Multiple Dark Excitons in Semiconductor CdSe Nanocrystals

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ABSTRACT: When excited with a low laser power, the dark excitons in semiconductor CdSe nanocrystals (NCs) are associated with a long radiative lifetime at the cryogenic temperature. With the increasing laser excitation power, there additionally appears a fast lifetime component that signifies the effective generation of multiple dark excitons. Similar to the case of multiple bright excitons, the Auger recombination of multiple dark excitons in large-sized CdSe NCs is greatly suppressed to render them a highly emissive nature. The introduction of multiple dark excitons to the current studies of semiconductor CdSe NCs will surely promote various potential applications such as in high-capacity energy storage and low-threshold optoelectronic lasing.

INTRODUCTION

Semiconductor CdSe nanocrystals (NCs) synthesized by the colloidal approach have been extensively investigated over the past decades due to their size- and shape-dependent photophysical properties that are attractive for both fundamental studies and practical applications.1,2 The enhanced electron–hole exchange interaction in the quantum-confined CdSe NCs, together with the intrinsic crystal field and the structural anisotropy, split the 8-fold degenerate band-edge exciton structure into four energy levels with the lowest being an optically forbidden one.3 The existence of such a dark state could be deduced in ensemble CdSe NCs from the appearance of a long photoluminescence (PL) lifetime at the cryogenic temperature4 and its significant shortening under an external magnetic field.5,6 The PL peak of dark excitons was later resolved in single CdSe NCs,7–10 their spectroscopic fingerprints have been firmly established, with the emissive nature being attributed to thermal mixing with the bright excitons or spin-related interactions with several proposed sources such as longitudinal phonons, surface ligands, and paramagnetic defects.3,5,6,9,11–14 A comprehensive understanding of the dark excitons in CdSe NCs would not only guide their emerging studies in colloidal NCs with other compositions15,16 as well as in other semiconductor nanostructures,17–19 but also facilitate their potential usages in solid state spintronics.20

Specifically, the long radiative lifetime of dark excitons is beneficial for the storage of excitation energy,1,2 but can then be efficiently extracted by molecular acceptors to sensitize fluorescent photons over those of the single dark excitons even with the laser excitation of an intermediate power.21,22 Here, we study two batches of ensemble CdSe NCs with small and large sizes, whose dark-exciton radiative lifetimes are approximately 240 and 70 ns, respectively, under the low-power laser excitation at the cryogenic temperature of 3.2 K. When the laser power is further increased, a fast lifetime component of about 10 ns appears for both samples, which can be attributed to the effective generation of multiple dark excitons. In the small-sized CdSe NCs, the multiple dark excitons suffer strongly from the nonradiative Auger recombination, so that their fluorescent photons are still significantly fewer than those of the single dark excitons for the highest laser power used in our experiment. Meanwhile, the Auger recombination of the multiple dark excitons is greatly suppressed in the large-sized CdSe NCs, leading to the dominance of their fluorescent photons over those of the single dark excitons even with the laser excitation of an intermediate power.

METHODS

The solution absorption and emission spectra measured at the room temperature for the small- and large-sized CdSe NCs (Qdot 605 and Qdot 655, from Thermo Fisher Scientific) are shown in Figure 1a, with the emission peaks located at 605 and 655 nm, respectively. According to the transmission electron microscopy (TEM) measurements, the Qdot 655 CdSe NCs (Figure 1c) have a prolate shape with an average aspect ratio of 0.22 (width 8.75 ± 0.88 nm, length 13.46 ± 1.69 nm), while the Qdot 605 CdSe NCs (Figure 1d) have a spherical shape with an average radius of 3.69 ± 0.40 nm. One drop of a toluene solution containing CdSe NCs was spin-coated onto a...
Figure 1. (a) Solution absorption and emission spectra of the Qdot 655 and Qdot 605 CdSe NCs. (b) PL intensities of the ensemble Qdot 655 and Qdot 605 CdSe NCs each plotted as a function of the laser excitation power. The two sets of data points are each fitted with a function form, $I \propto 1 - e^{-\alpha P}$, where $\alpha$ is a fitting constant and $P$ is the laser excitation power. The above optical measurements were performed at room temperature. (c) Statistical distribution for the aspect ratio of the Qdot 655 CdSe NCs. Inset: TEM image for a representative Qdot 655 CdSe NC. (d) Statistical distribution for the radius of the Qdot 605 CdSe NCs. Inset: TEM image for a representative Qdot 605 CdSe NC.

