Supporting Information

For

Electron Trapping and Extraction Kinetics on Carrier Diffusion in Metal Halide Perovskite Thin films

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Experimental methods

Film fabrication: Fluorine-doped tin oxide (FTO) were rinsed with diluted detergent, deionized water, acetone, and isopropyl alcohol (IPA), successively. Tin oxide (SnO_2) solution (0.1128 g $SnCl_2 \cdot 2H_2O$ in 5 mL ethanol) was spin-coated at 2000 rpm for 60 s on the completely dried substrates after 15 min UV-ozone treatment. SnO_2 electron transport layer is annealed at 200 °C for 30 min. Perovskite solution was prepared as reported [1 M formamidinium iodide (FAI), 1.1 M lead iodide (PbI_2), 0.2 M methylamine bromide (MABr), 0.22 M lead bromide ($PbBr_2$) in 1 mL dimethylformamide (DMF): dimethyl sulfoxide (DMSO) (4:1 vol%) mixed solvent]. This solution is mixed with 1.5 M cesium iodide in DMSO solvent in 95:5 vol %, resulting in the composition of $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$. Resulting solution was spin-coated on the UV-ozone treated SnO_2 substrates in two steps: 1st: 1000 rpm for 10 s, 2nd: 6000 rpm for 20 s, chlorobenzene is dropped 5 s before the end of 2nd step. Then, perovskite is annealed at 100 °C for 45 min.

Time resolved photoluminescence measurement: Time-resolved photoluminescence measurements were performed using time correlated single photon counting (TCSPC) system (HAMAMATSU/C11367-31). For TCSPC measurements, a pulsed laser source was laser diode with a wavelength of 464 nm, a repetition rate of 100 kHz, fluence of ~ 4 nJ cm^{-2} and a pulse width of 70 ps.

Supplmentary note

Calculation of absorption coefficient

The absorption (A) was calculated using:

$$A = -\log_{\alpha}\left(\frac{I_s}{I_0}\right) \tag{S1}$$

where I_0 is the reference intensity measured with the blank and I_s is the intensity measured with the sample. The absorption coefficient α was obtained from:

$$T = \frac{I_s}{I_0} = e^{-\alpha L} \tag{S2}$$

where T represents transmittance and L is the sample thickness. From Equation S1 and S2, we can get the absorption coefficient by the value of A:

$$\alpha = A\ln 10/L \tag{S3}$$

The absorption coefficient for is as a function of wavelength. The penetration depth (x) is then calculated as $x = 1/\alpha(\lambda)$.

Fluence of the absorbed photons

The fluence (F) of the absorbed photons upon excitation at 464 nm was calculated using Equation S4:

$$F(\lambda) = P(\lambda)\lambda(1 - e^{-\alpha(\lambda)L})/hcf_{rep}A \tag{S4}$$

where, $P(\lambda)$ is a pump power, f_{rep} is a repetition rate of pump, A is the area of pump beam, λ is a wavelength of excitation and $\alpha(\lambda)$ is the wavelength dependent absorption coefficient and L is the sample thickness. The h and c correspond to Planck constant and speed of light, respectively.

Calculation of average lifetime in stretched exponential function

The average lifetime, $<\tau>$, can be calculated by below equation:

$$<\tau> = \frac{\tau_1}{\beta}\Gamma\left(\frac{1}{\beta}\right) \tag{S5}$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^{\infty} x^{(1-\beta)/\beta} e^{-x} dx \tag{S6}$$

where, $\Gamma\left(\frac{1}{\beta}\right)$ is gamma function, β is the stretching exponent between 0 and 1.

Table S1. Summary of parameters extracted from fitting TRPL decay curves to perovskite samples of different thicknesses.

Samples	Condition	τ_1 (ns)	τ_2 (ns)	β	$<\tau>$ (ns)[a]	A_1	A_2	$A_1/A_1 + A_2$ (%)
P490	Bi-exponential function	5.2	916.1	-		0.63	0.25	71.8
P140		5.3	897.6	-		0.33	0.41	44.7
P70		5.3	907.7	-		0.20	0.44	30.1
P490	Dynamic trapping model	13.8	1219.8	0.78	15.9	0.76	0.28	73.5
P140		6.7	1127.5	0.87	7.2	0.38	0.43	46.8
P70		5.4	1178.2	0.95	5.5	0.23	0.48	32.6

[a]The calculation method of the average lifetime, $<\tau>$, is explained in the supplementary note.

