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Tuning Energy Splitting and Recombination Dynamics of Dark and Bright Excitons in CdSe/CdS Dot-in-Rod Colloidal Nanostructures

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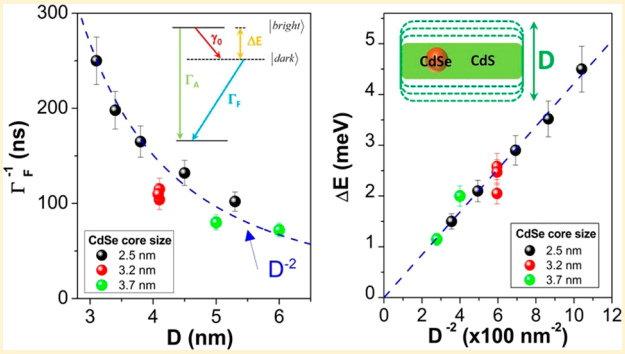
ABSTRACT: We report on a time-resolved study of the photoluminescence of core/shell CdSe/CdS dot-in-rod colloidal nanocrystals having various geometries. By studying the exciton recombination dynamics, we unveil a quadratic dependence of the bright−dark exciton energy splitting and the dark exciton radiative recombination rate on the inverse CdS rod width, regardless of the CdSe core size. We also evidence a strong dependence of the spin-flip rate between bright and dark exciton states on the shell thickness that suggests an acoustic phonon bottleneck. This work highlights the possibility to fully control and tune the optical properties of colloidal nanocrystals by shape engineering of the CdS shell.



INTRODUCTION

The continuous interest in CdSe-based colloidal heteronanostructures throughout the past decades has led to a deeper understanding of their optical properties. The high expertise in synthesis enables the growth of nanocrystals (NCs) with sphere-shape, rod-shape, or platelet-shape with zero-,[1] one-,[2] and two-dimensional[3] confinement, respectively. Besides a high flexibility in the core-shape growth, the colloidal synthesis possesses an additional knob to tune the photophysical properties: the shell, which is typically made of a wide band gap semiconductor such as ZnS or CdS and plays a major role for the optical properties of NCs. Adding a shell around the bare core helps to passivate the surface and enables dramatic increasing of the ensemble quantum yield from less than 10% to more than 50%.[4] Among various materials available for designing shells, a greater attention has been given to CdS, since it gives a high flexibility for the shell growth due to the small lattice mismatch between CdSe and CdS (about 4%). Several new spherical CdSe/CdS core/shell heteronanostructures with unique optical properties have been recently synthesized.[5−7] For example, NCs with a CdS shell thicknesses of 10 nm around a spherical CdSe core exhibit remarkable emission properties at cryogenic temperature. Notably, the emission can be stable (blinking-free) and is governed by radiative recombination of charged excitons with a quantum yield close to 100%.[8] This behavior contrasts with thin-shell CdSe/ZnS and CdSe/CdS NCs, where the emission arises from the radiative recombination of the two thermally populated lowest fine structure levels of the neutral exciton.[9,10] Apart from an increase of the shell thickness, the optical properties of NCs can be further affected by means of anisotropic growth of the shell. In this regard, recent studies reported on CdS shells with tetrapod-shape,[11] plate-shape,[12] or rod-shape[13] surrounding a CdSe spherical core. The latter structure is typically referred to as dot-in-rod (DiR) and has attracted much attention because of its superior optical properties such as suppressed Auger processes[14] or high optical gain.[15] Besides these striking properties, DiRs allow for electron−hole wave function overlap engineering due to the small conduction band offset between CdSe and CdS.[16,17] These remarkable features are very attractive for quantum optics applications, notably to generate polarized entangled photon pairs based on the biexciton−exciton radiative cascade. A prerequisite for such generation is the comprehensive knowledge of the exciton fine structure and its dynamics.

In nearly spherical CdSe/ZnS core/shell NCs, the 8-fold degenerated exciton ground state is split into 5 fine structure levels, due to the electron−hole exchange interaction, the crystal field (for wurtzite structures), and the spin−orbit interaction. It has been shown both theoretically and experimentally that, in CdSe/ZnS NCs, the relative position of the exciton fine structure levels and the energy splittings strongly depend on the core size,[18] the core shape,[19] and the crystal structure.[20] In the effective mass approximation framework, the optical transition from the lowest energy level of the exciton fine structure is always forbidden in the electric dipole approximation, regardless the size, the shape, and the crystal structure of the core.[18,21] This optically passive state,

