Supplementary Materials for

*High grain boundary recombination velocity in polycrystalline metal halide perovskites*

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Supplementary Text

Two-dimensional (2D) carrier diffusion model and simulation details

MATLAB Partial Differential Equation (PDE) Toolbox was used for 2D carrier diffusion simulation based on finite element analysis of 2D diffusion PDE equation. A square frame with 5 μm was created first with four corners coordinated at (0, 0), (0, 5), (5, 0) and (5, 5). Then meshes with triangular elements were generated uniformly within the square. All the nodes between these meshes will become numeric approximations of a PDE equation’s solution at their corresponding coordinates, including nodes on the edges. A total number of 283225 nodes were generated in our simulations to ensure the accuracy of spatial resolution.

The 2D diffusion PDE equation describing the laser-excited carriers transport in perovskites without external electrical and magnetic fields is given by: (24, 25)

\[
\frac{\partial n(x,y,t)}{\partial t} = D \left( \frac{\partial^2 n(x,y,t)}{\partial x^2} + \frac{\partial^2 n(x,y,t)}{\partial y^2} \right) - A n(x,y,t) - B n^2(x,y,t) - C n^3(x,y,t),
\]

where \( n(x,y,t) \) is the carrier density (holes or electrons) at coordinates \((x,y)\) and time \( t \). \( D \) is the diffusion coefficient. \( A, B \) and \( C \) are trap-assisted, bimolecular and auger recombination rate constants respectively. For the time resolution, \( m_t \) frames with equal intervals were divided between the starting time \( t_{\text{start}} \) to the ending time \( t_{\text{end}} \). \( m_t, t_{\text{start}} \) and \( t_{\text{end}} \) were decided according to experimental conditions.

The initial condition of the 2D diffusion PDE equation is given by:

\[
n(x,y,t_{\text{start}}) = n_0 e^{-(\frac{(x-x_0)^2}{2\sigma_x^2} + \frac{(y-y_0)^2}{2\sigma_y^2})},
\]

where \( n(x,y,t_{\text{start}}) \) is the initial carrier density (holes or electrons) at coordinates \((x,y)\) and \( t_{\text{start}} \). \((x_0,y_0)\) is the center of laser excitation position. A 2D gaussian carrier density function was implemented to mimic the laser pulse intensity distribution in the axial plane, and \( \sigma_x \) and \( \sigma_y \) are standard derivations in the \( x \) and \( y \) directions, which could be decided by fitting the normalized experimental PL profile data at the start time with the normalized \( n(x,y,t_{\text{start}}) \) (Fig. S1b). Then \( n_0 \) is estimated according to the equation:

\[
\iint n_0 e^{-(\frac{(x-x_0)^2}{2\sigma_x^2} + \frac{(y-y_0)^2}{2\sigma_y^2})} \, dx \, dy = n_{\text{photons}},
\]

where \( n_{\text{photons}} \) is the total photon counts generated by laser excitation per pulse, which was assumed to be equal to the photon flux of 6000 photons per laser pulse used in this work, as most
of our perovskite solar cells had over 90% EQE in the excitation wavelength range. As a result, a typical $n_0$ value of $10^4$ was used in our simulations.

Two different boundary conditions were considered during the simulation depending on the location of the laser excitation spot. When the laser is focused onto the grain center and the distance of excitation spot to grain edges $L_{GB}$ is larger than the carrier diffusion length $L_D$, boundary condition

$$\vec{n} \cdot \nabla n(x,y,t) = 0$$

was used for simulating the PL profiles and confocal TRPL. When the laser is focused near a grain boundary, e.g., $L_{GB} < 1 \mu$m, Neumann boundary conditions on the edges satisfy the equation below:

$$\vec{n} \cdot \nabla n(x,y,t) + \frac{S_{GB}}{D} n(x,y,t) = 0 \big|_{(x,y)}$$

where $\vec{n}$ is the outward unit normal vector and $S_{GB}$ is the grain boundary recombination velocity.

