Comparison Studies of the Linear and Nonlinear Optical Properties of CsPbBr$_{3-x}$ Nanocrystals: The Influence of Dimensionality and Composition

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ABSTRACT: The optoelectronic properties of all-inorganic perovskite nanocrystals (NCs) have been widely investigated, but the relevant studies have mainly focused on CsPbBr$_3$ NCs. The photophysical properties of other all-inorganic perovskite NCs, such as CsPbBr$_3$ (0 ≤ x < 3), have not been fully explored. Herein, we report comprehensive comparison studies on the linear and nonlinear optical (NLO) properties of colloidal CsPbBr$_{3-x}$ NCs, that is, CsPbBr$_{2.7}$, CsPbBr$_{1.3}$ two-dimensional nanoplatelets (2D NPs) and cubic NCs of CsPbBr$_{3}$ and CsPbI$_3$. Temperature-dependent photoluminescence (PL) measurements confirm that the 2D NPs exhibit higher PL color purity at elevated temperatures than their cubic counterparts. By using femtosecond-transient absorption spectroscopy, the linear absorption cross sections are determined. Importantly, it is found that the 2D NPs show more efficient volume-normalized two-photon absorption than their cubic counterparts due to the contribution of strong electronic confinement. Studies on the relevant influences of dimensionality and composition on the linear and NLO properties of perovskite NCs are not only interesting for relevant applications but also important for fundamental physics.

1. INTRODUCTION

Colloidal semiconductor nanocrystals (NCs), currently synthesized with various methods, have been intensively investigated for their various optoelectronic properties. Among them, lead halide perovskite NCs and all-inorganic CsPbX$_3$ (X = Cl, Br, I) NCs are emerging as a family of promising light emitters owing to their size- and composition-dependent band gap from the violet to near-infrared region and extremely narrow full width at half-maximum (FWHM). The photoluminescence (PL) quantum yields of CsPbBr$_{3-x}$ (0 ≤ x < 3) can reach over 90% in the green and red spectral regions, which enable promising applications as light-emitting diodes and nonlinear optical (NLO) materials. Since CsPbBr$_3$ NCs show better stability than CsPbBr$_{3-x}$ NCs, only great progress in the NLO properties of CsPbBr$_3$ NCs has been achieved, while the optical properties of CsPbBr$_{3-x}$ NCs have not been fully elucidated, which significantly hampers their relevant applications. Compared with CsPbBr$_3$ NCs, CsPbBr$_{3-x}$ NCs possess some unique properties, mainly (1) longer PL emission wavelengths, (2) longer photoexcited carrier lifetimes and diffusion lengths, and (3) no deep state defects and very small Urbach energy, which are preferable for some special applications, such as solar cells and biological imaging. In addition, the structural stability of CsPbBr$_{3-x}$ NCs has been rapidly improved, supported by efforts in recent studies. Therefore, a thorough understanding of their linear and NLO properties is important for the realization of their relevant applications.

It is well known that the NLO properties of semiconductor NCs can be effectively influenced by their geometries. He et al. reported a linear dependence of the three-photon absorption cross section ($\sigma_3$) of CdSe NCs on their volume. Xing et al. reported that the $\sigma_3$ of CdSe/CdS nanorods follows a superlinear dependence on volume with an exponent of $\sim$1.5. Semiconductor two-dimensional nanoplatelets (2D NPs) offer advantageous optical properties, including narrow PL emission at room temperature together with their large oscillator strength, which can be tuned by their vertical thickness. Due to these favorable features, 2D NPs have become appealing for numerous applications, including NLO devices. For example, Scott et al. found that the magnitudes of the two-photon absorption (2PA) cross sections of CdSe 2D NPs and nanorods are proportional to the square of the volume. The different relationship between the 2PA cross section and volume is attributed to the different degrees of quantum confinement, which is weak for spherical NCs and strong for 2D NPs and nanorods. Although some progress on the geometric influence on the NLO properties of semiconductor NCs has been achieved in recent years, the relevant...
studies in perovskite NCs have not been well elucidated. It is expected that the strong quantum confinement of perovskite 2D NPs in the vertical direction can greatly improve both their linear optical and NLO properties, which are crucial for high performance in NLO applications.

Herein, we reveal the linear optical and 2PA properties of CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs and cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$. Compared with the cubic counterparts, the CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs possess better PL color purity at elevated temperatures. Importantly, CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs exhibit enhanced volume-normalized (NV) 2PA properties over the wavelength range of 720–880 nm, which will enable new approaches for various applications.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$ were prepared according to the previously published method described in ref 2 with slight modifications. Additionally, CsPbBr$_{2.7}$I$_{0.3}$ NPs were synthesized according to the procedures provided in ref 19.

