Slow Auger Recombination of Charged Excitons in Nonblinking Perovskite Nanocrystals without Spectral Diffusion

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ABSTRACT: Over the last two decades, intensive research efforts have been devoted to the suppressions of photoluminescence (PL) blinking and Auger recombination in metal-chalcogenide nanocrystals (NCs), with significant progresses being made only very recently in few specific NC structures. Here we show that nonblinking PL is readily available in the newly synthesized perovskite CsPbI$_3$ NCs and that their Auger recombination of charged excitons is greatly slowed down, as signified by a PL lifetime about twice shorter than that of neutral excitons. Moreover, spectral diffusion is completely absent in single CsPbI$_3$ NCs at the cryogenic temperature, leading to a resolution-limited PL line width of $\sim$200 $\mu$eV.

KEYWORDS: Perovskite, nanocrystal, blinking, spectral diffusion, Auger recombination

Auger recombination describes an intriguing optoelectronic phenomenon in semiconductor nanocrystals (NCs) whereby the exciton energy is nonradiatively transferred to an extra charge instead of being converted to a photon. For regular metal-chalcogenide NCs (e.g., CdSe), the Auger processes of multie excitons and charged excitons normally occur at the subnanosecond time scale, much shorter than the radiative lifetime of tens of nanoseconds for single neutral excitons. This limited survival time of multie excitons in semiconductor NCs makes it difficult to achieve long optical gain in lasers as well as to obtain high power conversion efficiencies in photodetectors and solar cells, based on the carrier multiplication effect. Meanwhile, multie exciton ioniza
tion and direct carrier trapping are the two main channels for the intermittent formation of charged excitons in a single NC, resulting in the photoluminescence (PL) blinking “off” periods that are detrimental to the single-photon emitting characteristics and the brightness of light-emitting diodes normally operated with imbalanced injection of charge carriers. So far, effective suppressions of both Auger recombination and PL blinking have been realized only in several specific NC structures such as “giant” CdSe/CdS NCs. Besides PL blinking, another notorious optical property of a single NC is the random shift of its PL peak energy that is denoted as the spectral diffusion effect. Although a PL line width as narrow as hundreds of $\mu$eV can be occasionally observed from single CdSe NCs, its stability over long measurement time periods is still being actively pursued in order to elongate the dephasing time for the implementation of coherent optical measurements. Ever since the first synthesis of semiconductor perovskite NCs of cesium lead halides in 2015, they have attracted a lot of research interest due to the size- and composition-dependent emission colors from the quantum confinement effect. At the ensemble level, the perovskite NCs have been characterized by the transient absorption and emission measurements to probe the exciton decay dynamics, and their capability of being used as laser materials have been demonstrated under both the single-photon and two-photon excitation conditions. At the single-particle level, the quantum-emitter nature of perovskite NCs have been confirmed from the single-photon emission measurements, and their reduced PL blinking has been observed at both room and cryogenic temperatures. Here we show that, at room temperature and with low-power excitation, nonblinking PL is easily achieved in single perovskite CsPbI$_3$ (cesium lead iodide) NCs synthesized from a facile colloidal approach. With high-power excitation, PL blinking is triggered in single CsPbI$_3$ NCs by the photoionization effect that creates two types of charged excitons with opposite signs. The “grey” intensity level in the PL blinking time trace is related to the charged exciton with Auger-mediated weak
fluorescence. Auger recombination in the other type of charged exciton is nearly eliminated so that its fluorescent photons contribute to the blinking “on” intensity level with a PL lifetime almost twice shorter than that of the neutral exciton. At cryogenic temperature and with low-power excitation, a resolution-limited PL line width of ~200 μeV is measured for single CsPbI3 NCs without the spectral diffusion effect.

According to a previous report,20 the CsPbI3 NCs were synthesized (see experimental details, Supporting Information) with an average size of ~9.3 nm (Figure S1, Supporting Information) and a PL peak around ~690 nm at room temperature (Figure S2, Supporting Information). Using the same method reported previously,25 the absorption cross sections measured at 400 nm for the ensemble and ~10 single CsPbI3 NCs are ~2.74 × 10⁻¹³ and (~2.69 ± 1.64) × 10⁻¹³ cm², respectively, which agree well with those obtained previously for ensemble and single CsPbBr3 NCs.25 Single CsPbI3 NCs placed on top of a silica substrate were excited at ~570 nm with a picosecond pulsed laser, and the PL signals were detected by a time-correlated single-photon counting system (see experimental details, Supporting Information). In Figure 1a, we plot the PL intensity time trace of a nonblinking CsPbI3 NC excited at ⟨N⟩ = ~0.03, where ⟨N⟩ represents the average number of photons absorbed per NC per pulse (Figure S3, Supporting Information). The above measurements were performed at room temperature for the same single CsPbI3 NC excited at ⟨N⟩ = ~0.03.

