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Abstract: CsPbBr₃ has attracted great attention due to unique optical properties. The understanding of the multiexciton process is crucial for improving the performance of the photoelectric devices based on CsPbBr₃ nanocrystals. In this paper, the ultrafast dynamics of CsPbBr₃ nanocrystals is investigated by using femtosecond transient absorption spectroscopy. It is found that Auger recombination lifetime increases with the decrease of the excitation intensity, while the trend is opposite for the hot-exciton cooling time. The time of the hot-carriers cooling to the band edge is increased when the excitation energy is increased from 2.82 eV (440 nm) to 3.82 eV (325 nm). The lifetime of the Auger recombination reaches the value of 126 ps with the excitation wavelength of 440 nm. The recombination lifetime of the single exciton is about 7 ns in CsPbBr₃ nanocrystals determined by nanosecond time-resolved photoluminescence spectroscopy. The exciton binding energy is 44 meV for CsPbBr₃ nanocrystals measured by the temperature-dependent steady-state photoluminescence spectroscopy. These findings provide a favorable insight into applications such as solar cells and light-emitting devices based on CsPbBr₃ nanocrystals.

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). **Keywords:** Auger recombination; hot-exciton cooling; transient absorption spectroscopy; temperaturedependent photoluminescence spectroscopy

1. Introduction

Nanocrystal quantum dots (QDs) are intensively studied for the next-generation optoelectronic materials [1]. Cesium lead halides QDs in the form of CsPbX₃ (X = Cl, Br, or I) show attractive properties such as tunable bandgaps, ultrahigh photoluminescence (PL) quantum yields, wide tunable emission range, high defect tolerance, and low-threshold optical gain [2–4]. With these exciting properties, CsPbX₃ semiconductors have emerged as promising materials in applications such as light-emitting diodes (LEDs), lasers, photodetectors, and solar cells [5–7].

In traditional semiconductors, photogenerated energetic carriers, i.e., hot-carriers or hot-excitons, relax rapidly to band edges by the emission of phonons [8,9]. The multiexciton generation is a process in which two or even more electron–hole pairs are created in nanostructured semiconductors by absorbing a single high-energy photon [10]. It is difficult to harvest the excess energy above the band edges of the hot carriers due to the carrier relaxation that usually occurs on a sub-picosecond timescale [8]. Quantum confined semiconductor nanocrystals (NCs), such as CsPbX₃ NCs, are predicted to have long-lived hot-carriers enabled by a phonon bottleneck where the large inter-level spacings in NCs result in inefficient phonon emissions. The long lifetimes of hot-excitons provide an opportunity for their extraction. However, there is another relaxation process—non-radiative Auger recombination (AR)—in CsPbBr₃ NCs. In the AR process, electrons and holes recombine directly, transferring their energy to a third particle which would be re-excited to a higher energy state [11,12]. The exciton energy is lost in the AR, which hampers

the PL efficiency and is disadvantageous for applications that rely on light emission [13]. Therefore, it is critical to understand the mechanism of the multiexciton process in $CsPbX_3$ NCs. Mondal et al. found that the hot-exciton cooling process is affected by the pump wavelength, and its lifetime increases with the pump-photon energy (140–700 fs) [14]. However, there are few reports for hot-exciton cooling at high excitation intensity and the AR at different excitation wavelengths to our best knowledge [15–17].

In this paper, the AR and the hot-exciton cooling lifetimes of CsPbX₃ NCs are investigated by using transient absorption (TA) spectroscopy with different pump fluences and excitation wavelength. The lifetime of hot-excitons increases gradually with the increase of pump fluence and/or with the decrease of excitation wavelength. AR lifetime increases with the decrease of pump fluence. Furthermore, it increases with the increase of the excitation wavelengths.

2. Experimental Section

2.1. Sample Preparation

CsPbBr₃ NCs were synthesized by modifying the hot-injection method [18]. First, 0.069 g of PbBr₂ was added to a 3-neck round-bottom flask containing 5 mL of 1-octadecene (ODE). The mixture was degassed at 120 °C for 1 h. Then, 0.5 mL of oleic acid and 0.5 mL of oleylamine were added to the mixture under N₂ atmosphere. After 30 min, the temperature of the mixture was raised to 180 °C. The solution of Cs-oleate (0.1 M, 0.4 mL) in ODE was preheated to 100 °C and then added rapidly to the mixture. When the color of the mixture turned green, the reaction was stopped by dipping the reaction flask into an ice bath. At room temperature, 6 mL of n-butanol was added to form CsPbBr₃ precipitates, followed by the centrifugation at 7000 rounds per minute (rpm). Finally, wet pellets of the CsPbBr₃ NCs were re-dispersed in the n-hexane.

