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## Deciphering the Role of Quantum Dots Size in the Ultrafast Charge Carrier Dynamics at the Perovskite-Quantum Dots Interface

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## EXPERIMENTAL SECTION

PbS QDs of 2.9 nm and 3.2 nm were synthesized according to procedure previously reported with a small modification. <sup>1-3</sup> Briefly, for 2.3 nm-PbS synthesis, a mixture of 0.9 g (4 mmol) of PbO, 2 g (7 mmol) of oleic acid (OA) and 36 ml of 1-octadecene (ODE) in a three-necked round-bottom flask was heated up to 120°C vacuum for 90 minutes to form Pb-oleate moieties. Then solution was opened to N<sub>2</sub> and temperature was increased to 150°C. 3 ml (6.7 mmol) of trioctylphosphine (TOP, 90%) was injected. A mixture of 0.42 ml (2 mmol) of hexamethyldisilathiane (HMDS) and 4 ml ODE was quickly injected to the flask when the temperature was reduced to 110°C. The solution was left to cool to room temperature. The reaction product was cleaned three times with ethanol/acetone (1:1, v/v), centrifuged (3,000 rpm for 10 minutes). For the synthesis of 3.2-nm PbS QDs, an identical procedure was applied for the synthesis of 2.3 nm QDs, however 2.7 g (9.6 mmol) of OA was used for PbS formation.

For the synthesis of 4.5-nm and 5.3-nm PbS QDs, we applied a similar process, however the concentration of precursors and reaction temperature were increased. Concretely a three-necked round-bottom flask containing 0.9 g (4 mmol) PbO, 4 g (14 mmol) OA and 18 ml ODE was prepared instead. And a mixture of 0.42 ml (2 mmol) of HMDS and 4 ml ODE was quickly injected to the flask at 150 °C. The reaction was maintained at this temperature for 3 and 15 minutes to grow PbS of 4.5 and 5.3 nm respectively. The cleaning process was applied identically to the cleaning of 2.9 nm and 3.2 nm PbS QDs.

A MAPbI<sub>3</sub> solution 0.25M is prepared dissolving 117 mg of PbI<sub>2</sub> (PbI<sub>2</sub>, >98%, from TCI) and 50 mg of MAI (98%, from Great Cell solar) in 1 ml of dimethylformamide (DMF). Then, 1.5 ml of QDs (10 mg/ml) in octane is added into 0.5 ml of MAPbI<sub>3</sub> solution 0.25 M. After stirring for 30 minutes, QDs are transferred from the top octane phase to the bottom DMF. After removing the octane, the QD solution is washed three times with fresh octane to remove the organic residue. Subsequently, the QDs are precipitated by the addition of toluene, then

centrifuged at 3,000 rpm for 5 minutes. After removing the supernatant, QDs are dried under vacuum for several hours.

The ligand exchange is analyzed by the Fourier Transform Infrared Spectroscopy (FT-IR) measurement of PbS based thin films. **Figure S3a,b** show the FT-IR transmission spectra of oleic acid (OA) capped PbS quantum dots films, and perovskite (PS) capped PbS quantum dots films, respectively. The spectra in **Figure S3a** clearly show the bands around 2,908 and 2,850 cm<sup>-1</sup>, attributed to the antisymmetric and symmetric C-H stretching vibration of the CH<sub>2</sub> group respectively, and the CH<sub>2</sub> vibration at 1,457 cm<sup>-1</sup>. The band at 3,006 cm<sup>-1</sup> is assigned to the stretching vibration of the =C-H and the band at 1,515 cm<sup>-1</sup> is associated to the stretching vibrations of the carboxylic group (COO-). As expected, the characteristic vibrations of oleic acid are strongly reduced in the PS/PbS films (**Figure S3b**). Furthermore, no differences observed can be imputable to the size of the PbS quantum dots.