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Table 1. Parameters of the CdSe/CdS Dot-in-Rod Samples[a]

	sample									
	1	2	3	4	5	6	7	8	9	10
CdSe core diameter (nm)	2.5	2.5	2.5	2.5	2.5	3.2	3.2	3.2	3.7	3.7
CdS rod width, D (nm)	5.3 (0.5)	4.5 (0.5)	3.8 (0.3)	3.4 (0.2)	3.1 (0.2)	4.1 (0.3)	4.1 (0.2)	4.1 (0.3)	6 (0.6)	5 (0.3)
CdS rod length, L (nm)	28.9 (1.5)	20 (1)	22 (2)	22.8 (1.8)	62 (2)	60 (5)	41 (2)	32 (1)	20.4 (1.3)	26.5 (2.7)
bright exciton lifetime (ns)	7.1 (0.7)	6.6 (0.7)	4.7 (0.5)	3.8 (0.4)	6.6 (0.7)	3.7 (0.4)	3.6 (0.4)	3.8 (0.4)	6.2 (0.6)	4.2 (0.4)
dark exciton lifetime (ns)	100 (10)	130 (13)	165 (17)	200 (20)	250 (25)	115 (12)	105 (10)	110 (11)	70 (7)	80 (8)
bright−dark splitting, ΔE (meV)	1.5 (0.15)	2.1 (0.2)	2.9 (0.3)	3.5 (0.35)	4.4 (0.4)	2.6 (0.26)	2.05 (0.2)	2.5 (0.25)	1.1 (0.11)	2 (0.2)

[a]The width and the length of the CdS rod are measured by transmission electron microscopy. The CdSe core size is determined from the energy of the first exciton in the absorption spectra.[27] Errors are indicated in parentheses.[28].

often referred to as the dark state, has a total angular momentum of 0 or ±2 depending on whether the light-hole (lh) or the heavy-hole (hh) band is the highest valence band, respectively. The dark state is located a few millielectronvolts below a bright optically allowed state whose total angular momentum is ±1. These two states are of great interest, since they have a pivotal role in the photoluminescence (PL) properties of NCs, especially at cryogenic temperatures.[9,10] Over the past decades, the energy splitting and the recombination dynamics of these states have been intensively investigated for spherical NCs. Notably it has been demonstrated that, by changing the size and the shape of the core, the exciton fine structure and thereby the optical properties of the NCs can be tuned.[9,19,20,22] Moreover, it has been shown that, by changing the shell thickness, the electron−hole wave function overlap can be controlled. This influences the electron−hole exchange interaction and leads to a change in the bright−dark energy splitting.[23]

While insightful regarding the influence of core size and shell thickness on the exciton fine structure, the aforementioned studies leave the role played by the shell shape undisclosed. However, especially in the case of anisotropic heteronanostructures, the shell strongly influences optical properties such as polarization[24] or lh−hh splitting.[12] In DiR, analysis of the early part of the PL decay at cryogenic temperatures unveiled a size dependence of the energy splitting between a lower and an upper bright state of the exciton fine structure.[25] However, in spite of more than a decade of experimental and theoretical studies on the optical properties of DiR NCs, neither the energy splitting between the two lowest exciton states, that is, the bright and the dark states, nor their recombination dynamics have been discussed yet. Therefore, in DiR, the possibility to tune and control the exciton fine structure through the shell thickness and the shell shape remains still unclear.

In this Letter, we report on a systematic study of the temperature dependence of the PL decay of CdSe/CdS DiR colloidal heteronanostructure ensembles. The results can be interpreted by a three level model that includes a ground state and two excited states, a higher energy bright state and a lower energy dark state. We clearly unveil the size dependencies of all the relevant parameters of the exciton fine structure such as the energy splitting between the lowest exciton states, the radiative recombination times, as well as the spin-flip time between bright and dark states. We find that, independently of the seed CdSe core size, the energy splitting between the two lowest exciton states, namely, the bright and the dark states, scales with the inverse square width of the CdS rod. This probably results from the significant leakage of the electron wave function into the CdS rod and the lack of confinement of the electron along the rod axis direction. Additionally, we show that the dark exciton recombination time has a prominent size dependence. While the bright exciton radiative lifetime does not exhibit systematic size dependence, the dark exciton radiative lifetime is shown to decrease with the inverse square of the rod width, regardless of the core size. Remarkably, the dark exciton lifetime in DiR is considerably reduced compared to spherical nanocrystals with similar core size. These striking features may help to unveil the origin of the dark exciton radiative recombination and clearly point toward a surface-assisted mechanism of dark exciton recombination. Interestingly, we find that the nonradiative spin-flip rate from the bright to the dark exciton state is strongly influenced by the shell thickness suggesting an acoustic phonon bottleneck effect. The detailed study of the exciton fine structure and its dynamics provided in the present work pave the way toward tailoring optical properties in DiR.