2.2. Size Characterization

The morphology of the CsPbBr₃ NCs was characterized by using a transmission electron microscopy (TEM, JEOL JEM-2010, Tokyo, Japan) operated at an accelerating voltage of 200 kV.

2.3. Spectroscopic Measurements

The steady-state (SS) absorption spectrum was measured by using an ultravioletvisible-near-infrared (UV-Vis-NIR) spectrophotometer (Cary-5000, Agilent, Palo Alto, CA, USA) at room temperature. The SS-PL spectrum was conducted with an optical fiber spectrometer (USB-4000, Ocean Optics, Dunedin, FL, USA) under the excitation of 400 nm. For the temperature-dependent SS-PL spectrum measurements, a thermostat (LNC-W, Lanhai Instrument LH, Beijing, China) with liquid nitrogen was employed. The data of the PL intensity were collected while the temperature was increasing.

The ultrafast TA spectra were performed using the femtosecond (fs) TA spectroscopy system, which is composed of a regenerative-amplified Ti: sapphire laser system (Coherent, Santa Clara, CA, USA, 800 nm, 35 fs, 7 mJ/pulse, and 1 kHz repetition rate) as the laser source and Helios pump–probe system (Ultrafast Systems LLC, Sarasota, FL, USA) as the spectrometer. The output pulse of the laser source was divided into two parts by the beam splitter. One part entered the optical parametric amplifiers (TOPAS, 800 fs), which generated laser pulses at 325 nm, 365 nm, and 440 nm as pump beams. The probe pulses from 320 nm to 650 nm were generated by focusing another part into the continuously rotating CaF₂ crystal. The pump and probe beam overlapped on the sample. After transmitting through the sample, the probe beam was focused into a fiber-coupled spectrometer with CMOS sensors. Time delays (0–8 ns) between the pump and probe pulses were controlled by a motorized optical delay line. The pump beam was chopped by a mechanical chopper rotating at 500 Hz. The instrument response function (IRF) of this system was measured to be 100 fs. The sample was continuously stirred throughout the spectral measurement to suppress the photo-charging effect [19]. All the TA experiments

were carried out at room temperature, and the collected data were analyzed by the Surface Xplore software (Surface Xplore 4.2.1, 2019).

The nanosecond time-resolved PL spectra were obtained by detecting the PL attenuation information of the samples at various wavelengths through the grating monochromator (Omni-l300, Zolix, Beijing, China) and oscilloscope (GDS-3354, GWINSTEK, Xinbei, China) with 400 nm excitation wavelength.

3. Results and Discussion

The TEM image of CsPbBr₃ is shown in Figure 1. The inset displays the size distribution of CsPbBr₃ NCs. The average size of CsPbBr₃ NCs is \sim 8.7 ± 0.5 nm.



Figure 1. TEM of CsPbBr₃ nanocrystals (NCs). The inset shows the size distribution of CsPbBr₃ NCs.

The SS absorption and PL spectra of CsPbBr₃ NCs are shown in Figure 2a. As the quantum confinement results in discrete levels, the optically allowed transitions between these levels produce discrete absorption bands in the SS UV–Vis absorption spectrum with the lowest energy exciton band centered at ~495 nm [20]. There is a strong and narrow PL peak at 509 nm, and the Stokes shift is about 44 meV. This Stokes shift is caused by the coupling of the electron transitions in the luminescent centers and vibrations of the CsPbBr₃ NCs [21]. Note that the peak position of the PL spectrum is the same whether the initial absorption is pumped at high or low energy. Figure 2b shows the contour of the TA spectrum of CsPbBr₃ NCs. There are three features: positive weak broadband in the 450 to 480 nm range (labeled PA1), ground state bleaching (GSB) with a peak at 505 nm, and the second positive absorption band in the 520 to 560 nm region (labeled PA2).



Figure 2. (a) SS absorption (black solid line) and PL spectra (blue dashed line) of CsPbBr₃ NCs. (b) TA contour with an excitation energy of $16 \mu J/cm^2$.

