs photodiode. The scan range was 190–1600 nm with spectral bandwidths of 0.5 nm in the UV–Vis region and -3 to 3 Abs in the NIR region. The photometric accuracy was  $\pm 0.0015$  Abs (0.0 to 0.5 Abs),  $\pm 0.0025$  Abs (0.5 to 1.0 Abs), and  $\pm 0.3\%$ T. The RMS noise was 0.00003 Abs.

**Investigation of charge carrier dynamics**. Steady-state PL spectra and TCSPC data were recorded using a FluoTime 300 (PicoQuant GmbH) instrument equipped with a PMA-C-192-M detector, high-resolution excitation monochromator, and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH). The LHP samples were placed in an integrating sphere. Charge excitation of the samples was conducted at 513 nm. The excitation fluence intensity was set to 1.5 mW·cm<sup>-2</sup>, as measured using a power meter (Thorlabs PM100D). The diode laser was controlled by a PDL 820 driver to control the picosecond pulses of the excitation light source (internal repetition rates between 196 kHz and 80 MHz) and was kept at 10 MHz during scanning TCSPC. The laser beam was incident onto the back side (LHP side) of the LHP film/glass substrate. TCSPC data were collected at the wavelength of the maximum PL intensity. The LHP precursors were coated on quartz glass substrates. The PL emission decay curves were fitted using the following equation:

$$Y = A_1 \exp(t/t_1) + A_2 \exp(t/t_2)$$
(1)

where *Y* is the time-dependent emission intensity,  $A_1$  and  $A_2$  are the relative amplitudes, and  $t_1$  and  $t_2$  are the fitted PL decay times. Eqn (1) demonstrates that the charge carrier dynamics are described by a combination of nonradiative recombination at defect sites and radiative recombination in bulk LHP films, which are assigned to  $t_1$  and  $t_2$  as the fast and slow components, respectively.

SCLC measurement for calculations of total trap densities. The J-V curves of three representative LHP samples were scanned by a source meter (Keithley 2636B) in a range from 0 to 2 V under dark conditions. The OHP films were deposited to indium tin oxide (ITO) glass substrate. The gold counter electrode had coated in a sandwich structure after the LHP/ITO glass substrate was prepared.

The evaluation of fabricated PSCs. The J-V curves were measured using a source meter (Keithley 2420) with a solar simulator (Newport, Oriel Class AAA, 94043A) at 100 mA·cm<sup>-2</sup> illumination (AM 1.5 G) and a calibrated Si reference cell (Newport, Model 91150V) certified by NREL. The calibrated 1 sun illumination was automatically maintained by an exposure control

instrument (Newport, Model 68951). The J-V curves were measured in reverse scan mode. The step voltage and delay time were fixed at 10 mV and 40 ms, respectively. The delay time was set at each voltage step before the current was measured. The J-V curves of each device were measured by masking the active area with a metal mask 0.096 cm<sup>2</sup> in area. The EQEs of each LHP solar cell were estimated using an IQE-200B system (Newport, Oriel). The steady-state current density was measured using AUTOLAB (model AUT302N). During all measurements for LHP solar cells had attached anti-reflection polymer onto front of FTO glass.



**Figure S1.** (a) UV–Vis absorption spectra of perovskite precursor solutions with various concentrations. (b) Tyndall effect on the perovskite precursor solution and the variation in colloidal size depending on the concentration



**Figure S2**. (a) Schematic illustration of objective-based TIRFM. L1 and L2: lenses, DM1 and DM2: dichroic mirrors, F1 and F2: filters, CAM1 and CAM2: EMCCDs, OBJ: objective lens, BFP: back focal plane. A 488 nm diode laser was focused onto the BFP of the objective lens. TIRF illumination was achieved by displacing the laser beam towards the periphery of the objective. Light emitted from the perovskite colloidal sample is separated from the lasers using DM1 and focused onto the EMCCD cameras, CAM1 and CAM2. To prevent degradation, the sample was placed in a sealed chamber. (b) TIRFM imaging of the precursor solution (scale bar = 2  $\mu$ m). Emission from the colloids is detected in two spectral ranges (500–550 nm for the blue spot and 570–630 nm for the red spot).



**Figure S3.** The cross-sectional TEM images for (a) control, (b) target and (c) excess conditions of LHP films.



**Figure S4.** (a) X-ray diffraction patterns for control, target and excess are displayed from 10 to 50 degrees. It is appeared the representing crystal orientations of (110)t and (220)t. (b) the magnified XRD peak at (110)t has shown. Three each peaks of (c) control, (d) target and (e) excess LHP film conditions have deconvoluted by Voigt (or pseudo-Voigt) to two crystal components that can assign to (1) envelopment, (2) (002)t and (3) (110)t phases in comparisons. (f) The ordered component (denoted as 3 for the deconvoluted peak) of control, target and excess LHP films.