Simulation process

Synopsys Sentaurus TCAD platform was used in this work. Drift-diffusion transport was adopted along with Poisson and carrier continuity equations self-consistently. 2-D ray tracer simulation was used for the light emission to the perovskite. To simplify the optical paths, the surface reflection due to the difference of refractive index between air (vacuum) and perovskite was omitted. Trap-assisted SRH recombination and radiative recombination in the experiment were described by adopting trap sites uniformly distributed within the perovskite. Simply, all the traps were situated at the middle of energy bandgap, and had sufficiently-long hole capture time compared to electron capture time so that the captured electrons do not escape from the traps. Proportionality constant (r) that regulates electron capture rate (R_{cn}) is written as

$$r = \sigma \cdot v_{th} \tag{S7}$$

where σ is the electron capture cross-section, v_{th} is the electron thermal velocity (1.5×10^7 cm/s). Sufficiently-long hole capture time has been done by decreasing the hole capture cross-section significantly so that the hole capture at the trap site is almost negligible during TRPL measurements. This simulation approach adopting trap sites was first introduced in our study for detailed and accurate analysis on the TRPL decay mechanisms.

For SQ-TRPL, SnO_2 is contacted directly with the perovskite, and there are no sources providing the free electrons and holes into the perovskite except for the light. Same as the experiment, SnO_2 works as the quencher that extracts free electrons from the conduction band of perovskite by adopting thermionic emission current at perovskite/SnO_2 hetero-interface. Thermionic current density at the hetero-interface is given by

$$J_{e,SnO2} = -J_{e,perov.} = Kq\left(v_{e,perov.}n_{perov.} - \frac{m_{e,perov.}}{m_{e,SnO2}}v_{e,SnO2}n_{SnO2}exp\left(-\frac{\Delta E_C}{kT}\right)\right) \quad \text{(S8)}$$

where $J_{e,SnO2}$ ($J_{e,perov.}$) are the electron current density leaving SnO_2 (perovskite), $v_{e,SnO2}$ ($v_{e,perov.}$) are the electron emission velocities for SnO_2 (perovskite) (2.573×10^6 cm/s), $m_{e,SnO2}$ ($m_{e,perov.}$) are electron effective masses for SnO_2 (perovskite), n_{SnO2} ($n_{perov.}$) are electron density of SnO_2 (perovskite), ΔE_C is the difference of conduction band (or electron affinity) between perovskite and SnO_2, and K is the thermionic emission coefficient. Because the difference of electron affinity between perovskite (3.94 eV) and SnO_2 (4.54 eV) is huge, thermionic current density is approximated as

$$J_{e,SnO2} = -J_{e,perov.} \approx Kqv_{e,perov.}n_{perov.} \quad \text{(S9)}$$

Changing K is similar to changing electron injection coefficient, but the thermionic current density also depends on the electron density of SnO_2 and perovskite, which is varied as a function of time. Transient simulation has been done from 0 to 5 μs. Electron density and distribution of the perovskite are obtained after the light is off. Calibration to the TRPL curves with different thickness of neat perovskite has been done by changing electron capture cross-section (directly proportional to electron capture rate by traps), trap density (proportional to trap-assisted SRH recombination), and electron lifetime for radiative recombination. Then, K values are additionally tuned to calibrate the SQ-TRPL curves. All the physical parameters are summarized and specified in Tables S2 and S3.

Table S2. Summary of the fixed parameters for perovskite.

Parameter	Value
Real refractive index	2.516
Absorption coefficient (cm^{-1})	1.6×10^5
Energy Bandgap (eV)	1.62
Electron affinity (eV)	3.94
Electron mobility ($cm^2V^{-1}s^{-1}$)	3

Table S3. Summary of calibrated parameters for perovskite.

