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# Top and Bottom Surfaces Limit Carrier Lifetime in Lead Iodide Perovskite Films

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## Supplementary Figures.

а		b		
	CH. CALIF. (310)		Unit cell dimensions	a = 8.878 ± 0.005 Å
	80 80			c = 12.643 ± 0.005 Å
	and a second second second			$\alpha = \beta = \gamma = 90^{\circ}$
			Volume	996.73 A <sup>3</sup>
			Density (calculated)	4.131 g/cm <sup>3</sup>
			Reflections collected	7946
		[	Unique reflections	261
			Inconsistent	10
			equivalents	
			R(int)	0.1255
		[	R (sigma)	0.0278
			Goodness-of-fit	1.217
		_		

Supplementary Figure 1. (a) Photograph of  $CH_3NH_3PbI_3$  single crystal showing rhombododecahedral shape. Crystal measures 8mm in width, 10 mm in length, and 4 mm in height. (b) Refined crystallographic data for the single crystal of  $CH_3NH_3PbI_3$ 



Supplementary Figure 2. Top view scanning electron microscope (SEM) image of the polycrystalline lead iodide perovskite sample.



Supplementary Figure 3. X-ray diffraction analysis of the polycrystalline perovskite film on a glass substrate.



Supplementary Figure 4. (a) Photocurrent density-voltage curves of a typical perovskite solar cell made from the optimized thickness ( $\sim$ 350 nm). (b) Stable output of the current density and power conversion efficiency of the cell in (a) biased near the maximum power point.



Supplementary Figure 5. Ellipsometry characterization of polycrystalline and single crystal perovskties. (a) The complex refractive indices as a function of photon energy  $(\hbar\omega)$ ,  $\tilde{n}(\hbar\omega) = n(\hbar\omega) + ik(\hbar\omega)$ , for both samples are measured by ellipsometry. The real (n) and imaginary (k) part of  $\tilde{n}(\hbar\omega)$  for polycrystalline and single crystal samples are shown separately. (b) The absorption coefficient spectra  $\alpha(\hbar\omega)$  for polycrystalline and single crystal samples determined from the respective  $k(\hbar\omega)$ . The relationship between  $\alpha(\hbar\omega)$  and  $k(\hbar\omega)$  is given by  $\alpha(\hbar\omega) = 2 \cdot \omega \cdot k(\hbar\omega)/c$ , where  $\omega$  and c are the photon angular frequency and light speed, respectively. The red and blue arrows point out the photon energies of the pump for polycrystalline and single crystal transient reflection measurements, respectively.

2.4

2.6



Supplementary Figure 6. Transient absorption (TA) measurement of polycrystalline perovskite film. (a) The pseudocolor images of TA spectra for the polycrystalline film. The horizontal and vertical axes are the probe photon energy and pump-probe delay, respectively. The color intensity indicated by the color bar represents the TA signal magnitude. The pump scattering leads to the noise near photon energy of 2.0 eV. No TA signals are collected beyond this energy point due to the lack of probe light passing through the films. (b) The transient spectrum of  $\Delta k(\hbar \omega)$  (red trace) obtained from the TA spectra captured at a single delay (5ps) according to the equation,  $\Delta k(\hbar \omega) = c \cdot \Delta \alpha(\hbar \omega)/2\omega$ , where  $\omega$  and c are the photon angular frequency and light speed. Also shown is the Hilbert transform (blue trace) of  $\Delta k(\hbar \omega)$ . According to the Kronig-Kramers relations, Hilbert transform of  $\Delta k(\hbar \omega)$  is  $\Delta n(\hbar \omega)$  that is proportional to the TR spectrum. (c) The HT of TA spectrum for polycrystalline sample is consistent with the TR spectrum for single crystals are consistent, suggesting that primary discrepancy of the measured TR spectra between the two samples is due to the additional photo-induced interference in the polycrystalline sample.