**TRPL profiles**

The TRPL profile is the PL intensity change with time $t$, which can be extracted from the 2D carrier diffusion simulation. Firstly, the maximum carrier density value is found in all the time frames from 0 s to $t_{end}$, and this time is defined as $t_{start}$. For $i$ th frame at time $t_i$ between $t_{start}$ and $t_{end}$, the simulated TRPL signal $F_{TRPL}(t_i)$ is defined with the maximum carrier density, i.e.,

$$F_{TRPL}(t_i) = \max_{x,y} n(x,y,t_i). \{t_i, F_{TRPL}(t_i) \mid i = 1, ..., m \}$$

are points of simulated TRPL profile. Here are $m_t$ frames from $t_{start}$ to $t_{end}$ are selected, and the maximum carrier density at each time frame is $\max_{x,y} n(x,y,t_i)$. Because the PL signal intensity is assumed to be the same with carrier density, the TRPL signal intensity $F_{TRPL}(t_i)$ at $t_i$ is $\max_{x,y} n(x,y,t_i)$. $F_{TRPL}(t_i)$ vs $t_i$ for all $t_i$ between $t_{start}$ and $t_{end}$ is the TRPL profile.

**PL profile and Carrier diffusion profile**

The PL profile is the PL intensity distribution along the specific line defined in the 2D mesh grids. For the PL profile $\{d_k, F_{PL}(d_k, t_i) \mid k = 1, ..., m_k \}$ ($m_k$ is the number of sampling points) at time $t_i$, profile origin $(x_{center}, y_{center})$ and degree $\theta$ were defined first. $d_k$ is the distance between one sampling point and the origin along the specific line. In most cases, the profile origin is the center of laser excitation position $(x_0, y_0)$. Profile degree $\theta$ is defined as $\theta = \arctan(k), \theta \in \ldots$
$(-\frac{\pi}{2}, \frac{\pi}{2})$, where $k$ is the slope of the profile line. The unit direction vector of the profile line is defined as $\vec{u} = \cos\theta \vec{u}_x + \sin\theta \vec{u}_y$, where $\vec{u}_x$ and $\vec{u}_y$ are unit vectors of x axis and y axis respectively. Because the simulation is based on nodes in the 2D mesh grids, which is discrete rather than continuous, to get accurate and smooth PL profile, the specific line here needs to have a width along the direction vertical to the line. All the nodes in the specific line with width are used to calculate the distance $d_k$, and the corresponding carrier densities are the PL intensity $F_{PL}(d_k, t_i)$. Here is a practical method to correctly select the sampling points. All the profiled nodes $\{(x_k, y_k) | k = 1, ..., m_k\}$ satisfy $|x_k \cos \theta - y_k \sin \theta - x_{center} \cos \theta + y_{center} \sin \theta| < w$, and $w$ is decided based on the mesh nodes density and profile width (distance along the direction perpendicular to $\vec{u}$). A typical value of $w$ is 0.05. After sampling all the nodes, $d_k$ is calculated by $d_k = (x_k \vec{u}_x + y_k \vec{u}_y) \cdot \vec{u}$, and the simulated TRPL signal $F_{PL}(d_k, t_i)$ is defined with the carrier density, i.e., $F_{PL}(d_k) = n(x_k, y_k, t_i)$. $F_{PL}(d_k, t_i)$ vs. $d_k$ is the PL profile.

After getting all the PL profiles at different time $t_i$ between $t_{start}$ and $t_{end}$. A 3D mapping plot by stacking all PL profiles from $t_{start}$ to $t_{end}$ is the carrier diffusion profile. In the carrier diffusion profile, the x axis is the distance $d_k$ of each PL profile, y axis is the time $t_i$ from $t_{start}$ to $t_{end}$ and z axis is the PL intensity $F_{PL}(d_k, t_i)$. With this stacking method, the carrier diffusion profile $F_{CD}$ can be defined as $\{F_{CD}(d_k, t_i, F_{PL}(d_k, t_i)) | k = 1, ..., m_k; i = 1, ..., m_t\}$. By assigning $\{d_k | k = 1, ..., m_k\}$ along x axis, $\{t_i | i = 1, ..., m_t\}$ along y axis and $\{F_{PL}(d_k, t_i) | k = 1, ..., m_k\}$ along z axis, a typical carrier diffusion profile is finished.

