Highly Luminescent Water-Soluble CdTe Quantum Dots

Sander F. Wuister,* Ingmar Swart, Floris van Driel, Stephen G. Hickey, and Celso de Mello Donegá

Debye Institute, Chemistry of Condensed Matter, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands

ABSTRACT

Colloidal CdTe quantum dots prepared in TOP/DDA (trioctylphosphine/dodecylamine) are transferred into water by the use of amino–ethanethiol•HCl (AET) or mercaptopropionic acid (MPA). This results in an increase in the photoluminescence quantum efficiency and a longer exciton lifetime. For the first time, water-soluble semiconductor nanocrystals presenting simultaneously high band-edge photoluminescence quantum efficiencies (as high as 60% at room temperature), monoexponential exciton decays, and no observable defect-related emission are obtained.

Research on semiconductor nanocrystals (NCs), also known as quantum dots (QDs), has increased rapidly in the past few decades.[1] The size dependence of their electronic and optical properties is one of the unique features of semiconductor NCs,[2] turning them into promising materials for a number of optical applications.[3,4] In particular, semiconductor QDs are very attractive as biological labels,[5,6] because of their small size, emission tunability, superior photostability and longer photoluminescence (PL) decay times in comparison with dyes.[5,6] One of the major challenges is to obtain water-soluble QDs with a high PL quantum efficiency (QE). Three different approaches have been used to obtain water-soluble semiconductor QDs: ligand-exchange,[7–11] encapsulation into a water-soluble shell (e.g., the silica[12] or phospholipids[13]) and arrested precipitation in water.[14–17] The ligand exchange method has been applied to highly luminescent (QE ≥ 50%) CdSe(ZnS),[6,11,12] CdSe(CdS),[5] or CdTe[10] QDs prepared in hot coordinating solvents, yielding water-soluble NCs with a lower QE (∼10−30%[5,10,11]). In the case of CdSe QDs the emission has been observed to be completely quenched after transfer into water, if no shell of a wider band gap material is used.[10] The encapsulation of the QDs into a water-soluble shell typically yields PL QEs of 20−30%.[12,13] Both of the above-mentioned methods for transferring QDs into water involve several steps and thus have the additional disadvantage of being rather complicated and time-consuming. Arrested precipitation in water in the presence of stabilizers (e.g., thiols) is a faster and simpler method to synthesize water-soluble QDs and has been applied to several semiconductors potentially relevant to biolabeling (e.g., CdS,

CdSe, CdTe[14−18]). For CdS[14,15] and CdSe,[16] this yielded NCs with defect-related emission and a low QE. For CdTe QDs,[17,18] both excitonic and defect-related emission bands were observed, and, although samples with no observable trap luminescence were also obtained[17], the typical PL QEs were only 3%−10%.[17] After post-preparative treatment, QEs up to ∼40% were obtained.[17] A strategy to prepare highly efficient (QE ≥50%) water-soluble QDs is thus still lacking.

In this letter we report a novel method that yields highly luminescent water-soluble CdTe QDs, either with a positive or negative surface charge, with no observable defect emission and monoexponential exciton decay.

First, highly luminescent CdTe QDs (QE up to 45%) were synthesized in a mixture of TOP/DDA (trioctylphosphine/dodecylamine) by a modified version of the method reported by Talapin et al.[19,20] A mixture of DDA (10 g) and TOP (7 mL) was heated to 50 °C. A 0.22 g portion of $Cd(Me)_2$ in 7 mL TOP and 0.16 g of Te powder (grain size <250 μm) were then added to the mixture, and the temperature was gradually raised to either 145 °C, 165 °C, or 180 °C, and then kept constant for a few hours, yielding green, yellow, or orange emitting NCs with QEs of up to 45% at room temperature. The CdTe QDs thus prepared were then transferred into water by exchanging the TOP/DDA molecules for amino-ethanethiol•HCl (AET) or mercaptopropionic acid (MPA), as described below.

To prepare CdTe NCs with a positively charged capping, 100 μL of the crude solution of CdTe QDs (with a QE of 48%) in the TOP/DDA coordinating mixture was dissolved in 5 mL chloroform. Subsequently a 0.5 M methanolic solution of AET was added until the particles flocculated. Directly after the flocculation, ultrapure water (16 MΩ·cm)

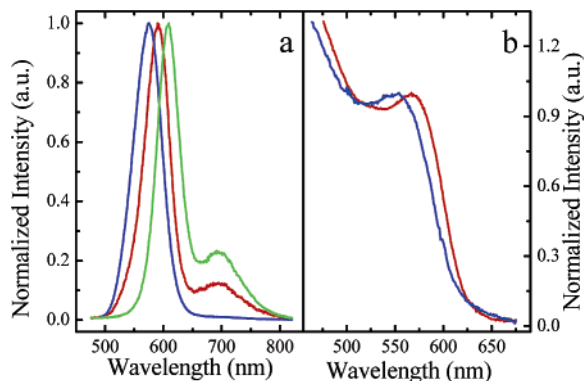* Corresponding author: Phone +31-30-2532207. Fax +31-30-2532403. E-mail: S.F.Wuister@phys.uu.nl.

