

# Large Blue Shift of the Biexciton State in Tellurium Doped CdSe Colloidal Quantum Dots

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## ABSTRACT

The exciton–exciton interaction energy of tellurium doped CdSe colloidal quantum dots is experimentally investigated. The dots exhibit a strong Coulomb repulsion between the two excitons, which results in a huge measured biexciton blue shift of up to 300 meV. Such a strong Coulomb repulsion implies a very narrow hole wave function localized around the defect, which is manifested by a large Stokes shift. Moreover, we show that the biexciton blue shift increases linearly with the Stokes shift. This result is highly relevant for the use of colloidal QDs as optical gain media, where a large biexciton blue shift is required to obtain gain in the single exciton regime.

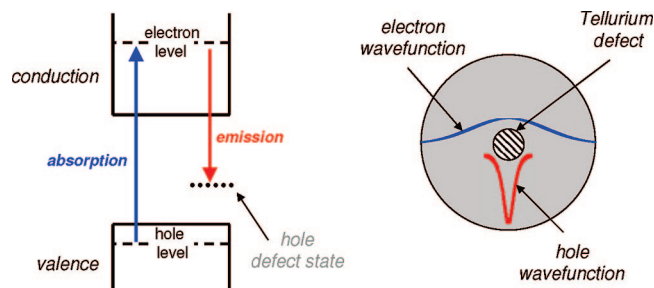
The progress in chemical synthesis of colloidal quantum dots provides a way to produce high quantum yield nanocrystals out of a variety of substances and allows control over their size, shape, and composition. Because of the strong charge confinement within the dots, their electronic excitation spectrum is discrete, with an increased energy gap as compared with its corresponding bulk material. In the strong confinement regime, the band gap is conveniently tuned simply by changing the quantum dot (QD) diameter. This particular property of colloidal small QDs serves as the prime motivation to further investigate and optimize their properties as optical gain media. The first successful attempt to measure optical gain from colloidal QDs<sup>1</sup> showed that, for CdSe, optical amplification requires high power density pumping. This is due to the degeneracy between the exciton (X) and the biexciton (BX) resulting from a small X–X interaction in doubly excited QDs. Since the electronic ground state is doubly degenerate, the threshold for population inversion requires that at least some of the dots are populated with two electron–hole pairs. However, the BX state decays through fast nonradiative Auger recombination, during which one electron–hole pair recombines and transfers its energy to a spectator charge carrier. Thus, in the strong confinement regime, the gain dynamics is dominated by a fast nonradiative decay, which is typically of the order of tens of picoseconds. This system is therefore impractical for achieving sustained gain from QD-based devices. In order to obtain optical gain from singly excited colloidal QDs, it is thus necessary to remove the X–BX degeneracy. In core only QDs, because of the Coulomb correlation term between the two excitons,

the BX state is bound.<sup>2</sup> This implies that the BX is red shifted in energy with respect to the energy of two noninteracting excitons. This red shift is, however, typically  $\leq 30$  meV, which is less than the inhomogeneous line broadening of the X and BX states. Therefore, the degeneracy is effectively not removed.

Recently, it was demonstrated that, in core/shell type II nanocrystals, the core and shell sizes can be changed in order to tune the relative position of the X and BX lines.<sup>3,4</sup> These dots are composed of two different materials with a staggered band diagram,<sup>5</sup> such that the holes tend to localize in one material and the electrons tend to localize in the other. This charge separation leads to a strong Coulomb repulsion that dominates the X–X interaction, resulting in a blue shift of the BX emission line.<sup>3</sup> Such a system was realized experimentally by using CdS/ZnSe core/shell QDs,<sup>4</sup> and a large BX blue shift of 100 meV was measured. This value is large enough to overcome the inhomogeneous broadening of the QDs ensemble. Therefore, the degeneracy is almost completely removed, resulting in a significantly reduced gain threshold. It should be noted, however, that in ref 4 the core and shell parameters and composition were chosen to maximize the BX blue shift<sup>6</sup> while still having a large enough transition moment. Thus, such a system lacks the robustness required for broadband color tunability.