**One-photon surface TRPL measurement**

The method that using one- and two-photon-excited TRPL to investigate the surface recombination velocity ($S_{Surf}$) was initially proposed by Wang et al., (38) and further developed for a wide range of semiconductor materials including perovskite bulk crystals. (39, 50) Fig. S14a shows the schematic of the one-dimensional (1D) diffusion model for this method. A 405 nm pulsed laser with a large spot size of around 1 mm was adopted for the measurement, where the lateral carrier diffusion could be ignored, and the evolution of carrier density along the vertical direction from the surface of the crystal $n(x, t)$ was governed by the diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau_B},$$

with an initial carrier density distribution of
\[ n(x, t = 0) = n_0 e^{-ax}, \]  

(S7)

and a surface flux-matching boundary condition of

\[ \frac{\partial n}{\partial x} \bigg|_{x=0} = \frac{s_{\text{surf}}}{D} n \bigg|_{x=0}, \]  

(S8)

where \( \tau_B \) is bulk recombination lifetime which can be derived from two-photon-excited TRPL, \( \alpha \) is the absorption coefficient at the excitation wavelength. A simplified solution can be derived by introducing an average decay time \( \tau_{av} \) that correlates \( S_{\text{surf}} \) with

\[ \frac{1}{\tau_{av}} = \frac{1}{\tau_B} + \frac{2a^2D}{1 + 18a^2D^2/S_{\text{surf}}^2}, \]  

(S9)

where the second part on the right side equals to the surface recombination rate \( 1/\tau_S \)

\[ \frac{1}{\tau_S} = \frac{2a^2D}{1 + 18a^2D^2/S_{\text{surf}}^2}. \]  

(S10)

Typically, \( \tau_{av} \) is adopted from the initial decay \( \tau_1 \) which is taken to indicate near-interface recombination from the one-photon-excited TRPL measurement, (39) for which two exponential data analysis model with deconvolution of the instrumental response is used

\[ I_{\text{PL}} = A_1 \exp \left( \frac{t}{\tau_1} \right) + A_2 \exp \left( \frac{t}{\tau_2} \right), \]  

(S11)

where \( A_1 \) and \( A_2 \) are amplitudes of the two decay components.

Here we measured the TRPL of MAPbI\(_3\), MAPbBr\(_3\) and MAPbBr\(_3\)-O\(_3\) single crystals with a 405 nm laser, as shown in Fig. S14b. The fitted \( \tau_1 \) for these three crystals were 160 ns, 21 ns and 66 ns, respectively. The \( \alpha \) for MAPbI\(_3\) and MAPbBr\(_3\) crystals at 405 nm are \( \sim 1.9 \times 10^5 \) and \( 9 \times 10^4 \) cm\(^{-1}\), respectively. (51) And the \( \tau_B \) obtained from two-photon-excited TRPL are \( \sim 4 \) and 4.5 \( \mu \)s for MAPbI\(_3\) and MAPbBr\(_3\) crystals, respectively. (50, 52) As a result, the \( S_{\text{surf}} \) for the MAPbI\(_3\), MAPbBr\(_3\) and MAPbBr\(_3\)-O\(_3\) single crystals derived from the one-photon surface TRPL measurement are \( \sim 60, 650 \) and 210 cm/s, respectively (Fig. S14c).

**Grain boundary passivation by TPDMP**

To figure out the grain boundary passivation mechanism for TPDMP treatment, we first checked the chemical reaction process between TPDMP and perovskites by mixing pure TPDMP with perovskite at room temperature. As shown in Fig. S30a, the reaction between TPDMP and perovskite films occurs at room temperature and results in a yellow semitransparent product first, followed by complete dissolving of the perovskite films. Then we measured the surface and bottom
PL intensity changes of perovskite films after coating dilute TPDMP solutions with different times before annealing. As shown in Fig. S30c-d, both the surface and bottom PL intensities kept decreasing after the coating of TPDMP for 2 to 30 min without annealing, indicating that TPDMP has reached the bottom side of the perovskite film through grain boundaries by reacting and dissolving the grain boundaries of the film at room temperature. After annealing of the TPDMP-reacted film, the PL intensity significantly enhanced, showing that annealing process is necessary to realize the grain boundary passivation effect. To find out the reaction products before and after annealing, we measured the XRD spectra of perovskite films coated with TPDMP before and after annealing. As shown in Fig. S30b, an intermediate phase with 2θ at 4.6° appeared in the unannealed TPDMP-treated film, which eventually turned into TPPbI₃ after annealing. These results demonstrate that it is TPPbI₃ that has grain boundary passivation effects for polycrystalline perovskite thin films.