Supplementary Figure 7. Total carrier dynamics in single crystal and polycrystalline perovskites. (a) The total carrier lifetime of polycrystalline films measured by nanosecond TA spectroscopy. The exciton bleach kinetics represents the total carrier lifetime that depends on both bulk and surface recombination (Eq. 5 in main text). The single exponential fitting gives the lifetime as 90 ns. After taking into account surface recombination, the bulk lifetime is estimated as 477 ns for the polycrystalline films in this work. (b) The time-resolved photoluminescence (TRPL) of the single crystal perovskite under two-photon excitation (2PPL). The excitation wavelength is 1400 nm, far below band gap. A diffusion limited surface recombination model (black trace) gives the bulk lifetime as 1.6 µs. (c) Theoretical simulation of the fast component in 2PPL kinetics. The fast component may originate from two sources. (1) Under uniform excitation (such as two-photon excitation) condition, surface carrier density will be lower than that in bulk due to the surface recombination, and there is a concentration gradient (See Eq 4a and 4b in main text) near surface. Then the carriers in the bulk will diffuse to the surface and undergo surface recombination. The fast component may arise from this diffusion limited surface recombination. (2) Under intensive optical excitation, higher order bulk recombination can result in a fast decay component in PL kinetics. However, for 2PPL measurement, the first cause is more likely because of the low carrier concentration. Panel (c) shows the carrier concentration distribution from the surface to the bulk in a single crystal after two-photon excitation as function of delay. The y-axis represents the normalized carrier density. The x-axis represents

the depth from the surface to the bulk (to focus on the near surface region, we only plot 50  $\mu$ m sub-surface depth). The traces in the panel (c) are produced by the analytical solution of Equation 1 in the main text, which is given by:

$$N(t,x) = \frac{1}{2} \exp\left(-\frac{x^2}{4Dt}\right) \left[ w\left(-\frac{x}{2\sqrt{Dt}}\right) - w\left(\frac{x}{2\sqrt{Dt}}\right) + 2w\left(S\sqrt{\frac{t}{D} + \frac{2x}{2\sqrt{Dt}}}\right) \right] \cdot \exp\left(-t/\tau\right)$$
(1)

where *t* is delay time, *x* is sub-surface depth, *D* is the ambipolar diffusion coefficient, S is surface recombination velocity,  $\tau$  is the first-order bulk recombination time constant, and  $w(z) = \exp(z^2) [1 - \exp(z)]$ . S and D are determined in the current report. We find at early delay, the carrier distribution is nearly flat due to the homogeneous excitation. As the delay increases, a carrier concentration gradient starts appearing at near surface region. The carrier concentration is always flat when the depth is larger than 50 µm. Due to self-absorption and other factors, the PL emitted inside the single crystal cannot always been collected, and the PL photon collection efficiency should decrease as the sub-surface depth increases. To simplify the simulation model, we can define an effective PL collection depth; only the PL photons emitted shallower than this depth can be collected, while those emitted beyond this depth cannot be collected. Therefore, the measured PL intensity will be proportional to the carrier population within the effective PL collection depth we can simulate the 2PPL kinetics by plotting the carrier population within the effect PL collection depth with respect to the delays. The initial amplitudes of 2PPL kinetics and the simulation are normalized to 1. As shown in panel (b), we find that with an effective collection depth of 1 µm, the simulation (black trace) matches the measured data (red circle) very well and used the S and D determined from TR.



Supplementary Figure 8. Time dependent carrier distribution in the single crystal perovskite sample. The pump photon energies are indicated in the figures. The left column (a, c, e, g) shows the carrier distribution within the sub-surface of 2  $\mu$ m. The right column (b, d, f, h) shows the carrier distribution in the effective detecting depth (~20 nm). The pump photon energy dependence arises from the different initial carrier distribution due to different pump penetration lengths. The carrier distribution evolution depends on the carrier diffusion coefficient and surface recombination velocity. The diffusion coefficient and surface recombination velocity are obtained from the TR kinetics fitting.



