Influences of light intensity on fluorescence lifetime of nanorods and quantum dots

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In this letter we investigate light-intensity dependence of the fluorescence lifetime for CdSe nanorods (NRs) and quantum dots (QDs) measured by time-correlated single photon counting techniques. We report extremely narrow lifetime distribution for NRs as the light intensity increases, although the change for QDs is not so pronounced. In addition, the averaged lifetimes for NRs and QDs all become shortened at higher light intensities. Some possible mechanisms for these effects are discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.3021366]

Semiconductor nanomaterials, such as quantum dots (QDs) and nanorods (NRs), have attracted extensive attention for scientific studies and technological applications due to their unique optical and electric properties.1–3 For example, the strong luminescence of QDs has found applications in biological imaging.4,5 Because of a larger surface area NRs exhibit greater optical absorption cross sections than QDs.6 Not only the emission and absorption spectra are size dependent but also the Stokes shift is strongly dependent on the aspect ratio of the NRs.7 Recently, there is increasing research interest in exploring fluorescence decay dynamics,8–13 fluorescence blinking statistics,14–16 and band edge exciton states17–20 of QDs and NRs. It is essential to establish the relationship between fluorescence intensity and fluorescence decay time, and the role of quantum yield fluctuation in the emission-intensity trajectory.21 In addition, the fluorescence lifetime of single CdSe/ZnS QDs shows a biexponential decay with a long time component strongly dependent on the temperature.22 The decrease in lifetime at higher excitation intensities was shown to be caused by increased formation of biexcitons.8,15 Until now, the studies of excitation intensity dependence of the fluorescence lifetime have been largely focused on QDs. In this letter, we report our study of CdSe NRs that display unusually sharp lifetime distribution and offer some possible mechanisms involving multie exciton formation and surface trapping to explain the dynamics.

The synthesis of CdSe QDs is well documented23,24 CdSe NRs were synthesized in our laboratory according to the reported methods,22 except a modification using various surfactants. Briefly, a selenium (Se) injection solution containing 0.073 g Se was prepared by dissolving Se powder in 1 ml of tri-octyl phosphine. 0.20 g of CdO and 0.71 g of tetradeceyl phosphonic acid (TDDA) were loaded into a 50 ml three-neck flask and heated to 200 °C under Ar flow.25 After the CdO was completely dissolved, judging by the vanishing of the brown color of CdO, the Cd-TDDA complex was allowed to cool down to room temperature. Subsequently, 3.00 g of tri-octyl phosphine oxide (TOPO) was added to the flask, and the temperature was raised to 320 °C to produce an optically clear solution. At this temperature, the Se injection solution was swiftly injected into the hot solution. The reaction mixture was maintained at 320 °C for growth of CdSe crystals. After 5 min, the temperature was quenched to 40 °C to terminate the reaction. 5 ml of toluene was then introduced to dissolve the reaction mixture, and a brown precipitate was obtained by adding 5 ml of isopropanol and centrifuged at 3000 rpm for 5 min. The precipitate was dispersed in toluene for the transmission electron microscope (TEM) characterization, and dried powder of the precipitate was obtained for the x-ray diffraction measurement.

The fluorescence of single NRs or QDs was measured using a time-resolved single-molecule confocal microscope, MT200 from PicoQuant, with PicoHarp 300 for data acquisition. The time-tagged time-resolved mode was used for fast dynamics measurements. Fluorescence from the sample was collected through an oil-immersion objective (Olympus). A picosecond diode laser with an excitation wavelength at 467 nm was used as a light source with excitation intensity from 38 to 570 W/cm2 and a repetition rate of up to 10 MHz. All samples were measured at room temperature in air. The TEM image in Fig. 1(a) shows a uniform structure of CdSe NRs with 7.9 nm in diameter and 40 nm in length. Figure 1(b) shows the fluorescence intensity time traces for a single CdSe NR with 300 s collection time, a binning time of 1 ms, and by Lorentzian fitting to QDs, we obtained the same decay parameters.

Figure 3 shows the dependence of 1Xc/W and the linewidth (W). Figure 3 shows the dependence of 1/Xc and 1/W on the excitation intensity. For QDs and NRs, 1/Xc and 1/W both increase with the excitation intensity. Interestingly, Fig. 3(a) shows a nice linear relationship between 1/Xc and the excitation intensity. Since Xc represents the mean lifetime, Fig. 3(a) indicates a greater intensity effect on fluorescence lifetime decay. The dependence of 1/W on the excitation intensity between QDs and NRs is compared and shown in Fig. 3(b). The dis-

Table 1. The fluorescence lifetime and the excitation intensity dependence of the fluorescence lifetime for CdSe QDs and NRs.

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<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Fluorescence Lifetime (ps)</th>
<th>Excitation Intensity (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QDs</td>
<td>25</td>
<td>38</td>
</tr>
<tr>
<td>NRs</td>
<td>22</td>
<td>570</td>
</tr>
</tbody>
</table>

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distribution width for QDs has slight changes but NRs exhibit a dramatic change. The inverse of the linewidth exhibits an abrupt increase at 380 W/cm² for both 40 and 20 nm NRs. Over the observed excitation intensity the linewidth for NRs changes by almost two orders of magnitude, a phenomenon that has not been reported previously.