To demonstrate the passivation effect of TPDMP, we measured the efficiencies of MAPbI₃ and Cs₀.₀₈FA₀.₉₂PbI₃ solar cells before and after TPDMP treatment with the device structure of indium tin oxide (ITO)/poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine](PTAA)/perovskite/fullerene(C₆₀)/bathocuproine (BCP)/copper (Cu), shown in Fig. S31. Note the solar cells with pristine films were fabricated without any passivation agents. The average PCEs of MAPbI₃ and Cs₀.₀₈FA₀.₉₂PbI₃ solar cells were increased by 1.16% and 1.05% in absolute value after TPDMP treatment, respectively, mostly stem from the increase of the open-circuit voltages, validating the passivation effect by TPDMP treatment.
Fig. S1. Schematic of 2D carrier diffusion model for the confocal PL mapping and carrier diffusion measurement. (a), Schematic diagram of the TRPL mapping and carrier diffusion measurement system (left), and the 2D carrier diffusion model for the confocal PL mapping and carrier diffusion measurement (right). (b), 2D gaussian initial carrier density distribution at coordinates \((x, y)\) and \(t_{\text{start}}\). \(\sigma_x = \sigma_y = 0.32 \ \mu\text{m}, \ n_0 = 10^4\).
Fig. S2. Influence of reabsorption on carrier diffusion measurement. (a) Schematic illustration of the measurement of the PL spectra at the grain center (GC) and grain boundary (GB) of a perovskite grain. The excitation laser is fixed at GC, and the PL spectra are measured at the GC and GB separately. The maximum distance between the GC and GB is about 1 μm. PL spectra measured at GC and GB of (b) MAPbI$_3$ and (c) Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films before and after sulfate and TPDMP surface treatment with the confocal PL system.
Fig. S3. Blocking of the carrier diffusion by GBs in perovskite thin films. (a) PL mapping image of a MAPbI$_3$ polycrystalline thin film. (b) carrier diffusion mapping images of grains marked in (a). The laser was focused onto the center of each grain. The carrier diffusion was limited inside the grain.
Fig. S4. Influence of $S_{GB}$ on PL center shift with time. Schematic illustration of the dependence of PL center shift on $S_{GB}$ for perovskites. PL intensity profiles of perovskites with (a) $S_{GB} = 1$ cm/s, (b) $S_{GB} = 100$ cm/s and (c) $S_{GB} = 10^4$ cm/s. The blue dashed line denotes the center location of the PL profile at initial excitation state. $n_{Left}$ and $n_{Right}$ denotes the carrier density at the left and right sides of the dashed line at different time delay after excitation, respectively. The yellow arrow denotes the carrier diffusion toward the grain boundary. The blue arrow denotes the carrier recombinations at grain boundary.
Fig. S5. Carrier diffusion measurement of a MAPbI$_3$ single crystal. (a), top-view optical microscopic image of a freshly cleaved MAPbI$_3$ single crystal near the crystal edge. The yellow crosses denote the laser excitation spots at the grain center (GC) or near the grain edge (GE). The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 3μm. (b) Measured and (c) simulated unnormalized (left) and normalized-to-each-frame (right) linear carrier diffusion profiles of the MAPbI$_3$ single crystal with laser excitation at the grain center. (d), measured (dots) and simulated (solid lines) linear PL profiles at different times after excitation of the MAPbI$_3$ single crystal with laser excitation at the grain center. (e), dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profile on time delay $t$ after laser excitation extracted from (d). The solid line is the linear fitting of the dot data, where the slope is $2D$. (f), measured (dots) and simulated (solid lines) confocal TRPL of the MAPbI$_3$ single crystal with laser excitation at the grain center.
Fig. S6. Carrier diffusion measurement of a MAPbBr$_3$ single crystal. (a), top-view optical microscopic image of a freshly cleaved MAPbBr$_3$ single crystal near the crystal edge. The yellow crosses denote the laser excitation spots at the grain center (GC) or near the grain edge (GE). The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 3μm. (b) Measured and (c) simulated unnormalized (left) and normalized-to-each-frame (right) linear carrier diffusion profiles of the MAPbBr$_3$ single crystal with laser excitation at the grain center. (d), measured (dots) and simulated (solid lines) linear PL profiles at different times after excitation of the MAPbBr$_3$ single crystal with laser excitation at the grain center. (e), dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profile on time delay $t$ after laser excitation extracted from (d). The solid line is the linear fitting of the dot data, where the slope is $2D$. (f), measured (dots) and simulated (solid lines) confocal TRPL of the MAPbBr$_3$ single crystal with laser excitation at the grain center.
Fig. S7. Carrier diffusion measurement of a MAPbBr₃-O₃ single crystal. (a), top-view optical microscopic image of a freshly cleaved MAPbBr₃-O₃ single crystal near the crystal edge. The yellow crosses denote the laser excitation spots at the grain center (GC) or near the grain edge (GE). The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 3μm. (b) measured and (c) simulated unnormalized (left) and normalized-to-each-frame (right) linear carrier diffusion profiles of the MAPbBr₃-O₃ single crystal with laser excitation at the grain center. (d), measured (dots) and simulated (solid lines) linear PL profiles at different times after excitation of the MAPbBr₃-O₃ single crystal with laser excitation at the grain center. (e), dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profile on time delay $t$ after laser excitation extracted from (d). The solid line is the linear fitting of the dot data, where the slope is $2D$. (f), measured (dots) and simulated (solid lines) confocal TRPL of the MAPbBr₃-O₃ single crystal with laser excitation at the grain center.
Fig. S8. Diffusion coefficient and recombination rate constants for perovskite single crystals.