0.4M MAPbI<sub>3</sub> solution is prepared by dissolving 403.8 mg of PbI<sub>2</sub> and 139.2 mg of MAI in the mixture of DMF: dimethyl sulfoxide (DMSO) 10:1 at 70 °C. Dried PbS QDs are dispersed in the MAPbI<sub>3</sub> solution, adding a volume needed to reach the desired concentration, 0.38wt%, 0.52wt%, 1.8wt% and 2.4wt%, for the PbS QDs of 2.9 nm, 3.2 nm, 4.5 nm and 5.3 nm respectively.<sup>4</sup> The MAPbI<sub>3</sub>-PbS films are prepared by spin-coating the solutions at 9,000 rpm for 50 seconds (acceleration of 4,000 rpm). The diethyl ether is dropped on the films at the 4<sup>th</sup> second of the spinning. The films are annealed at 65 °C for 1 minute and at 100 °C for 2 minutes. All the solutions and films are prepared in glove box filled with nitrogen.

The main diffraction peaks, at the angles 14.05 °, 28.38 °, 31.74 ° and 40.63°, are assigned to the (110), (220), (310) and (224) faces, confirming the formation of a perovskite in the tetragonal phase<sup>5</sup> in the presence of the PbS QDs 4.5nm. (b) The XRD patterns of the PbS QD films on glass substrates confirm the formation of PbS crystals with lattice constant comparable

to the values of JCPDS card (no 5-592), that are not displayed in the perovskite pattern because of the low QDs weight percentage loaded.

**The X-ray diffraction (XRD)** patterns of the MAPbI<sub>3</sub> films and PbS QDs are recorded using an X-ray diffractometer (D8 Advance, Bruker AXS) (Cu K $\alpha$ , wavelength of 1 = 1.5406 Å) within the range of 10–60°.

**Transmission electron microscopy (TEM)** images are taken on W JEOL JEM 1010 transmission electron microscope, using an accelerating voltage of 100 kV, with a resolution of 0.4 nm.

**FTIR** spectra of the PbS QDs are collected with a FTIR Equinox 55 (Bruker) with an ATR Pro (Jasco) equipped with a diamond crystal, in standard conditions (in the range 600 - 4,000 cm<sup>-1</sup>).

The photoluminescence (PL) of PbS\_OA QDs in solution was carried out using a CCD detector (InGaAs Andor-iDUS DU490A-2.2) coupled with an adaptive focus imaging spectrograph (Kymera KY-193i-B2). A commercial continuous laser (532 nm, GL532RM-150) was used as an excitation source. A long-pass filter 20CGA-590 was placed front of the detector to block the excitation source.

The femtosecond (fs) transient UV-visible setup used here has been described elsewhere.<sup>6</sup> The femtosecond (fs) transient UV-visible-near-IR experiments were done using a chirped pulse amplification setup. It comprises a Ti:sapphire oscillator (TISSA 50, CDP Systems) pumped by a 5 W diode laser (Verdi 5, Coherent). The seed pulse (30 fs, 450 mW at 86 MHz) centered at 800 nm is directed to an amplifier (Legend-USP, Coherent). The amplified fundamental beam (50 fs, 1Wat, 1 kHz) is directed through an optical parametric amplifier for wavelength conversion (CDP Systems).<sup>6</sup> The 800 nm and its second harmonic 400 nm or the

second harmonic of the output of the OPA (600 nm) were used as the pump. The ratio of the spot size of the pump with respect to the probe was always bigger than 3:1. The spot size was measured using the razor (knife)-edge method.<sup>7</sup>

The time-resolved terahertz spectrometer is described elsewhere.<sup>8</sup> The amplified fundamental beam centered at 800 nm (50 fs, 1W, 1 kHz) is split into three parts. The first one (~700 mW) is doubled in 1-mm BBO crystal or it is first converted by an optical parametric amplifier and then doubled in 1-mm BBO crystal to give the desired pumping wavelength. The resulting beam is sent through a long (up to 10 ns) delay line (H2W Technologies) to excite the sample in the time-resolved terahertz (THz) experiment. The second part of the fundamental beam (~ 200 mW) generates the THz probe in a ZnTe crystal by optical rectification. The third part (~1 mW) is used for electro-optic detection of THz in another ZnTe crystal. During the measurements the setup is continuously purged with dry nitrogen.