As illustrated in Fig. 2, the mean lifetime for NRs and QDs becomes shorter as the excitation intensity increases. Previous studies have shown that the biexciton in QDs exhibit a faster decay than the exciton because the decay of biexciton involves nonradiative Auger recombination but the exciton involves radiative decay. Based on the work in QDs by Fisher et al.,10 the slow component of the decay at low excitation intensity is due to emission from the exciton, and the fast component at high excitation intensity is due to the biexciton and triexciton emission. The pumping rate from the ground state to the exciton state is proportional to the photoabsorption cross section (proportional to volume) of a QD and the light intensity.26 For a QD of 3.3 nm in radius, at an intensity of 200 W/cm² the pumping rate is about 10⁷ s⁻¹, which is comparable to the fluorescent decay rate. Therefore, at a higher intensity further excitation from the photoexcited state (exciton) to higher states (multiexciton) could occur and would be more probable for a NR that is much larger than a QD.

We observed significant differences between NRs and QDs in their mean fluorescence lifetime and distribution width. The actual mechanism is presently unknown; yet we offer here some possible explanations. The mean lifetime is shorter for NRs (~10⁻⁹ s) than that for QDs (~10⁻⁸ s), likely due to the elongated NRs having less percentage of TOPO molecules attached on the surface and, therefore, having less complete surface passivation. The lifetime of CdSe QDs capped with ZnS was found to increase with surface passivation.27 This fast decay is related to the less effective surface trapping and increased multiexciton formation.28 In addition, photoabsorption and multiexciton excitation can be more efficient for NRs for their larger size. Previous studies have shown that single QDs could exhibit different fluorescence lifetimes.21,29 Each band edge state could have a different oscillator strength and a different transition rate to the ground state. The formation of multiexciton states depends on the excitation intensity, and their subsequent relaxation to the exciton states and then radiative transition to the ground state could be highly dependent on photoexcitation and Auger relaxation. Our observation of narrow lifetime distribution could imply that for NRs, the radiative transition to the ground state involves fewer band edge exciton states, i.e., the radiative transitions from some closer band edge states, resulting in an extremely narrow fluorescence lifetime distribution. Additionally, less percentage of TOPO molecules were attached on the surface of NRs, and a larger number of

![FIG. 1. (a) TEM image (7.9 × 40 nm²) of CdSe NRs. (b) Fluorescence intensity time traces for a single NR with excitation intensity at 38 W/cm², excitation wavelength λ, at 467 nm, and binning time of 1 ms. (c) The zoom-in area from 100 to 110 s.](image)

![FIG. 2. (Color online) The lifetime distribution at different excitation intensities for a single (a) 40 nm, (b) 20 nm NR, and (c) 3.3 nm QD. The excitation intensities are 95 [(a) black], 190 [(b) red], 380 [(c) blue], and 570 [(d) cyan] W/cm². Unlike NRs that can be fitted by a Gaussian, for QDs with a broader wing the distribution could be fitted better by a Lorentzian.](image)

![FIG. 3. (Color online) (a) The inverse of the central position (X) of the lifetime distribution vs the excitation intensity for a single NR with lengths of 40 nm (blue) and 20 nm (red) NR, and a single QD with radius of 3.3 nm QD (black). (b) The inverse of the linewidth (W) vs the intensity.](image)
nonpassivated surface traps could affect the fluorescence decay. Furthermore, a stronger excitation could saturate the surface traps,\textsuperscript{30,31} attributing to simpler decay dynamics in NRs and QDs. We reported unusually sharp lifetime distribution for NRs at high light intensities. Over the observed excitation intensity from 100 to about 600 W/cm\textsuperscript{2}, the linewidth for NRs changes by almost two orders of magnitude. The detailed mechanism is presently unclear but we think that multie excitons might play a role. Due to a larger surface area and stronger light absorption for NRs, the light-intensity effects can be more pronounced than QDs. We also observed a shift of the lifetime distribution of both QDs and NRs to a shorter time scale. The shift could be due to multie exciton formation. Because NRs are much larger in size, the band edge exciton states become much closer and the Auger relaxation from the multie exciton states to the lowest exciton state is more effective. The radiative relaxation from these states to the ground state could become more uniform. In addition, due to more nonpassivated surface trapping states for NRs, the fluorescence lifetime distribution appears to be broader and the shape is closer to a Gaussian. In contrast, the surface of QDs was almost attached by TOPO molecules, and the intensity induced saturation effects do not affect the lifetime distribution significantly.

In conclusion, we have investigated the excitation intensity dependence of fluorescence lifetime for CdSe NRs and QDs. We reported unusually sharp lifetime distribution for NRs at high light intensities. Over the observed excitation intensity from 100 to about 600 W/cm\textsuperscript{2}, the linewidth for NRs changes by almost two orders of magnitude. The detailed mechanism is presently unclear but we think that multie excitons might play a role. Due to a larger surface area and stronger light absorption for NRs, the light-intensity effects can be more pronounced than QDs. We also observed a shift of the lifetime distribution of both QDs and NRs to a shorter time scale. The shift could be due to multie exciton formation. Because NRs are much larger in size, the band edge exciton states become much closer and the Auger relaxation from the multie exciton states to the lowest exciton state is more effective. The radiative relaxation from these states to the ground state could become more uniform. In addition, due to more nonpassivated surface trapping states for NRs, the fluorescence lifetime distribution appears to be broader and the shape is closer to a Gaussian. In contrast, the lifetime distribution for QDs is closer to a Lorentzian and the ratio of the distribution width over the average lifetime is smaller.

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\textsuperscript{7}L. S. Li, J. Hu, W. Yang, and A. P. Alivisatos, Nano Lett. \textbf{1}, 349 (2001).