METHODS

CdSe/CdS DiR heteronanostructures were grown following a standard protocol described in ref 11; the dimensions of the different samples studied here are listed in Table 1. The samples were prepared for ensemble measurements by drop casting the CdSe/CdS DiR solution on a quartz plate. For experiments at low temperatures the sample was mounted in a helium bath cryostat. The DiR samples were excited non-resonantly using a pulsed diode laser (photon energy, 3.06 eV; pulse duration, 50 ps; repetition rate, 1 MHz) with a weak average excitation power (<0.02 W·cm^{-2}) to prevent contributions from radiative recombination of multiexcitons. The PL was filtered from scattered excitation light by a long-pass filter to avoid experimental artifacts[26] and was dispersed with a 0.55 m spectrometer and detected by a liquid-nitrogen-cooled charge-coupled-device camera or by an avalanche photodiode connected to a conventional time-correlated single-photon counting setup. The instrumental response function of the setup was 200 ps.

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RESULTS AND DISCUSSION

Bright and Dark Exciton States in CdSe/CdS Dot-in-Rod. Figure 1a shows normalized PL spectra of CdSe/CdS DiR samples with a seeded CdSe core diameter of 2.5 nm and various rod widths measured at T = 4.2 K. We observe a continuous red shift of the PL maximum with increasing rod width from 2.317 eV for the bare core sample to 2.172 eV for the sample with the thickest shell (sample **1**). This can be explained by considering the small conduction band offset between CdSe and CdS that allows for a leakage of the electron wave function in the CdS shell, thereby reducing the confinement energy. Figure 1b shows the rod length dependence of the PL spectra of CdSe/CdS DiR samples having a rod width of 4.1 nm and a CdSe seed core of 3.2 nm at T = 4.2 K. The lack of rod length dependence for the maximum PL energy indicates that the length does not play a significant role regarding the optical properties at low temperatures. The full width at half-maximum (fwhm) of the PL spectra is ~70 meV as a result of the DiR size dispersion. Inhomogeneously broadened structureless PL spectra allow for neither the identification of the fine structure levels involved in the exciton recombination nor the size dependence of the exciton fine structure parameters. To get deeper insight into the exciton recombination processes in DiR, we measured a temperature dependence of the PL decay from 2.2 up to 70 K.

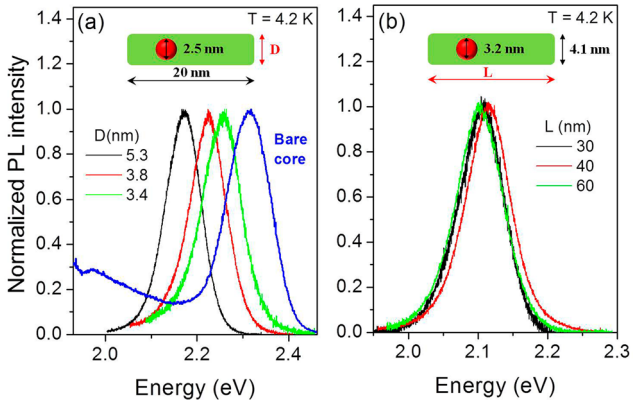

Figure 1. (a) PL spectra of CdSe/CdS DiR at T = 4.2 K for various rod widths with a fixed CdSe core diameter of 2.5 nm (samples **1**, **3**, **4**) together with the bare CdSe core spectrum (blue). Note that the red tail in the bare core sample arises from deep trap emission. (b) Same as (a) but for DiR having for various rod lengths (CdSe core diameter is 3.2 nm, and rod width is 4.1 nm) (samples **6**–**8**).

Figure 2a shows the spectrally integrated normalized PL decays of sample **1** at various temperatures. The geometric parameters are indicated in the inset of the figure. At T = 2.2 K, the PL decay occurs on two very different time scales: it consists of a short component in the 1-ns range and a long component in the 100-ns range. When increasing the temperature, the long component shortens, while the intensity of the short component drops until it eventually vanishes at temperatures above 20 K. Such a behavior is well known for the emission of two thermally populated exciton levels with very different oscillator strengths.[9,10,29,30] Figure 2b depicts a model of dark and bright exciton states commonly used in the literature. It is composed of a vacuum state |G⟩ and two states, denoted |A⟩ and |F⟩, which correspond to the bright (optically allowed) and dark (optically forbidden) exciton states, respectively. Because of the electron–hole exchange interaction, these two exciton states are separated by a bright–dark