2.2. TEM and Steady-State Spectroscopy. The morphology and size distribution of the NCs were examined using transmission electron microscopy (TEM; JEOL, JEM-2010). Linear absorption measurements were carried out using a UV–vis–NIR spectrophotometer (Lambda 950, PerkinElmer, Inc.). The one-photon PL spectra and absolute quantum yields were collected with a spectrometer (Zolix, SENS-9000).

2.3. Lifetime Measurements. Time-resolved PL experiments were carried out at room temperature. The excitation source was a pulsed ultraviolet picosecond diode laser operating at 375 nm, and the pulse width and repetition rate of the laser were 80 ps and 50 MHz, respectively. The signal was dispersed by a 320 mm monochromator (HR320 from Horiba, Ltd.) combined with suitable filters and detected by a time-correlated single photon counting technique.

2.4. Measurements of Temperature-Dependent PL Spectra. The PL measurements were performed between 10 and 300 K within a closed-cycle helium cryostat. A CW He–Cd laser emitting at 325 nm was used as the PL excitation source, and the signal was dispersed by a 750 mm monochromator combined with suitable filters and detected by a photomultiplier by using a standard lock-in amplifier technique.

2.5. Measurements of Femtosecond-Transient Absorption (fs-TA) Spectrum. The fs-TA spectra and dynamics were recorded using a standard pump–probe configuration at 350 nm, ~100 fs pump pulses at 1 kHz repetition rate, and a broadband white-light supercontinuum probe (18SIS0466 Rev.1, Newport). The excited spot diameter was 300 μm, and the measured quantity was the normalized transmission change, that is, ΔA/A, which was performed on NC solutions with an optical density below 1 at the excitation wavelength.

2.6. Measurements of Two-Photon Excited PL Spectra and 2PA Cross Sections. Room-temperature two-photon excited PL spectra of the perovskite NCs were also measured with laser pulses (1000 Hz, 100 fs) from an optical parameter amplifier combined with a traveling-wave optical parameter amplifier system (TOPAS, Spectra-Physics, Inc.) with a tunable wavelength range. The emission from the samples was collected at a backsattering angle into an optical fiber that was coupled to a spectrometer (Acton, SpectraPro 2500i). The 2PA cross sections of perovskite NCs in toluene solution were investigated via the standard Z-scan technique with the same excitation source as that used in the measurements of the two-photon excited PL.

3. RESULTS AND DISCUSSION

As shown in Figure 1, CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs were crystallized with lateral sizes of 16 and 26 nm. The majority of the 2D NPs had a thickness of ~2.4 nm, which corresponds to four unit cells. The as-formed colloidal NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$ were ~19 and ~15 nm in size with nearly cubic shapes, respectively. The volumes were calculated as ~998, ~6859, and ~3375 nm$^3$ for the 2D NPs and cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$, respectively. The UV–vis absorption and PL spectra of the perovskite NCs were measured (Figure 2a). For the 2D NPs, a clear excitonic absorption peak can be observed at 459 nm, while the other two samples do not exhibit such peaks. All three samples show bright PL emission (inset of Figure 2a), and each PL spectrum clearly comprises only a single peak, with the central peak positions at 471, 550, and 598 nm, respectively.

Figure 2. (a) UV–vis absorption and PL spectra of the perovskite NCs. The inset shows their colloidal solutions under UV illumination (λ = 365 nm). (b) Time-resolved fluorescence decay curves of the perovskite NCs. 1, 2, and 3 represent 2D NPs and cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$, respectively.
and 691 nm for the 2D NPs and cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$, respectively. The absolute PL quantum yields of CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs and cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$ were determined to be 4.5, 9.5, and 15.1%, respectively. In addition, the determination of lifetime values of semiconductor NCs is important for many applications, such as various nonlinear photonic devices and two-photon lifetime bioimaging. In the latter case, the signals from short-lived autofluorescence can be greatly reduced if the semiconductor NCs with long lifetime are used. $^{23}$ Time-resolved fluorescence decay curves of the NCs were then measured (Figure 2b). By fitting with a single exponential or biexponential function, we obtained average radiative lifetime values of 3.2, 10.1, and 12.2 ns, respectively. The much shorter lifetime of the 2D NPs is generally considered to be due to a high density of structural defects and trap states. $^{22}$ Additionally, the lifetime values of all-inorganic perovskite NCs are much smaller than those of hybrid inorganic–organic perovskite NCs. $^{23}$ Actually, the nature of the longer lifetime of hybrid inorganic–organic perovskite NCs is unclear and often argued. Several microscopic mechanisms have been proposed to interpret their long lifetime, such as formation of large polarons, Rashba effect, ferroelectric domains, photon recycling, and the screening of band-edge charge carriers by rotation of organic cation molecules. $^{24}$ However, recent work demonstrated that the screening effect was nonessential. $^{25}$