Figure 2. PL decay curves of the ensemble (a) Qdot 655 CdSe NCs and (c) Qdot 605 CdSe NCs measured at the room temperature for $\langle N \rangle = 0.05, 1.0, 2.0, 3.0, \text{ and } 4.0$, respectively. The PL decay curve measured at $\langle N \rangle = 0.05$ is fitted by a single-exponential function, while the others are each fitted by a biexponential function. The PL decay curves in (a) and (c) are offset to each other for clarity. The relative PL efficiency of $N(\tau_{\text{me}})/N(\tau_{\text{se}})$ between the multiple and single bright excitons plotted as a function of the exciton number $\langle N \rangle$ for the (b) Qdot 655 CdSe NCs and (d) Qdot 605 CdSe NCs, respectively. The solid lines in (b) and (d) are guides for the eye.
fused silica substrate to form a solid film. The NC film sample was mounted in a helium-free cryostat and excited through an internally integrated objective (N.A. = 0.82) by the 490 nm output beam from a picosecond fiber laser with a repetition rate of 1.9 MHz. Fluorescent signals from the ensemble CdSe NCs were collected by the same objective and sent through a 0.5 m spectrometer to either a charge-coupled-device camera for the PL spectral measurements or an avalanche photodiode for the PL decay measurements with a time resolution of ~250 ps.

**RESULTS AND DISCUSSION**

In Figure 1b, we plot the PL intensities of the Qdot 605 and Qdot 655 CdSe NCs measured at the room temperature as a function of the exciton number \( \langle N \rangle \) for the (b) Qdot 655 CdSe NCs and (d) Qdot 605 CdSe NCs, respectively. The solid lines in (b) and (d) are guides for the eye.

When \( \langle N \rangle \) is increased to 0.5 and beyond, all the PL decay curves can be fitted well only with a biexponential function of \( A e^{-t/\tau_{se}} + B e^{-t/\tau_{me}} \), where \( \tau_{me} \) is the PL lifetime of the multiple excitons, while \( A \) and \( B \) are the fitting amplitudes for the two lifetime components. Since \( \tau_{me} \) is not dependent on the laser excitation power, its value of 31.55 ns can be fixed in the biexponential decay fittings to yield \( \tau_{me} \) at various exciton numbers. At \( \langle N \rangle = 0.5 \), the \( \tau_{me} \) value of 4.02 ± 0.01 ns is close to the biexciton Auger recombination lifetime measured previously for a similar sample. When \( \langle N \rangle \) is further varied from 1.0, 2.0, 3.0 to 4.0, the \( \tau_{me} \) values of 3.19 ± 0.02, 2.48 ± 0.01, 2.02 ± 0.01, and 1.73 ± 0.01 ns are acquired, signifying the sequential generations of higher-order multiple excitons with increasing Auger interactions. For each of the biexponential PL decay curves measured at high laser powers, the total photons emitted by the multiple and single excitons can be estimated from \( N(\tau_{me}) = B\tau_{me} \) and \( N(\tau_{se}) = A\tau_{se} \), respectively. Then the ratio of \( N(\tau_{me})/N(\tau_{se}) \) should reflect the relative PL efficiency between the multiple and single excitons, which increases sublinearly from 19.40 ± 0.12% at \( \langle N \rangle = 0.5 \) to 56.37 ± 0.48% at \( \langle N \rangle = 4.0 \) in Figure 2b.

For comparison, we plot in Figure 2c several representative PL decay curves measured at the room temperature for the Qdot 655 CdSe NCs excited at \( \langle N \rangle = 0.05, 1.0, 2.0, 3.0, \) and 4.0, respectively. The PL decay curve obtained at \( \langle N \rangle = 0.05 \) can be fitted with a single-exponential lifetime of \( \tau_{se} = 31.55 ± 0.05 \) ns arising from the radiative recombination of the single excitons. When \( \langle N \rangle \) is increased to 0.5 and beyond, all the PL decay curves can be fitted well only with a triexponential function, while the others are each fitted by a tetraexponential function. The PL decay curves in (a) and (c) are offset to each other for clarity. The relative PL efficiency of \( N(\tau_{me})/N(\tau_{se}) \) between the multiple and single dark excitons plotted as a function of the exciton number \( \langle N \rangle \) for the (b) Qdot 655 CdSe NCs and (d) Qdot 605 CdSe NCs, respectively. The solid lines in (b) and (d) are guides for the eye.

