Direct and Indirect Recombination and Thermal Kinetics of Excitons in Colloidal All-Inorganic Lead Halide Perovskite Nanocrystals

Huafeng Shi,†,‡ Xiaoli Zhang,† Xiaowei Sun,† Rui Chen,*† and Xinhai Zhang*†

†Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen 518055, China
‡Harbin Institute of Technology, Harbin 150001, China

ABSTRACT: In recent years, the colloidal all-inorganic lead halide perovskite nanocrystal has become one of the most notable optoelectronic materials. The kinetics of excitons directly influence the device performance, but it is very complicated and still unclear. Here, we have presented the investigation of thermal kinetics of excitons in colloidal all-inorganic lead halide perovskite nanocrystals. As temperature increases from 4 K to room temperature, the photoluminescence (PL) intensity follows the Arrhenius equation with interruption at 130–150 K, while the average PL lifetime follows the double-Boltzmann function fitting, discontuing at the same temperature. These experimental results could be explained by direct and indirect recombination of excitons. The excitons directly recombine with a short lifetime of about 300 ps. Indirect recombination is completed by the photo-excited electrons (holes) along the path of trapping, detrapping, and then recombination with holes (electrons). The excitons mainly undergo indirect recombination at low temperature and balance at the temperature of 130–150 K because of thermal activation, while direct recombination happens at high temperature. Our experimental results provide insight into the recombination mechanism of excitons in colloidal all-inorganic lead halide perovskite nanocrystals, which will be helpful to unravel their potential for high-performance optoelectronic devices.

INTRODUCTION

Lead halide perovskites have been recognized as a promising functional material for optoelectronic device applications, including high-efficiency photovoltaic cells,1 light-emitting diodes,2,3 terahertz source,4,5 photo detectors,6 and other optoelectronic functional devices.7,8 All-inorganic lead halide perovskite shows high stability compared to those organic ones, which have attracted intensive research attention.5,10 Bulk crystal of all-inorganic lead halide perovskite showed poor photoluminescence (PL) because of the ionic characteristic which leads to the dissociation of excitons.11 However, with size reduction to the nanoscale, extraordinary properties have been produced.5,12 Colloidal all-inorganic lead halide perovskite nanocrystals present wide and tunable absorption ability, narrow emission, strong luminescence, and excellent PL quantum yield even up to nearly 100%.13 Therefore, colloidal all-inorganic lead halide perovskite nanocrystals have been considered as a promising optoelectronic material.

The kinetics of carriers during the photo-excitation process in colloidal all-inorganic lead halide perovskite nanocrystals is very complicated, which directly influences the device performance. Random formation of charged carriers and the associated nonradiative Auger recombination result in emission blinking.14,15 The decay of charged carriers in perovskite is caused by much faster Auger recombination than common quantum dots and seems to deviate from “universal volume scaling”.16,17 Dark states for carriers may suppress PL emission and could mix with bright states under thermal activation.18–20 Self-trapped carriers in perovskite that could produce warm white light break the band gap limitation.21,22 Different diffusion of electrons and holes could generate terahertz emission.23,24 Alkali cation (Cs) could lead to a more homogeneous spacing between various lattice planes for increasing carrier lifetime and charge recombination.25 The band bending of grain boundaries in mixed phases could improve photocurrent performance of all-inorganic lead halide perovskite.26 To fully realize the potential of perovskites, it is imperative to obtain a deeper understanding of the underlying photophysics of all-inorganic lead halide perovskite nanocrystals.

During the photon excitation of the perovskite CsPbBr3 nanocrystal, photo-excited carriers may exist as the exciton (bound electron–hole pair), biexciton (double bound electron–hole pair), and trion (charged exciton, electron–hole pair binding one more electron). The direct recombination of the exciton could be fitted by single-
exponential decay perfectly with a time constant around 300 ps for the CsPbBr₃ nanocrystal. Biexcitons have much shorter decay time because of faster Auger recombination. The double exponential function could be used to describe these PL decay including the biexciton and defect/dark state. Trions need higher excitation power and always come along with the exciton and biexciton in the perovskite CsPbBr₃ nanocrystal. PL decay could be fitted by the tri-exponential function. PL dynamics in the perovskite CsPbBr₃ nanocrystal strongly depends on temperature, and therefore, tri-exponential fitting is often used to analyze these experimental data. It is necessary to mention that the temperature-dependent PL is obviously different from the process including excitons, biexcitons, and trions. The thermal kinetics need more information to determine physical processes when temperature changes. Also, the mechanism responsible for long PL lifetimes observed in many lead halide perovskites is still under debate.