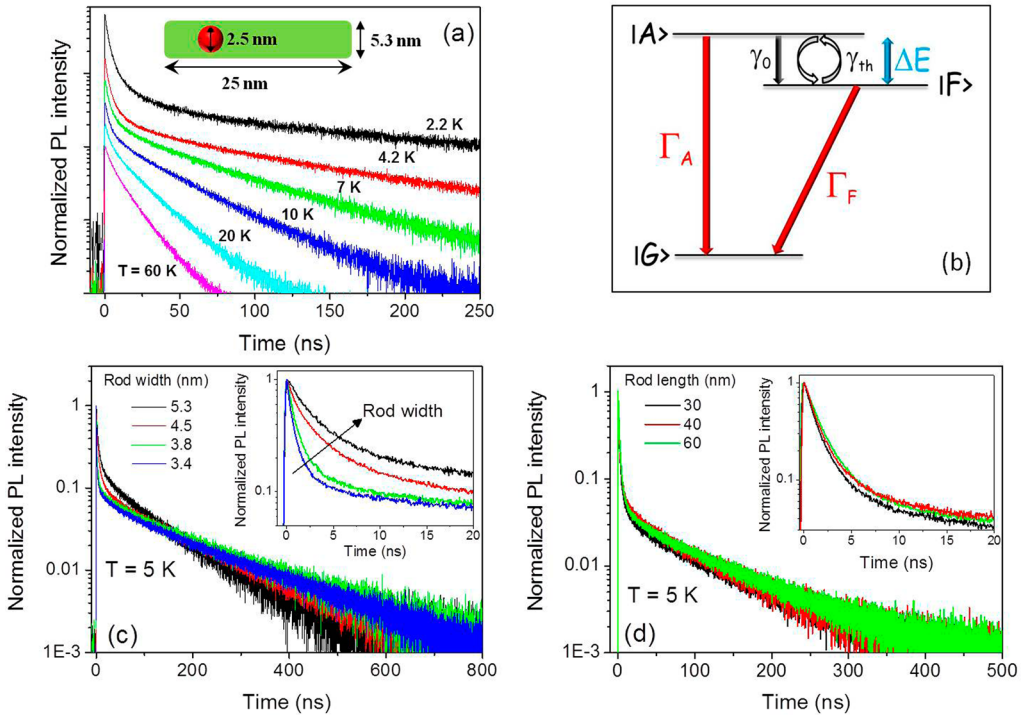

Figure 2. (a) PL decay at different temperatures of sample **1**. For clarity, the PL decays are shown with a vertical offset. (b) Three level system used to interpret the data. (c) PL decay at T = 5 K of DiR with different width but having the same CdSe seed core size of 2.5 nm and a length of about 20 nm (samples **1**–**4**). Inset: early part of the PL decay. (d) PL decay at T = 5 K of DiR with different rod lengths having the same CdSe core size of 3.2 nm and a rod width of 4.1 nm (samples **6**–**8**). Inset: early part of the PL decay.

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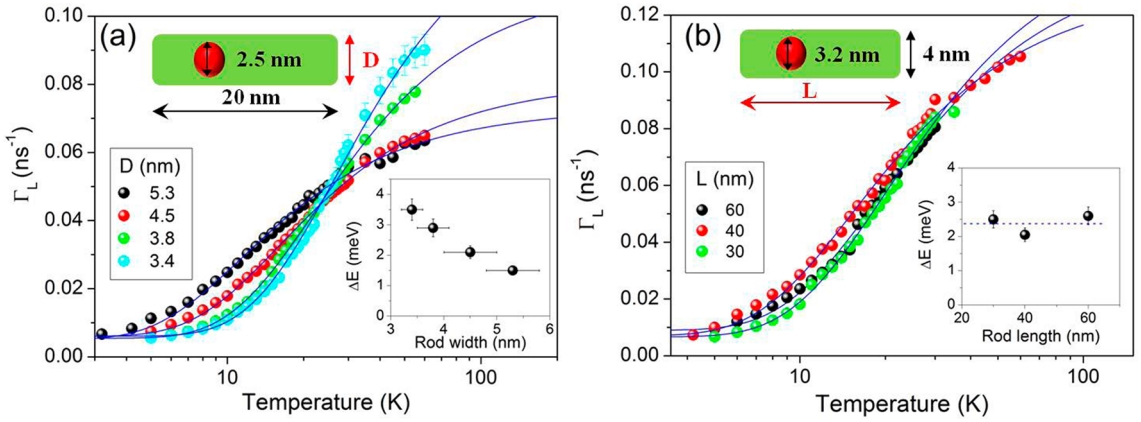

Figure 3. (a) Temperature dependence of the long decay rate for DiR with various widths (samples **1**–**4**). Solid lines are fits according to the three level system (see text). Note that the error bars are representative for all the samples. Inset: rod width dependence of the bright–dark splitting obtained from the fits. (b) Temperature dependence of the long decay rate for DiR with different rod lengths (samples **6**–**8**). Solid lines are fits according to the three level system (see text). Inset: rod length dependence of the bright–dark splitting obtained from the fits.

splitting ΔE. They have radiative recombination rates Γ_A and Γ_F, respectively. γ_0 is the spin-flip rate from the bright to the dark exciton state, and $\gamma_{th} = \gamma_0 N_B$ the spin-flip rate induced by thermal mixing of bright and dark exciton states. $N_B = 1/(\exp(\Delta E/k_B T) - 1)$ is the Bose–Einstein phonon occupation.