To measure the carrier dynamics, the ultrafast TA spectral experiments were performed with a pump pulse at 365 nm. The absorbance variation of the detection beam was recorded in the wavelength range of 380 to 650 nm. Figure 3a,b shows TA spectra of the CsPbBr₃ NCs with pump fluence of 0.6 μ J/cm² and 318 μ J/cm², respectively. The delay time ranges from 0 to 500 ps, and the arrows indicate the evolution of the delay time. The PA1, GSB, and PA2 appear in the TA spectra after the pulse excitation, and these characteristic peaks recovered gradually over time. The PA1 signal is attributed to transitions of newly state-filling excited-state carriers to higher levels [22]. The GSB signal at \sim 505 nm is induced by the state-filling of the low energy state of band edges [20,23], corresponding to the first exciton absorption peak in Figure 2a. The GSB amplitude, as well as the bandwidth at low pump fluence of $0.6 \,\mu$ J/cm², is smaller than that with a high pump fluence of 318 μ J/cm². Furthermore, the recovery of the GSB signal in 500 ps is ~30% at $0.6 \,\mu$ J/cm² but 60% at 318 μ J/cm². This fast GSB recovery process indicates that there is an exciton–exciton extinction process (e.g., non-radiative AR). The PA2 signal at \sim 520 nm can be assigned to a transient Stark effect caused by the Coulomb interactions between the hot-excitons and the band-edge excitons [11,24–26]. Moreover, the decay of PA2 is accompanied by an increase of GSB from 500 fs to 7 ps. It should be noted that the GSB reaches the maximum around 6 ps, however, the delay time is 500 fs for the PA2 signal.



Figure 3. (a) TA spectra of CsPbBr₃ NCs at the indicated delay time under the lowest pump fluence at 365 nm. (b) TA spectra of CsPbBr₃ NCs at higher pump fluence at 365 nm.

Figure 4a shows the TA dynamics with excitation intensity of $16 \mu J/cm^2$ at 446 nm, 503 nm, and 519 nm in the early time, respectively. The inset displays the formation time (~450 fs) for the PA2 signal. The PA2 signal at 519 nm decays with the buildup of the GSB signal at 503 nm. This phenomenon is caused by the formation of band-edge excitons during the relaxation of hot-excitons [8]. The attenuation time 580 ± 50 fs is obtained by fitting the PA2 signal of 519 nm, corresponding to the hot-exciton intraband cooling-time. The buildup time constant of the GSB signal is 450 ± 20 fs. The PA2 decay time and GSB buildup time are similar, validating the cooling dynamics of hot-excitons, i.e., intraband relaxation [11]. The origin of the GSB signal is attributed to the state-filling effect [20,23]. However, the origin of PA2 is different from GSB because of the difference in the dynamic curves. It is believed that the origin of PA2 is polarons formed by pump-excitons [17]. The PA1 signal at 446 nm is attributed to the absorption arising from the lowest exciton state, as its formation time (520 \pm 90 fs) is close to that of GSB [14].

The influence of pump fluence on the bleaching recovery kinetics is conducted for CsPbBr₃ NCs. Figure 4b displays the normalized kinetic curves of the GSB peak at 500 ps with different pump fluences. The TA trace with a low-intensity of $0.6 \ \mu$ J/cm² is almost flat, meaning that there is only a single-exciton recombination process. The amplitude of the initial TA spectra increases from 1.3 to 3.1 optical density (OD) when the excitation intensity rises from 0.6 to 318 μ J/cm². Moreover, the amplitude of the initial TA spectra is directly proportional to the number of band-edge excitons generated in the pumping

process. The amplitude of the initial TA spectra with the excitation intensity of $318 \ \mu J/cm^2$ is close to that of $159 \ \mu J/cm^2$, indicating that the band-edge states are saturated.



Figure 4. (a) TA dynamics detected at the peaks of PA1 (446 nm), PA2 (519 nm), and GSB (503 nm) early scale. Inset: zoomed-in view of the early time for PA2 band. The black-line is IRF. (b) Pump fluence dependence of the normalized TA dynamics at the GSB peaks on the long time delay.

The information about the degeneracy of the band-edge states can be extracted. The initial TA amplitude is ~3.1 for the highest pump fluence of 318 μ J/cm² in Figure 4b. It is ~3.1 times higher than that at 500 ps after the excitation. This implies that the degeneracy for the lowest band-edge states is bigger than two. Makarov et al. found that the band-edges states were twofold degenerate because there are only the lifetimes of biexcitons in the pump fluence-dependent PL and TA spectra for cesium lead halide perovskite QDs [11]. There are biexcitons and multiexcitons with the fluence higher than the threshold value of 1.6 μ J/cm² generated in CsPbBr₃ NCs.