Here, we have presented the investigation of the exciton dynamics in the colloidal all-inorganic lead halide perovskite nanocrystal. At room temperature (293 K), steady-state PL demonstrates a linear relationship with excitation power while maintaining the same shape. As temperature increases from 4 K to room temperature, the integrated PL intensity follows the Arrhenius equation with an interruption at 130−150 K. The temperature-dependent time-resolved PL (TRPL) data show that the average PL lifetime follows the double-Boltzmann function, which also shows a turning point at the same temperature. The experimental data could be fitted by using the tri-exponential function. The exciton is directly recombined with a short lifetime of about 300 ps. The indirect recombination is due to the photo-excited electrons (holes) along the path of trapping, detrapping, and recombination with holes (electrons), corresponding to the intermediate (long) lifetime. The direct and indirect recombination has a balance at the temperature of 130−150 K. Our experimental results provide insight into the direct and indirect recombination mechanism for excitons in the colloidal all-inorganic lead halide perovskite nanocrystal, which is helpful to unravel their potential for high-performance optoelectronic devices.

■ METHODS

The colloidal all-inorganic lead halide perovskite nanocrystal samples were synthesized using the hot-injection method, and a detailed description of the synthesis procedures can be seen in the Supporting Information. The steady-state PL spectra were measured by using a spectrometer (SP2300) with a CCD detector (PIX400BRX) under excitation by He−Cd gas laser with a wavelength of 325 nm. The sample was mounted with silver paint on the cold finger of a Janis closed-cycle cryostat, providing a varying temperature range from 4 K to room temperature (293 K). The lifetime of samples were measured by a time-correlated single photo counting system under excitation of 375 nm pulse laser (~40 ps).

■ RESULTS AND DISCUSSION

The characteristic of the perovskite nanocrystal is shown in Figure 1. The X-ray diffraction (XRD) results of perovskite CsPbBr₃ nanocrystals. The electron beam of TEM could reshape the morphology of the perovskite nanocrystal. As shown in the high-resolution TEM (HRTEM) of single perovskite nanocrystal, four direct corners of the nanocrystal cube shape disappear and the center of the nanocrystal cube can be seen more clearly as in Figure 1c. The distance of the nearest neighboring atoms in both the vertical and horizontal directions are about 0.58 nm, which agrees well with the (100) face value of the cubic phase of CsPbBr₃. Figure 1d shows the absorption and the PL spectra of the perovskite CsPbBr₃ nanocrystal measured at room temperature. The absorption edge is identified by the sharp band edge and excitonic feature at about 522 nm. The PL peak position is around 524 nm with a width of about 20 nm, which slightly red-shifted from the excitonic peak position. This red-shift phenomenon, also known as Stokes shift, is commonly observed in perovskite, which may be ascribed to the spectral diffusion-exciton fusion-exciton...
relaxation process.\textsuperscript{39,40} The TRPL curves are necessary to analyze the physical process of the emission in the perovskite CsPbBr\textsubscript{3} nanocrystal, illustrating in Figure 1e. The average PL lifetime of the perovskite CsPbBr\textsubscript{3} nanocrystal is about 2 ns. Note that it is orders of magnitude faster than other optoelectronic materials with a typical decay time (larger than 100 ns), such as CdSe, ZnO, and Au nano-particles.\textsuperscript{41–-44} This makes the perovskite nanocrystal suitable for application in light-emitting diodes, light display, lasers, photodetectors, and other optoelectronic devices.