The nanosecond (ns) flash photolysis setup was the same as previously described.<sup>9</sup> Briefly, it consists of a LKS.60 laser flash photolysis spectrometer (Applied Photophysics) and a Vibrant (HE) 355 II laser (Opotek). To excite the sample, we used the signal from OPO (pumped by a Q-switched Nd:YAG laser, Brilliant, Quantel) at 460 nm. The pump fluence was 80  $\mu$ J/cm<sup>2</sup>. The much higher pump fluence in flash photolysis experiment as compared to transient absorption one might be risky in terms of determination of first order recombination constant due to domination of higher order processes under such conditions. However, the time resolution of the experiment is approximately 6 ns, while the time scale of higher order processes is below 1 ns. This means that in the **ns flash photolysis** experiment, we will observe only the photoresponse of trapped charge carriers (first order recombination). To probe the system, we used the light source of a 150 W Xenon arc lamp. The light transmitted through the sample was then dispersed by a monochromator and detected by visible photomultiplier (Applied Photophysics R928), which is coupled to a digital oscilloscope (Agilent Infinium

DS08064A, 600 MHz, 4 GSa/s). The measured IRF of the system was ~6 ns. The kinetic traces were collected at 580 nm and were fit by a bi-exponential function.

The authors declare no competing financial interests.

## Average distance between QDs:

Cubic approximation per cm<sup>3</sup> of PS:1 dm<sup>3</sup> =  $10^{24}$  nm<sup>3</sup>.

Mean distance ( $r_{ec}$ ) between QDs in  $10^{24}$  nm<sup>3</sup> volume (cubic approximation):

$$r_{ec}[nm] = \sqrt[3]{\frac{10^{24}nm^3}{N_A \times n_{QDs}}}$$

QD diameter (nm)	QD volume V <sub>QDs</sub> (nm <sup>3</sup> )	Number of unit cells in QD	Number of lead atoms in sphere	Concentration of PbS QDs in perovskite C <sub>QDs</sub> (10 <sup>-5</sup> mol/L)	Mean Distance $r_{es}^{(1)}/r_{ec}^{(2)}$ (nm)
2.9	12.76	61	793	8.04	25/28
3.2	17.15	82	1066	8.18	24/27
4.5	47.69	228	2964	9.0	22/26.5
5.3	77.91	372	4836	9.35	21/26

**Table S1.** Parameters used for calculation of distance between neighboring QDs in perovskite matrix. <sup>(1)</sup>Distance between surfaces of neighboring QDs. <sup>(2)</sup>Distance between centers of neighboring QDs.

QD size	$k_1(10^6 \text{s}^{-1})/\text{A}_1$	$k_2 (10^6 \text{s}^{-1}) / \text{A}_2$	$k_3(10^4 \text{s}^{-1}) / \text{A}_3$	$k_4(10^4 \text{s}^{-1}) / \text{A}_4$	k <sub>mono</sub> (10 <sup>6</sup> s <sup>-1</sup> )
(nm)					
5.3	20/0.73	1.9/0.15	53/0.10	4.8/0.02	14.9
3.2	20/0.78	1.9/0.15	53/0.05	4.8/0.02	17.7
2.9	20/0.81	1.9/0.11	53/0.05	4.8/0.03	16.4
PS	20/0.78	1.9/0.22	-	-	16.0