**Figure 3.** PL decay curves of the ensemble (a) Qdot 655 CdSe NCs and (c) Qdot 605 CdSe NCs measured at 3.2 K for \( \langle N \rangle = 0.05, 1.0, 2.0, 3.0, \) and 4.0, respectively. The PL decay curve measured at \( \langle N \rangle = 0.05 \) is fitted by a triexponential function, while the others are each fitted by a tetraexponential function. The PL decay curves in (a) and (c) are offset to each other for clarity. The relative PL efficiency of \( N(\tau_{me})/N(\tau_{se}) \) between the multiple and single dark excitons plotted as a function of the exciton number \( \langle N \rangle \) for the (b) Qdot 655 CdSe NCs and (d) Qdot 605 CdSe NCs, respectively. The solid lines in (b) and (d) are guides for the eye.


\[ \tau_{\text{medium}} \text{ being } 68.61 \pm 0.62, 8.77 \pm 0.05, \text{ and } 2.27 \pm 0.01 \text{ ns, respectively.} \]

A re-reading the recombination dynamics of bright excitons at room temperature for the Qdot 655 and Qdot 605 CdSe NCs, we next move to the cryogenic temperature of 3.2 K to perform our PL decay measurements. In Figure 3a, we plot the PL decay curve measured for the Qdot 655 CdSe NCs at \( \langle N \rangle = 0.05 \), which can be fitted well only with a triexponential function of \( A \ e^{-t/\tau_{\text{t}}} + B \ e^{-t/\tau_{\text{short}}} + \frac{\tau_{\text{medium}}}{\tau_{\text{t}}} + D \ e^{-t/\tau_{\text{short}}} \) (also see Figure 4) with the lifetime values of \( \tau_{\text{t}}, \tau_{\text{short}}, \) and \( \tau_{\text{medium}} \) as shown. The two sets of PL decay curves are offset to each other for clarity.

**Figure 4.** PL decay curves of the ensemble Qdot 655 CdSe NCs measured at 3.2 K for \( \langle N \rangle = 0.05 \) and 4.0, respectively. The PL decay curve measured at \( \langle N \rangle = 0.05 \) can be fitted well by a biexponential function (red solid line), while a biexponential function \( A \ e^{-t/\tau_{\text{t}}} + B \ e^{-t/\tau_{\text{medium}}} + \frac{\tau_{\text{short}}}{\tau_{\text{t}}} + D \ e^{-t/\tau_{\text{short}}} \) (also see Figure 4) with the lifetime values of \( \tau_{\text{t}}, \tau_{\text{short}}, \) and \( \tau_{\text{medium}} \) as shown. The two sets of PL decay curves are offset to each other for clarity.

<table>
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<th>( \langle N \rangle )</th>
<th>0.05</th>
<th>0.5</th>
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<tr>
<td>( \tau_{\text{t}} )</td>
<td>68.61 ± 0.62</td>
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<tr>
<td>( \tau_{\text{medium}} )</td>
<td>8.77 ± 0.05</td>
<td>4.79 ± 0.11</td>
<td>4.78 ± 0.09</td>
<td>4.97 ± 0.07</td>
<td>4.56 ± 0.06</td>
<td>4.18 ± 0.05</td>
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<tr>
<td>( \tau_{\text{short}} )</td>
<td>2.27 ± 0.01</td>
<td>1.55 ± 0.02</td>
<td>1.50 ± 0.01</td>
<td>1.39 ± 0.01</td>
<td>1.24 ± 0.01</td>
<td>1.12 ± 0.01</td>
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<tr>
<td>( N(\tau_{\text{short}})/N(\tau_{\text{t}}) ) (%)</td>
<td>105.55 ± 9.05</td>
<td>161.09 ± 12.49</td>
<td>210.05 ± 21.77</td>
<td>304.96 ± 28.27</td>
<td>366.25 ± 33.36</td>
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\*The four lifetime components of \( \tau_{\text{t}}, \tau_{\text{medium}}, \tau_{\text{short}}, \) and \( N(\tau_{\text{short}})/N(\tau_{\text{t}}) \) are in the unit of ns, while \( N(\tau_{\text{short}})/N(\tau_{\text{t}}) \) reflects the relative PL efficiency between the multiple and single dark excitons.
The long survival lifetime of about 10 ns for the multiple dark excitons would elongate the storage time of multiple excitations as well as facilitate their efficient extractions to the acceptor materials. Low-threshold lasing devices could also be anticipated to take advantage of the long optical gain associated with the multiple dark excitons in semiconductor CdSe NCs.

### ACKNOWLEDGMENTS

This work is supported by the National Basic Research Program of China (2017YFA0303700), the National Natural Science Foundation of China (Nos. 11574147 and 11621091), and the PAPD of Jiangsu Higher Education Institutions.

### REFERENCES