Competition between zero-phonon and phonon-assisted luminescence in colloidal CdSe quantum dots


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We determine the low-temperature optical properties of dark-exciton states in CdSe/CdS nanocrystal quantum dots (NQDs). By using resonant laser excitation we distinguish zero-phonon from phonon-assisted photoluminescence. The NQDs show a decreasing zero-phonon intensity with decreasing temperature, resulting in a redshift of the nonresonant photoluminescence. This redshift is undone by application of a magnetic field. Our results show that dark-exciton luminescence originates from the intricate competition of phonon-assisted and zero-phonon transitions, the latter of which are enhanced by dark–bright-exciton mixing due to unpassivated surface states or a magnetic field.

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The spectrum was fitted by a single Gaussian to obtain the peak energy. Figure 1 shows the peak energy (a,c,e,g), integrated intensity (b,d,f,h), and the degree of circular polarization (DCP) \([\sigma^-/(\sigma^+ + \sigma^-)]\) as function of \(B\) at 1.2 and 4.2 K for QD1 and QD2. We recognize the following trends: at \(B=0\) T the PL energy is lower at 1.2 K than at 4.2 K, namely, \(\approx 4\) meV for QD1 [Figs. 1(a) and 1(c)], and \(\approx 2\) meV for QD0 (not shown) and QD2 [Figs. 1(e) and 1(g)]. This redshift at 1.2 K is undone by a magnetic field of \(\approx 10\) T [Figs. 1(a) and 1(e)]. With increasing \(B\) the PL becomes circularly polarized, where the \(\sigma^-\) emission shifts to higher energy with increasing intensity and the \(\sigma^+\) emission shifts to lower energy with decreasing intensity. The corresponding DCP equals 0.5–0.6 at \(B=33\) T, and only slightly depends on temperature [Figs. 1(i) and 1(j)]. Remarkably, we measured the highest intensity at the highest energy for both temperatures, similar to an earlier report. Finally, for all samples the total normalized PL intensity only marginally increases with \(B\) from 2 (\(B=0\) T) to 2.4 at \(B=33\) T.

To determine the contributions of different recombination mechanisms, PL was measured under resonant excitation (FLN). The sample was mounted on a fiber coupled probe, and resonantly excited by a tunable dye laser using circularly polarized light. Excitation and detection occurred under crossed polarization to minimize scattered laser light. Spectra were recorded in 60 s exposures.

Typical FLN spectra are shown in Fig. 2(a) and can be roughly understood in terms of the exciton level scheme in Fig. 2(c). Excitons are excited by the laser into the bright \(F=\pm 1\) levels, resulting in emission from the dark \(F=\pm 2\) excitons, i.e., the zero-phonon line (ZPL) 6 meV below the laser energy, and several phonon replicas (1PL, 2PL), superimposed on a small nonresonant PL background. The energy positions and intensities of all resolved peaks were obtained by fitting a Lorentzian laser line and Gaussian peaks for the ZPL, 1PL, and 2PL, and the nonresonant background. Figure 2(b) shows the ZPL and 1PL intensities as a function of temperature, relative to the ZPL intensity at 4.2 K (QD2). The ZPL intensity steadily decreases with decreasing temperature, whereas the 1PL intensity slightly increases, a
The measured exchange splittings of the exciton lines have been omitted in this figure.13,14 and direct zero-phonon transitions.24

Figure 3(b) plots the fitted ZPL and 1PL intensities as a function of temperature, magnetic field, and surface passivation. Let us first consider the temperature dependence of the nonresonant PL. This redistribution among the ZPL and 1PL lines17 is characterized by the recombination lifetime $\tau_{\text{phonon}}$. Direct recombination of the dark excitons can only occur through mixing with the bright excitons, either due to a magnetic field ($\tau_{\text{field}}$) (Refs. 14, 15, 19, and 25) or due to unpassivated surface states ($\tau_{\text{surface}}$).11 Clearly, this schematic model ignores recombination of charged excitons or biexcitons, as well as the chemical details of the actual states at the NQD surface, which might lead to modifications of the exciton fine structure and the optical recombination.11,21 Within the experimental resolution of our FLN experiment, however, we did not find any deviations from this simple level scheme.

The actual dark-exciton recombination is governed by the competition between the different transitions, depending on temperature, magnetic field, and surface passivation. Let us first consider the temperature dependence of the NQD emission. In the FLN experiment we observed a reduced ZPL emission with decreasing temperature, whereas the intensity of the phonon replicas only marginally increases [Fig. 2(b)].17 This redistribution among the ZPL and 1PL lines20 is responsible for the temperature dependence of the nonresonant PL. The nonresonant spectrum is the averaged PL emission of an ensemble of NQDs with slightly different sizes. For typical size variations of about 5%, the ensemble PL linewidth is almost constant (open diamonds).

To describe the data we consider the different recombination channels of neutral excitons that are schematically shown in Fig. 2(c), taking into account bright $F=\pm 1^L$ and dark $F=\pm 2$ levels. Note that for sake of clarity the Zeeman splittings of the exciton lines have been omitted in this figure. Given the measured exchange splitting $\Delta_{\text{bd}}$ of $\sim 6$ meV, the $F=\pm 2$ levels are not populated at the low temperatures used here. Therefore, we only need to include recombination from the $F=\pm 2$ levels, where we distinguish three recombination processes: surface-state assisted transitions,11 phonon-assisted transitions,13,14 and direct zero-phonon transitions.