Figure 1. (a) Emission spectra (λ_{ex} = 450 nm) and b) absorption spectra of TOP/DDA-capped CdTe NCs in chloroform (red), after addition of 140 μL of 0.5 M AET in methanol (green) and after transfer into water (blue).

Figure 2. (a) Emission spectra (λ_{ex} = 490 nm) and (b) absorption spectra of TOP/DDA-capped CdTe NCs in chloroform (red) and after transfer into water with the use of MPA (blue).

was added to the suspension, resulting in a two-phase system (water above chloroform). Upon shaking, the NCs were transferred into the water phase.

To prepare negatively charged MPA capped water-soluble CdTe NCs, a similar procedure was used, but adding a 0.05 M methanolic solution of MPA−KOH (with 20 mol % excess of KOH) instead of an AET solution. The KOH solution was added to the MPA solution in order to deprotonate the carboxylic groups of MPA. A different batch of TOP/DDA-capped CdTe NCs, with a lower QE (9%), was used in order to see the effect of QE improvement by the thiol capping for particles with a lower efficiency. The preparation of TOP/DDA-capped CdTe NCs and their subsequent transfer into water was performed under argon or nitrogen. No post-preparative steps were required to clean up the CdTe QDs solution, since TOP and DDA stay in the chloroform phase rather than in the water phase.

Emission spectra were measured at room temperature using a SPEX Fluorolog spectrofluorometer, equipped with two monochromators (double-grating, 0.22 m, SPEX 1680, model F2002) and a 450 W xenon lamp as the excitation source. A Princeton Instruments liquid nitrogen cooled CCD camera was used to detect the luminescence spectra. Absorption spectra were recorded on a Perkin-Elmer Lambda 16 UV/vis spectrometer. Luminescence lifetime measurements were performed with a Pico Quant picosecond laser (λ_{ex} = 406 nm, 2.5 MHz repetition rate) and monochromator (0.1 m focal length, 1350 lines mm^{-1} grating, blazed at 500 nm) in combination with a fast Hamamatsu photomultiplier tube (H5738P-01) for light detection. Luminescence decay curves were obtained by pulse height analysis using a Time Harp 100 computer card. Quantum efficiencies of the samples were determined using commercial laser dyes as standards (Rhodamine B and Coumarine 153, QE = 90%), as described in detail elsewhere.[21]

Figure 1a shows the emission spectra of a sample of TOP/DDA-capped CdTe NCs in chloroform (red curve, optically clear solution), after addition of 140 μL of a 0.5 M methanolic solution of AET (green curve, turbid suspension), and after transfer to water (blue curve, optically clear solution). The AET-capped CdTe QDs in water are charge-
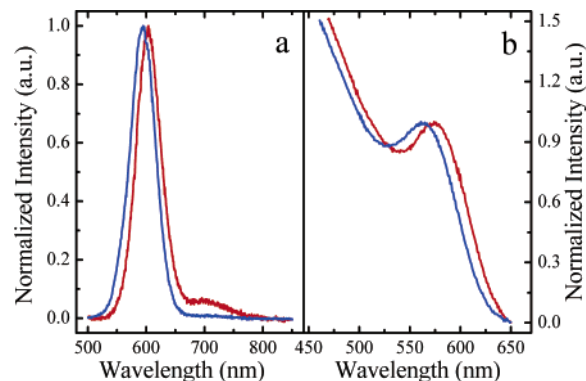
stabilized by a positive surface charge, since the dissociated AET molecules have an NH_3^+ group. Figure 2a shows the emission spectra of TOP/DDA-capped CdTe NCs in chloroform (red curve, optically clear solution) and after transfer into water (blue curve, optically clear solution) by ligand exchange with MPA (negatively charged NCs). The absence of light scattering (optically clear solution) after transfer into water indicates that the clusters of QDs, which were causing the turbidity, fully redisperse in water as individual QDs. The low PL intensity of the flocculated MPA-capped CdTe QDs in chloroform prevented the measurement of emission spectra (Figure 2) or luminescence decay curves (Figure 5, see below) for this sample.