Since understanding the interactions between carriers and lattice vibrations (phonons) is a prerequisite for the fabrication of nonlinear optoelectronic devices, the exciton–phonon interactions of perovskite NCs should be investigated. Although such properties of other perovskite NCs have been widely reported, $^{26-28}$ the relevant studies on our materials have not been revealed. To shed more light on the exciton–phonon interactions of NCs, we conducted temperature-dependent PL measurements for thin films of perovskite NCs obtained by a drop-casting method. Pseudocolor maps of the temperature-dependent PL spectra of perovskite NCs with different geometries in the temperature range of 30 to 300 K are presented in Figure 3a–c. A double-peak PL spectrum was observed for CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs but not for the other two samples (Figure 3d). The PL at low energy is attributed to emission from bound excitons, which are trapped at shallow energy defects before recombination, while the PL at high energy results from free excitons. $^{29}$ Compared with their cubic counterparts, 2D NPs have appreciable defect states that produce PL emission from bound excitons. It can be seen that the PL peaks of the NCs were continuously blue-shifted with increase in temperature from 30 to 300 K (Figure 3e). Thermal changes in the band gap were fitted using the empirical Varshni relation as follows

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T}$$

where $E(T)$ and $E(0)$ are the band gaps at temperature $T$ and 0 K, respectively, $\alpha$ is the coefficient of the band gap change, and $\beta$ is the Debye temperature for the material. $^{30}$ The values of $\alpha$ were determined to be $-2.1 \times 10^{-3}$ K$^{-2}$ for the 2D NPs and $-1.5 \times 10^{-4}$ and $-1.6 \times 10^{-4}$ K$^{-2}$ for the cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$, respectively. The thermal change in the band gaps of the cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$ is 1 order of magnitude larger than that of CsPbBr$_{2.7}$I$_{0.3}$ 2D NPs, indicating their high PL color purity at elevated temperatures. The strong quantum confinement in the 2D NPs can greatly enhance their exciton binding energy ($E_b$). $^{31}$ The higher $E_b$ value indicates that the excitons are highly stable and the probability for their dissociation is less, in particular at temperatures $T < 300$ K. As a result, the thermal change in the band gap of 2D NPs was much smaller than that of the cubic NCs of CsPbBr$_{2.7}$I$_{0.3}$ and CsPbI$_3$. The thermal broadening of the excitonic peak is generally interpreted as an exciton–phonon interaction. The temperature dependence of the PL FWHM can be approximately described by the following equation:

$$\Gamma(T) = \Gamma_0 + \Gamma_{e\text{-}c} + \Gamma_{e\text{-}LO} = \Gamma_0 + \gamma_e T + \gamma_{LO} N_{LO}(T) = \Gamma_0 + \gamma_e T + \frac{\gamma_{LO}}{e^{\frac{\hbar c}{k_B T}} - 1}$$

In eq 2, $\Gamma_0$ is the inhomogeneous peak width at 0 K, while $\Gamma_{e\text{-}c}$ and $\Gamma_{e\text{-}LO}$ are homogeneous PL emission broadening terms, which result from acoustic and longitudinal optical (LO) phonon scattering, respectively. The coefficients $\gamma_e$ and $\gamma_{LO}$ represent the weights of the exciton–phonon coupling strengths. $N_{LO}(T)$ describes the occupation numbers of the...
respective LO phonons, and $E_{\text{LO}}$ is the phonon energy involved in LO phonon scattering.\textsuperscript{32} Figure 3f shows the temperature dependence of the PL FWHM of the free excitons of the perovskite NCs. The solid lines represent the fitting results based on eq 2. The best-fitted values of $\gamma_{\text{LO}}$ for the 2D NPs and cubic NCs of CsPbBr\textsubscript{2.7}I\textsubscript{0.3} and CsPbI\textsubscript{3} are 38, 32, and 31 meV, and the values of $E_{\text{LO}}$ were determined to be 14.9, 20, and 14.2 meV, respectively.

Then, we estimated the linear absorption cross sections ($\sigma_{\text{lin}}$) of the perovskite NCs from the excitation intensity-dependent one-photon-induced ground state bleaching (GSB) signals via fs-TA spectroscopy.\textsuperscript{33} As shown in Figure 4a, we present the fs-TA spectra of the perovskite NCs excited by pump pulses at 350 nm. For all perovskite NCs, the fs-TA spectra exhibit two broad positive bands spanning the visible region and a broad negative band. The broad negative band is attributed to the superposition of GSB and simulated emission due to the close resemblance to the spectra of steady absorption and PL, while the positive spectral features are assigned to photoinduced absorption of the excited state.\textsuperscript{34} It was found that the photoinduced absorption feature develops a multimodal feature for the 2D NPs, indicating the strong confinement regime. However, such a feature has not been observed in the cubic NCs of CsPbBr\textsubscript{2.7}I\textsubscript{0.3} and CsPbI\textsubscript{3}, suggesting weak quantum confinement. The different features can be understood in terms of the different confinement regimes defined based on the NC dimensions relative to the exciton Bohr radius. After fast Auger recombination within the initial hundreds of picoseconds, the samples contain only a single exciton in the subsequent time period. The amplitude of the GSB signal under different excitation intensities varies based on the following equation