**Figure S5.** The PL spectra for three represented LHP films such as (a) control, (b) target, (c) excess with Gaussian fitted results in Figure 4(a2). The A, B peaks are attributed to disorder and order phases, respectively. According to previous investigation,<sup>7</sup> the order and disorder phases of MAPbI<sub>3</sub> on PL peak had depended on the values of FWHM (comparatively large FWHM is disorder amongst two components).



**Figure S6.** ToF-SIMS spectra of (a) lead (Pb<sup>+</sup>), (b) iodide (I<sup>-</sup>), (c) hydrogen (H<sup>-</sup>) and (d) carbon (C<sup>-</sup>) for LHP films deposited using control, target and excess conditions. Pb<sup>+</sup> had measured at a positive polarity mode. I<sup>-</sup>, H<sup>-</sup> and C<sup>-</sup> were detected at a negative polarity mode.



**Figure S7.** (Top) Spatial CPD maps  $(4\mu m^2)$  with are shown that dark, light with (Bottom) surface photovoltage (SPV) profiles for (a) control, (b) target and (c) excess LHP samples of the white lines indicated on each spatial CPD maps, respectively.



**Figure S8.** (a) CPD distribution over-occurrence (256 x 256 pixels over 16  $\mu$ m<sup>2</sup>), (b) Average CPD plot of grain interiors (GI) and grain boundaries (GB) for control, target and excess LHP samples. (c) Summary of calculated work function of each sample. Note that the work function of the diamond-coated conductive probe (DCP20) is measured to be 4.0650eV.<sup>5</sup>



**Figure S9.** The (a) transmittance and (b) absorbance spectra for three representative LHP films shown in Figure 4(a1).



**Figure S10.** TCSPC spectra of three representative LHP films such as (a) control, (b) target, (c) excess with bi-exponential curves fitted with results shown in Figure 4(a3).



**Figure S11.** TCSPC spectra of LHP layer with and without HTM layer for three LHP samples; control, target, and excess.



**Figure S12.** Distributions of (a)Voc, (b) Jsc, (c) FF and (d) PCEs from each 15 samples with various  $I_3^-$  added to MAPbI<sub>3</sub> precusor solution. The box is determined by the 25th and 75th percentiles. The whiskers are determined by the 5th and 95th percentiles. The open square and line in the box represents mean and median respectively. Other closed squares mean individual data point and the minimum/maximum values are shown in X mark.



**Figure S13.** The J-V curves of the device of control, target, and excess sample under both reverse-and forward-scan direction.



Figure S14. Dynamic stability test under 1 Sun radiation condition in N2 condition



**Figure S15.** J-V curves of the FAPbI<sub>3</sub>-based perovskite solar cell with  $I_3$ - IPA solution. Control device is FAPbI<sub>3</sub> without additional  $I_3$ - insertion. In case of target and excess sample, 20 and 50 mmol% of  $I_3$ - IPA solution are used respectively based on the control sample.

	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	FF	PCE [%]
Control	1.07	22.47	0.73	17.51
Target	1.11	23.43	0.79	20.60
Excess	1.07	22.80	0.73	17.88

Table S1. The solar cell performances from three represented LHP samples in Figure 4(c1).

## Reference

- Betzig E.; Patterson, G. H.; Sougrat, R.; Lindwasser, O. W.; Olenych, S.; Bonifacino, J. S.; Davidson, M. W.; Schwartz, J. L.; Hess, H. F. Imaging Intracellular Fluorescent Proteins at Nanometer Resolution. *Science* 2006, *313*, 1642-1645.
- 2 Rust, M. J.; Bates, M.; Zhuang, X. Sub-diffraction-limit imaging by stochastic optical reconstruction microscopy (STORM). *Nat Methods* **2006**, *3*, 793-795.
- de Keijser, Th. H.; Langford, J. I.; Mittemeijer, E. J.; Vogels, A. B. P., Use of the Voigt function in a single-line method for the analysis of X-ray diffraction line broadening, *J. Appl. Cryst.* **1982**. *15*, 308-314
- 4 Stoumpos, C. C.; Malliakas, C, D.; Kanatzidis, M. G., Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties, *Inorg. Chem.* **2013**, *52(15)*, 9019-9038.
- Kim, D.; Yun, J.; Lyu, M.; Kim, J.; Lim, S.; Yun, J. S.; Wang, L.; Seidel, Probing Facet-Dependent Surface Defects in MAPbI3 Perovskite Single Crystals. J. J. Phys. Chem. C 2019, 123, 14144-14151
- 6 Stern, E. A.; Newville, M.; Ravel, B.; Yacoby, Y.; Haskel, D. The UWXAFS analysis package: philosophy and details. *Physica B: Condensed Matter* **1995**, *208-209*, 117-120.
- Park, B.; Zhang, X.; Johansson, E. M. J.; Hagfeldt, A.; Boschloo G.; Seok, S. I.; Edvinsson,
  T. Analysis of crystalline phases and integra-tion modelling of charge quenching yields in
  hybrid lead halide perovskite solar cell materials. Nano Energy 2017, 40, 596-606