Here, we suggest an alternative way to control the Coulomb repulsion between two Xs inside a QD, by incorporating dopant atoms into a host nanocrystal. This method has already shown to induce large X–X repulsion in an organic–inorganic two-dimensional semiconductor system.<sup>7</sup> Although widely used in bulk semiconductors,

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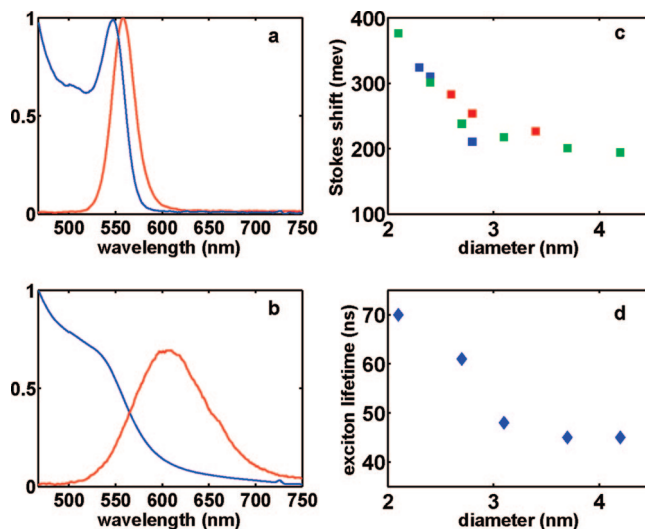


**Figure 1.** Schematics of a doped QD. Left: The energy band structure is composed of the energy structure of the host nanocrystal, plus an additional level which resides inside the host band gap. Right: spatial structure of doped QDs. The electron wave function (blue) width is determined by the size of the host nanocrystal. The hole wave function (red) is spatially localized around the Te defect.

doping of colloidal nanocrystals became a practical possibility only recently. Doped nanocrystals exhibit a large Stokes shift between the absorption edge and their emission, since absorption is determined by the (large) host band gap, while emission is due to defect states inside the gap (see schematic representation in Figure 1). Some successful examples include Mn doped ZnSe,<sup>8,9</sup> Cu doped ZnSe,<sup>10</sup> and Mn doped CdS<sup>11</sup> (see also a review by Norris et al.).<sup>12</sup> Here, we investigate the effect of Te doping on the optical properties of the X and BX states in colloidal CdSe nanocrystals. In analogy to type II CdTe/CdSe QDs where the BX repulsion is due to charge separation,<sup>3</sup> we have chosen to work with doped QDs in which the dopant atoms form a defect state, which spatially localizes only the holes.<sup>13</sup> We show that a few atoms of Te incorporated in each dot can have a significant effect not only on the linear<sup>13</sup> but also on the nonlinear properties of the entire nanocomposite.

The synthesis of Te doped CdSe (CdSe:Te) was performed by following the procedure suggested by Franzl et al.<sup>13</sup> with minor modifications. The QDs were synthesized in a non-coordinating solvent (octadecene) with 3,3-tetradecyl phosphonic acid (TDPA) as a ligand replacing trioctylphosphine oxide (TOPO) and 1-hexadecanamine (HDA) as in ref 13. The Se and Te precursors were dissolved in a single 2 mL TOP solution, with Te percentage ranging from 0–12%, and injected into a vigorously stirred Cd solution at a temperature of 300 °C. The particles were grown at a temperature of 250 °C, and aliquots were taken at several time intervals corresponding to particle diameters in the range 2–4 nm. Further details can be found in Supporting Information.

Typical absorption and emission spectra of a colloidal solution of CdSe:Te 5% (5% Te content in the injected solution) is shown in Figure 2b, along with those of undoped CdSe QDs (Figure 2a) prepared under similar conditions. The emission spectrum was taken using a 405 nm continuous wave (CW) laser, and the absorption measurements were carried with a UV–vis spectrophotometer. The absorption curve shows the first electronic excitation of the QDs at about 540 nm, where for the CdSe:Te 5% QDs (with the same mean size as the undoped CdSe) this peak is partially smeared because of a broader size distribution. The emission of the undoped QDs reveals the familiar emission profile of



**Figure 2.** (a,b) Absorption (blue) and emission (red) spectra of undoped CdSe (a) and CdSe:Te 5% (b) QDs, with similar average diameter. For the doped dots, the absorption peak is smeared because of size inhomogeneity and the band edge emission is substantially broader. (c) Stokes shift vs dot diameter for CdSe:Te 3% (blue), CdSe:Te 5% (green), and CdSe:Te 7% (red) QDs. (d) X lifetime vs dot diameter for the CdSe:Te 5% QDs.

