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Exciton lifetimes of CdTe nanocrystal quantum dots in high magnetic fields


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I. INTRODUCTION

The optical properties of colloidal semiconductor nanocrystal quantum dots (NQDs) have attracted much interest in recent years. Control over their composition and size makes it possible to tune their exciton confinement energies, and thereby their emission wavelength, over a wide range.1,2 Furthermore, the high photoluminescence (PL) quantum efficiency of high-quality NQDs at room temperature3,4 is important for applications.5–9 To date, wurtzite NQDs have been mostly investigated, with CdSe as the prototypical example,10–12 since the PL wavelength of CdSe NQDs can be tuned across the visible wavelength region. Alternatively, zinc-blende (e.g., CdTe, CdS, ZnSe, and ZnS) and rock-salt (e.g., PbS and PbSe) NQDs have been fabricated, which have considerably enlarged the wavelength emission range.13,14

From a fundamental point of view, it is interesting to study NQDs with different crystal structures because the lattice symmetry is one of the parameters to tune the lowest energy levels of the excitons that are responsible for the NQD optical properties.15,16 It is well established that, in wurtzite NQDs, the electron-hole exchange interaction and the intrinsic crystal/shape anisotropy lift the spin degeneracy of the exciton levels, leading to five distinct states, which are characterized by their spin projection (\( m_s \)) along the nanocrystal c axis. The resulting exciton fine structure is characterized by a lowest energy exciton state (\( E_{1,\text{m}} \approx \pm 2 \)), which is forbidden for direct radiative recombination (thus optically dark), and a higher energy exciton state (\( E_{1,\text{m}} \approx \pm 1/2 \)), which is dipole allowed (thus optically bright). Evidence for this exciton fine structure has been given by the size-dependent Stokes shift from fluorescence line-narrowing experiments15,17 and by the dependence of the radiative lifetime on both temperature1,2,8–22 and magnetic fields.11,23,24 In these latter experiments, it was found that the dark ground state acquires oscillator strength in a magnetic field by field-induced mixing of the exciton states, thereby significantly decreasing the exciton lifetime. These experiments demonstrate that application of high magnetic fields is a powerful tool to determine the exciton fine structure in NQDs.11,15,23–25 Similar high-field data are scarce for NQDs with a crystal lattice different from wurtzite.26

In this paper, we report on the radiative lifetimes of excitons in zinc-blende CdTe NQDs as a function of strong magnetic fields (\( B \)), as determined from the PL decay times. We have found that the exciton lifetime strongly decreases with increasing magnetic field, as well as with increasing temperature and size, which is similar to the behavior of wurtzite CdSe NQDs. We describe the \( B \) dependence of the exciton lifetime with a phenomenological model that includes \( B \)-induced exciton mixing. Based on the fact that the theoretically predicted exciton fine structure is similar for spherical NQDs with the wurtzite crystal structure and for prolate NQDs with the zinc-blende crystal structure, we conclude that the close resemblance of the CdTe and the CdSe data is caused by the nonspherical shapes of the CdTe NQDs investigated in this work.

II. EXPERIMENT

We have measured the magnetic-field dependence of the PL decay time for five different chemically synthesized CdTe NQD samples, with diameters (\( d \)) ranging from 2.6 to 3.8 nm, and for one CdSe NQD sample, with \( d = 3.6 \) nm (size dispersion <10% in all cases). The synthesis and characterization of the NQDs have been described elsewhere.27,28 Powder x-ray diffraction measurements revealed that the CdTe NQDs have the zinc-blende crystal structure [Fig. 1(c)]. Transmission electron microscopy showed that NQDs fabricated by this method possess a variety of faceted and nonspherical shapes, sometimes slightly elongated in one direction (aspect ratio: 1.1–1.2) [Figs. 1(a) and 1(b)]. The samples were prepared by freezing a suspension of randomly organized, organically capped NQDs in toluene. Time-correlated single-photon counting experiments were performed in high magnetic fields up to 30 T (using a Florida-Bitter magnet in Faraday geometry) at low temperatures (4.2 K), using a standard PL setup with optical fibers. The excitation was provided by a picosecond pulsed laser operating at 445 nm (PicohQuant). The PL emission was passed through a high pass filter and detected by an avalanche photon detector (MPD PD5CTC) connected to a single-photon counter (Picoharp 300).

