Microscopic morphology independence in linear absorption cross-section of CsPbBr₃ nanocrystals

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ABSTRACT Multiple morphologies of colloidal perovskite nanocrystals (NCs) diversify their optical and electronic properties. Among them, the linear absorption cross-section (σ) is a primary parameter to determine their intrinsic photophysical features, and consequently, application potential. Herein, three morphologies of all-inorganic hybrid colloidal perovskite CsPbBr₃ NCs, nanocubes (NBs), nanoplatelets (NLs), and nanowires (NWs), were targeted, and their linear σ values were obtained through femtosecond transient absorption (TA) spectroscopy analysis. At high excitation energy well above the bandgap, the σ per particle of all CsPbBr₃ NCs linearly increased with the particle volume (V_{NC}) regardless of the morphology with the value of $\sigma_{400} = 9.45 \times 10^4 \text{ cm}^{-1} \times V_{\text{NC}} (\text{cm}^3)$. Density functional theory (DFT) calculation confirmed the negligible influence of shapes on the optical selection rules. The Einstein spontaneous emission coefficients calculated from the σ values define the intrinsic radiative recombination rate. However, reduced size dependence is observed when the excitation energy is close to the bandgap (i.e., at 460 nm) with the value of $\sigma_{460} = 2.82 \times 10^8 \text{ cm}^{0.65} \times (V_{\text{NC}})^{0.45} (\text{cm}^2)$. This should be ascribed to the discrete energy levels as well as lower density of states close to the band edge for perovskite NCs. These results provide in-depth insight into the optical characteristics for perovskite NCs.

Keywords: multiple morphologies, absorption cross-section, transient absorption spectroscopy, density functional theory, radiative recombination

INTRODUCTION

Lead-halide perovskites nanocrystals (NCs) have attracted immense attention in the past few years profiting from

their prominent optoelectronic characteristics [1–4]. The bench-marked all-inorganic colloidal CsPbX₃ NCs (X = I, Br, Cl) can achieve narrow photoluminescence (PL) emission and near-unity quantum yields with high stability. Besides, their optical absorption and emission can be conveniently adjusted *via* size and chemical composition engineering [5]. Recently, CsPbX₃ NCs with modified morphologies from conventional nanocubes (NBs) have been extensively investigated, involving one-dimensional nanowires (1D NWs) and 2D nanoplatelets (2D NLs) [6–10]. The morphologic diversity of those nanostructures empowers the flexibility of device assembly. More importantly, the asymmetric quantum confinement can arise from those asymmetric structures fulfilling the special requirement of optoelectronic devices where anisotropic optical absorption or electric conduction is needed [11–13].

In order to elucidate the fundamental optical properties and provide guidance for the device application, lots of photophysical studies on the excited state dynamics, charge carrier transport, defect trapping, etc., have been discussed in recent literatures [14–17]. Most of these studies still utilized the primary optical parameters, especially the absorption cross-section (σ) of bulk materials or conventional NBs. The σ of CsPbBr₃ NBs and their size dependence have been extensively investigated in literature including our own previous studies [18–20]. While, the morphology dependence of light absorption in strongly quantum-confined systems (e.g., quantum dots, quantum wells) is so far not systematically investigated. Here the Coulomb interactions within confined excitons are responsible for additional renormalization effects

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which can play important role [21,22]. In this scenario, the σ values in other morphologies of NCs could deviate from the NBs due to their asymmetric local field factor as well as dielectric surrounding induced from the capping agent [21]. In addition, dominant exposure facets of NCs are morphology-dependent while the contribution of surface states can modulate the oscillator strength [23]. Therefore, it is indispensable to revisit the σ of perovskite NCs with specific morphologies and provide accurate parameters for fundamental studies as well as device engineering.