Statistical results of (a) diffusion coefficients ($D$), (b) monomolecular and (c) bimolecular recombination rate constants for MAPbI$_3$, MAPbBr$_3$ and MAPbBr$_3$-O$_3$ single crystals.
Fig. S9. Influence of diffusion coefficient on carrier diffusion profiles. Simulated linear carrier diffusion profiles along the normal direction of grain boundaries of MAPbI$_3$ single crystals with different $S_{GB}$ for (a) $D = 1$ cm$^2$/s and (b) 0.5 cm$^2$/s. The grain boundary is at the right edge of each figure. Simulated traces of the peak-shifting of the diffusion profiles for the MAPbI$_3$ single crystals with different $S_{GB}$ and (c) $D = 1$ cm$^2$/s and (d) 0.5 cm$^2$/s.
Fig. S10. Influence of $L_{GB}$ on carrier diffusion profiles. Simulated linear carrier diffusion profiles along the normal direction of grain boundaries of MAPbI$_3$ single crystals with different $S_{GB}$ for (a) $L_{GB} = 0.4$ μm and (b) 0.8 μm. The grain boundary is at the right edge of each figure. Simulated traces of the peak-shifting of the diffusion profiles for the MAPbI$_3$ single crystals with different $S_{GB}$ and (c) $L_{GB} = 0.4$ μm and (d) 0.8 μm.
Fig. S11. Surface recombination velocities of MAPbI₃ single crystals. (a) – (d), statistics of measured carrier diffusion profiles near the grain edges of different MAPbI₃ single crystals, and their peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines). The white dashed lines denote the locations of the grain edges.
**Fig. S12.** Surface recombination velocities of MAPbBr$_3$ single crystals. (a) – (d), statistics of measured carrier diffusion profiles near the grain edges of different MAPbBr$_3$ single crystals, and their peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines). The white dashed lines denote the locations of the grain edges.
Fig. S13. Surface recombination velocities of MAPbI$_3$-O$_3$ single crystals. (a) – (d), statistics of measured carrier diffusion profiles near the grain edges of different MAPbBr$_3$-O$_3$ single crystals, and their peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines). The white dashed lines denote the locations of the grain edges.
Fig. S14. One-photon surface TRPL measurement. (a), schematic diagram of the 1D carrier diffusion model for the one-photon surface TRPL measurement. (b), measured TRPL on the surfaces of freshly cleaved MAPbI$_3$ and MAPbB$_3$ crystals, and MAPbB$_3$ crystal with ozone treatment (MAPbBr$_3$-O$_3$). The wavelength of the laser is 405 nm. (c), dependence of surface recombination velocities ($S_{Surf}$) of MAPbI$_3$ and MAPbB$_3$ single crystals on the surface recombination lifetime $\tau_S$ that measured at excitation wavelength of 405 nm. The dashed lines mark the measured $\tau_S$ and corresponding $S_{Surf}$ for the MAPbI$_3$, MAPbB$_3$ and MAPbB$_3$-O$_3$ single crystals.
Fig. S15. Influence of laser repetition rate on the carrier diffusion measurement. (a), measured confocal TRPL in a grain of the MAPbI$_3$ polycrystalline thin film with different laser repetition rates. The size of the grain is around 3 μm. (b), initial linear PL intensity ($I_{PL}$) profiles measured with laser excitation at repetition rates of 20, 5 and 2 MHz. The orange solid line denotes the Gaussian fitting of the PL intensity profile. (c), dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profile on time delay $t$ after laser excitation extracted from (b) with different laser repetition rates.
Fig. S16. Time trace of the PL intensity during the confocal PL mapping and carrier diffusion measurement for MAPbI$_3$ and Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films.
Fig. S17. Diffusion coefficients of the grains in MAPbI$_3$ polycrystalline thin films. Time-resolved PL mapping images of (a) pristine, (c) sulfate- and (e) TPDPM-treated MAPbI$_3$ polycrystalline thin films. Statistical results of dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profiles on time delay $t$ after laser excitation for multiple grains in the (b) pristine, (d) sulfate- and (f) TPDPM-treated MAPbI$_3$ thin films.