Parameter	Value
Trap density (cm^{-3})	3.5×10^{15}
Proportionality constant (cm^3s^{-1})	7.5×10^{-9}
Thermionic emission coefficient	7.0×10^{-5}

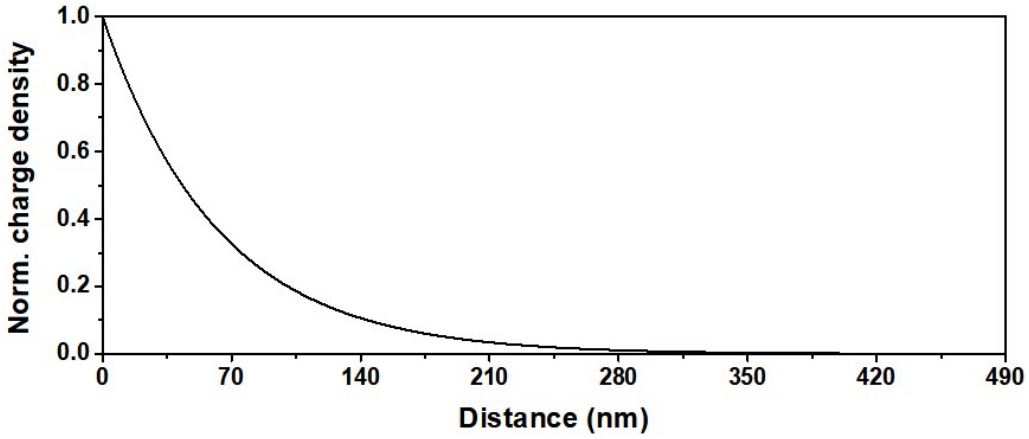

Figure S1. The charge generation rate in perovskite with excitation wavelength of 464 nm. The rate exponentially decreases throughout the material as can be seen following equation, $G = N_0 e^{-\alpha x}$ where N_0 = photon flux at the surface, α = absorption coefficient and x = distance into the material.

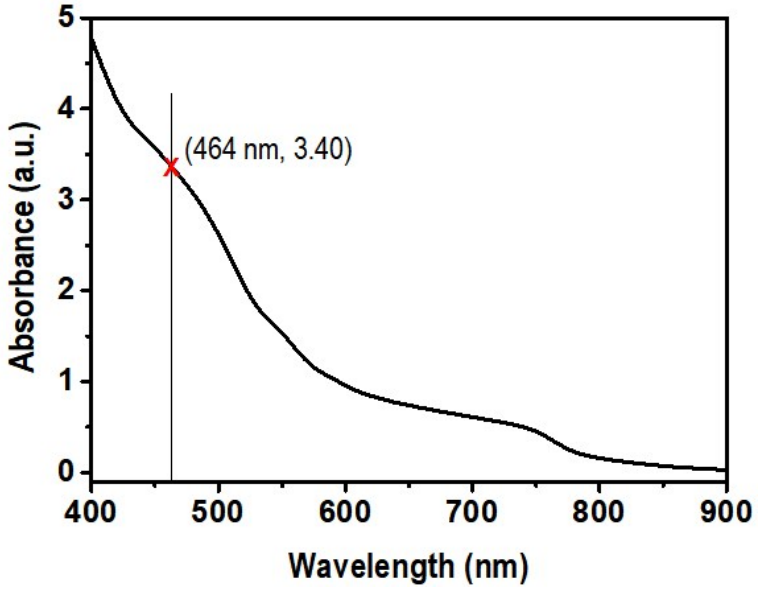

Figure S2. UV-vis absorption spectrum of polycrystalline perovskite thin film.

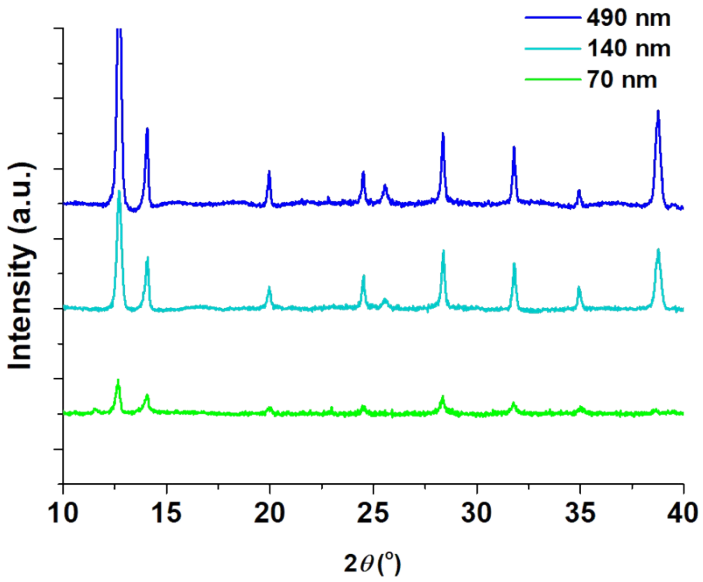

Figure S3. XRD spectra of perovskite thin films with thickness of 490, 140 and 70 nm.

