Supplementary Information for:

Modulating Hot Carrier Relaxation and Trapping Dynamics in Lead Halide Perovskite Nanoplatelets by Surface Passivation

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Experimental section

Materials

Cesium Bromide (CsBr, 99.99%, from Xi'an Polymer Light Technology Corp.), Cesium Carbonate (Cs_2CO_3, 99.99%, from Xi'an Polymer Light Technology Corp.), Oleic acid (OA, 90%, from Alfa Aesar reagent), Oleylamine (OAm, 80–90%, from Aladdin reagent), Toluene (Macron Fine Chemicals), Hexane (98.5 %, Fisher Chemicals), Acetone (Fisher Chemicals).

Synthesis of NPLs

The NPLs were synthesized according to the reported literature with minor modifications.[1, 2] The Cs-oleate and $PbBr_2$ precursors are first prepared. 0.1 mmol Cs_2CO_3 was added into 10 mL oleic acid. The mixture was stirred at 100°C under Ar atmosphere for ~30 minutes to dissolve the solid. The solution was then kept in air as the Csoleate precursor. The $PbBr_2$ precursor was prepared by dissolving 0.2 mmol $PbBr_2$, 200 µL oleic acid and 200 µL oleylamine in 20 mL toluene at 100 C under Ar atmosphere. To synthesize the 2 monolayer (2L) NPLs, 3 mL of the $PbBr_2$ precursor was loaded into a 20 mL vial and stirred at 1200 rpm. 150 µL of the Cs-oleate precursor was added in to the $PbBr_2$ precursor and stirred for 10 seconds. 2 mL acetone was then quickly injected into the precursor mixture to induce the formation of NPLs. The mixture was stirred for another 1 minutes to allow for the complete reaction. The resulting NPLs was then separated from the reactants by centrifuging the mixture at 4000 rpm for 3 minutes. The precipitated NPLs were finally redispersed in 2 mL hexane for future characterization. The synthesis method was the same for 3L and 4L NPLs only the amount of $PbBr_2$ precursors was changed to 1.5 ml and 1.2 ml, respectively.

Surface passivation of NPLs

The passivation of NPLs is followed the reported method with minor modifications.[3] The $PbBr_2$-ligand solution is prepared by dissolving 0.1 mmol $PbBr_2$ in 10 mL of hexane with the aid of 100 µL each of oleylamine and oleic acid at 100°C which help to dissolve the $PbBr_2$. Typically, 0.1 mL $PbBr_2$ precursor was added into 0.9 mL hexane solution of NPLs. The mixture was shaken for 5 seconds to uniformly distribute the $PbBr_2$ on the NPL surface. Bright blue emission was observed immediately after

passivation. In order to ensure a consistent sample concentration in future spectroscopic experiments, a hexane solution was also added proportionally to the prinstine NPLs.

Steady-State Characterizations

UV-vis absorption spectra were carried out on a Cary 5000 UV-Vis-NIR spectrophotometer. PL spectra were acquired from a Perkin Elmer LS 55 fluorescence spectrometer. The transmission electron microscopy (TEM) images were performed on a JEOL JEM-2100 microscope operating at an acceleration voltage of 200 kV. X-ray diffraction (XRD) was acquired with a DX-2700. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe delay line detector (DLD) spectrometer equipped with a monochromated Al Kα X-ray source.

Transient absorption and time-resolved fluorescence spectra

TA measurements were performed on a commercial femtosecond TA spectrometer (HELIOS, Ultrafast Systems). The excited pulse was obtained from an optical parametric amplifier (TOPAS) pumped by an 800 nm pulse from a femtosecond amplifier laser system (Astrella Vitara-S, Coherent) with the pulse width of 110 fs, centered at 800 nm, and repetition rate of 1 kHz. A small fraction of the 800 nm beam was focused on a CaF_2 crystal in the HELIOS to generate broadband white-light continuum pulses as probe pulses. Pump and probe beams were focused onto the sample, and the time delay was controlled by a motorized delay stage. The excitation-induced transmission change of the probe light was collected by a fiber-coupled spectrometer with CMOS sensors. The time-resolved photoluminescence (TRPL) spectra were performed on FLS980E (Edinburgh Photonics) spectrometer with a 375 nm laser diode.