Figure 1. (a) PL intensity time trace plotted with a binning time of 30 ms. (b) “On”-level PL decay curve fitted with a single-exponential lifetime of ~43.4 ns. (c) Second-order autocorrelation function g(2)(τ). The above measurements were performed at room temperature for the same single CsPbI3 NC excited at ⟨N⟩ = ~0.03. (d) PL intensity distribution plotted with a binning time of 10 ms for the same NC excited at ⟨N⟩ = ~0.15. (e) “On”- or “grey”-level PL decay curve of this NC excited at ⟨N⟩ = ~0.02 or ~1.7. See text for more details. (f) (from top to bottom) Fitting residuals for the first three PL decay curves plotted in (e). (g) Second-order autocorrelation function g(2)(τ) measurements for this NC excited at ⟨N⟩ = ~0.02 (top) and ~1.7 (bottom). The above measurements were performed at room temperature.

Although the PL blinking effect was suppressed in most of the single CsPbI3 NCs excited at low power, it was triggered in all of the single CsPbI3 NCs excited at high power due to the formation of charged excitons from the multie exciton ionization process.27,29 In Figure 2a, we plot the nonblinking PL time trace of a single CsPbI3 NC excited at ⟨N⟩ = ~0.02, whose PL intensity distribution is shown in Figure 2b with a single “on”-level peak. The blinking PL time trace of the same single NC excited at ⟨N⟩ = ~1.7 is plotted in Figure 2c, where a “grey” intensity level can be clearly resolved in addition to the normal “on” and “off” ones. As can be seen in Figure S5 of the Supporting Information from an enlarged part of this PL time trace marked by the red box and in Figure 2d from the PL intensity distribution, the “grey” intensity level is associated with a PL efficiency of ~15% relative to that of the “on” intensity level. This kind of “grey” intensity level was previously reported in single metal-chalcogenide CdSe NCs as a sign of slightly reduced Auger recombination in charged excitons.35–38 When a single CsPbI3 NC is excited at ⟨N⟩ = ~1.7 to create mainly Xs and neutral bie excitons (XXs), we assume for convenience that it is the electron in the X being pumped to a
higher excited state after receiving the XX recombination energy in an Auger process. The probability for this electron to be captured by an external trap is higher than would it stay in the band-edge state, thus leaving an unpaired hole in the NC. A positively charged two-exciton state would be prepared in the next excitation event so that PL photons of the "grey" intensity level should be mainly contributed by positively charged single excitons (X’s) when assuming that its PL efficiency is significantly higher than that of positively charged bieexcitons.

As mentioned earlier in the text, with the low-power pulsed laser excitation at 570 nm, most of the studied CsPbI3 NCs were nonblinking (Figure 1a), while the rest of them showed occasional changes of the PL intensity to lower levels (Figure S4, Supporting Information). In our experiment, we also employed a pulsed laser at 400 nm for the low-power excitation in which case only a small amount of the studied NCs were still nonblinking, while the others showed either occasional or frequent changes of the PL intensity to lower levels. This strongly implies that the number of accessible carrier traps increases when the photoexcited carriers are staying at higher energy states. With the high-power laser excitation at 570 nm, the single-exciton charge carriers would be pumped to even higher excited states after receiving the biexciton recombination energy so that a more drastic PL blinking behavior is expected (Figure 2c).

The "on"-level PL decay curve of the CsPbI3 NC excited at \( \langle N \rangle = \sim 0.02 \) is plotted in Figure 2e, which can be well fitted by a single-exponential function with a radiative lifetime of \( \sim 55.3 \) ns for Xs (fitting residual in Figure 2f). At \( \langle N \rangle = \sim 1.7 \), the "on"-level PL decay curve shown in Figure 2e can only be roughly fitted by a single-exponential function with a shortened PL lifetime of \( \sim 42.0 \) ns (fitting residual in Figure 2f), which is unexpected for the radiative lifetime of Xs since it should be independent of the excitation power. However, the same PL decay curve can be well fitted by a double-exponential function of \( A_1 e^{-t/t_1} + A_2 e^{-t/t_2} \) (fitting residual in Figure 2f), with \( A_1 \) (\( A_2 \)) and \( t_1 \) (\( t_2 \)) being the amplitude and the value of the slow (fast) lifetime component, respectively. The slow lifetime \( t_1 \) of \( \sim 51.0 \) ns is close to the radiative lifetime of \( \sim 55.3 \) ns measured at \( \langle N \rangle = \sim 0.02 \) for Xs, while the fast lifetime \( t_2 \) of \( \sim 33.4 \) ns could be related to negatively charged excitons (X’s) with strongly reduced Auger recombination that was previously observed in single “giant” CdSe/CdS NCs. In contrast to the "grey"-level case, the "on"-level X should be formed after a photoexcited hole is ejected out of the NC in a XX Auger ionization process. The ratio of \( t_1/t_2 \) was calculated to be \( \sim 1.53 \) for this specific NC and \( \sim 1.83 \) on average for the \( \sim 20 \) NCs studied in our experiment (Figure S6, Supporting Information), which is close to the value of two predicted for the radiative lifetime ratio between Xs and charged excitons. Now that the blinking "grey" ("on") level has been associated with the X’s (Xs and X’s), the appearance of the blinking “off” level could be caused by multiply charged excitons or the exciton trapping process.