The GSB kinetic curves with different excitation intensities at 325 nm, 365 nm, and 440 nm pump wavelengths are fitted using the exponential Formula (1) [27,28],

$$\Delta A(t) = a_1 exp(-t/\tau_1) + a_2 exp(-t/\tau_2) - c_1 exp(-t/\tau_{et})$$
(1)

where a_1 , a_2 , and c_1 are the amplitude; τ_1 and τ_2 are the decay time constants; and τ_{et} is the rise-time constant. Decay includes fast and slow components. Figure 5a shows the variation of the fast decay component τ_1 with the pump fluences at 325 nm, 365 nm, and 440 nm excitation. As the pump fluence increases from 1.6 to 318 μ J/cm², the fast decay τ_1 decreases from 75 \pm 18 ps, 104 \pm 19 ps, and 126 \pm 41 ps to 41 \pm 6 ps, 46 \pm 4 ps, and 58 ± 7 ps for 325 nm, 365 nm, and 440 nm, respectively. (The error drops by more than a factor of 2 indicating that the signal-to-noise ratio of the collected data is increased when the pump fluence increases.) It indicates that the fast lifetime τ_1 reduces when the pump fluence increases. The fast decay component τ_1 is attributed to the non-radiative AR of multiexcitons generated by the absorption of multiple photons in a single NC. Furthermore, the number of photons absorbed by per NC should increase with the increase in excitation intensity, which will amplify the number of excitons, speeding up the AR rate [9,16]. The AR rate can be represented by $dn/dt = -Cn^3$, where n is the carrier density and C is the effective Auger constant, and the carrier density-dependent instantaneous AR time (τ_n) is described by $\tau_n = (Cn^2)^{-1}$ in bulk semiconductors [12]. For the case of NCs, τ_n is related to the N-exciton Auger lifetime (τ_{NX}) by $\tau_n = \tau_{NX} < N > |_{\langle N \rangle = N}$, where *n* is defined as $n = \langle N \rangle / V_{NC}$ (here $\langle N \rangle$ is the ratio of the average number of electron-hole pairs per NC, V_{NC} is the NC volume) [29]. The effective Auger coefficient can be expressed as $C = V_{NC}^2/(8\tau_{2X})$, where τ_{2X} is the biexciton lifetime [11]. Thus, the Auger constant of $CsPbBr_3 NCs$ is obtained between 9.4 × 10⁻²⁸ to 1.3 × 10⁻²⁷ cm⁶s⁻¹ based on the measured lifetime with the pump fluence of 1.6 μ J/cm². Moreover, the AR lifetime with 440 nm excitation wavelength is much longer than that with 325 nm. It should be noted that there are no fast decay component τ_1 at the low pump fluence of 0.6 μ J/cm², and there is only

a single exciton recombination process. The time constant of the slow decay component τ_2 caused by the single-excitons recombination is about a few nanoseconds [13,30]. As shown in Figure 5b, the single-excitons recombination lifetimes fitted from the GSB data are \sim 7.2 \pm 1.2 ns, 6.3 \pm 1.1 ns, and 6.8 \pm 1.1 ns with pump wavelengths of 325 nm, 365 nm and 440 nm, respectively.



Figure 5. (a) Decay time constant of fast decay component the GSB dynamic as a function of pump fluence with 325 nm, 365 nm, and 440 nm pump wavelengths. (b) Single-excitons recombination lifetimes with 325 nm, 365 nm, and 440 nm at 0.6 μ J/cm², and (c) rise-time constant of the GSB dynamic as a function of pump fluence with 325 nm, 365 nm, and 440 nm.