Conventional approaches to evaluating the NCs σ , including ion concentration and gravimetric analysis, may cause uncertainty given the uneven NCs size distribution and disturbance from the surface ligands. Herein, a well-established method using femtosecond transient absorption (TA) spectroscopy was employed to characterize the σ of three CsPbBr₃ NCs (NBs, NLs and NWs) per particle, which tracks the Poissonian distribution of photo-generated excitons at excited states [20,24–27]. We conclude that the σ at high photon energy (400 nm) above the band edge strictly follows the bulk behavior and linearly scales up with the volume of the NCs regardless of the NC morphology with the relation of $\sigma_{400} = 9.45 \times 10^4 \text{ cm}^{-1} \times V_{\text{NC}}$ (V_{NC} is the volume of a single NC in the unit of cm^3). Very different size dependence was observed when the excitation energy is close to the absorption band edge (460 nm), which is ascribed to the discrete energy levels

with less density of states (DOS) close to the band edge. To our surprise, σ values at 460 nm exhibit the exponential dependence on the volume of NCs with the relation of $\sigma_{460} = 2.82 \times 10^8 \text{ cm}^{-1} \times (V_{\text{NC}})^{0.65}$ for three morphologies with different symmetry of the confinement. This is because in the direction of critical confined dimensions (i.e., the dimension in the direction with strongest quantum confinement regime) of NCs, the overlap between electron and hole wave functions does not change with size any more. Our findings unify the utilization of the σ in colloidal perovskite NCs with various morphologies.

RESULTS AND DISCUSSION

Three types of colloidal CsPbBr₃ NCs with different morphologies, including NBs, NLs and NWs, were synthesized by the typical hot-inject method [5,28,29]. The steady-state absorption and emission spectra of the three samples are presented in Fig. 1a with the absorption edge located at 503, 513 and 445 nm, while PL emission peaks at 513, 518 and 473 nm for NBs, NLs, NWs, respectively. Transmission electron microscopy (TEM) images in Fig. 1b confirmed the three distinct morphologies of those NCs, and the respective sizes are summarized in Fig. 1c. Herein, NWs displayed the most pronounced exciton peak in the absorption spectrum. In contrast, inconspicuous exciton peak can be observed in NBs, which is primarily correlated to the critical confined

Figure 1 (a) Absorption (solid line), PL (dotted line) spectra and (b) TEM images of CsPbBr₃ NCs with different morphologies. (c) The size distribution histogram for the key dimensions of CsPbBr₃ NBs and NLs and NWs, respectively.

dimensions of the NCs. The excitons of NWs therefore are extremely quantum-confined in the radial direction with a diameter of 2.2 nm, while the thickness of 3.1 nm is responsible for the confined excitons in NLs. As for 0D NBs, their excitons are evenly confined in three directions with an edge length of ~ 6.2 nm. Such critical dimension instead of the total volume determines the confinement regime as the volumes of NCs follow the trend of $V_{\text{NBs}} > V_{\text{NLs}} > V_{\text{NWs}}$.

To extract the linear σ of quantum-confined NCs, we utilized the ultrafast TA spectroscopy, where the dynamics of the excited state population were probed (Figs S1 and S2). Fig. 2 presents the typical TA signals of the three different CsPbBr₃ NCs. All samples featured distinct band-edge ground state bleach (GB) band (blue color). In addition, positive excited state absorption (ESA) appeared at the blue side of the GB of all three samples. According to the singular value decomposition (SVD) fitting, TA dynamics can be decomposed into three components as denoted in Fig. 2. The ultrafast component at femtosecond time-scale (400 to 500 fs) corresponds to the hot carrier cooling [30]. The component of tens to hundreds of picoseconds is ascribed to nonradiative recombination processes [20]. The third component on nanosecond timescale is the typical monomolecular radiative recombination of the photo-

generated carriers [20,31]. The ratio of the amplitudes at the GB minimum between the second and third components almost complies with the photoluminescence quantum yield (PLQY) (Fig. S3), which justifies the assignment. In particular, the radiative recombination lifetimes of the three samples are 12 ns (NBs), 13 ns (NLs) and 3 ns (NWs), respectively, being consistent with the other reports in the literatures [32–34]. The fastest radiative recombination lifetime of 3 ns in CsPbBr₃ NWs should be attributed to the larger exciton binding energy evidenced by more pronounced band-edge exciton peak in Fig. 1a.