A possible origin of the fast lifetime \( t_2 \) from Xs can be ruled out based on the following reasons. First, the X+ PL decay of the "grey" intensity level is dominated by Auger recombination with a fitted rate \( K_{XX} \) of \( \sim 1.5/8.1 \) ns\(^{-1} \) in Figure 2e. Meanwhile, the X- PL decay of the "on" intensity level is dominated by radiative recombination so that its Auger rate \( K_{XX} \) should approach zero. Then the XX PL decay rate can be expressed as \( K_{XX} = 2(K_{XX} + K_{Xs}) \approx 2K_{Xs} \) to yield a maximum PL lifetime of \( \sim 2.9 \) ns that is much shorter than the \( t_2 \) value of \( \sim 33.4 \) ns. In fact, a XX Auger lifetime of \( \sim 90 \) ps was previously reported for ensemble CsPbI3 NCs with similar sizes to the ones studied here. Second, as shown in Figure 2g, the average area ratio between the central and the side \( g_{2}(t) \) peaks was calculated to be \( \sim 0.08 \) (\( \sim 0.04 \)) for this single NC excited at \( \langle N \rangle = \sim 0.02 \) (\( \sim 1.7 \)), implying that the XX PL efficiency is at most \( \sim 4\% \) relative to that of Xs. This extremely low PL efficiency of XXs contradicts the fact that the fast lifetime component contributes \( \sim 40\% \) of the total photons in the “on” intensity level from the calculation of \( (A_1t_1 + A_2t_2) \). It should be noted that, although we focused on a specific CsPbI3 NC in Figure 2, similar appearances of two charged-exciton species were observed in all of the \( \sim 20 \) single CsPbI3 NCs excited at high power (Figure S7, Supporting Information).

After room-temperature characterizations, we switched to the cryogenic temperature of \( \sim 4 \) K to measure the optical properties of single CsPbI3 NCs. As in the case of perovskite CsPbBr3 NCs studied previously, the PL peak energy measured at 4 K for CsPbI3 NCs is red-shifted relative to that at room temperature, the exact origin of which might be revealed in future work to see whether a phase-transition process is involved from the temperature-dependent PL measurements with a single-NC precision. With the excitation at \( \langle N \rangle = \sim 0.1 \), nearly all of the single CsPbI3 NCs possessed an ultranarrow PL line width of \( \sim 200 \) \( \mu \)eV that is limited only by our system resolution (Figure 3a). Moreover, both the PL blinking and the spectral diffusion effects are completely suppressed, as can be seen in Figure 3b from the time-dependent PL spectral image of a representative NC. In Figure 3c, we plot the PL decay curve measured for a representative CsPbI3 NC, which can be fitted by a single-exponential function with a radiative lifetime of \( \sim 1.02 \) ns. Similar to the case previously reported for single CsPbBr3 and CsPb(Cl/Br)3 NCs, no long-lifetime component of dark-exciton emission.
commonly observed in single CdSe NCs\textsuperscript{65} was resolved here from the PL decay dynamics of single CsPbI\textsubscript{3} NCs.