**Excitation Power-Dependent PL Measurement at Room Temperature.** Under continuous wave (CW) laser (325 nm) excitation, we measured the steady-state PL with various excitation powers at room temperature, as shown in Figure 2. To determine the integrated PL intensity \(I_{PL}\), the average excitation power was controlled from 4 \(\mu W\) to 18 mW. As shown in Figure 2a, \(I_{PL}\) shows a linear relationship with the excitation laser power \(P_{ex}\) and the slope is about 1.34, which is under full thermal equilibrium conditions. There is no saturation effect or rapid increase observed with increasing excitation power. It means that the PL is mainly due to the spontaneous radiation rather than amplified spontaneous emission or other optical nonlinear phenomenon.\textsuperscript{36,45} For the normalized PL spectra, no obvious peak shift or broadening can be observed, as shown in Figure 2b.

**Temperature-Dependent PL Measurement.** Figure 3 shows the temperature-dependent PL of the perovskite CsPbBr\textsubscript{3} nanocrystal from 4 K to room temperature. The PL spectra were obtained under an excitation power of 20 \(\mu W\) by a 325 nm CW laser, as shown in Figure 3a. Lower excitation power is necessary to discuss the intrinsic emission processes, avoiding the heating effect,\textsuperscript{36–49} lattice expansion,\textsuperscript{50} and structural transition\textsuperscript{51} induced by intensive laser excitation. As the temperature increases from 4 K to room temperature, the peak position has a blue-shift (530–524 nm) and the peak width broadening (6 to nearly 20 nm), as shown in Figure 3a. The band gap theory could be used to explain the temperature-dependent PL peak position.\textsuperscript{52} As the temperature increases, the band gap narrowing about 27 meV results in the PL peak position blue-shift from 530 to 524 nm, as shown in Figure 3b. The broaden PL peak width can be attributed to the phonon-assisted broadening effect.

As the temperature increases, the integrated PL intensity shows a monotonic decrease which interrupts at 130–150 K, where the integrated PL intensity slightly increases and then continues to decrease, as shown in Figure 3c. As the temperature increases, more excitation energy transfers to the lattice and other electrons, which results in the decreased integrated PL intensity. The temperature-dependent PL data could be described by the Arrhenius equation as given below:\textsuperscript{38,45}

\[
\frac{I_0}{I(T)} = 1 + A_1 e^{-E_1/kT} + A_2 e^{-E_2/kT}
\]

(1)

\(I_0\) is the integrated PL intensity at 0 K. \(I(T)\) is the integrated PL intensity at temperature \(T\). \(A_1\) (\(A_2\)) relates to the density of recombination centers. \(E_1\) (\(E_2\)) is the activation energy of recombination center.

The temperature-dependent PL could be fitted by the Arrhenius equation, respectively, in two ranges of low temperature (red solid line) and high temperature (blue solid line), which is separated by the interruption (130–150 K), as shown in Figure 3d. As indicated from the PL process, photo-excited carriers may exist as excitons, biexcitons, and trions; and the carrier recombination may have direct or indirect recombination. As the temperature increases, population of biexcitons and trions raise because of the photon-phonon coupling effect,\textsuperscript{53} which may result in slight emission increase and then continues to decrease. However, the biexciton and trion are hard to exist in perovskite at very low excitation power. Moreover, there are no obvious information in the PL peak position and width, which could evidence the existence of the bie exciton and trion. Thus, carrier’s recombination may play a major role. To further analyze the mechanism, TRPL characterizations are necessary, as the following results in Figure 4.

**Temperature-Dependent Evolution of Carriers’ Dynamics.** At room temperature, the PL decay contains two lifetimes with different time scales, a fast decay and a slow decay, as shown in Figure 4a. To further analyze the physical process, TRPL measurement was performed from 4 K to room temperature. The temperature-dependent TRPL of the perovskite CsPbBr\textsubscript{3} nanocrystal is illustrated in Figure 4b. These TRPL results could be fitted with a tri-exponential function convoluted with the instrument response function (IRF) to obtain the accurate average PL lifetime.\textsuperscript{54}
The double-Boltzmann Fitting curve of the average PL lifetime.

The average PL lifetime decreases as the temperature increases.

