Visualizing Photoinduced Ion Migration in Halide Perovskite Grains

Hoyeon Choi¹, Jack Chun-Ren Ke¹, Stefan Skalsky², Christopher A. Castle³, Kexue Li⁵, Katie L. Moore⁶, Wendy Flavell⁷, and Patrick Parkinson³⁺

a. Department of Physics and Astronomy and the Photon Science Institute, The University of Manchester

b. Department of Materials and the Photon Science Institute, The University of Manchester

Experimental Details

Sample preparation

Substrate sanitizing

For all photoluminescence experiments, perovskite samples were prepared on z-cut quartz substrates. All substrates were thoroughly cleaned via common cleaning processes used in fabrication of perovskite solar cells: First, the substrates were cleaned using a sequence of Helimax III (3 vol % in deionised (DI) water), DI water, and acetone, with the substrate placed into each solution and ultrasonicated for 10 minutes. Subsequently, the washed substrates were dried using dry air, followed by UV-O³ treatment for 15 minutes in order to remove organic residuals prior to deposition of the MAPI films.

AACVD MAPI

First, 0.405 g of lead iodide (PbI₂, 99.9985 %, Alfa Aesar) was dissolved in 3 mL of warm (~70 °C) anhydrous N,N-dimethylformamide (DMF, 99 %, Sigma-Aldrich) solvent with stirring for 30 minutes to generate a clear yellow solution (concentration 0.3 M). Subsequently, a stoichiometric amount (0.147 g, 0.3 M) of methylammonium iodide (MAI, CH₃NH₃I, 98 %, Ossila) was poured into the solution under continuous stirring for another 30 minutes at room temperature to form a translucent light-yellow perovskite solution (0.3 M). The prepared solution was directly used as the supply for the AACVD without further steps. The apparatus used for the AACVD has been previously described in detail by Ramasamy et al. and employed in synthesis of Cs₂SnI₆ double perovskite.¹¹ First, 3 mL of the DMF solution was poured into a two-necked 100 mL round-bottom flask with a gas inlet that allows Ar carrier gas (at a flow rate of ~300 sccm) to travel into the solution to transport mist produced by a domestic humidifier. Prior to deposition, the solution was pre-humidified for 10 minutes to ensure a homogeneous perovskite solution before opening the gas valve for deposition. This flask was connected to a long glass tube (50 cm) in a furnace where the temperature during deposition was set to be 100 °C. The deposition time was fixed for an hour to obtain a film thickness of ~600 nm. After the deposition, the samples were annealed at 100 °C in ambient atmosphere for 30 minutes to completely remove residual solvents from both the samples and the AACVD tube. The MAPI samples were then removed from the AACVD tube and stored in relevant sample containers in a vacuum desiccator.

Spin-coated MAPI

For production of spin-coated films, the chemicals used are identical to those utilized for the preparation of AACVD-grown samples. First, 0.254 g of lead iodide was dissolved in the mixture of 100 µl anhydrous dimethyl sulfoxide (DMSO, 99.9 %, Sigma-Aldrich) and 400 µl DMF at 70 °C with stirring for 30 minutes to generate a clear yellow solution (with a concentration of 1.0 M). Subsequently, a stoichiometric amount (0.092 g, 1.0 M) of MAI was added into the solution under continuous stirring for another 30 minutes at room-temperature to form a translucent light-yellow perovskite solution (1.0 M) for use in spin coating. Prior to spin coating, the substrates were heated at 70°C and only removed from a hot place just before spin coating (within 10 seconds). In the spin...
coating steps, a small volume (50μl) of the perovskite solution was poured on top of the substrate and the film was then spun at 4000 rpm for 30 seconds. Subsequently, the as-deposited samples were subsequently transferred to a hot plate for annealing at 100 °C in ambient air for 10 minutes. The resultant MAPI samples were then stored in the same way as the AACVD-grown films.