Next at 4 K, we excited the same single CsPbI\textsubscript{3} NCs at both $\langle N \rangle = \sim 0.1$ and $\sim 0.8$. As shown in Figure 4a for a representative CsPbI\textsubscript{3} NC, there existed mainly a single PL peak from Xs at $\langle N \rangle = \sim 0.1$, and an additional one emerged at a lower energy after $\langle N \rangle$ was increased to $\sim 0.8$. The spectral diffusion effect is slightly induced at $\langle N \rangle = \sim 0.8$ especially for the X peak, as can be seen in Figure 4b from the time-dependent PL spectral image. This can be explained by the existence of fluctuating local fields to disturb the exciton energy from the Stark effect.\textsuperscript{55,17} We attribute the red-shifted PL peak to be from X's, whose PL photons are mixed with those from Xs in the “on” intensity levels of the room-temperature PL time trace measured at $\langle N \rangle = \sim 1.7$ in Figure 2c. The spectral diffusion effect is not significant for the X'' PL peak, which possesses a resolution-limited line width of $\sim 200$ meV. Auger recombination should be still efficient for both Xs and X's at the cryogenic temperature since no other PL peaks were resolved from single CsPbI\textsubscript{3} NCs excited at $\langle N \rangle = \sim 0.8$. When $\langle N \rangle$ was further increased to $\sim 2.0$ and beyond, several additional PL peaks appeared in a very small amount of the single CsPbI\textsubscript{3} NCs studied in our experiment. PL energies of these peaks are even smaller than that of the charged excitons, and due to the extremely weak PL emissions, their exact origins cannot be determined at the current stage.

In Figure 4c, we plot the PL intensity of the X peak as a function of the laser excitation power, where a linear increase toward saturation can be observed. Meanwhile, the PL intensity of the X'' peak demonstrates a sublinear (instead of quadratic) dependence on the laser excitation power to exclude again its possible origin from Xxs.\textsuperscript{40} As shown in Figure 4d, the PL decay curve measured at $\langle N \rangle = \sim 0.8$ for the X peak can be fitted with a single-exponential lifetime of $\sim 1.08$ ns, which is close to the one of $\sim 1.04$ ns measured at $\langle N \rangle = \sim 0.1$ (Figure S8, Supporting Information). This independence of the X radiative lifetime on the laser excitation power is difficult to be revealed from the ensemble-NC measurement reported previously\textsuperscript{21} or the single-NC measurement performed here at room temperature (Figure 2e). In this cases, the X photons are spectrally mixed with those from multie excitons and charged excitons whose contributions increase with the increasing laser excitation power. The PL decay curve measured at $\langle N \rangle = \sim 0.8$ for the X'' peak is also plotted in Figure 4d and fitted with a single-exponential function to yield a PL lifetime of $\sim 0.42$ ns, from which a X/X'' lifetime ratio of $\sim 2.57$ can be obtained. From statistical measurements on $\sim 10$ single CsPbI\textsubscript{3} NCs, an average X/X'' lifetime ratio of $\sim 2.38$ was obtained that is comparable to the one of $\sim 1.83$ measured at room temperature in Figure S6 of the Supporting Information. In Figure 4e, we plot a histogram of energy separations between the X and X'' PL peaks measured over 15 single CsPbI\textsubscript{3} NCs, and the average value of $\sim 8.1$ meV roughly reflects the binding energy between a single exciton and an extra electron with an attractive interaction. In contrast, the binding energies of charged excitons obtained previously for perovskite CsPbBr\textsubscript{3} NCs\textsuperscript{27} and metal-chalcogenide CdSe NCs\textsuperscript{47} fall within the ranges of $\sim 10-20$ and $15.5-18.5$ meV, respectively.

To summarize, we have demonstrated slow Auger recombination of charged excitons and nonblinking PL behavior in single CsPbI\textsubscript{3} NCs at both room and cryogenic temperatures. Moreover, a resolution-limited PL line width of $\sim 200$ meV without the influence of spectral diffusion was measured for single CsPbI\textsubscript{3} NCs at the cryogenic temperature. A combination of the above optical properties has been actively pursued in previous optical studies of single metal-chalcogenide NCs without any success but is easily and repeatedly realized here in single CsPbI\textsubscript{3} NCs from many batches of samples synthesized by us with a facile colloidal approach. The above findings mark the emergence of a potent semiconductor nanostructure that will surely stimulate intensive research efforts in both fundamental studies and practical applications.

We tentatively attribute the suppressed PL blinking and spectral diffusion effects in single CsPbI\textsubscript{3} NCs to the nonexistence of defect traps for band-edge charge carriers to form charged excitons. Meanwhile, the sign assignments for the two types of charged excitons and the exact origins for their slightly- and strongly reduced Auger recombination are yet to be determined from future experimental and theoretical works.
Experimental details, transmission electron microscopy image, solution absorption and emission spectra of ensemble NCs, laser-power dependence of the PL intensity of a single NC, PL intensity time trace of a single NC with the appearance of lower intensity levels, PL intensity time trace of a single NC with "grey" levels, slow and fast PL decay lifetimes measured for ~20 single NCs, room-temperature optical properties of a single NC excited at both low and high powers, and PL decay curve of a single NC measured at 4 K with low-power excitation (PDF).