Supplementary Figure 9. Time dependent carrier distribution in the polycrystalline perovskite samples. The pump photon energies are indicated in the figures. The left column (a, c, e, g) shows the carrier distribution in the whole film (the film thickness is 950 nm). The right column (b, d, f, h) shows the carrier distribution in the effective detecting depth ( $\sim$ 20 nm). The pump photon energy dependence arises from the different initial carrier distribution due to different pump penetration lengths. The carrier distribution evolution depends on the carrier diffusion coefficient and surface recombination velocity. The diffusion coefficient and surface recombination the TR kinetics fitting.



Supplementary Figure 10. Exciton band kinetics of the polycrystalline perovskites. The kinetics are extracted from the TR spectra collected from the front surface (red trace) and the back surface (blue trace). The back surface is also the interface between the perovskite film and the quartz substrate. The consistency of the two kinetic traces suggests that the surface recombination velocities for the front and back surfaces are similar.



Supplementary Figure 11. X-ray photoelectron spectroscopy (XPS) measurements of single crystal (SC) and polycrystalline (PC) samples. (a) The survey spectra of single crystal and polycrystalline samples are shown. The high-resolution spectra of I, N, C and Pb atomic peaks are shown in panel b, c, d and e, respectively. Compared with the single crystal, the polycrystalline sample shows higher binding energies for each element, which is attributed to the differences in surface stoichiometry and consequently surface energetics. In panel d, the higher binding energy feature is due to mostly the C–N environment; the lower energy shoulder/peak is due to C contamination, In panel e [SC (original)], the lower binding energy feature is due to metallic lead.<sup>1,2</sup>



Supplementary Figure 12. Surface kinetics extracted from TR spectra with indicated pump energies for the single crystal with a polished surface. The maxima of the surface carrier kinetics for the indicated pump photon energies are normalized to 1. The crystal surface is polished by sand paper with grain size of 100 nm. We use the diffusion model described in the main text to fit the kinetic traces. The black solid traces are the best-fit curves. The x-axis is split into two parts to clearly show the kinetics and fits. The first part (-5-1000 ps) and second part (1-200 ns) are plotted on linear and logarithm scale, respectively. The diffusion coefficient (*D*) and surface recombination velocity (*S*) are determined as  $1.2\pm0.1 \ cm^2 \ s^{-1}$  and  $(2.1\pm0.1)\times 10^3 \cdot cm \ s^{-1}$ , respectively.

### Supplementary Tables.

Supplementary Table 1. The relative atomic ratios determined from XPS for the three samples. For the single crystals, the stoichiometry indicates a Pb-rich surface, whereas the stoichiometry of the polycrystalline sample has an excess amount of N and C, implying that the surface is methylammonium  $(CH_3NH_3^+)$  rich.

	Pb	Ι	Ν	*C
Single Crystal	1.0#	2.2	0.65	1.3
Polycrystalline	1.0	2.9	1.2	1.3
Single Crystal (polished surface)	1.0	2.5	0.83	0.84

\* The amount of C is determined by integrating the higher energy XPS C1s feature, which is due to mostly C in the C-N environment.

<sup>#</sup> The lead peak was integrated to exclude the metallic feature at lower binding energy.

Supplementary Table 2. Pump photo fluence for the TR measurements of the single crystal sample.

Photon Energy (eV)	2.48	2.07	1.77	1.57
Fluence (cm <sup>-2</sup> )	$1.9 \times 10^{12}$	2.7×1012	8.0×1012	$1.7 \times 10^{14}$
Average carrier density (cm <sup>-3</sup> )	$2.4 \times 10^{17}$	$1.1 \times 10^{17}$	$1.7 \times 10^{17}$	3.4×10 <sup>17</sup>

Supplementary Table 3. Pump photo fluence for the TR measurements of the polycrystalline sample.

Photon Energy (eV)	3.1	2.48	2.07	1.77
Fluence (cm <sup>-2</sup> )	$2.2 \times 10^{12}$	2.6×1012	3.3×10 <sup>12</sup>	$7.4 \times 10^{12}$
Average carrier density (cm <sup>-3</sup> )	5.0 ×10 <sup>17</sup>	3.4×1017	$1.4 \times 10^{17}$	$1.7 \times 10^{17}$

#### Supplementary Notes.

Supplementary Note 1. Kramers-Kronig relationship between TR and TA spectra.