The optical phonon-assisted 1PL lies typically $\hbar \omega_{\text{LO}} =25–26$ meV below the $F=\pm 2$ level [Fig. 2(a)].17 and is due to resonant recombination of the dark excitons can only occur through mixing with the bright excitons, either due to a magnetic field ($\tau_{\text{field}}$) (Refs. 14, 15, 19, and 25) or due to unpassivated surface states ($\tau_{\text{surface}}$).11 Clearly, this schematic model ignores recombination of charged excitons or biexcitons, as well as the chemical details of the actual states at the NQD surface, which might lead to modifications of the exciton fine structure and the optical recombination.11,21 Within the experimental resolution of our FLN experiment, however, we did not find any deviations from this simple level scheme.

The actual dark-exciton recombination is governed by the competition between the different transitions, depending on temperature, magnetic field, and surface passivation. Let us first consider the temperature dependence of the nonresonant PL. This redistribution among the ZPL and 1PL lines20 is responsible for the temperature dependence of the nonresonant PL. The nonresonant spectrum is the averaged PL emission of an ensemble of NQDs with slightly different sizes. For typical size variations of about 5%, the ensemble PL linewidth is larger than the LO phonon energy, which implies that the nonresonant PL spectrum is an average of nonphonon and phonon-assisted lines. We simulate this average PL by combining the extracted energies and intensities of the ZPL and 1PL emissions in the FLN spectra [Fig. 2(b)] to calculate the

![Figure 2](image-url)
compared to the phonon replica emission of the ZPL emission at 1.2 K with bright excitons. The strength of the mixing depends on the exciton levels. First, the field causes the mixing of dark excitons. Second, the field changes the relative importance of the ZPL and phonon-assisted emission, leading to an increased quantum yield with an optical thickness thus changes the relative importance of the ZPL and phonon-assisted emission, leading to an increased quantum yield with an optimum at a certain shell thickness (∼1–2 ML). A reduced surface-assisted emission results in a diminished ZPL emission ($\tau_{\text{surface}}$ becomes longer). Changing the shell thickness thus changes the relative importance of the ZPL and phonon-assisted emission, leading to a sample-dependent redshift upon cooling, which also explains the wide range of values, up to 13 meV, reported in literature.

The competition between zero-phonon and phonon-assisted recombination is further supported by the results in high magnetic fields. A magnetic field has several effects on the exciton levels. First, the field causes the mixing of dark with bright excitons. The strength of the mixing depends on the angle of the NQD $c$ axis with respect to the direction of $B$. On average it will lead to an enhanced ZPL intensity compared to the phonon replica emission [Figs. 3(b) and 3(c)]. Calculating the intensity weighted average energy position of the ZPL and 1PL [see Fig. 3(c)], we find that at 1.2 K the average energy shifts 2 meV upward from 2110 (0 T) to 2112 meV at 10 T. This behavior matches very well with the observed shifts in the nonresonant PL experiment [compare with Figs. 1(e) and 1(g)]. The redshift upon cooling is canceled by application of a magnetic field of 10 T.

The second important effect of $B$ is the Zeeman splitting of the exciton levels, which is visible in the FLN data as an increasing separation between the laser line and the $F=-2$ and $F=-1^\pm$ emission with growing field [Fig. 3(a)]. Furthermore, as a result of the Zeeman effect, we observed an energy separation of ∼1 meV at $B=33$ T, between the $\sigma^-$ and $\sigma^+$ polarizations, and a profound DCP [Figs. 1(i) and 1(g)]. The $B$ dependence of the DCP appears to be described well within the exciton fine-structure model, a fact that was repeatedly used to support this model. However, with the parameters used to fit the DCP, the model fails to describe three other characteristic features: (i) the peculiar polarization of the PL emission, i.e., that the highest energy has the highest intensity, (ii) the actual value of the observed energy splitting (Fig. 1), and (iii) the nonzero intensity of the low-temperature PL. Therefore, we find that the exciton fine-structure model cannot fully describe the high magnetic-field experiments, which confirm that a complete description of the dark-exciton PL should include multiple recombination channels.

A complete theory for dark-exciton recombination that is capable of explaining all experimental observations is still lacking. Therefore, we propose the schematic dark-exciton recombination scheme of Fig. 2(c), which combines ingredients from several different theoretical descriptions. The starting point is an exciton fine structure, in which bright-
dark-exciton levels are split due to exchange interactions. This fine structure has been calculated by either an effective-mass approximation model or atomistic pseudopotential calculations. To explain the finite lifetime of the dark-exciton ground state, mixing of bright and dark excitons is needed, for instance due to unpassivated surface states. This lifetime, however, is still very long (~μs) and therefore phonon-assisted transitions should also be taken into account. The competition between these direct and phonon-assisted transitions explains the redshift of the dark-exciton emission upon cooling from 4.2 to 1.2 K and the cancellation of this redshift by a magnetic field. This magnetic-field effect is due to the mixing of the dark- and bright-exciton states, as described by the effective-mass model. Although this model describes the enhancement of bright-exciton states, as described by the effective-mass approximation model or atomistic pseudopotential model, the exciton fine structure, also phonon-assisted and surface-state assisted recombinations.

In conclusion, we have found that the low-temperature dark-exciton emission of CdSe/CdS NQDs is determined by the competition between phonon-assisted and zero-phonon recombinations. The relative importance of the different recombination processes depends strongly on internal factors, such as shell thickness and surface passivation, and on external factors, such as temperature and a magnetic field. Our results prove that any model that attempts to fully describe the optical properties of CdSe NQDs should include, besides the exciton fine structure, also phonon-assisted and surface-state assisted recombinations.

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