CdSe featuring a small Stokes shift, while the doped CdSe exhibits a large Stokes shift of about 60 nm and a much broader emission distribution. The emission profile shown in Figure 2b for the CdSe:Te 5% is in complete agreement with previous results.<sup>13</sup>

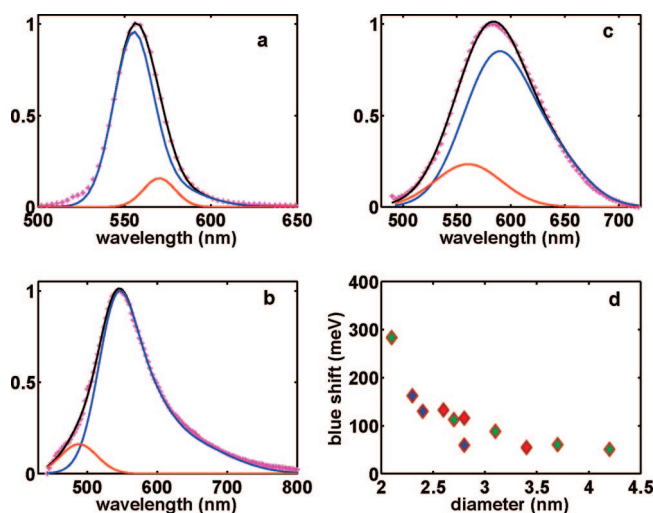
In ref 13, it was shown that, for QDs with a fixed size, the emission wavelength is further red shifted as a function of the amount of Te injected during the synthesis, while the absorption onset remains unchanged. As discussed in ref 13, the red-shifted emission results from a hole trap state inside the CdSe gap, which is caused by few atoms of Te bunched together during the nucleation. The absorption onset is determined by the energy gap of the host material, and its position is hardly affected by the dopant. The size distribution is, however, clearly affected by the introduction of the Te atoms, especially at the early stages of the growth.

In addition to the dependence of the Stokes shift on the amount of Te incorporated into the CdSe QDs, as presented in ref 13, it is interesting to further investigate its dependence on the QDs size. Since the energy level of the hole trap state is expected to weakly depend on size, the Stokes shift should follow the spectral position of the hole ground state in the host nanocrystal. Figure 2c shows the CdSe:Te 5% QD Stokes shift as a function of the dot diameter. For the two largest dots, the absorption peak is smeared, so we define it as the point where the slope of the absorption decreases, after the onset of the band edge absorption. As expected, the Stokes shift decreases as a function of the crystal size. For the 2.1 nm diameter dots (the smallest dots from which band edge, rather than trap state, fluorescence could be measured), the Stokes shift is as high as 380 meV. For large dots (4 nm diameter), it approaches a value of about 180 meV which corresponds to the energy difference between the Te defect level and the bulk CdSe valence band edge. On the same graph, we plot the Stokes shift which results from the

synthesis of QDs with other contents of Te, namely, CdSe:Te 7% (red) and CdSe:Te 3% (blue). As can be seen, a larger Te percentage upon injection results in a somewhat larger Stokes shift. However, we have found that working above 7% of Te is difficult because of the nucleation of pure CdTe QDs.

In order to observe emission dynamics, we excited a dilute QD solution in toluene with 4 ns pulses at 450 nm, at a repetition rate of 10 Hz. The emission was spectrally filtered by a monochromator, and transient emission traces were recorded with a fast detector and a digital oscilloscope. When the excitation level is low enough ( $I_{\text{input}} \ll 1$  photon/pulse/dot) we observe only the X (linear) dynamics. Multiexciton transient spectra were measured at higher photon fluences ( $I_{\text{input}} \gg 1$  photon/pulse/dot). A more detailed description of the set up and the detection scheme can be found elsewhere.<sup>3,14</sup> In Figure 2d, we present measurements of the X lifetime of a colloidal CdSe:Te 5% solution, as a function of the QDs diameter. The results clearly show that for small dots the lifetime decreases as a function of size, while for larger dots it only weakly depends on size, similar to undoped CdSe QDs. Surprisingly, this result is opposite to the lifetime size dependence measured on both type II CdTe/CdSe QDs<sup>3</sup> and on quasi type II CdSe/CdS QDs, where the hole wave function is localized and the electron is extended.<sup>15</sup> In type II QDs, the lifetime increases continuously from about 30 ns for core only QDs to about 150 ns for a 2.5 nm thick shell. In such a core/shell system, the electron wave function is spread over the entire shell, while the hole wave function is almost unaffected by the shell growth, leading to a smaller electron–hole overlap for thicker shells. In the quasi type II case, the wave functions overlap is less sensitive to the shell thickness, and the exciton lifetime increases only slightly with the shell size.<sup>15</sup> The lifetime measurements presented in Figure 2 imply that this picture is not correct in our case. Here, the depth of the Te hole trap is determined by the energy difference between the trap and the host valence band edge, which is by definition the Stokes shift. Thus, as the CdSe particle grows, the hole becomes less localized in the trap. This results in a larger overlap with the electron, despite the fact that the electron is spread over a larger volume. As we show below, this picture is consistent also with the measured BX size dependent spectra.