As the GB in TA measurement is induced by the state filling of the band edge exciton states, we can utilize the kinetics at GB to follow the evolution of exciton population in the NCs. Furthermore, the number of excitons per QD is discrete and the lifetimes corresponding to different numbers of excitons can be easily distinguished from TA kinetics. Disregarding the possible coherent effects caused by short laser pulses, the exciton population of NCs follows the Poissonian distribution [35–38]:

$$P_N = \frac{e^{-\langle N \rangle} \cdot \langle N \rangle^N}{N!}, \quad (1)$$

where P_N is the fraction of NCs with N excitons, N and $\langle N \rangle$ denote the number of excitons and the average exciton

Figure 2 TA spectra of CsPbBr₃ (a) NBs, (b) NLs and (c) NWs, and (d–f) the corresponding SVD fittings, at 300 nm excitation.

number per NC, respectively. When the optical density of the sample is low, the excitation intensity does not vary in the sample volume and $\langle N \rangle$ can be expressed as

$$\langle N \rangle = \sigma \cdot I, \quad (2)$$

where I is the excitation fluence (photons per pulse per excitation area) and σ is the absorption cross-section at specific excitation wavelength. Combining Equations (1) and (2), the fraction of excited NCs can be calculated as follows [36]:

$$P_{\text{exc}} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 - e^{-\sigma \cdot I}. \quad (3)$$

Multiple excitations in a QD decay through Auger process which is significantly faster than the radiative decay of the single excitation. This means that once the Auger process is completed, the signal amplitude is proportional to P_{exc} .

To eliminate the many-body effect, we fitted the linear region in the TA kinetics' logarithmic plot from the long-time delay and extrapolated such linear fitting to $t = 0$ to get the $\Delta A_{0,\text{max}}$ ($\Delta A_{0,\text{max}}$ represents the highest single-exciton signal (all QDs excited) rescaled to $t = 0$) that we need for the σ calculation. The reason is when mono-molecular recombination for the last remaining electron-

hole pair dominates, it should reflect in TA kinetics as a single exponential decay and exhibit linearity in the logarithmic plot. At the early time scale, the TA kinetics deviates from this linearity due to the occurrence of high-order recombination processes such as Auger recombination in the QDs. As discussed, all excited CsPbBr₃ NCs contain a single exciton at long timescale [35]. In this scenario, $\Delta A(I)$ is merely proportional to P_{exc} and decays mono-exponentially. We can rescale it to the corresponding signal at $t = 0$, which is named as $\Delta A_0(I)$.

$$\Delta A_0(I) = \frac{\Delta A(I)}{e^{-t/\tau}} = \Delta A_{0,\text{max}} \cdot \left(1 - e^{-(I/I_0) \cdot \langle N \rangle_0}\right). \quad (4)$$

Here the lowest pump intensity utilized in TA measurement was defined as I_0 . We used such low intensity that the existence of multiple excitons in one NC can be neglected. Clearly, $\langle N \rangle_0$ can be obtained from the performed exponential fit of the $\Delta A_0(I)$ vs. (I/I_0) plots as described in Equation (4), and σ can be calculated according to Equation (2). Fig. 3 presents the pump-intensity dependence of TA dynamics on the three types of NCs. As collected in Table S1, the calculated σ values are $1.87 \times 10^{-14} \text{ cm}^2$ (NBs), $2.68 \times 10^{-14} \text{ cm}^2$ (NLs), $1.67 \times 10^{-14} \text{ cm}^2$ (NWs) at the excitation wavelength of 400 nm. When excitation wavelength is closer to the band

Figure 3 Pump-intensity dependence of TA dynamics for CsPbBr₃ NBs, NLs and NWs, pumped at (a–c) 400 nm and (d–f) 460 nm, respectively.

edge (i.e., 460 nm), the obtained σ values were dropped to 1.24×10^{-14} , 1.34×10^{-14} and $0.97 \times 10^{-14} \text{ cm}^2$, respectively.