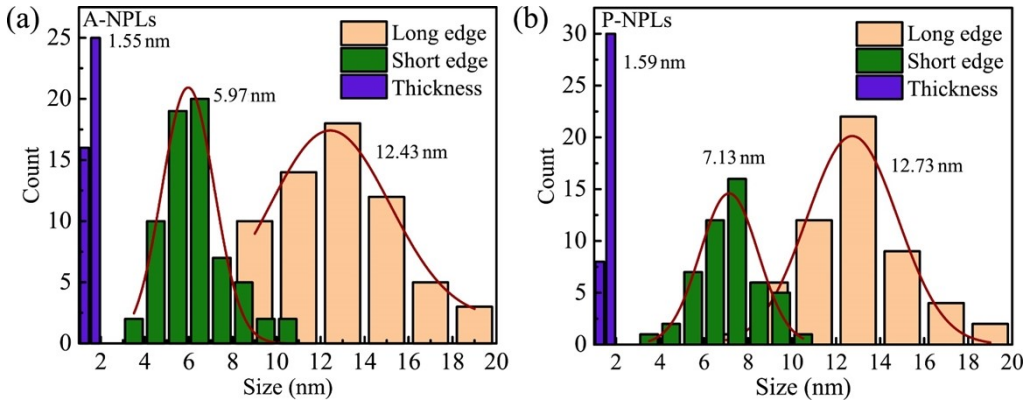

Figure S1. Size distributions of pristine (a) and surface passivated (b) 2L $CsPbBr_3$ NPLs.

Note 1. Calculation of PL QY.

The PL QY of NPLs were obtained using a relative method with quinine sulfate as the standard sample at room temperature. The standard sample is quinine sulfate, with 57.7% PL QY in 0.1 mol/L H_2SO_4 while the cuvette is 10 mm. The refractive index of 0.1 mol/L H_2SO_4 was 1.3443 and that of 1.388 for hexane were applied, respectively.[4] According to the following formula, PL QY of NPLs were obtained,

$$\Phi_1/\Phi_2=F_1/F_2*A_2/A_1*(n_1/n_2) \qquad (S1)$$

where Φ_1 and Φ_2 are the quantum yields of the standard sample and NPLs sample, respectively. $A_1$and A_2 are the absorbances of the standard sample and NPLs sample at the excitation wavelength; F_1 and F_2 are the integrated PL emission intensity of the standard sample and NPLs sample; n_1 and n_2 are the refractive indexes of the standard sample and NPLs sample solution.

Note 2: PL emission dynamics fitting.

The PL dynamical curves are fitted using a double exponential function as below:[5]

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad \text{(S2)}$$

Here, the method of intensity-weighted average was used to calculate the average lifetime of PL dynamics due to the population obtained from time-resolved emission measurements is proportional to integrated emission intensity.[6, 7]

The intensity-weighted average PL lifetime <τ> is calculated according to the following equation:

$$<\tau> = \frac{A_1 {\tau_1}^2 + A_2 {\tau_2}^2}{A_1 \tau_1 + A_2 \tau_2} \quad \text{(S3)}$$

Table S1. Fitted time constants for PL decay curves in Figure 2f.