**Table S2.** Monomolecular recombination rate constants  $(k_i)$  in neat perovskite (PS) and PS/QDs having QDs of different sizes. A<sub>i</sub> are the normalized (to 1) contributions of the component to the TA signal. As the recorded dynamics are dominated by  $k_1$  and  $k_2$  constants, the monomolecular recombination  $(k_{mono})$  value was calculated using only  $k_1$  and  $k_2$  values

according to 
$$k_{mono} = \sum A_i k_i$$
, where  $i = 1,2$ 



<u>20 nm</u>

**Figure S1.** TEM images of the different size PbS QDs with oleic acid as ligand (PbS/OA) and QDs embedded in thin PS film. The TEM images show the PbS QDs at different sizes, in accordance with the steady-state photoluminescence peaks (**Figure S2**).<sup>10</sup>



**Figure S2.** a) Steady state photoluminescence (PL) of the PbS/OA QDs in octane. b) PL after the ligand exchange with the perovskite precursors in DMF.



Figure S3. FTIR of the PbS QDs films before PbS/OA and after the ligand exchange (PbS/PS).



**Figure S4.** X-ray diffraction (XRD) patterns of bare MAPbI<sub>3</sub> and of MAPbI<sub>3</sub>/PbS (4.5 nm) films on FTO substrates.



**Figure S5.** Transient absorption spectra of (1) neat PS (black solid line) and PS containing QDs having size of (2) 2.9 nm (blue dashed line), (3) 3.2 nm (red solid line), (4) 4.5 nm (green dashed line) and (5) 5.3 nm (brown solid line) at 1 ps pump-probe delay time. The samples were excited at 600 nmwith a fluence of the absorbed photons of  $8.2 \times 10^{12}$  ph/cm<sup>2</sup>.



**Figure S6.** (a,b) Transient absorption decays of PS and PS/QDs (3.2 nm) films having QDs of different sizes; (b) zoom of the short time window. The observation wavelength was 760 nm.



**Figure S7.** Absorption spectra of neat perovskite and PS/PbS QDs of different size. The spectra of different samples were normalized to 1 at 750 nm.



**Figure S8.** Transient absorption spectra of neat QDs film of (a) 3.2 and (b) 4.8 nm size at pumpprobe delay times 2, 50 and 1500 ps. Transient absorption decays of PbS of 3.2 nm size observed at 880 and 950 nm in (c) picosecond and (d) nanosecond time window. Data were obtained upon excitation at 600 nm, using fluence of the absorbed photons of  $20 \times 10^{12}$  ph/cm<sup>2</sup>. Solid lines are from the best monoexponential fit of the obtained data.



**Figure S9.** Flash photolysis  $\mu$ s-TA decays of (a) PS (blue open dots), (b) PS/PbS QDs (2.9 nm) and (c) PS/PbS QDs (5.3 nm) films. The measurements were carried out upon excitation at 460 nm (10 mJ/cm<sup>2</sup>) and observation at 580 nm. The solid lines are from the best multi-exponential fits of the experimental data.



**Figure S10.** TA spectra for (a) perovskite and (b) perovskite/QDs of 3.2 nm at different pumpprobe delay times upon excitation at 600 nm with a fluence of  $8.2 \times 10^{12}$  ph/cm<sup>2</sup>.



**Figure S11.** TA spectra for (a) perovskite and (b) perovskite/QDs of 3.2 nm at different pumpprobe delay times upon excitation at 600 nm with a fluence of  $8.2 \times 10^{12}$  ph/cm<sup>2</sup>.



**Figure S12.** TA decays for (a) perovskite and (b) perovskite/QDs of 3.2 nm at different observation wavelengths upon excitation at 600 nm with a fluence of  $1.23 \times 10^{15}$  ph/cm<sup>2</sup>.





(b) 1.0

0.8

0.6

 $\Delta t = 2 \, \text{ps}$ 

(a) 1.0 8.2×10<sup>12</sup> ph/cm<sup>2</sup>

0.8

0.6

<u>∆t</u> = 2 ps

gure S13. Deconvolution (using Lorentz functions) of the TA bleaching band in neat perovskite film at the indicated pump-probe delay times and pump fluences.

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**Figure S14.** Deconvolution (using Lorentz functions) of the TA bleaching band in PS/PbS films at the indicated pump-probe delay times and pump fluences.

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