By assuming a quantum yield of 100% for both the bright and the dark exciton,[31] the luminescence signal $S(t)$ is proportional to $(\Gamma_A \rho_A + \Gamma_F \rho_F)$, where ρ_A and ρ_F are the time-dependent populations of the bright and the dark exciton states, respectively. With the approximation $\gamma_0 \gg \Gamma_A, \Gamma_F$,[10] we obtain

$$S(t) = \frac{\Gamma_A N_B + \Gamma_F}{1 + 2N_B} e^{-\Gamma_L t} + \frac{\Gamma_A}{2(1 + 2N_B)} e^{-\Gamma_S t} \quad (1)$$

Here, Γ_L and Γ_S are the long component and the short component of the PL decay, respectively, given by

$$\Gamma_L = \frac{\Gamma_A + \Gamma_F}{2} - \frac{\Gamma_A - \Gamma_F}{2} \tanh\left(\frac{\Delta E}{2k_B T}\right) \quad (2)$$

$$\Gamma_S = \gamma_0 (1 + 2N_B) \quad (3)$$

At low temperature ($k_B T \ll \Delta E$), the signal displays a biexponential decay with a short component that arises from radiative recombination of the bright exciton before its relaxation into the dark state and a long component that stems from the radiative recombination of the dark exciton. When the thermal energy becomes comparable to ΔE, the amplitude of the second term in eq 1 decreases and eventually vanishes at high temperatures ($k_B T \gg \Delta E$). At these temperatures, the signal displays a single exponential decay with a characteristic rate $\Gamma_A/2$.

Figure 2c shows the rod width dependence of the PL decay at $T = 5$ K for rods having the same CdSe seed core of 2.5 nm and a length of about 20 nm (samples **1**–**4**). The clear shortening of the long component of the PL decay in combination with the reduced relative weight of the short component with increasing rod width indicates a decrease of the bright–dark energy splitting. The striking observation of the lengthening of the short component with increasing rod width suggests a reduced spin-flip rate from the bright to the dark state due to an acoustic phonon bottleneck.[9,32,33] A markedly different behavior can be observed for the length dependence of the PL decay (Figure 2d, samples **5**–**7**), since the long and the short components remain constant for different rod lengths. These results, together with those obtained on PL spectra, clearly indicate that the rod length does not influence the exciton fine structure.

Bright–Dark Energy Splitting. In order to get a deeper understanding of the bright–dark energy splitting, we analyzed the temperature dependence of the PL decay for various DiR structures, according to the bright–dark exciton model described above. Figure 3a shows the temperature dependences of the long decay component of DiR having various widths together with fits according to eq 2, in which the energy splitting ΔE and the recombination rates Γ_A and Γ_F are used as adjustable parameters.

In the inset of Figure 3a, one can clearly see that the bright–dark energy splitting decreases from 3.5 to 1.5 meV when the rod width is increased from 3.4 up to 5.3 nm. This results from a reduced electron–hole exchange interaction due to a change in the electron–hole spatial overlap.[23] Because of the small conduction band offset between CdSe and CdS, the electron wave function can leak into the CdS shell while the hole remains strongly confined in the CdSe core.[8,23] However, as seen in Figure 3b, the electron–hole wave function overlap is not significantly changed when the rod length is increased. Indeed, as it is shown in the inset of Figure 3b, ΔE remains constant when the rod length is increased from 30 to 60 nm. These results are further supported by recent numerical calculations for CdSe/CdS DiR. These predict a distribution of the electron density in the vicinity of the CdSe core rather than spread over the full rod length.[17]

In Figure 4 we show that in DiR the bright-dark energy splitting scales with the inverse square width of the rod. It is noteworthy that spherical core/shell NCs exhibit a D^{-3} dependence for ΔE.[30]

This reduced size dependence in DiR can be understood when considering the distribution of the electron density within the rod. Indeed, in the DiR NCs we studied, the length of the rod is larger than the calculated spread of the electron wave function along the rod length.[17] Therefore, the electron–hole exchange interaction depends only on the rod width. Strikingly, ΔE decreases with increasing rod width, regardless of core size and rod length. The lack of core size dependence provides strong evidence that, in stark contrast to spherical CdSe/CdS