Fig. S18. Diffusion coefficients of the grains in Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films. Time-resolved PL mapping images of (a) pristine, (c) sulfate- and (e) TPDPM-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films. Statistical results of dependence of the mean-square-distribution $\sigma^2$ of the Gaussian-distribution-fitted PL profiles on time delay $t$ after laser excitation for multiple grains in the (b) pristine, (d) sulfate- and (f) TPDPM-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films.
Fig. S19. Recombination rate constants of the grains in MAPbI₃ polycrystalline thin films. Measured (dots) and simulated (solid lines) linear PL intensity (Iₘ) profiles at different delay times after laser excitation at grain centers for grains of (a) pristine, (c) sulfate- and (e) TPDPM-treated MAPbI₃ thin films. Measured (dots) and simulated (red lines) confocal TRPL of the grains in the (b) pristine, (d) sulfate- and (f) TPDPM-treated MAPbI₃ thin films with laser excitations at grain centers.
Fig. S20. Recombination rate constants of the grains in Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films. Measured (dots) and simulated (solid lines) linear PL intensity ($I_{PL}$) profiles at different delay times after laser excitation at grain centers for grains of (a) pristine, (c) sulfate- and (e) TPDPM-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. Measured (dots) and simulated (red lines) confocal TRPL of the grains in the (b) pristine, (d) sulfate- and (f) TPDPM-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films with laser excitations at grain centers.
**Fig. S21.** Diffusion coefficient and recombination rate constants of perovskite polycrystalline films. Statistical results of (a) diffusion coefficients ($D$), (b) monomolecular and (c) bimolecular recombination rate constants for grains of pristine, sulfate- and TPDMP-treated MAPbI$_3$ and Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films.
**Fig. S22. Passivation of perovskite thin films by sulfate and TPDMP treatments.** PL spectra of (a) MAPbI₃ and (b) Cs₀.₀₈FA₀.₉₂PbI₃ thin films before and after sulfate and TPDMP surface treatments measured with light illumination from the top of the films. PL spectra of (c) MAPbI₃ and (d) Cs₀.₀₈FA₀.₉₂PbI₃ thin films before and after sulfate and TPDMP surface treatments measured with light illumination from the bottom of the films. The wavelength of the laser is 405 nm.
Fig. S23. Grain boundary recombination velocities of pristine MAPbI₃ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of pristine MAPbI₃ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 2 μm. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Fig. S24. Grain boundary recombination velocities of sulfate-treated MAPbI$_3$ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of sulfate-treated MAPbI$_3$ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 2 μm. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Fig. S25. Grain boundary recombination velocities of TPDMP-treated MAPbI$_3$ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of TPDMP-treated MAPbI$_3$ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Fig. S26. Grain boundary recombination velocities of pristine Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of pristine Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 2 μm. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Fig. S27. Grain boundary recombination velocities of sulfate-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of sulfate-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 2 μm. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Fig. S28. Grain boundary recombination velocities of TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. (a) - (e), statistics of measured carrier diffusion profiles near the grain boundaries of multiple grains of TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. The PL mapping images of the measured grains are correspondingly shown on the top. The yellow crosses denote the laser excitation spots which are around 0.6 μm away from the grain boundaries. The white dashed lines denote the directions for the carrier diffusion profiles. Scale bar: 2 μm. The bottom panel shows the measured peak-shifting traces with time (red dots) overlapped with those obtained from simulation results with different $S_{GB}$ (colored lines).
Grain boundary passivation of perovskite thin films by TPDMP. IR spectra measured by AFM-IR mapping for (a) pristine Cs$_{0.08}$FA$_{0.92}$PbI$_3$ and (b) TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films. The IR signals at wavenumbers of 1713 and 965 cm$^{-1}$ correspond to C=N stretching in FA and C-H bending vibrations in tributyl(methyl)phosphonium (TP), respectively.
Fig. S30. Chemical reaction between perovskite and TPDMP. (a), schematics (top) and photographs (bottom) of the chemical reaction between a MAPbI₃ polycrystalline thin films and pure TPDMP fluid before annealing. (b), XRD spectra of pristine MAPbI₃, TPDMP-treated MAPbI₃ films before and after annealing. PL spectra of MAPbI₃ polycrystalline thin films before and after TPDMP treatment with different time followed by annealing when the laser is excited from the (c) top and (d) bottom sides of the films. The wavelength of the laser is 405 nm.
Fig. S31. Passivation of perovskite solar cells with TPDMP. (a), current density-voltage ($J-V$) curves of MAPbI$_3$ polycrystalline thin film solar cells before and after TPDMP treatment. (b), current density-voltage ($J-V$) curves of Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin film solar cells before and after TPDMP treatment. (c), statistics of PCEs of MAPbI$_3$ and Cs$_{0.08}$FA$_{0.92}$PbI$_3$ solar cells before and after TPDMP treatments.
Fig. S32. Surface recombination velocities of Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films. Time-resolved PL mapping images of cross-sections of (a) pristine, (d) sulfate- and (g) TPDMP-surface-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. Scale bar: 2 μm. The yellow crosses denote the laser excitation spots. Carrier diffusion profiles along the normal direction of grain surfaces in (b) pristine, (e) sulfate- and (h) TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films. The white dashed lines denote the locations of grain surfaces. Statistics of measured peak-shifting traces with time from the carrier diffusion profiles near the grain boundaries for (c) pristine, (f) sulfate- and (i) TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ thin films.
Fig. S33. Influence of \( L_{\text{GB}} \) on the quantitative relationship between the normalized peak shift \( d_{\text{max}}/L_{\text{GB}} \) and \( S_{\text{GB}} \) for perovskites. Variation of the quantitative relationship between \( d_{\text{max}}/L_{\text{GB}} \) and \( S_{\text{GB}} \) for perovskites with different \( D \) when \( L_{\text{GB}} \) changes from 0.4 to 0.8 \( \mu \text{m} \).
Fig. S34. Influence of the recombination rate constants on the quantitative relationship between the normalized peak shift $d_{\text{max}}/L_{\text{GB}}$ and $S_{\text{GB}}$ for perovskites. Variations of the quantitative relationship between $d_{\text{max}}/L_{\text{GB}}$ and $S_{\text{GB}}$ for perovskites with different $D$ when (a) $A$ changes from 0.01 to 1 ns$^{-1}$ and (b) $B$ changes from $10^{-4}$ to $10^{-2}$ cm$^2$/s.
Table S1.
Statistic results of fitted $D$, $A$, $B$ and $C$ values for MAPbI$_3$, MAPbBr$_3$ and MAPbBr$_3$-O$_3$ single crystals.