For all the TR measurements conducted in this paper,  $\Delta R(\hbar\omega)/R$  is small (~0.005) and the refractive index  $n(\hbar\omega)$  is much larger than the extinction coefficient  $k(\hbar\omega)$  in the spectral region of interest (Supplementary Fig. 5a), and thus  $\Delta R(\hbar\omega)/R$  can be approximated as:

$$\frac{\Delta R}{R}(\hbar\omega) = \frac{4}{n(\hbar\omega)^2 - 1} \Delta n(\hbar\omega)$$
(2)

The transient spectrum of  $\Delta k(\hbar \omega)$  can be obtained from the TA spectrum according to the equation,  $\Delta k(\hbar \omega) = c \cdot \Delta \alpha(\hbar \omega)/2\omega$ . Because  $n(\hbar \omega)$  and  $k(\hbar \omega)$  are the real and imaginary components of the complex refractive index function  $\tilde{n}(\hbar \omega)$ , respectively, according to the Kramers-Kronig (KK) relations,  $n(\hbar \omega)$  can be calculated from  $k(\hbar \omega)$  (or vice versa). The KK relations are given by:

$$n(\hbar\omega) = -\frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{k(\hbar\omega')}{\omega-\omega'}d\omega' (3)$$

and

$$k(\hbar\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{n(\hbar\omega')}{\omega - \omega'} d\omega'$$
(4)

where *P* means Cauchy principal value of the integral. The KK relations between the TR and TA spectrum can also be derived from Supplementary equation (2) and (3), which are given by:

$$\Delta n (\hbar \omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta k (\hbar \omega')}{\omega - \omega'} d\omega'$$
(5)

and

$$\Delta k (\hbar \omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta n(\hbar \omega')}{\omega - \omega'} d\omega'$$
(6)

Therefore, in mathematics,  $\Delta n$  is the inverse Hilbert transform of  $\Delta k$ , and  $\Delta k$  is the Hilbert transform of  $\Delta n$ . The operation of the Hilbert and inverse Hilbert transformation can be realized by commercial software. For example, we use Igor pro procedure to call the built-in function "HilbertTransform" in the current paper.

Supplementary Note 2. Demonstration of excluding bulk recombination from the surface carrier dynamics within 5 ns delay time.

For the polycrystalline samples, total carrier depopulation can be directly measured by TA kinetics or interference kinetics from TR measurement. Both kinetic traces show negligible decay (< 5%) within 5 ns (green and black traces, Fig. 3 in main text), while surface carrier kinetics (red trace, Fig.3 in main text) decays > 70% by 5 ns for the same excitation condition. Therefore, the bulk carrier recombination (first order and higher order recombination) shows negligible contribution in carrier depopulation out of the TR probing region, and it is not included in the diffusion model (Equation 1 in the main text).

For the single crystal TR measurements, the average carrier densities are controlled to be similar to those for the polycrystalline film TR measurements. The bulk recombination contributions should also be negligible within 5 ns delay time. To confirm this, the pump fluence dependent experiments were conducted. We use pump energy of 2.48 eV as an example. Supplementary Fig. 13a shows the TR kinetics of the single crystal sample for different pump fluences. After normalization, the TR kinetic traces are identical (Supplementary Fig. 13b), which rules out the higher order recombination contribution. Furthermore, the first order recombination time constant is orders-of-magnitude longer than 5 ns (Supplementary Fig. 7), and thus the first order recombination contribution is negligible within 5 ns. However, for the pump with photon energy of 1.55 eV, the TR spectra were measured in a longer time window (0-200 ns), and the first-order bulk carrier recombination was included in the fitting model.



Supplementary Figure 13. Pump fluence dependent TR kinetics. (a) TR kinetics for different pump fluences. (b) Normalized TR kinetics. The 1.9x10<sup>12</sup> cm<sup>-2</sup> pump fluence data (black trace) is the data used in the main text. The x-axis is on log-scale. The pump photon energy is 2.48 eV.

#### Supplementary References.

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