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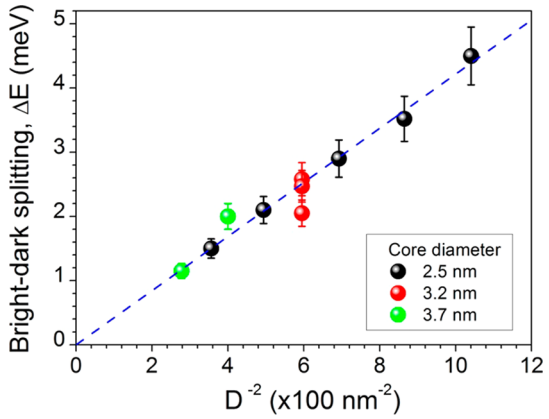

Figure 4. Bright−dark energy splitting as a function of the inverse square width of the rod for different CdSe core sizes. Dashed line is a linear fit.

NCs,[23] the changes in the electron−hole exchange interaction in CdSe/CdS DiR arise from the changes in the overall width of the NCs.

Bright Exciton Recombination Dynamics. Let us now discuss the size dependence of the DiR recombination rates. In Figure 5a, we show the values of the bright exciton lifetimes, determined from the fit of the temperature dependence of the long component of the PL decay, for DiR samples having different core size, rod width, and rod length. The bright exciton lifetime varies weakly between 3 and 7 ns for all studied samples, without a clear dependence on the DiR dimensions. Since the bright exciton radiative rate is directly proportional to the electron−hole wave function overlap, the fast recombination time of the bright exciton found for all DiR samples further evidence strong localization of the electron wave function near the CdSe core.[23]

The optical properties at cryogenic temperatures of colloidal nanostructures are strongly dependent on the spin-flip rate between bright and dark exciton states.[9,10] Therefore, the ability to monitor the spin-flip rate is of major interest regarding the use of colloidal nanostructures notably in quantum optics applications. In spherical CdSe and CdSe/ZnS NCs, this process has been shown to be mediated by confined acoustic phonon modes,[9,32] in particular with acoustic phonon modes with angular momentum $l = 2$. Remarkably the spin-flip rate has been shown to decrease as the core size is increased, that is, when the energy splitting between bright and dark exciton states becomes smaller.[9,33] These results suggest the existence of a phonon bottleneck effect in NCs. While the bright-to-dark spin-flip rate has been studied as a function of the core size[33] and/or the material,[32] the role played by the shell remains unclear.

In the case of CdSe/CdS heteronanostructures, the effect of the size and shape of the CdS shell on the acoustic phonon confinement is expected to be of major importance, since CdSe and CdS have only a small lattice mismatch and therefore acoustic phonons can propagate over the entire nanostructure.[34,35] The shell influence might be even more pronounced in DiR, due to the rod shape. In extended nanostructures, such as nanoplatelets (NPLs), acoustic phonons can be treated as a continuum of states.[36] The lack of phonon confinement has dramatic consequences especially on the bright-to-dark spin-flip rate. In NPLs, it has been shown that the latter is a very efficient process that only weakly depends on the NPL thickness, that is, the bright−dark energy splitting. Furthermore, the spin-flip rate in NPLs is found to be 2 orders of magnitude larger than in spherical NCs having a comparable bright−dark energy splitting (∼2 meV).

In order to unveil the impact of the shell on the spin-flip rate in DiR, we analyzed the short component of the PL decay of DiR samples having the same CdSe seed core and various CdS thicknesses (samples **2**−**5**). Because of the multiexponential behavior of the short component, we have considered the time at an intensity $1/e$ in the PL decay at $T = 4.2$ K, where the PL decays do not show any temperature dependence. Therefore, from eq 3, assuming $k_BT \ll \Delta E$, the fast component can be written as $\Gamma_S = \gamma_0$. So, at $T = 4.2$ K, the short component directly reflects the bright-to-dark spin-flip rate. Figure 5b shows the short rate as a function of the bright−dark energy splitting. Interestingly, the rates are found to be of the order of 1 ns^{-1}, comparable to those found for spherical core/shell NCs[9,22] and orders of magnitude smaller compared to CdSe colloidal NPLs with similar energy splitting.[36] If the phonons had to be treated as a continuum of states in DiR, the spin-flip rates would be of the order of those in NPLs, in contrast to our

