Supporting Information

Deciphering excited-state dynamics and multicarrier interactions in perovskite core-shell hetero-nanocrystals

Yinjuan Ren, ‡[a,b] *Zhonghui Nie,* ‡[a] *Fei Deng,* [a] *Ziming Wang,* [a] *Siyang Xia* [a] and *Yue Wang** [a]

[a]MIIT Key Laboratory of Advanced Display Materials and Devices, Institute of Optoelectronics & Nanomaterials, College of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

[b]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

‡ These authors contribute equally to this work

*Author to whom correspondence should be addressed, electronic email: ywang@njust.edu.cn

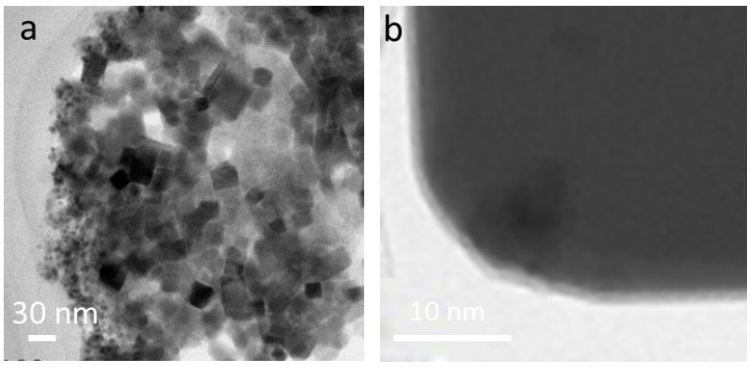

Figure S1: (a) Transmission electron microscopy (TEM) image of the fabricated $CsPbBr_3$@ZnS nanocrystal ensemble. (b) Zoom-in TEM image of a single nanocrystal, revealing the core-shell like structure.

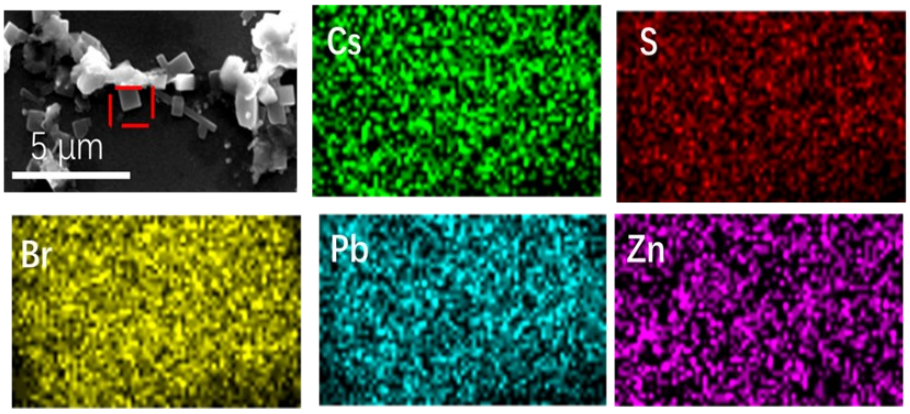

Figure S2: Elemental mapping by energy-dispersive X-ray spectroscopy (EDS) of the $CsPbBr_3$@ZnS nanocrystals, showing the uniform distribution of Zn and S along with Cs, Pb, and Br.