$$-A(I/I_0) = -A_{\text{max}}[1 - e^{-(I/I_0)\sigma_{\text{lin}}}]$$ \hspace{1cm} (3)

where $A(I/I_0)$ denotes the GSB signal amplitude of the NCs after a long time delay as a function of excitation intensity and $I_0$ is the minimum excitation intensity used in the fs-TA experiment.\textsuperscript{33} As shown in Figure 4b, the excitation intensity-dependent GSB signal amplitude with a delay time of 1 ns could be well fitted with eq 3, from which the values of $\sigma_{\text{lin}}$ at 350 nm were extracted and determined to be $\sim7.4 \times 10^{-14}$, $\sim9.7 \times 10^{-14}$, and $\sim6.2 \times 10^{-14}$ cm$^2$ for the 2D NPs and cubic NCs of CsPbBr\textsubscript{2.7}I\textsubscript{0.3} and CsPbI\textsubscript{3}, respectively. Their NV linear absorption cross sections were calculated to be $\sim7.4 \times 10^{-17}$, $\sim1.4 \times 10^{-17}$, and $\sim1.8 \times 10^{-17}$ cm$^2$/nm$^2$, respectively. The largest NV linear absorption cross section of 2D NPs is due to their strongest quantum confinement effect. Correspondingly, their molar distinction coefficients were determined to be $\sim1.93 \times 10^7$, $\sim2.54 \times 10^7$, and $\sim1.63 \times 10^7$ L·cm$^{-1}$·mol$^{-1}$ at 350 nm.

From Figure 2a, one can also see that there is one spectral window for the perovskite NCs with negligible one-photon absorption, that is, from $\sim700$ to $\sim900$ nm, which is suitable for two-photon excitation. The 2PA mechanism can be confirmed by measurements of the power-dependent PL intensity (inset of Figure 5a). The logarithm–logarithm plot of the quadratic dependence of the PL intensity versus pumping power with a slope of approximately 2 clearly confirms the existence of the 2PA process.\textsuperscript{35} To quantitatively determine the 2PA cross sections of the 2D NPs and cubic NCs, Z-scan measurements were carried out and relevant experimental data are presented in Figure 5b. To understand the influence of quantum confinement on the 2PA properties, comparing the
2PA cross section at a single excitation wavelength is less than ideal because it does not account for the spectral dependence of the 2PA. Thus, we measured the 2PA spectra of the perovskite NCs in the spectral region between 720 and 880 nm. Since the volume of the NCs greatly influence the 2PA but does not alter the spectral course, we plot the NV 2PA cross section (in GM/nm³) rather than the absolute cross section (Figure 5c).⁸,3⁶ For all samples, the NV 2PA values increase when the excitation wavelength is tuned from low to high energies. However, the 2PA cross sections of the perovskite NCs can be 1 order of magnitude larger than those of CsPbCl₃ and CsPb(Cl₀.₅₃Br₀.₄₇)₃,⁴⁰ indicating that the addition of Br and I elements can more effectively amplify the 2PA of perovskite NCs compared with the addition of the CI element. However, the 2PA cross section of the perovskite NCs can only be slightly modified by partially changing the halide element from Br to I. Thus, compared with the change in the halide element in their cubic counterparts, the fabrication of CsPbBrₓIₙ₋ₓ NPs with 2D geometry can more efficiently amplify the 2PA cross sections. It can be concluded that the electronic confinement effects could also result in very high NV 2PA cross sections for CsPbI₃ 2D NCs if their poor stability could be overcome.

4. CONCLUSIONS
In conclusion, our findings reveal that a family of halide perovskite colloidal NCs that is, 2D NCs and cubic NCs of CsPbBr₂.₇₃I₀.₃ and CsPbI₃ cubic NCs, possesses dramatically different linear and NLO properties. Compared with their cubic counterparts, the 2D NCs of CsPbBr₂.₇₃I₀.₃ exhibit higher PL color purity but more dramatic FWHM broadening at elevated temperatures. Importantly, the perovskite NCs with a 2D geometry offer amazing NV 2PA cross sections that are much larger than those of their cubic counterparts, highlighting their potential for nonlinear optics and bioimaging applications.

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Notes

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