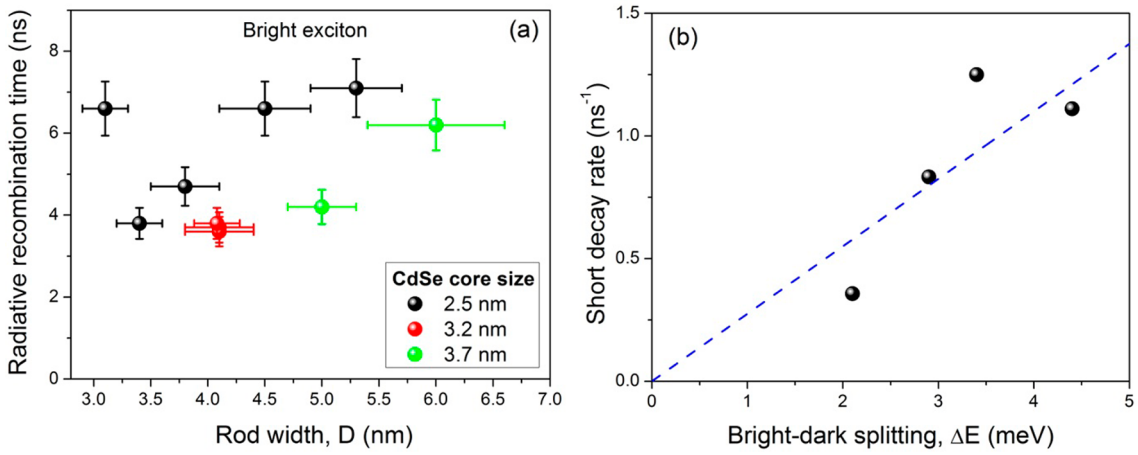

Figure 5. (a) Rod width dependence of the bright exciton radiative recombination time, deduced from the fitting for DiR with various characteristics (See Table 1). (b) Short decay rate at an intensity of $1/e$ in the PL decay as a function of the bright−dark energy splitting for DiR with a 2.5 nm CdSe core diameter (samples **1**−**5**). Dashed line is a linear interpolation.

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experimental results. Therefore, in agreement with a recent publication, our results indicate that the spin-flip in DiR is assisted by confined acoustic phonons.[37] The existence of confined modes in DiR is supported by the experimental results obtained for CdSe nanorods, for which confined acoustic phonon modes, whose energy is given by the rod width only, have been observed.[38] Like in spherical NCs, the bright−dark spin-flip rate in DiR is assisted by confined acoustic phonon modes whose energy is given by the overall thickness of the rod. This assumption is further supported by the lack of rod length dependence on the spin-flip rate, as it was observed in Figure 2d. Despite a change of the rod length by a factor of 2, the short component of the PL decay remains unchanged.

It is noteworthy that the spin-flip rate is dramatically reduced as the shell thickness is increased, that is, ΔE is decreased. This result highlights the possibility to tune the spin-flip rate and concomitantly the bright exciton population at cryogenic temperature through shell thickness engineering. These results suggest an acoustic phonon bottleneck effect in the bright-to-dark spin-flip process of DiR heteronanostructures.

Dark Exciton Recombination Dynamics. While the bright exciton state in DiR has been studied both theoretically[17] and experimentally,[16] the dark exciton state has attracted far less attention. Despite its major role in the recombination dynamics at cryogenic temperatures, the dark exciton recombination in CdSe/CdS DiR has not been studied so far. Here, we report on the influence of the rod parameters (width, length) and core size on the dark exciton lifetime. Figure 6a shows a dramatic shortening of the dark exciton lifetime from ∼250 to ∼70 ns, as the rod width is increased from 3 to 6 nm.

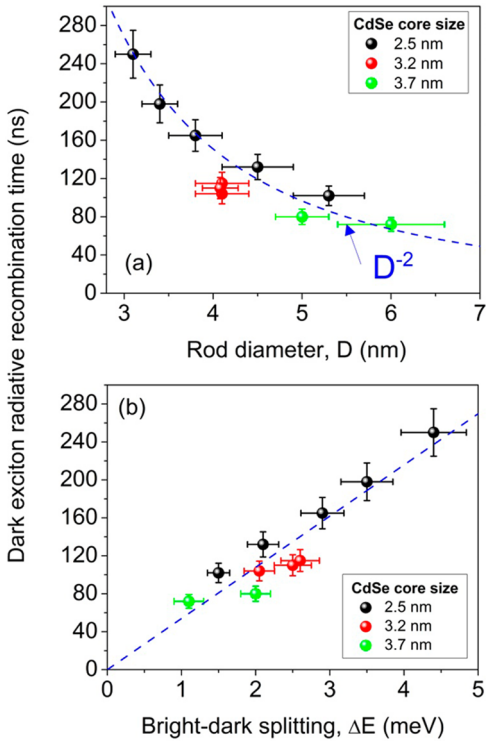

Figure 6. (a) Rod width dependence of the dark exciton radiative recombination time, deduced from the fitting for DiR with various characteristics (Table 1). Dashed line is an inverse square width interpolation. (b) Dark exciton radiative recombination time as a function of the bright−dark splitting. Dashed line is a linear fit.