Characterization

Confocal PL mapping
The schematic of the home-built μ-PL scanning microscope is shown in Fig. S1. A He-Ne continuous wave laser at 632.8 nm was employed to excite the sample. The excitation beam is split by two 50:50 beam-splitters; the first divides the beam to the sample and an integrated power meter. The sample stage is attached to an encoded xy stage, and a 60× objective lens (Olympus) is attached to a stepper-motor controlled z axis. The 3-dimensional freedom allows 3D scanning in which the spatial resolution of the translation stage is ~100 nm. Fluorescence emitted from the sample was split by the second beam splitter. One branch was detected to a fibre coupler with ~30× magnification; this could be coupled to a spectrometer (Ocean Optics) through a multimode optical fibre of diameter 105μm, to give a detection collection diameter of ~3.5 μm. The other beam branch was simultaneously monitored using a CCD camera.

Grazing incidence X-ray diffraction (GIXRD)
X-ray diffraction (XRD) were conducted using a Bruker D8 Advance at a grazing incidence(GI) angle of 3° to probe signals from thin films. The scanning range (2θ) was 10-50° with a theta step of 0.05° and dwell time of 4.5 s.

i-TCSPC
A 405 nm pulsed diode laser at a frequency of 500 kHz and pulse duration 80 ps was used to excite the samples. The same sample stage of confocal scanning microscope was used to excite and detect the samples (Figure S1). Instead of the spectrometer, a single-mode optical fibre was used to transport the photoluminescence signal to the i-TCSPC system. Briefly, a folded-Michelson interferometer with dual channel SPAD (idQuantique 100) detectors was combined with TCSPC (Hydraharp 400) hardware in T2 mode. The interferometer was continually scanned, and each detected photon was binned according to arrival time, channel and interferometer position; this permits spectral, decay and kinetics to be resolved in post-processing.

Scanning electron microscopy (SEM)
The morphology of the MAPI films (by AACVD, and spin coating) deposited on ITO-coated glasses was probed using a Zeiss Sigma SEM instrument, with an acceleration voltage of 10 kV using secondary electron images.

NanoSIMS analysis
A NanoSIMS 50L (CAMECA, France) was used to map the elemental distribution and depth profile the samples. A 16 keV Cs⁺ beam with a beam current of 1.6 pA was scanned over the surface using a raster size of 20×20 μm over 256×256 pixels with 1500 μs dwell time per pixel. The secondary ions; 12C⁺, 16O⁺, 12C₂⁺, 12C¹⁴N⁺, 28Si⁺, 28Si²⁺, and 127I⁻ were analyzed in a double focusing mass spectrometer and the ion-induced secondary electron (SE) signal was also collected. Apertures and slits were set to D1-3, ES-3, AS-2 and EnS-open. 200 images were acquired from each position to obtain a depth profile of the selected elements. ImageJ with the OpenMIMS plugin (Harvard, Cambridge, MA, USA) was used for data analysis. To avoid topography artifacts at the edges of the particles, only regions from the center of the particles were selected as shown in Figure 4 (main manuscript) and Figure S10. 12C¹⁴N⁺ was used as a reference signal to reflect the unaffected matrix composition and shows a
stable $^{12}\text{C}^{14}\text{N}^-$ signal intensity. Secondary ion ratios, $^{16}\text{O}^-/^{12}\text{C}^{14}\text{N}^-$ and $^{127}\text{I}^-/^{12}\text{C}^{14}\text{N}^-$, were used to show the depth distribution of oxygen and iodine.

**Supplementary Results**

Additional results referred to in the main manuscript are provided in Figures S2, S4, S5, S6, S7, S8, S9, S10 and S11. These figures are described in the main text where introduced.