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III. RESULTS

Figure 2 shows typical PL decay curves as a function of temperature [Fig. 2(a)], NQD size [Fig. 2(b)], and magnetic field [Fig. 2(c)]. The data are background corrected and plotted on a semilogarithmic scale. The decay of all the NQDs we have investigated is biexponential, with a fast ($\approx$ ns) and a slow component. The biexponential shape indicates the high quality of the NQDs used in this study and also that interdot energy transfer plays a negligible role. The fast component is assigned to emission from the bright state prior to relaxation to the lowest energy exciton state. The slow decay time reflects the lifetime for the lowest energy exciton state (the dark state). The full magnetic-field, size, and temperature dependence of the exciton lifetimes of the NQDs are shown in Fig. 3. The data points have been obtained by fitting the slow part of the PL decay curves (from 100 to 1000 ns) by a single exponent. Figure 3(a) shows the results for the five CdTe NQDs used and demonstrates that the exciton lifetimes shorten with increasing magnetic field, similar to the behavior of the reference CdSe NQD, shown in Fig. 3(b). Figure 3(a) also shows that the exciton lifetime decreases with increasing diameter, despite the deviation from this trend for the NQDs with $d = 2.9$–$3.3$ nm. Finally, Fig. 3(c) shows that the exciton lifetime of the 2.6-nm-diameter CdTe NQD decreases with increasing temperature. Below 4 K (the temperature used for the $B$-dependent measurements), the lifetime is constant and equal to the lifetime of the dark exciton ground state. This overall size- and temperature-dependent behavior is consistent with earlier reports for CdTe NQDs at $B = 0$, and is remarkably similar to the behavior of CdSe NQDs.

IV. DISCUSSION

To explain the behavior of the exciton decay times, we take a closer look at the exciton fine structure of both CdSe and CdTe NQDs, as shown in Fig. 4. The energy levels have been calculated using the effective-mass model of Efros$^{15}$ and depend strongly on the radius $a = d/2$ and the crystal structure of the NQDs. In these calculations, we have used the following parameters: the exchange splitting
Exciton lifetimes of CdTe nanocrystal quantum dots (QDs) are analyzed in this document. Measurements show a decrease in lifetime with increasing magnetic field and temperature. The exciton lifetime, $\tau$, is given by $\tau = v^{-1} e^{\hbar \omega_{ST} / k_B T}$, where $v$ is the exciton wave number, $\hbar \omega_{ST}$ is the exciton energy, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The product $\hbar \omega_{ST}$ is determined by the exciton fine structure, which is influenced by the electric field and quantum confinement effects.

The exciton fine structure is modified by crystal anisotropy and exchange interaction. For zinc-blende crystals, the fine structure splitting $\Delta_{\text{exch}}$ is given by $\Delta_{\text{exch}} = \epsilon_{\text{exch}} + \epsilon_{\text{crystal}}$, where $\epsilon_{\text{exch}}$ is the exchange interaction energy and $\epsilon_{\text{crystal}}$ is the crystal anisotropy energy. For wurtzite crystals, the fine structure splitting is $\Delta_{\text{exch}} = \epsilon_{\text{exch}} - \epsilon_{\text{crystal}}$.

The magnetic-field dependence of such an exciton fine structure is shown in Fig. 4(d). Although this level structure is calculated using the parameters of a 3.6-nm-diameter spherical CdSe QD, we assume that it is also approximately valid for a prolate CdTe QD of similar size. The degenerate levels $F_m = \pm 2$ and $F_m = \pm 1^{1/2}$ excite levels each split into two components as a result of the Zeeman effect. The splitting depends on the angle $\theta$ between the $c$ axis of the crystal and the magnetic field. The insets of (a) and (b) show the unit cells of the crystal lattices of CdTe and CdSe. Solid (dashed) lines correspond to spherical CdTe QDs ($\theta = 0^\circ$) and CdSe prolate QDs ($\theta = 90^\circ$). The insets of (a) and (b) show the unit cells of the crystal lattices of CdTe and CdSe. Solid (dashed) lines correspond to spherical CdTe QDs ($\theta = 0^\circ$) and CdSe prolate QDs ($\theta = 90^\circ$).
of the NQD ($\theta$) (Ref. 15):

$$\frac{1}{\tau(B, \theta)} = \frac{\sqrt{1 + \zeta^2 + 2 \zeta \cos \theta} - 1 - \zeta \cos \theta}{\sqrt{1 + \zeta^2 + 2 \zeta \cos \theta} 3} \frac{1}{4 \tau_{\text{rad}}},$$