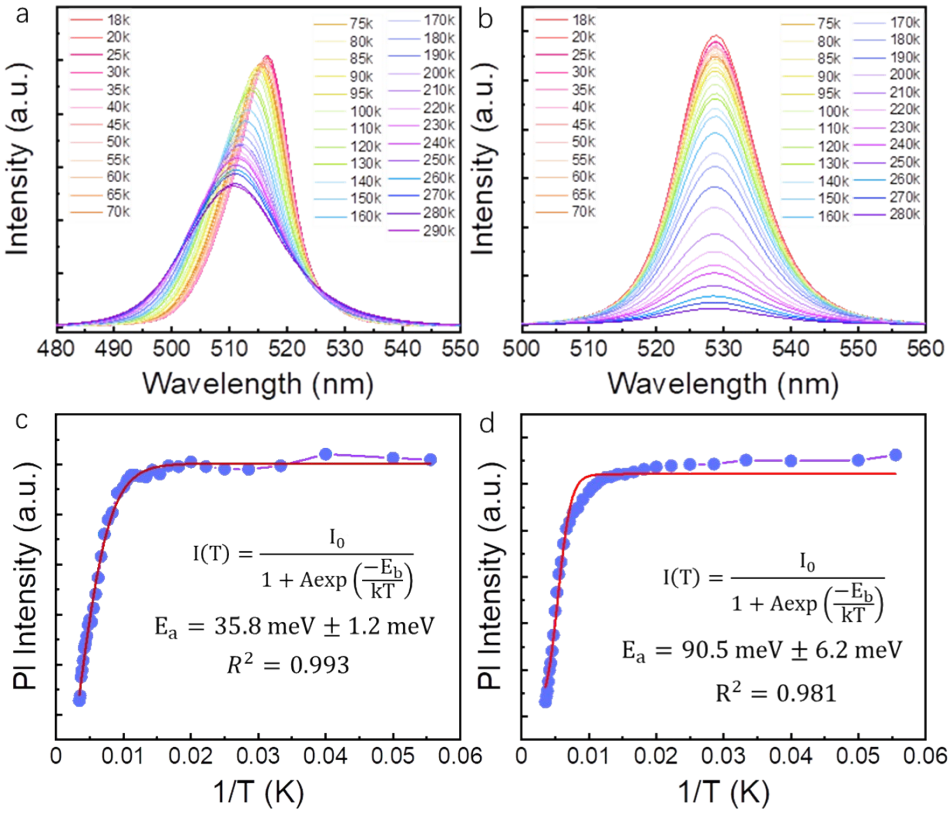

Figure S3. Temperature dependent PL spectra from $CsPbBr_3$ (a) and $CsPbBr_3$@ZnS NCs (b) and the integrated PL intensity as a function of temperature of $CsPbBr_3$ (c) and $CsPbBr_3$@ZnS NCs (d) The red line in Figure S1d shows the Arrhenius function fitting with single activation energy, revealing the large error.

The temperature dependent PL measurements have unraveled the different emission behavior of the samples. For $CsPbBr_3$ NCs (Figure S3a), the temperature dependent PL intensity can be well fitted by the Arrhenius function with thermal activation energy of 35.8 meV, agreeing with the literature.[1] In contrast, the results for $CsPbBr_3$@ZnS NCs can only be fitted by the Arrhenius plot with dual activation energy model:[2]

$$I(T) = \frac{I(0)}{\left[1 + a_1 \exp\left(-\frac{E_1}{\kappa T}\right) + a_2 exp(\frac{-E_2}{\kappa T})\right]}$$

where κ is the Boltzmann constant, T is the temperature, E_1 and E_2 are the activation energies. The determined E_1 (~21.7 meV) and E_2 (~154.0 meV) can be ascribed to the diminished exciton binding energy in $CsPbBr_3$/ZnS and the thermally activated carrier

capture by the core-shell interface.[3]

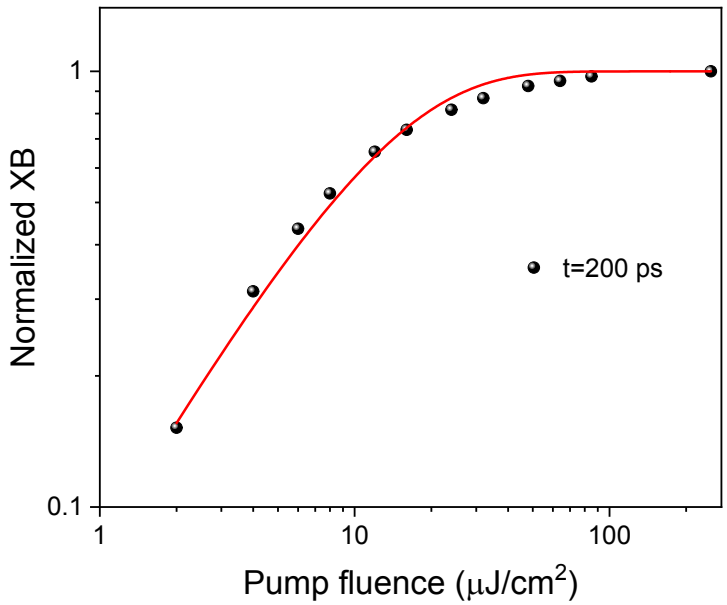

Figure S4. Normalized band edge bleaching signal of $CsPbBr_3$ NCs at a delay time of 200 ps as a function of the pump intensity and its fit to a Poisson statistics model to extract the average electron-hole pair number per NCs.

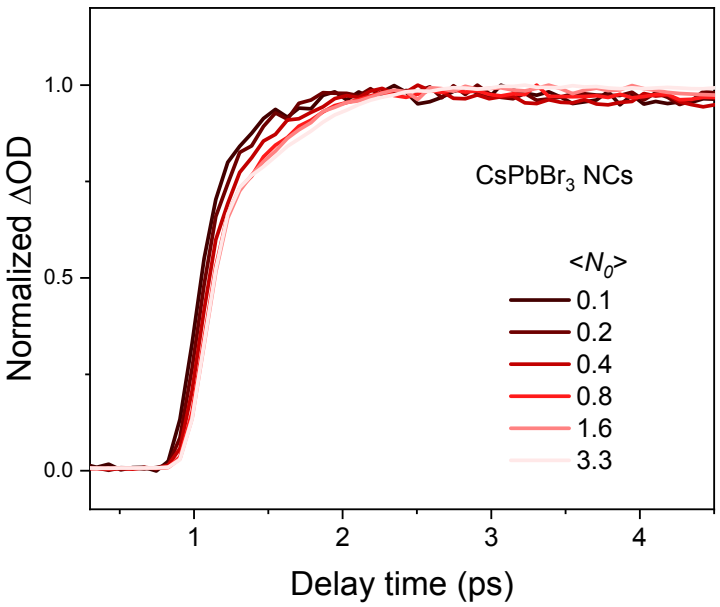

Figure S5. The normalized band edge bleaching signal of $CsPbBr_3$ NCs with different $\langle N_0 \rangle$. The rising edge can be elongated with the increase of pump fluence.