The calculated σ showed a perfect linear relationship vs. particle volume within the margin of error when CsPbBr₃ NCs (NBs, NLs and NWs) were pumped at 400 nm, as plotted in Fig. 4a. In addition, such a linear relationship complies again with the trend for NBs with different sizes. This indicates the absorption transition well above the optical band edge in CsPbBr₃ NCs is independent of the particle morphology and exhibits bulk-like behavior. The σ value can be expressed as $\sigma_{400} = 9.45 \times 10^4 \text{ cm}^{-1} \times V_{\text{NC}} (\text{cm}^3)$ extracted from the slope in Fig. 4a. On the other hand, the σ at wavelength closer to the optical band edge possesses reduced size dependence. To our surprise, those σ values exhibited exponential dependence on the particle volume instead of critical dimensions within different morphologies, as presented in Fig. 4b.

In order to rationalize the morphology independence of the σ , we first calculated the DOS of CsPbBr₃ NCs with different morphologic lattice clusters corresponding to different preferential exposure facets as shown in Fig. 5 based on previous reports [6,29,39]. The conduction band minimum (CBM) and valence band maximum (VBM) in all three cases are mainly composed of Pb 6p and Br 4p orbitals, respectively. As the optical absorption in CsPbBr₃ perovskites is dominantly contributed by the optical transition electrons transfer from Br 4p to Pb 6p [40–42], such similar electronic structures indicate the conservation of angular momentum, energy, and linear momentum should be identical among all three samples during the optical transition. Therefore, we can conclude the morphology of CsPbBr₃ NCs has a negligible effect on the optical selection rules. On the other hand, as well accepted in other quantum dot system, the DOS can be

approximated as a continuum for absorption far above the band edge identical to the bulk counterparts (Fig. 4c) [43]. The above two factors elucidate the morphology independence of the σ at high excitation photon energy.

At the regime close to the absorption band edge of the NCs, σ is expected to deviate from bulk behavior as quantum confinement effect dominates. One well-accepted explanation is that the optical strength per NC of the first-exciton transition positively correlated to the particle volume will be canceled by the quantum confinement negatively correlated to the NC size [44,45]. This should be the main reason for the reduced size dependence of the σ with 460 nm excitation as shown in Fig. 4b. The σ value in this case can be expressed as $\sigma_{460} = 2.82 \times 10^8 \text{ cm}^{-1} \times (V_{\text{NC}})^{0.45} (\text{cm}^3)$. Such size dependence on band edge σ is weaker than that in most of semiconductor QDs (i.e., CdSe, PbSe, PbS) [46–48]. What surprises us is that the σ is in exponential dependence of particle volume for all three morphologies with different symmetry of the confinement. The main reason should be that the oscillation strength in strong quantum confinement regime is dimension-irrelevant on the overlap between wave functions of electron and hole [49]. In this regard, we can expect that the overlap of wave functions in the perovskite NCs is fixed as long as one critical dimension reaches strong quantum confinement regime as indicated in Fig. 4c and cannot deviate the oscillation strength.

The σ at other wavelength of CsPbBr₃ NCs can be extrapolated from steady-state absorption spectra (Fig. S4). We can now calculate the Einstein spontaneous emission coefficient (A_i) according to the integrated σ over the first-exciton band using Gaussian function as follows [50,51]:

$$A_i = \frac{8\pi}{\lambda^2} \int_{\nu_1}^{\nu_2} \sigma(\nu) d\nu, \quad (5)$$

Figure 4 The absorption cross-section of CsPbBr₃ NBs, NLs and NWs as a function of NCs volume with (a) 400 nm excitation and (b) 460 nm excitation, respectively. The hollow black circle represents the trend in CsPbBr₃ NBs with different sizes. The error bar for the volume is calculated from NC size distribution. The error bar for σ is propagated from the error of excitation fluence and $-\Delta A/A$. (c) The schematic of overlap between electron and hole wave functions in NCs with different morphologies.