Figure 5c demonstrates the relation between rise-time constant τ_{et} and pump fluences with excitation wavelengths of 325 nm, 365 nm, and 440 nm for CsPbBr₃ NCs, respectively. τ_{et} is corresponding to the hot-exciton intraband cooling-time. As the pump fluence increases from 0.6 to 318 μ J/cm², the rise time τ_{et} increases from 0.28 \pm 0.08 ps, 0.27 ± 0.08 ps, and 0.12 ± 0.07 ps to 1.13 ± 0.04 ps, 1.07 ± 0.03 ps, and 1.04 ± 0.06 ps for 325 nm, 365 nm, and 440 nm, respectively. The extension for the hot-exciton cooling time indicates that there is a hot phonon bottleneck [31]. With rising excitation intensity, the number of absorbed optical phonons per NC increases, leading to an increase in the occupancy of the lowest energy levels at the band edge. The hot phonon bottleneck effect slows down the hot-excitons' relaxation, resulting in the long-lived hot carriers' population [15,31]. On the other hand, at the same pump fluence, the hot-exciton cooling life τ_{et} shows an increasing trend with decreasing excitation wavelength. For example, at 0.6 μ J/cm², τ_{et} is 0.12 \pm 0.07 ps, 0.27 \pm 0.08 ps, and 0.28 \pm 0.08 ps for the pump wavelengths of 440 nm (2.82 eV), 365 nm (3.40 eV) and 325 nm (3.82 eV), respectively; at $1.6 \,\mu\text{J/cm}^2$, τ_{et} is $0.17 \pm 0.04 \,\text{ps}$, $0.42 \pm 0.03 \,\text{ps}$, and $0.46 \pm 0.06 \,\text{ps}$ for 440 nm, 365 nm, and 325 nm, respectively; at 16 μ J/cm², τ_{et} is 0.44 \pm 0.05 ps, 0.55 \pm 0.06 ps, and 0.60 \pm 0.05 ps for 440 nm, 365 nm, and 325 nm, respectively; and at 160 μ J/cm², τ_{et} is 0.65 \pm 0.03 ps, 0.78 ± 0.02 ps, and 0.83 ± 0.03 ps for 440 nm, 365 nm, and 325 nm, respectively. It means that the time of the hot-carriers cooling to the band edge is increased by increasing the excitation energy. Because the lowest excitation energy (2.82 eV) is close to the bandgap with little excess excitation energy, the GSB signal appears near the time resolution of the IRF (100 fs). However, for the higher excitation energy (3.40 eV or 3.82 eV) well above the bandgap, it generates a larger rising component τ_{et} .

The fast dynamical processes of CsPbBr₃ NCs have been analyzed using TA spectroscopy. To shed more light on the exciton nature of CsPbBr₃ NCs, the nanosecond time-resolved PL and variable temperature PL are performed with an excitation wavelength of 400 nm. Figure 6a demonstrates the time-resolved PL contour for the CsPbBr₃ NCs. The PL lifetime is 6.9 ns, which matches well with the single-exciton recombination lifetimes (7.2 ± 1.2 ns, 6.3 ± 1.1 ns, and 6.8 ± 1.1 ns) mentioned above. The exciton binding energy, as a key physical parameter of semiconductors, is especially crucial for excitation and recombination during the PL process of inorganic perovskite QDs at room temperature [32]. Figure 6b shows the SS-PL spectra for the CsPbBr₃ NCs. The PL peak shifts monotonously from 516 nm to 512 nm as the temperature increases from 100 K to 300 K. The blue-shift of this emission peak is caused by the electron–phonon coupling [33]. It indicates that the band-gap energy increases with the increase of the temperature. On

the other hand, the intensity of PL peaks reduced greatly with the increased temperature. This phenomenon is caused by thermally activated non-radiative recombination channels at high temperatures [34]. The dependence of the PL intensity with temperature is shown in Figure 6c fitted with Formula (2) [35],

$$I(T) = \frac{I_0}{1 + Aexp(-E_b/K_BT)}$$
(2)

where I_0 is the integrated PL intensity at 100 K. A is the radiation attenuation constant, E_b is the exciton binding energy, and K_B is the Boltzmann constant. The fitting yields an E_b value of 44 meV, close to the value reported by Li et al. [33]. This value is larger than the thermal disturbance energy at room temperature (\approx 26 meV), which indicates that CsPbBr₃ NCs can generate excitons at room temperature and recombine with a high rate [32].



Figure 6. (a) Nanosecond time-resolved PL contour. (b) Temperature-dependent SS-PL spectra of CsPbBr₃ NCs. (c) Integrated PL intensity as a function of temperature. The black solid line represents the fit based on the Formula (2).

4. Conclusions

The dynamics of hot-exciton cooling and AR for CsPbBr₃ NCs is investigated by using the TA spectroscopy. Processes of hot-exciton cooling and AR show a significant dependence on excitation fluence and pump wavelength. With high excitation intensity, the AR dominates the decay kinetics. AR lifetime increases with decreasing pump fluence, and the recombination rate (~126 ps) at 440 nm excitation wavelength is significantly suppressed at low pump power. The hot-exciton cooling time is 0.12–1.13 ps, and the cooling rate increases with the decrease of the excitation intensity and pump-photon energy of the pump light, respectively. The long lifetimes of hot-excitons are achieved by changing the pump light conditions. At low pump fluence, single exciton recombination is the main recombination in CsPbBr₃ NCs, and its lifetime is about 7 ns. The exciton binding energy of CsPbBr₃ NCs is 44 meV. The dynamics results for multiexcitons interactions and relaxation in CsPbBr₃ NCs provide a favorable insight into the applications including solar cells and light-emitting devices based on CsPbBr₃ NCs.

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