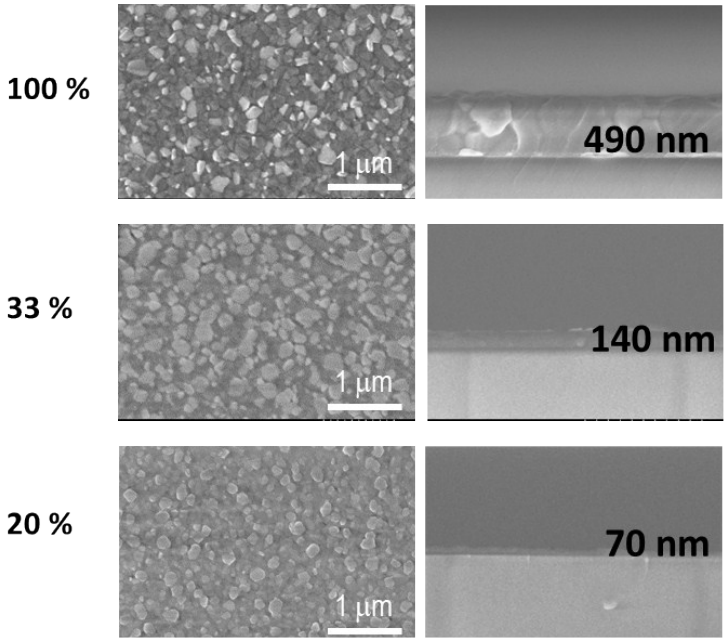

Figure S4. Top and cross-section SEM images of perovskite thin films with thickness of 490, 140 and 70 nm.

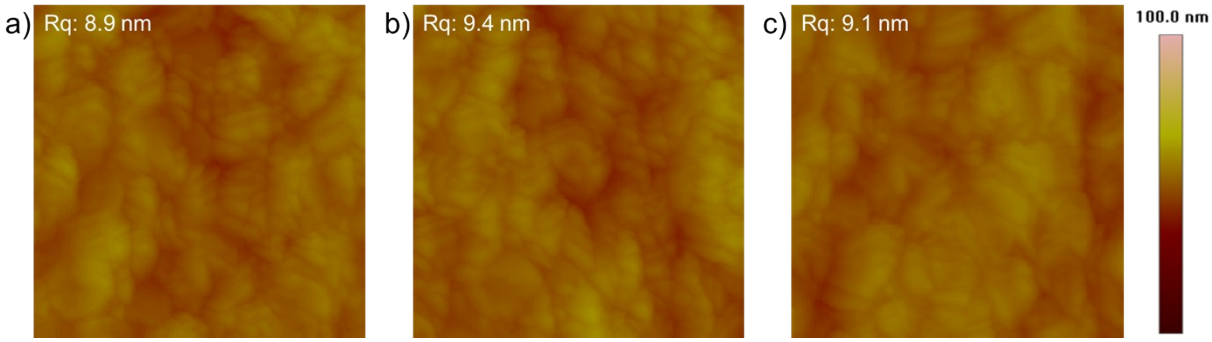

Figure S5. AFM images (3 μm × 3 μm) of perovskite thin films with thickness of a) 490, b) 140 and c) 70 nm. The root-mean-squared roughness calculated for each film are to be 8.9, 9.4 and 9.1 nm, respectively.