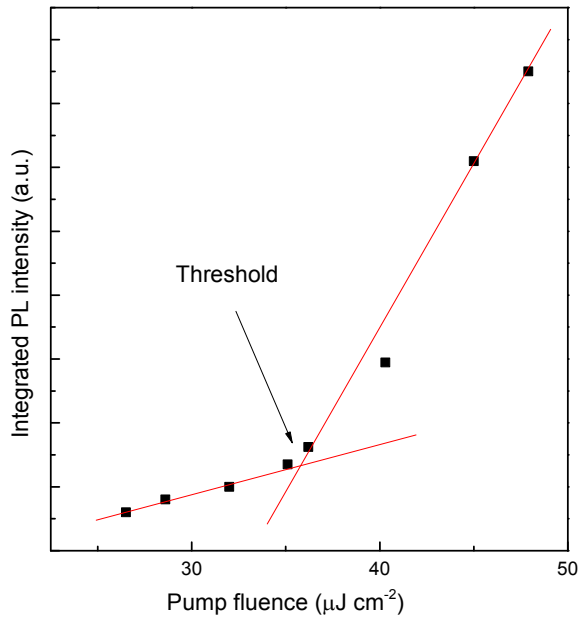

Figure S6. Integrated PL intensity as a function of pump fluence from $CsPbBr_3$@ZnS NCs

Supporting Note 1: transient absorption setup

The transient absorption (TA) measurements in this work were performed at room temperature with 400 nm pump and femtosecond white-light probe. A femtosecond amplified Ti:sapphire laser source (Solstice Ace) is employed to provide 100 fs, 1 kHz pulses with central wavelength at 800 nm. The output of laser is divided into two parts, and the major power is used to generate 400-nm pump beam through a BBO crystal and then focused using a 60-cm lens onto the sample surface. The rest part of laser is adopted to generate supercontinuum as the white-light source to probe the broadband photo-response. The spot sizes of the pump and probe beams were measured by a standard beam profiler, being ~ 400 and 350 μm, respectively. The time delay between pump and probe beams was controlled through a motorized stage. The transient probe transmission was measured directly on a commercial spectrometer.

Supporting Note 2: the determination of the average electron-hole pair number per NCs

In this work, we measured the TA spectra of $CsPbBr_3$@ZnS and $CsPbBr_3$ NCs with various pump fluences (j_p). The dynamical curves at XB have been selected to set the long-term values (> 300~ 400 ps) at to 1. As shown in Figure 4(a, b), a new and fast component emerge at the initial stage with increasing of pump fluences. According to the multi-carrier model in DQs, the fluence-dependent long-lived values (I) at 200 ps can be fitted well by $I = 1 - e^{-Cj_p}$, where C is the a parameter related to the absorption cross section of NCs. Thus, C is extracted from the fitting, shown in Figure S4, and then the average electron-hole pair number per NC can be obtained through calculating $\langle N_0 \rangle = Cj_p$.

Supporting Note 3: the extraction of electronic temperatures from TA

After the initial elastic scattering, hot carriers could form a quasi-thermal distribution, which obey a Fermi-Dirac distribution and has a corresponding electronic or hole temperature. Due to the similar effective mass of electrons and holes in halide lead perovskites, electronic temperature T_e can represent the

temperature of hot carriers. Since the excess energy of hot carriers is relative large, T_e can be obtained by fitting the high-energy tail of prominent PB with a simplified Maxwell-Boltzmann function: $\Delta A(\hbar\omega) = -\Delta A_0(\hbar\omega)\exp\left(\frac{E_f - \hbar\omega}{K_B T}\right)$, where A_0 is the static absorption, and E_f is the quasi-Fermi energy level, and K_B is the Boltzmann's constant. The extracted T_e of $CsPbBr_3$@ZnS and $CsPbBr_3$ NCs have been shown in Figure 3(d).

References

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2 H. D. Sun, S. Calvez, M. D. Dawson, J. A. Gupta, G. C. Aers, G. I. Sproule, *Applied Physics Letters*. 2006, **89**, 101909.

3 U. Manna, Q. Zhang, S. Dhomkar, I. F. Salakhutdinov, M. C. Tamargo, I. C. Noyan, G. F. Neumark, I. L. Kuskovsky, *Journal of Applied Physics*. 2012, **112**, 063521.