

Supporting Information

Revealing Photoluminescence Mechanisms of Single CsPbBr₃/Cs₄PbBr₆ Core/Shell Perovskite Nanocrystals

Huafeng Ding^{#1}, Yansu Shan^{#1}, Jizhou Wang^{#2}, Qinfeng Xu^{*1}, Jing Han¹, Mengmeng Jiao¹, Kunjian Cao¹, Mingliang Liu¹, Haifeng Mu^{*1}, Shufang Zhang¹, and Chuanlu Yang^{*1}

¹Department of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, People's Republic of China

²Lanzhou Institute of Space Technology and Physics, Lanzhou 730000, People's Republic of China

*Corresponding author:

E-mail address: xuqf5678@163.com (Qinfeng Xu);

hai-fengmu@163.com(Haifeng Mu);

yangchuanlu@126.com (Chuanlu Yang).

H. F. Ding[#], Y. S. Shan[#], J. Z. Wang[#] contributed equally to this work.

EXPERIMENTAL METHODS

sample preparation of CsPbBr₃/Cs₄PbBr₆ core/shell NCs and Cs₄PbBr₆ NCs

Synthesis of CsPbBr₃ NCs. PbBr₂ (0.188mmol), ODE (5mL), OA (0.5mL) and OLA (0.5mL) were mixed in a 50mL 3-neck flask, heated to 100°C and purged under vacuum for 30min. Then, the temperature was increased to 170°C and 0.058 mmol Cs-oleate solution was quickly injected. The reaction mixture was cooled with the water bath in 10 seconds.

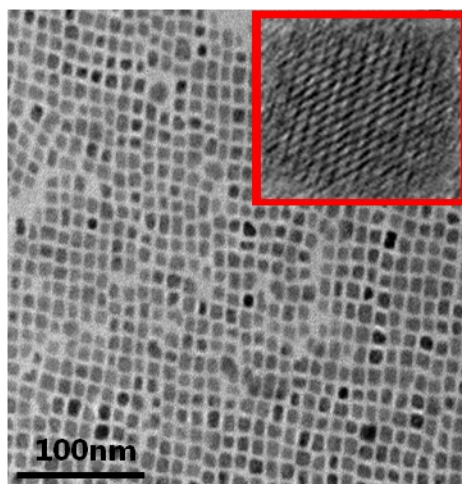


Figure S1. TEM images of CsPbBr₃ perovskite NCs and corresponding magnified individual core/shell NC (top right corner)

Synthesis of CsPbBr₃/Cs₄PbBr₆ core/shell NCs.

The resulting CsPbBr₃ NCs solution was lowered to room temperature and 0.1mmol (or 0.2 mmol) ZnBr₂ was added to the flash, degassed at 50°C for 20 min under vacuum. Afterward the temperature was raised to 70°C under a nitrogen atmosphere, Cs-oleate with different amount (0.203mmol corresponding to a shell thickness of 1.5 nm) was quickly injected. The solution was lowered to room temperature using a water bath after 3min. The solution turned bright green again. To collect the NCs, the crude solution was then centrifuged at 8000 rpm for 5 min. After centrifugation, the supernatant was discarded and the NCs were re-dispersed in 1 mL hexane.

Synthesis of pure Cs₄PbBr₆ NCs.

The Cs₄PbBr₆ NCs were synthesized according to a reported method with slight modifications, i.e. the amount of Cs-oleate and the temperature. PbBr₂(0.2mmol) was first added to a mixture of ODE(8mL), OA(0.4mL) and OLA(2mL) in a 50mL reaction flask. The mixture was degassed for 30 min at 100°C. Then the solution was allowed to cool down under N₂. When

the temperature reached 70°C, 0.46 mmol of Cs-OA (0.325g Cs₂CO₃ dissolved in 5mL OA in a 50ml 3-neck flask, the details were the same as preparation of Cs-oleate) was swiftly injected. After 3min, the solution was quickly cooled down using a water bath.

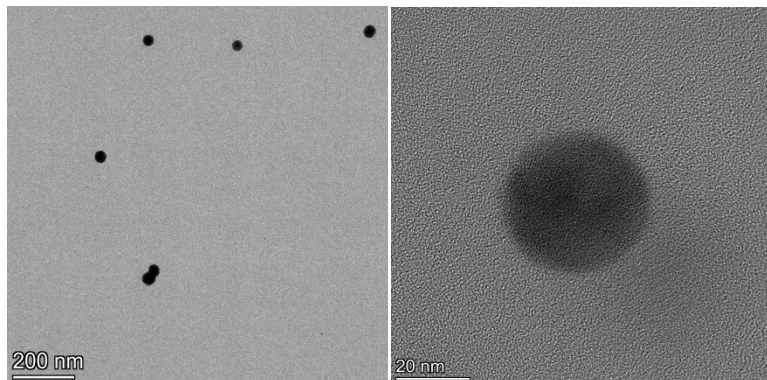


Figure S2. TEM images of Cs₄PbBr₆ perovskite NCs (Left) and corresponding magnified individual Cs₄PbBr₆ perovskite NCs (Right).

Experimental setup

Optical Characterizations of Single CsPbBr₃/Cs₄PbBr₆ core/shell NCs and Cs₄PbBr₆ NCs.