|        | $D$ (cm$^2$/s) | $A$ (1/ns) | $B$ (cm$^2$/s) | $C$ (cm$^4$/s) |
|--------|----------------|------------|----------------|----------------|
| MAPbI$_3$ | 0.67          | 0.75       | 2.5E-3         |                |
|         | 0.68          | 0.60       | 1.1E-3         |                |
|         | 0.68          | 0.70       | 2.4E-3         |                |
|         | 0.67          | 0.50       | 1.0E-3         |                |
| MAPbBr$_3$ | 0.49          | 0.72       | 1.1E-3         | <1E-16         |
|         | 0.50          | 0.65       | 2.0E-3         |                |
|         | 0.50          | 0.70       | 1.5E-3         |                |
|         | 0.49          | 0.65       | 1.5E-3         |                |
| MAPbI$_3$-O$_3$ | 0.48          | 0.75       | 1.3E-3         |                |
|         | 0.49          | 0.65       | 1.5E-3         |                |
|         | 0.50          | 0.68       | 2.0E-3         |                |
Table S2.

Statistic results of fitted $D$, $A$, $B$ and $C$ values for pristine, sulfate- and TPDMP-treated MAPbI$_3$ polycrystalline thin films.

|                  | $D$ (cm$^2$/s) | $A$ (1/ns) | $B$ (cm$^2$/s) | $C$ (cm$^4$/s) |
|------------------|----------------|-------------|----------------|----------------|
| **MAPbI$_3$**    |                |             |                |                |
|                  | 0.98           | 0.2         | 0.8E-3         |                |
|                  | 0.88           | 0.22        | 1.0E-3         |                |
|                  | 0.95           | 0.25        | 0.7E-3         |                |
|                  | 1.10           | 0.3         | 1.5E-3         |                |
|                  | 1.05           | 0.32        | 1.5E-3         |                |
| **Sulfate-treated MAPbI$_3$** |                |             |                | $< 1E-16$       |
|                  | 1.1            | 0.26        | 1.4E-3         |                |
|                  | 1.03           | 0.20        | 0.5E-3         |                |
|                  | 1.1            | 0.25        | 0.4E-3         |                |
|                  | 1.05           | 0.15        | 0.8E-3         |                |
|                  | 0.98           | 0.15        | 1.1E-3         |                |
| **TPDMP-treated MAPbI$_3$** |                |             |                |                |
|                  | 1.13           | 0.25        | 1.4E-3         |                |
|                  | 1.01           | 0.23        | 1.3E-3         |                |
|                  | 1.1            | 0.15        | 0.5E-3         |                |
|                  | 0.96           | 0.1         | 0.6E-3         |                |
|                  | 1.00           | 0.12        | 1.2E-3         |                |
Table S3.
Statistic results of fitted $D$, $A$, $B$ and $C$ values for pristine, sulfate- and TPDMP-treated Cs$_{0.08}$FA$_{0.92}$PbI$_3$ polycrystalline thin films.

|                  | $D$ (cm$^2$/s) | $A$ (1/ns) | $B$ (cm$^2$/s) | $C$ (cm$^4$/s) |
|------------------|----------------|------------|----------------|----------------|
| CsFAPbI$_3$      | 1.02           | 0.1        | 0.95E-3        |
|                  | 1.22           | 0.22       | 1.5E-3         |
|                  | 1.05           | 0.17       | 2.0E-3         |
|                  | 1.01           | 0.19       | 2.2E-3         |
|                  | 1.13           | 0.15       | 2.0E-3         |
| Sulfate-treated  | 0.99           | 0.18       | 1.5E-3         |
| CsFAPbI$_3$      | 1.16           | 0.13       | 2.4E-3         |
|                  | 1.20           | 0.15       | 2.2E-3         |
|                  | 1.08           | 0.11       | 1.0E-3         |
|                  | 1.06           | 0.12       | 2.0E-3         |
| TPDMP-treated    | 1.02           | 0.15       | 2.0E-3         |
| CsFAPbI$_3$      | 1.11           | 0.10       | 1.2E-3         |
|                  | 1.17           | 0.09       | 1.6E-3         |
|                  | 1.06           | 0.17       | 0.8E-3         |
|                  | 1.03           | 0.12       | 1.5E-3         |
|                  |                |            |                | $< 1E-16$      |
**Movie S1.**
Simulated dynamic diffusion process in a MAPbI$_3$ grain with $S_{GB} = 1$ cm/s.

**Movie S2.**
Simulated dynamic diffusion process in a MAPbI$_3$ grain with $S_{GB} = 10^4$ cm/s.

**Movie S3.**
Measured dynamic diffusion process in a MAPbI$_3$ single crystal near grain edge.
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