A polynomial interpolation reveals that, in DiR, the dark exciton radiative recombination time scales with the inverse square width of the rod, that is, as D^{-2}. To the best of our knowledge, previous reports have evidenced that, in spherical NCs, the dark exciton lifetime is compelled by the size of the CdSe core and depends only weakly on the shell material (ZnS, CdS), shell thickness, and so forth.[29,36] Instead, our results indicate that, in DiR, the dark exciton radiative recombination time strongly depends on the rod width regardless of the CdSe core size. This finding is of great importance, since it highlights a new possibility to tune the dark exciton lifetime and provides a new clue to unveil the origin of dark exciton radiative recombination.

As it was stated before, the radiative recombination of the dark exciton is forbidden in the electric-dipole approximation.[30] Therefore, the emission of a photon must be accompanied by a spin-flip of the electron or the hole for conservation of the angular momentum. Previous works have shown that such a spin-flip can be arranged by emission of optical and acoustic phonons.[9,36,39−42] In this regard, the lack of core size dependence observed in DiR clearly shows that the dark exciton recombination is accompanied by an electron spin-flip. If the hole were involved, the dark exciton recombination would not be affected by a modification of the shell shape, since the hole is strongly confined in the CdSe core.

Although such a phonon-assisted mechanism can explain dark exciton radiative recombination, it fails to explain several experimental observations such as the absolute value of the dark exciton lifetime that can vary from less than 100 ns to more than 1 μs depending on the size of the NCs,[9,10,29] the lengthening of the dark exciton lifetime with the magnetic field,[43] or the dark exciton zero phonon line (ZPL) seen in the PL spectra.[19,44] These observations suggest that, in addition to a phonon-assisted mechanism, the radiative recombination of the dark exciton involves a mixing between the dark and the bright exciton states. The origin of this mixing remains however puzzling, and many hypotheses have been stated: surface-assisted process (dangling bonds, surface ligands),[43] paramagnetic defects,[18] and valence band mixing.[45]

It is noteworthy that such a mixing is expected to be stronger when the bright−dark energy splitting is small, in agreement with our experimental results. In Figure 6b, we clearly show that the dark exciton lifetime shortens linearly with ΔE and more importantly does not depend on the CdSe core size. This lack of CdSe core size dependence provides strong evidence that the dark exciton radiative recombination is neither due to defects located in the CdSe core or at the CdSe/CdS interface nor due to a valence band mixing. In both cases, the dark exciton lifetime would not change systematically with increasing shell thickness or varying shell shape.

Interestingly, in DiR, the dark exciton lifetime is more than four times shorter than in spherical nanocrystals having a similar CdSe core size and about the same CdS shell thickness.[23,46] Although similar regarding the core size and the shell thickness, these NCs strongly differ by the nature of the surface experienced by the electron (ligands, dangling bonds). Therefore, the dramatic change in the dark exciton lifetime can reasonably be attributed to a change in the NCs surface. Thus, besides phonon-assisted processes, the radiative recombination of the dark exciton can be mediated by a surface-assisted process. The latter is of great importance, since it allows for explaining the origin of the remaining undisclosed experimental observations such as the dark exciton ZPL on PL

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spectra. Further experimental and theoretical works are needed to get a deeper insight into the surface-assisted process.

CONCLUSION

In conclusion, we have performed temperature-dependent studies of the PL decay of CdSe/CdS DiR nanostructures having various structural properties (core size, rod width, and rod length). By carefully analyzing the long component of the PL decay, we demonstrate that the energy splitting between the bright and the dark excitons scales quadratically with the rod width regardless the core size. This results from the lack of confinement of the electron along the rod length. Besides the ability to control the fine structure energy splitting, we evidence that shape engineering of the shell provides a way to further control spin relaxation among the fine structure levels. Moreover, we demonstrate that, in DiR, the dark exciton lifetime exhibits a strong dependence on the rod width and is significantly reduced compared to spherical nanocrystals. These stimulating results, in combination with the lack of core size dependence of the dark exciton lifetime, point to a radiative recombination of the dark exciton through a surface-induced mixing between the bright and the dark exciton states. These findings reopen the long-standing debate on the origin of the dark exciton radiative recombination and pave the way toward a control of the dark exciton in colloidal nanostructures. This work points out the manifold possibilities to tailor the optical properties of colloidal NCs by shape engineering of the CdS shell. We believe these results will further stimulate experimental and theoretical work to fully capture the origin of exciton recombination in colloidal core/shell nanostructures.

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Notes

The authors declare no competing financial interest.

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