Figure 5 The side and top views of calculation model, as well as calculated DOS for (a–c) CsPbBr₃ NBs, (d–f) NLs and (g–i) NWs, respectively. The unit cells of CsPbBr₃ NCs are highlighted with red dashed lines.

where λ represents the wavelength in centimeter for the first-exciton transition peak, ν_1 and ν_2 denote the start and end frequencies in Hertz at first-exciton absorption band. Furthermore, the first-exciton radiative lifetime τ for CsPbBr₃ NCs with different morphologies was obtained from the inverse of A_i [51].

$$\tau = \frac{1}{A_i}. \quad (6)$$

This calculated τ value can predict the intrinsic radiative lifetime in a given system. Here, both the calculated

radiative lifetimes and the experimental results are listed in Table S2 and plotted in Fig. 6. The experimental values from TA measurement are significantly longer than the calculated lifetimes *via* using A_i , though, the similar trend among three samples, namely NBs > NLs > NWs still holds. We explain the discrepancy by the fact that the absorption of a semiconductor nanocrystal consists of many energetically overlapping transitions which all contribute to the A_i calculation. At the same time, emission is induced by a single transition. This conclusion is well supported by the atomistic calculations of the

Figure 6 The calculated lower limit of radiative lifetimes and the experimental results for CsPbBr₃ NBs, NPs and NWs measured from TA studies, respectively.

semiconductor nanocrystals [52]. Furthermore, many processes prior to the ‘true’ radiative recombination including the diffusion of the charge carriers, trapping and detrapping from the shallow trap states, or the dark-bright state splitting at the band edge of the nanoparticles can all prolong the lifetime measured in TA [53].

CONCLUSIONS

We have successfully synthesized CsPbBr₃ NCs with three morphologies by the hot injection method, including NBs, NPs, and NWs with different aspect ratios. The linear σ values per NC are calculated from the excited state depopulation kinetics based on TA studies. Results showed that the value of σ at high photon energy above the band edge strictly follows the bulk-like behavior and linearly scales up with the volume of NCs regardless of the morphologies. This is due to the bulk-like continuum band structure at high energy and morphologic independent optical band transition visualized from DFT calculation. When the photon energy is close to the optical band edge, the σ exhibits reduced size dependence due to the enhanced quantum confinement. However, such confinement effect is also morphologic (or aspect ratio) independent, whereas it is more dominated by the reduced dependence of NC volume. Our observation indicates the utilization of basic absorption parameters from conventional NBs in other morphologies of colloidal CsPbBr₃ nanostructures is practicable without worrying about the surface or dimensional effects.

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CsPbBr₃纳米晶微观形貌非依赖的线性吸收截面

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摘要 胶体钙钛矿纳米晶的形貌变化赋予其不同的光学和电子特性, 其中, 线性吸收截面是决定材料本征光物理特性及其应用潜力的主要参数. 本文研究了三种不同形貌的全无机钙钛矿CsPbBr₃纳米晶(纳米立方体、纳米片和纳米线), 通过飞秒瞬态吸收光谱分析了它们的线性吸收截面 σ . 在高于带隙的能量激发下, 单个CsPbBr₃纳米晶的吸收截面与形貌无关, 且随着粒子的体积(V_{NC})呈 $\sigma_{400} = 9.45 \times 10^4 \text{ cm}^{-1} \times V_{\text{NC}} (\text{cm}^3)$ 趋势变化. 密度泛函理论证实了形貌对光学选择规则基本没有影响, 同时, 根据吸收截面也计算得到了定义本征辐射复合率的爱因斯坦自发辐射系数. 然而, 当激发能接近带隙(460 nm)时, 吸收截面值对纳米晶尺寸的依赖关系变弱, 取值满足 $\sigma_{460} = 2.82 \times 10^8 \text{ cm}^{0.65} \times (V_{\text{NC}})^{0.45} (\text{cm}^3)$, 这主要归因于钙钛矿纳米晶的离散能级及靠近带边的较低的态密度. 本文的研究结果为洞悉钙钛矿纳米晶的光学特性提供了深入的见解.