One drop of the diluted solution of CsPbBr₃/Cs₄PbBr₆ core/shell NCs and Cs₄PbBr₆ NCs was spin-casted onto glass coverslip for the optical characterizations of single NCs at room temperature. The 405nm output of picosecond diode laser was used as the excitation source. The laser beam was focused onto the sample substrate by an immersion-oil objective (N.A.=1.4). The PL signal of single NPLs was collected by the same objective and sent through a 0.5m spectrometer to a charge coupled-device camera for the PL spectral measurements. The PL signal of single NPLs can be alternatively sent through a nonpolarizing 50/50 beam splitter to two avalanche photodiodes (APDs) in a time-correlated single photon counting(TCSPC) system with a time resolution of ~250ps. The TCSPC system was operated under the time-tagged, time-resolved mode so that the arrival times of each photon relative to the laboratory time and the laser pulse time could both be obtained, which allowed us to plot the PL time trajectory and the PL decay curve, respectively. Moreover, the delay times between photons collected by one APD and those by the other could be summed up to yield the second-order autocorrelation $g^2(\tau)$ functions.

Determination of absorption cross section and estimation of $\langle N \rangle$

Single CsPbBr₃/Cs₄PbBr₆ core/shell NCs and Cs₄PbBr₆ NCs present photoluminescence (PL) blinking under the high laser powers excitation. After spin coating the quantum dots onto glass coverslip, we added P-Phenylenediamine solution over the sample to protect the NCs from PL blinking. The PL saturation curve of single NCs can be fitted with the functional form $1 - e^{-j\sigma_{abs}}$, where σ_{abs} and j are the absorption cross section and the laser pump fluence, respectively. The pump fluence j can be calculated from $j=P/FE$, where the laser power density P can be directly measured, F is the laser repetition rate of 20MHz, and E is the laser photon energy at 405nm. To determine excitation intensity, the average excitation power was measured directly, and the focal spot size area (Area = $\pi D^2/4$, where D =diameter) was calculated from the Gaussian full width at half-maximum (fwhm) of representative emission spot size scans. The average number of excitons formed per pulse was calculated according

$$\langle N \rangle = \frac{I_{ex} \sigma_{abs}}{E_{\lambda=405} f}$$

where $E_{\lambda=405}$ is the energy of 405nm excitation, and Γ_{rep} is the laser repetition rate. The absorption cross section σ_{abs} ($\lambda=405$ nm) is the cross section for single photon absorption at 405 nm. Therefore, we calculated the absorption cross section σ of single NCs by fitting the PL saturation curves. Then the value of $\langle N \rangle$ in our experiment can be determined by $\langle N \rangle = \sigma j$.

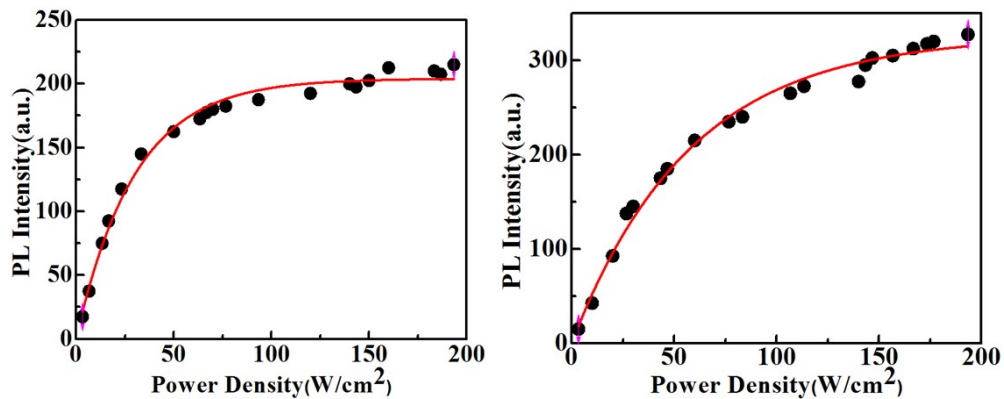


Figure S3. PL intensity of CsPbBr₃ NCs (a) and CsPbBr₃/Cs₄PbBr₆ core/shell NCs (b) measured as a function of the pump fluence j and fitted with the function $1 - e^{-j\sigma_{abs}}$, where σ_{abs} is a fitting constant related to the absorption cross section.

In Figure S3, we also plot the PL intensity of CsPbBr₃ NCs and CsPbBr₃/Cs₄PbBr₆ core/shell NCs as a function of the laser power density. With $\langle N \rangle$ representing the average number of photons absorbed per NC per pulse, Since the pump fluence j is a

controllable parameter in our experiment, the average absorption cross section $\sigma \sim 1.21 \times 10^{-13} \text{ cm}^2$ and $\sigma \sim 1.79 \times 10^{-13} \text{ cm}^2$ corresponding to CsPbBr₃ NCs and CsPbBr₃/Cs₄PbBr₆ core/shell NCs can be obtained from the PL saturation curve shown in Figure S3, which can be treated as the average absorption cross section of ensemble CsPbBr₃ NCs and CsPbBr₃/Cs₄PbBr₆ core/shell NCs at the excitation wavelength of 405nm.