We now turn to the measurements of the X and BX spectra in CdSe:Te dots. The transient spectra measurements are taken at the peak of the excitation pulse, assuming that the Auger lifetime is much shorter than the pulse duration (as we verify with transient photoluminescence measurements, not shown). Spectra measured at low photon fluence provide the line shape of the X, to which we add a Gaussian peak to numerically fit the width and position of the BX peak in the high power regime. In Figure 3a, we plot the measured transient spectrum of undoped 3 nm diameter CdSe, along with its fit as described above. On top, we plot the break up of the fitted spectrum into its X and BX components. In Figure 3b,c, we plot similar spectra of CdSe:Te 5% QDs with diameters  $d = 2.1$  nm and  $d = 2.7$  nm, respectively. The dots in Figure 3a,c have approximately the same



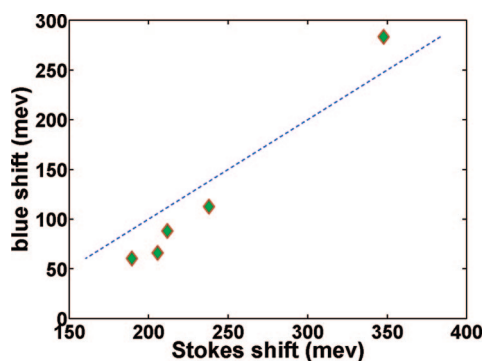
**Figure 3.** BX spectroscopy of CdSe:Te 5% QDs. (a–c) Experimental transient emission spectra are shown in magenta pluses along with its numerical fit (black). We decompose the fit into a low power X profile (blue) and an additional Gaussian peak to account for the BX emission (red). (a) Undoped 3 nm diameter CdSe. (b) 2.1 nm diameter CdSe:Te 5%. (c) 2.7 nm diameter CdSe:Te 5%. (d) BX blue shift vs dot diameter for CdSe:Te 3% (blue), CdSe:Te 5% (green), and CdSe:Te 7% (red) doped QDs. Adding more than 5% Te does not increase the blue shift substantially.

absorption onset (at about 530 nm), while the dots in Figure 3a,b have the same emission peak wavelength of about 540 nm. In agreement with previous reports,<sup>16</sup> the BX line of the undoped CdSe QDs is found to be about 30 meV red shifted compared with the X peak. In contrast, we have found that, for a CdSe:Te 5% QDs, the BX is substantially blue shifted. In fact, for the smallest dot (see Figure 3b) at the peak wavelength of the X emission, the BX content is vanishingly small. In Figure 3d, we plot the BX blue shift as a function of the dot diameter. As can be seen, the blue shift is larger for small QDs, approaching a remarkably large value of 300 meV, where for larger dots it saturates at about 50 meV. The BX blue-shift values of the CdSe:Te 7% and CdSe:Te 3% are plotted as well on Figure 3d, where it is seen that working above 5% Te content does not significantly improve the results.

This extraordinary blue shift is of the same order as the Te defect state offset (Stokes shift), and is explained by strong charge confinement around the Te atoms. The blue shift of the smaller dots is even larger than that of an optimized type II system<sup>4</sup> and therefore indicates a much stronger confinement of the holes. This leads to a huge unscreened local electric field which Stark shifts the BX energy level.

The size dependence of the BX blue shift shown in Figure 3d resembles that of the Stokes shift shown in Figure 2c. Following the arguments given to explain the size dependence of the X lifetime, a large Stokes shift implies a narrower hole wave function. Since the Coulomb repulsion between the holes is determined by the local positive charge density, we expect the blue shift to be an increasing function of the Stokes shift. In Figure 4, we plot the BX blue shift versus the corresponding Stokes shift. The dashed blue line





**Figure 4.** BX blue shift as a function of the Stokes shift for CdSe:Te 5% doped QDs. Green diamonds: experimental data. Dashed blue line: Stokes shift minus 100 meV as a function of the Stokes shift itself. The blue shift roughly follows the size dependence of the Stokes shift, with an additional offset of about  $-100$  meV.

represents the Stokes shift minus 100 meV as a function of the Stokes shift itself and is plotted as a guide. The dependence of the blue shift on the Stokes shift is roughly linear with a slope of about unity, implying that the BX repulsion is pinned to the Stokes shift. The agreement between the guide and the measurements suggests that, independently of size, the BX level always lies approximately 100 meV below the host valence band edge. In other words, the holes in the BX state are weakly localized to the same extent, independent of the dot diameter. It is important to note that, unlike type II QDs<sup>6</sup> for CdSe:Te QDs, the BX blue shift cannot be calculated simply by using perturbation theory. Since the BX Coulomb repulsion we measure is of the same order as that of the Stokes shift (see Figure 4), the wave functions of the holes in the X and BX states differ significantly. This has to be treated self-consistently in order to theoretically account for the large value of the BX blue shift. Thus, we believe that an exact description of such a system, in which one charge carrier is spatially confined to a defect state inside the gap, poses a highly relevant theoretical question.