**Figure S1.** A schematic of the optical configuration of the home-built $\mu$-PL scanning microscope. BS1, BS2 represent 50:50 non-polarizing beam-splitters. FM is a flick mirror, F1, F2 are 650 nm long pass filters, OF is optical fibre, and PM is calibrated silicon power meter. The $x$ and $y$ position of the sample was controlled using an encoded stage, while the $z$ position of the objective was set using a stepper motor. A quasi-confocal arrangement was achieved using the collection fibre as aperture.
Figure S2. Photoluminescence (PL) mapping images of the AACVD sample a) and spin-coated reference sample d). b) and d) are corresponding SEM images to a) and c) with the same magnification respectively. The scale bars in a-b), d-e) are 25μm in length. c) and f) are SEM images of AACVD and spin-coated sample with higher magnification respectively. The scale bars in c) and f) are 5 μm in length. The PL spectrum of the pristine spin coated perovskite film is displayed in e) (For the comparison to the AACVD sample, we added the grey dash line standing for the PL spectrum of the AACVD sample in the main text.)
Figure S3. GIXRD diffractograms of the MAPI films fabricated via AACVD (upper) and spin coating (lower). The reflection of a tetragonal-phase MAPI are indicated where (110) is the highest diffraction park, along with (001) and (101) stands for the contribution of a hexagonal PbI$_2$.
Figure S4. The photo-brightening and degradation in the AACVD MAPI with different illuminations, a) Switching on/off PL measurement on the AACVD MAPI film with the CW laser at 2 eV, with detailed behaviors in each region (I,II,III, and IV) elaborated in c), b) The same measurement with 3 eV pulsed laser. Higher-resolution data from region (I,II, III and IV) are shown in d).
Figure S5. Excitation power dependence on the AACVD MAPI with a continuous laser at 2 eV a), and a pulsed diode laser at 3 eV b).
Figure S6. a) Intensity and b) median emission energy maps for the AACVD MAPI sample, showing the early time evolution driven by the light soaking effect. The scale bars are all 25μm in length. A steady brightening in emission and growth of homogeneous emission size is observed over the first 10 hours. Concomitantly the sample emission redshifts, with an increasing homogeneity in emission energy.
Figure S7. An example of the spatial analysis carried out on each frame used to identify small grains a), large grains b), the centers of grains c) and the edge of grains d) from intensity data. The scale bar in the each PL maps are 10μm in length.
Figure S8. Comparable linear correlation study for spin-coated MAPI, showing a) spectrum and emission energy evolution, b) the PL evolution of the higher energy regions (median emission $E_{\text{em}} > 1.6115$ eV) and lower energy regions ($E_{\text{em}} < 1.6115$ eV) of the film.
Figure S9. The evolution of emission lifetime over 300 s of acquisition time under i-TCSPC conditions. The lifetime were obtained using a biexponential fitting function $I(t) = P_1 \exp\left(-\frac{t}{\tau_1}\right) + P_2 \exp\left(-\frac{t}{\tau_2}\right)$ where $I(t)$ is the intensity of the detected fluorescence, $P_1, P_2$ are the amplitude, and $\tau_1, \tau_2$ are the decay times. The evolution in the slow decay term, $\tau_2$ as a function of measurement time are plotted in a) pristine, b) air exposed, c) light-soaked and d) degraded states. The small grain and center and edge of large grain regions were selected manually.
Figure S10. The changes in the center of the emission energy. Gaussian fitting on the each emission by the time was exploited to obtain the central position of the emission spectrum. The evolution in the central energy of a small grain are plotted in a) pristine, b) air exposed and c) light soaked. That of the edge of a large grain are plotted in d) pristine, e) air exposed and f) light soaked. That of the center of a large grain are plotted in g) pristine, h) air exposed and i) light soaked.
Figure S11. NanoSIMS results showing the final secondary electron (SE) images (assumed to be at the substrate of the sample) for the sample without illumination a), with illumination b) and the row counts of each ion species, c-f) the counts of $^{127}$I$^-$, $^{16}$O$^-$, $^{12}$C$^{14}$N$^-$ and $^{28}$Si$^2$- respectively.

References