Supporting Information for Subgrain Special Boundaries in Halide Perovskite Thin Films Restrict Carrier Diffusion

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For the photoluminescence (PL) intensity distribution measurement, thin film samples of polycrystalline $FAPbI_3$ (thickness ∼500 nm) are excited by a focused 532 nm laser (Verdi, Coherent) with a 100X Nikon oil immersion objective (spot size around 250 nm, average power density around 320 mW/cm^2) in an inverted microscope system (TE2000, Nikon). PL signal is collected by the same objective and imaged with a CCD camera (Pixis 1024B, Princeton Instruments). The PL spectrum of the sample has a peak centered at 810 nm with a 40 nm full-width at half-maximum (FWHM). Note that PL collected from a given region of the sample may have two distinct spatial origins: (1) light directly produced by recombination in the collection volume, and (2) light indirectly produced by recombination elsewhere but which is waveguided within the high index ($n_r = 2.4$)[1] perovskite film and gets scattered out in collection volume. Fortunately, the process of light absorption and remission events as light travels through the film red-shifts the spectrum of the indirectly scattered PL over long distances (through the photon recycling effect[2]), and thus it is possible to reduce the indirect spatial contribution by placing a 800 nm shortpass filter in the collection path.

For confocal PL intensity and lifetime measurements, samples are excited with a 408-nm pulsed laser (MDL 300, PicoQuant) with a 2.5 MHz repetition rate and 40 μJ/cm^2 pulse energy density (pulse width 180 ps). The PL signal is coupled into a single-mode fiber (P1-780A-FC-2, Thorlabs), detected by a single-photon avalanche photodiode (τ-SPAD, PicoQuant), and recorded with a time-correlated single-photon counting system (PicoHarp 300, PicoQuant).

The time-resolved PL data was first normalized so that $I(0) = 1$ and then fitted with a bi-exponential decay model $I(t) = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2}$. Least squares method was used for fitting the model with uncertainties obtained from background and shot noises added in quadrature $\sqrt{N_{\text{shot}}^2 + N_{\text{bg}}^2}$. Figure S1 shows an example of such fitting.

The average lifetime used in the main text is a weighted average of τ_1 and τ_2. The weights being proportional to the total photons of the two decays: $w_i = \int_0^\infty I_i e^{-t/\tau_i} dt = I_i \tau_i$.

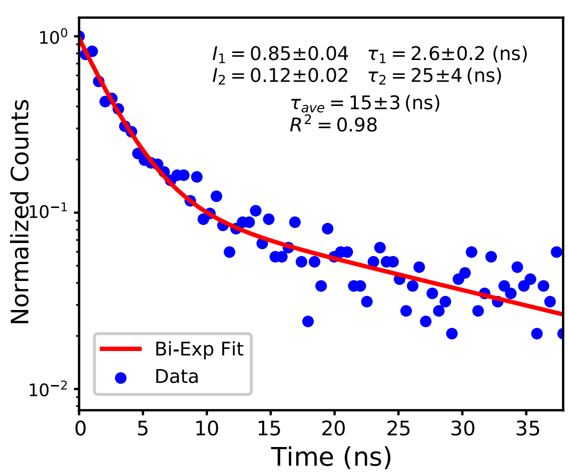

Figure S1: Time resolved PL intensity data and bi-exponential decay fitting

Note that the SEM image shown in Fig. 2 of the main text was taken at a tilted angle of 70° for purposes of the EBSD measurement. The raw SEM image is shown here in

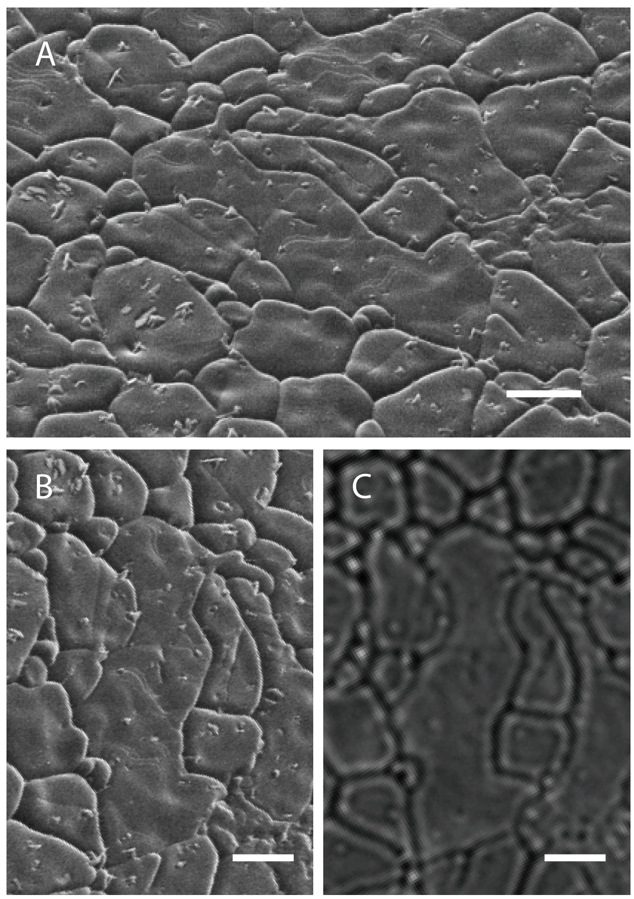

Figure S2: (a) Raw SEM image. (b) Rotated and scale-corrected SEM image. (c) Optical microscopy image. All scale bars are 3 μm.

Fig. S2a. Figure S2b shows the image corrected for perspective using the corresponding optical reference image shown in Fig. S2c.

The atomic force microscopy (AFM) measurements in Fig. 1c were obtained in contact mode using a commercial system (MFP3D Origin, Asylum Research with ASYELEC.01R2 probe tips, Asylum Research). The optical micrographs shown in Figs. 1a, 2a-c, and S2c as well as the TOC image were recorded in transmission mode under Kohler illumination with a halogen white-light source using the same inverted microscope and camera setup described above for the PL measurements (TE2000, Nikon; Pixis 1024B, Princeton Instruments). The SEM image shown in panels b,d-f of Figure 1 in the main text was obtained using a field-emission SEM (Zeiss, LEO 1530 VP) at an acceleration voltage of 5 kV.

Electron backscatter diffraction (EBSD) patterns were collected on a Cartesian grid (at 500 nm intervals) across all five regions of the large grain in the main text shown in Fig. 2d in the main text. Due to the varying sizes of the subgrain regions, the number of patterns used for the averages for regions 1 through 5 were 40, 17, 43, 40, and 67, respectively. The EBSD detector used was model *Symmetry* from Oxford Instruments. The parameters used during data acquisition were a 30 kV acceleration voltage and 0.34 nA beam current.

References

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(2) Fang, Y.; Wei, H.; Dong, Q.; Huang, J. Quantification of Re-absorption and Re-emission Processes to Determine Photon Recycling Efficiency in Perovskite Single Crystals. *Nat. Commun.* **2016**, *8*, 14417.