Although the BX blue shifts we have measured in CdSe:Te QDs are huge, these dots exhibit a broader emission line than undoped CdSe QDs prepared by the same method (compare Figure 2a,b). As is evident from the broadening of the absorption peaks (see Figure 2b) this inhomogeneous broadening is partially the result of a broad size distribution of the CdSe host QDs. In addition, fluctuations in the number of Te atoms in each dot and their specific location inside the dot may contribute to this inhomogeneity as well. Similar to the results presented in ref 4 for type II CdS/ZnSe, the

results presented here show only a partial removal of the X–BX degeneracy. However, this degeneracy can be more efficiently removed either by an improved synthetic procedure or by choosing different materials and morphology.

To conclude, we have performed a multiexciton analysis of Te doped CdSe QDs. Unlike core only QDs, we showed that the BX is blue shifted with respect to the X emission line. Moreover, we found that the BX blue shift is linearly proportional to the Stokes shift with a slope of approximately unity. Our results imply that pushing the defect state deeper inside the gap will further increase the Coulomb repulsion between the holes in a BX state. Another surprising property of Te doped CdSe QDs is that their BX blue shift as well as their X lifetime reveals an opposite size dependence than that of an analogous type II system. In doped QDs, the small size of the defect can lead to an extremely large Coulomb repulsion of about 300 meV, which is of the order of the band offsets. This regime is dramatically different than that observed in core/shell particles, opening new possibilities of controlling X–X in quantum confined systems.

**Supporting Information Available:** Synthesis of CdSe:Te 5%. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H.-J.; Bawendi, M. G. *Science* **2000**, *290*, 314.
- (2) Banyai, L.; Koch, S. W. *Semiconductor Quantum Dots World Scientific*, 1993.
- (3) Oron, D.; Kazes, M.; Banin, U. *Phys. Rev. B* **2007**, *75*, 035330.
- (4) Klimov, V. I.; Ivanov, S. A.; Nanda, J.; Achermann, M.; Bezel, I.; McGuire, J. A.; Piryatinski, A. *Nature* **2007**, *447*, 441.
- (5) Sungjee, K.; Fisher, B.; Eisler, H.-J.; Bawendi, M. *J. Am. Chem. Soc.* **2003**, *125* (38), 11467.
- (6) Piryatinski, A.; Ivanov, S. A.; Tretiak, S.; Klimov, V. I. *Nano Lett.* **2007**, *7*, 108.
- (7) Fujisawa, J.-I.; Ishihara, T. *Phys. Rev. B* **2004**, *70*, 205330.
- (8) Pradhan, N.; Peng, X. *J. Am. Chem. Soc.* **2007**, *129*, 11.
- (9) Norris, D. J.; Yao, N.; Charnock, F. T.; Kennedy, T. A. *Nano Lett.* **2001**, *1*, 1.
- (10) Pradhan, N.; Goorskey, D.; Thessing, J. Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 17586.
- (11) Nag, A.; Sarma, D. D. *J. Phys. Chem. C* **2007**, *111*, 37.
- (12) Norris, D. J.; Efros, A. L.; Erwin, S. C. *Science* **2008**, *319*, 28.
- (13) Franzl, T.; Müller, J.; Klar, T. A.; Rogach, A. L.; Feldmann, J.; Talapin, D. V.; Weller, H. *J. Phys. Chem. C* **2007**, *111*, 2974.
- (14) Oron, D.; Kazes, M.; Banin, U. *Phys. Rev. B* **2006**, *74*, 115333.
- (15) Zeng, Q.; Xianggui, Q.; Yajuan, S.; Youlin, Z.; Langping, T.; Jialong, Z.; Hong, Z. *J. Phys. Chem. C* **2008**, *112*, 8587–8593.
- (16) Woggon, U. In *Optical Properties of Semiconductors and Their Nanostructures*; Kalt, H., Hetterich, M., Eds; Springer-Verlag: Berlin, 2004.

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