There are always defect states, surface states, or dark recombination but also indirect recombination for excitons.

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Figure 4. Temperature-dependent PL lifetime of the perovskite CsPbBr₃ nanocrystal. (a) Fast and slow decay of PL lifetime. (b) Color mapping of temperature-dependent PL lifetime and the average value. (c) Double-Boltzmann function fitting lifetime at 4 K and room temperature. (d) Diagram of the exciton direct and indirect recombination.

\[ I_{\text{conv}}(t) = \int_0^t \text{IRF}(\tau^*) \sum_{i=1}^{3} A_i e^{-t/\tau_i} d\tau^* \]

(2)

\[ \tau_{av} = \sum_{i=1}^{3} A_i \tau_i^2 / \sum_{i=1}^{3} A_i \tau_i \]

(3)

\[ I_{\text{conv}}(t) \] is the convolved model decay that is to be compared to the measured decay. \[ A_i e^{-t/\tau_i} \] is the model decay law. \( \tau_{av} \) is the average PL lifetimes. IRF(\( \tau^* \)) is the normalized measured IRF.

All these TRPL curves could be globally fitted smoothly with a short time \( (\tau_1 = 0.294 \text{ ns}) \), an intermediate time \( (\tau_2 = 1.261 \text{ ns}) \), and a long time \( (\tau_3 = 6.054 \text{ ns}) \) with different amplitudes. The average PL lifetime decreases as the temperature increases. The double-Boltzmann Fitting curve of the average PL lifetime discontinues at 130–150 K, as shown in Figure 4c, which is the same with the interruption of the integrated PL intensity. The excitation pulse width and repetition rate both have significant influence on photo-carrier lifetime in perovskite, which should be taken into consideration.

In our experiment, excitation laser pulse width is about 40 ps and the IRF is about 120 ps. Thus, there is only the exciton considered in the following discussion. The exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. This is because the exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. This is because the exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. This is because the exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. This is because the exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. This is because the exciton decay is about 300 ps in the perovskite CsPbBr₃ nanocrystal, while the biexciton decay is about 1500 ps. 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CONCLUSIONS

To summarize, we have synthesized colloidal all-inorganic lead halide perovskite CsPbBr₃ nanocrystals by a solution method. The steady-state PL intensity performs as a linear function of excitation power and the spectra invariant at room temperature. The temperature-dependent PL intensity follows the Arrhenius equation. Temperature-dependent TRPL shows that there are two distinct different time scales, fast decay and slow decay. The TRPL curves could be fitted by the tri-exponential function with a short time constant \( (\tau_1 = 0.294 \text{ ns}) \), an intermediate time constant \( (\tau_2 = 1.261 \text{ ns}) \), and a long time constant \( (\tau_3 = 6.054 \text{ ns}) \). The short time corresponds to the direct recombination for excitons, which contributes to the PL fast decay in colloidal all-inorganic lead halide perovskite CsPbBr₃ nanocrystals. The intermediate (long) time constant corresponds to the photo-excited electrons (holes) path along trapping-detrapping-recombination with holes (electrons), contributing to the PL slow decay. The thermal effect could increase the TS and reduce the detrapping effect, changing the occupied percentage of indirect and direct recombination for excitons. The exciton mainly undergoes indirect recombination at low temperature, balance at the temperature of 130–150 K, and direct recombination at high temperature. Our experimental results provide insights into the direct and indirect recombination mechanism for excitons in colloidal all-inorganic lead halide perovskite nanocrystals and help to unravel their potential for high-performance optoelectronic devices.
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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b04532.

Synthesis and characterization; photos of synthesized perovskite samples; experiment system and temperature increase; system noise and PL stability; peak position and width (fwhm); temperature-dependent lifetime of samples; framework of a kinetic model for recombination of excitons, electrons, and holes; and TEM images and size distributions of perovskite nanocrystals (PDF)

AUTHOR INFORMATION

Corresponding Authors

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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REFERENCES


24. Chakrabarty, J.; Harnagea, C.; Celikin, M.; Rosei, F.; Nechache, R. Improved Photo voltaic Performance from Inorganic