(1)

where $\tau_{\text{rad}}$ is a size-independent radiative lifetime, $\zeta = \mu_B g_{\text{ex}} \chi\beta B / 3 \eta$ (with $\mu_B$ the Bohr magneton), $g_{\text{ex}}$ is the dark exciton $g$ factor, and $\eta = (a_{\text{ex}} / a)^3 \hbar \omega_{\text{ST}} \chi(\beta)$ is a factor that accounts for the size-dependent exchange splitting, using a dimensionless scaling factor $\chi(\beta)$, which can take values between 0.6 and 0.8. This formula successfully describes the experimentally observed decreasing exciton lifetime with magnetic field of CdSe NQDs, and is also used to explain their field-induced circular polarization. In this regard, it is important to note that the lifetime of excitons in spherical CdTe NQDs is expected to be independent of the magnetic field: the $|F| = 2$ and $|F| = 1$ states of such zinc-blende NQDs do not mix, resulting in an exciton ground state that should be dark at all magnetic fields, in contrast to our experimental results.

Motivated by the predicted similarity of exciton fine structures of spherical CdSe and elongated CdTe NQDs [Figs. 4(b) and 4(c)], we use Eq. (1) to model the lifetimes of excitons in CdTe NQDs. The angle $\theta$ is now defined as the angle between the magnetic field and the elongated axis of the nanocrystal. To account for the finite exciton lifetime at $B = 0$, we introduce a field-independent lifetime $\tau_0$:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau(B)},$$

(2)

where the value of $\tau_0$ is given by the experimental PL decay time at $B = 0$, which equals 800, 500, and 200 ns for NQDs with 2.6, 3.0, and 3.8 nm diameters, respectively. This size dependence of the exciton lifetime is typical for both CdSe and CdTe systems. Longer lifetimes are observed at 4.2 K for decreasing NQD diameter. The size dependence of the lifetime is explained by an increase in the exchange splitting between the dark and bright states for smaller NQDs and by higher energies of acoustic phonon modes that enable the transition from the dark state. The $\tau_0$ has no effect on the magnetic-field dependence of the exciton lifetime determined by $\frac{1}{\tau(B)}$, which is obtained by the average over all angles $\theta$ between 0° and 180°:

$$\frac{1}{\tau(B)} = \int_0^\pi \frac{1}{\tau(B, \theta)} \sin \theta d\theta.$$  

(3)

Figure 5 schematically shows the resulting exciton lifetimes as a function of the magnetic field. The parameters used are $\hbar \omega_{\text{ST}} = 0.04$ meV, $a_{\text{ex}} = 6.7$ nm, and $\chi(\beta) = 0.61$, which were taken from the literature. $\tau_{\text{rad}}$ and $g_{\text{ex}}$, the $g$ factor of the dark exciton, were used as adjustable parameters, leading to values $\tau_{\text{rad}} = 10$ ns and $g_{\text{ex}} = 4$. The actual decrease of the PL decay time with $B$ is entirely determined by the value of $\chi$ (cf. Eq. (1)); so, in our case, this is determined by the free parameter $g_{\text{ex}}$. The value found for $g_{\text{ex}}$ is larger than that reported in the literature, but close to the theoretically expected value $g_{\text{ex}} \approx 4$ for the dark exciton ground state.}

V. CONCLUSIONS

In conclusion, we have shown that the PL decay time of CdTe NQDs decreases when their size is increased and when an external magnetic field is applied. The decrease of the PL decay time of a NQD in a magnetic field is caused by the magnetic-field-induced mixing of dark and bright exciton states. The latter phenomenon can only be explained when a slight shape asymmetry of the CdTe NQDs is assumed. These results show that it is not possible to distinguish the exciton fine structure of a spherical NQD having a wurzite lattice from a slightly elongated NQD having a zinc-blende lattice.

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EXCITON LIFETIMES OF CdTe NANOCRYSTAL QUANTUM . . .

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