	τ_1/ns	τ_2/ns	τ_{av}/ns
A-NPLs	1.00 ± 0.01 (80%)	5.60 ± 0.35(20%)	3.68 ± 0.57
P-NPLs	2.20 ± 0.09 (77%)	10.70 ± 1.18 (23%)	7.24 ± 0.90

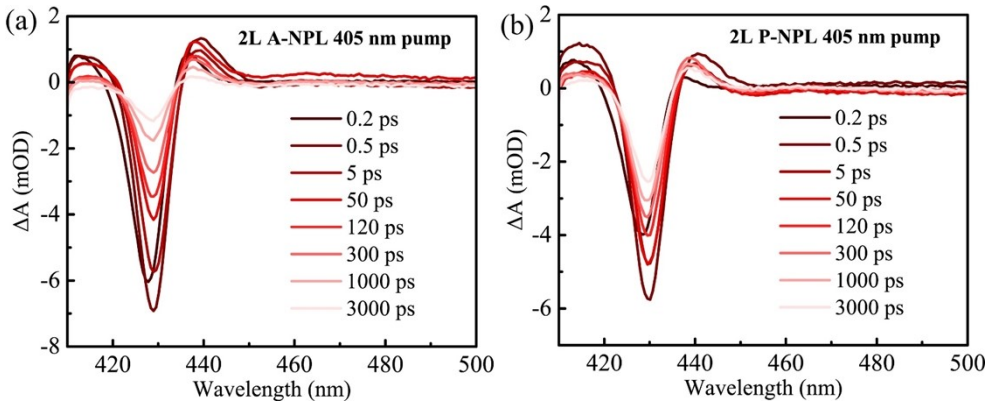

Figure S2. TA spectra of pristine (a) and surface passivated (b) 2L $CsPbBr_3$ NPLs probed at the selected delay times under exaction at 405 nm.

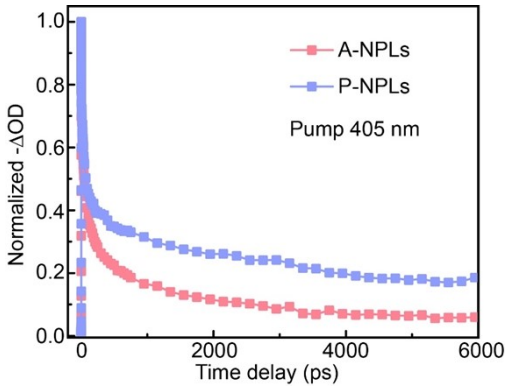

Figure S3. Normalized exciton dynamics of pristine and surface passivated 2L $CsPbBr_3$ NPLs excited at 405 nm.

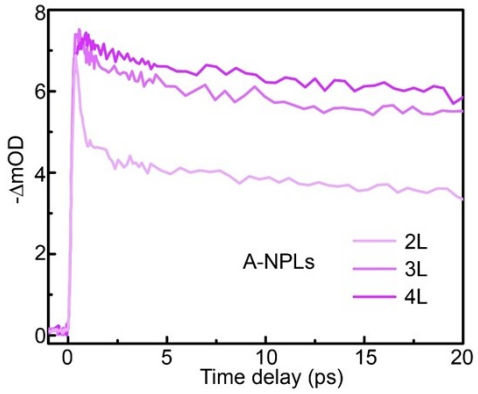

Figure S4. Exciton dynamics of pristine 2L, 3L, and 4L NPLs excited at 360 nm, 375 nm, and 384 nm, respectively.

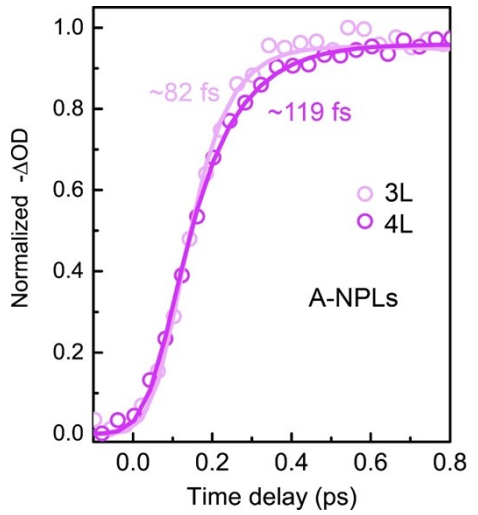

Figure S5. Exciton dynamics at early time delay of pristine 3L, and 4L NPLs excited at 375 nm, and 384 nm, respectively.

Reference

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