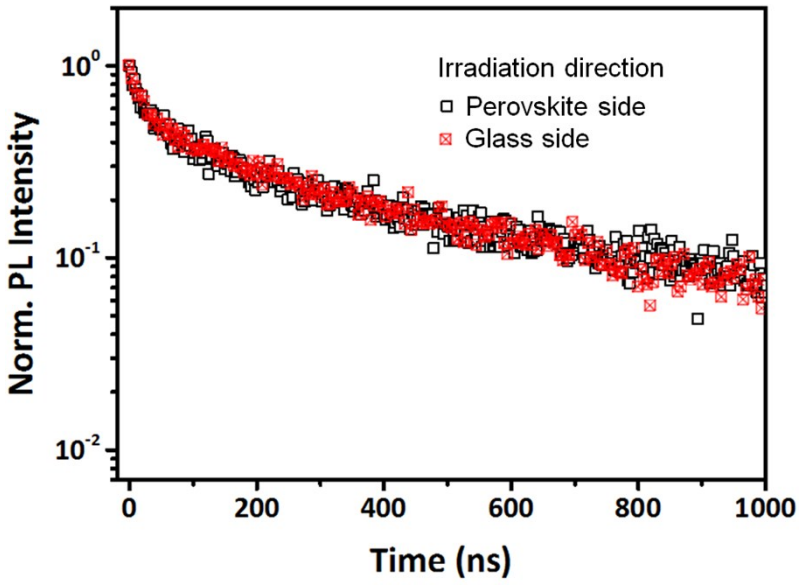

Figure S6. Time resolved PL decay curves after illumination on the perovskite side (black square) or on the glass side (red square).

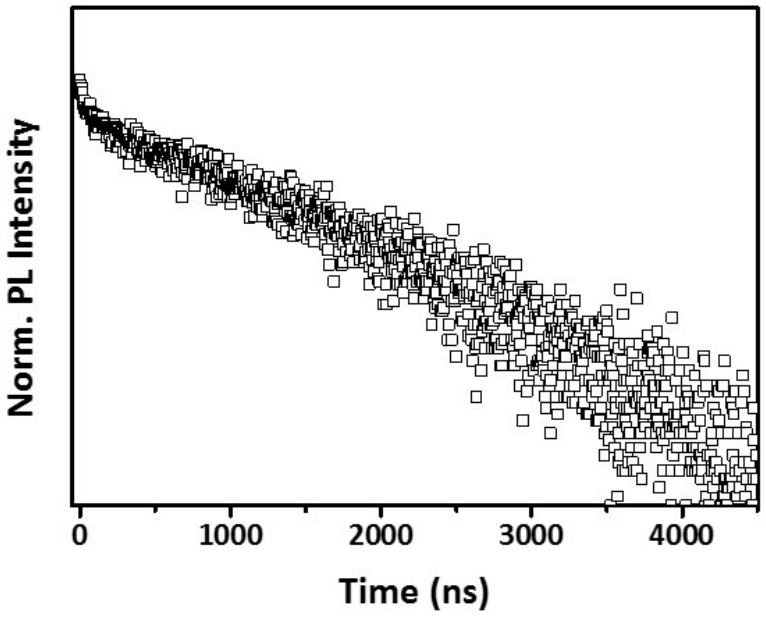

Figure S7. Time resolved PL decay curve of neat perovskite film plotted in reciprocal y-axis

Table S4. Summary of parameters extracted from fitting the SQ-TRPL decay curves to perovskite samples with different thicknesses.

	Samples	Condition	τ_1 (ns)	τ_2 (ns)	β	A_1	A_2	$A_1/A_1 + A_2$ (%)	k_2 ($cm^3\ s^{-1}$)
SnO_2	P490	Dynamic trapping model	13.5	133.2	0.79	0.65	0.45	59.0	-
	P140	Second-order	-	-	-	-	-	-	8.47×10^7
	P70	Second-order	-	-	-	-	-	-	1.16×10^8

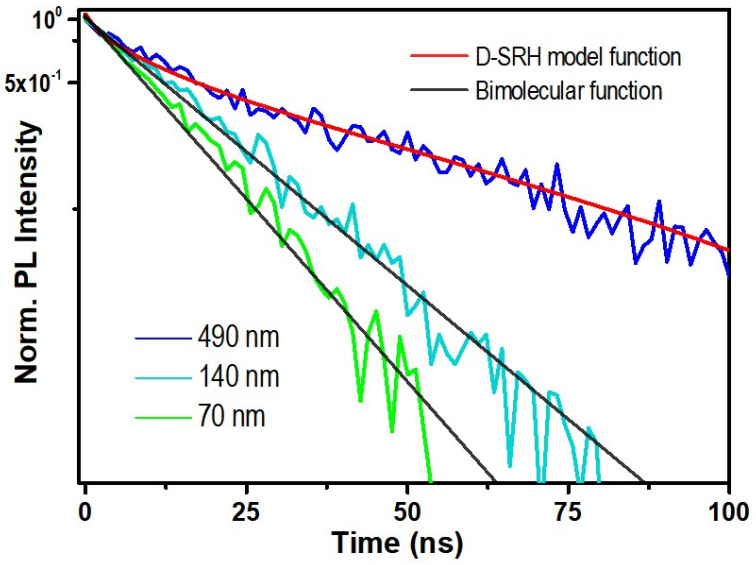

Figure S8. Linear-reciprocal plots of SQ-TRPL decays for perovskite films with SnO_2 ETL.

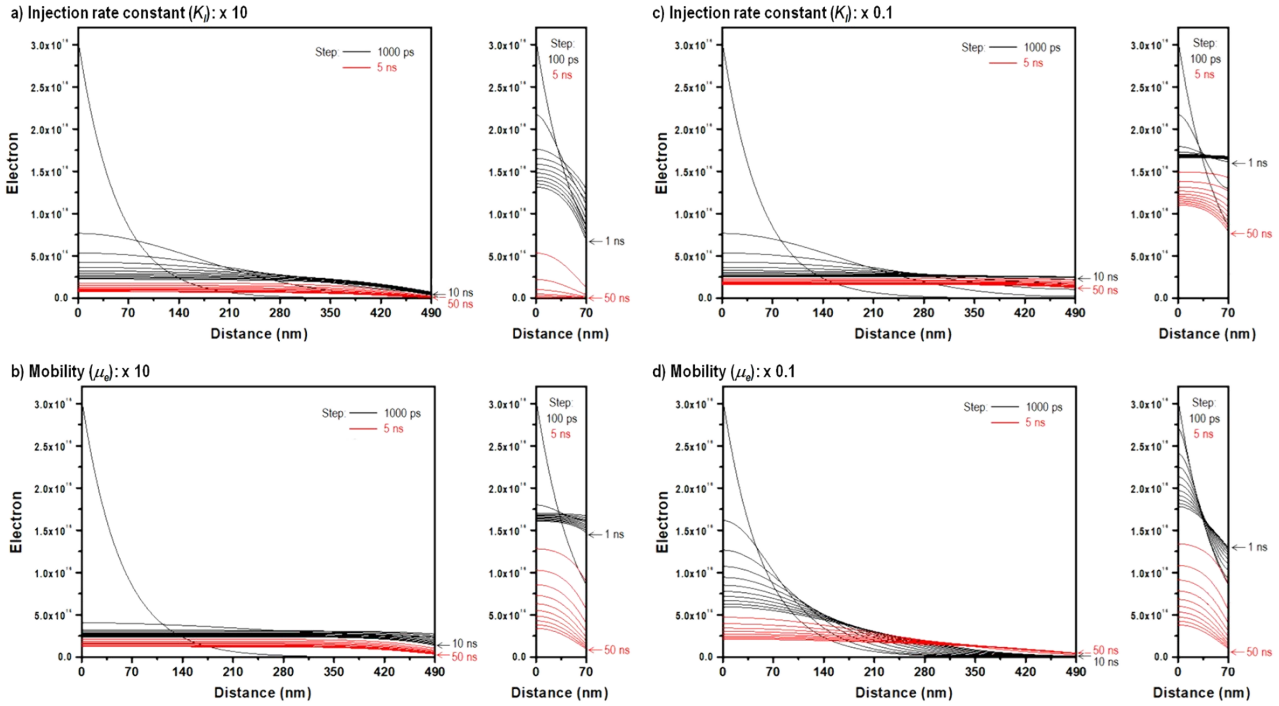

Figure S9. Spatiotemporal evolution of the electron by simulation study with an order of magnitude low (a) and high (c) k_i, and an order of magnitude low (b) and high (d) μ_e from the initial values for the P490 and P70, respectively.