The CdTe QDs in chloroform present two emission peaks. The narrower peak at higher energy is ascribed to the exciton radiative recombination (band-edge PL), and the broader peak at lower energy is attributed to radiative recombination at defects (trap emission). The relative intensity of the trap emission increases as AET is added to the CdTe QDs in chloroform (Figure 1a, green curve). Moreover, a red shift (61 meV) in the band-edge PL is also observed. The changes observed after the addition of AET can be ascribed to clustering of the QDs due to the modification of the surfactant shell. Since the Cd−thiol bond is much stronger than the Cd−amine bond, AET will replace the TOP/DDA capping molecules of the CdTe QD as soon as it is added. DDA stabilizes the CdTe NCs sterically, while AET-capped dots are surface charged and therefore charge stabilized in polar media. Since chloroform is not polar enough, the AET-capped CdTe QDs will tend to aggregate in chloroform. It must be emphasized that aggregation takes place only when AET or MPA is used. The addition of the same amount of pure methanol does not induce any observable flocculation of the colloidal suspension of DDA−TOP-capped CdTe QDs in chloroform.

It has been shown that energy transfer can occur between semiconductor QDs.[22,23] Smaller dots in the excited state can transfer their excitation energy to nearby larger dots in the ground state. The efficiency of this process is strongly dependent on the donor−acceptor distance. In view of the fact that the transitions involved have an electric dipole character, energy transfer via dipole−dipole interaction and
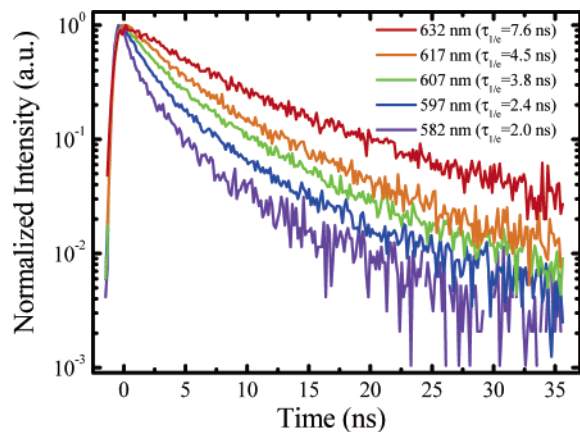
Figure 3. Luminescence decay curves taken at different emission wavelengths for TOP/DDA-capped CdTe NCs in chloroform, flocculated after addition of 130 μL 0.5 M AET in methanol (λ_{ex} = 406 nm). $\tau_{1/e}$ is the time at which the PL intensity has decreased to 1/e of its initial value.

Figure 4. Luminescence decay curves (λ_{ex} = 406 nm, measured at the maximum of the exciton emission peak) of TOP/DDA-capped CdTe QDs in chloroform (red), after addition of 140 μL 0.5 M AET in methanol (green) and after transfer into water (blue).

a R^{-6} distance dependence is expected.[24] Upon aggregation the average inter-QD distance becomes much shorter. Consequently, efficient energy transfer from the smaller NCs (higher energy emission) to the larger NCs in the ensemble (lower energy emission) can take place. This explains the red shift observed in the emission spectrum of the CdTe dots after the flocculation induced by the addition of AET.

The increase of the relative intensity of the trap emission in the spectra of the CdTe QDs after the addition of AET can also be explained by the aggregation of the NCs and the accompanying increase of the inter-QD energy transfer rates. Trapping of the exciton at a defect leads to localization of at least one of the charge carriers and to energy relaxation and therefore prevents the QD from transferring its excitation energy to a neighboring QD, since the resonance condition is no longer fulfilled. Therefore, when a smaller QD with exciton emission transfers its excitation energy to a larger QD with a defect-related emission, further energy transfer will be hindered, resulting in a relative increase of the defect related emission accompanied by a decrease in the quantum efficiency.

The energy transfer from the smaller to the larger QDs is also reflected in the lifetimes of the exciton emission. Figure 3 shows the luminescence decay curves of a sample of flocculated CdTe NCs in chloroform (with 130 μl AET solution in methanol added) as a function of the emission wavelength (λ_{max} = 607 nm). The time at which the PL intensity has decreased to 1/e of its initial value ($\tau_{1/e}$) is used as a parameter to compare the lifetimes. The lifetime becomes shorter and the exciton decay more nonexponential upon shifting the detection to higher energies (smaller dots). The shortening of the lifetime for smaller dots is expected because an extra path for depopulating the excited state is created. Since energy transfer happens at a different (faster) rate than the decay of the exciton and a distribution of inter-QD distances is present, a multiexponential decay is expected. By shifting the detection to the lower energy side of the emission peak the PL decay of the larger QDs in the ensemble is probed and the contribution of the energy transfer
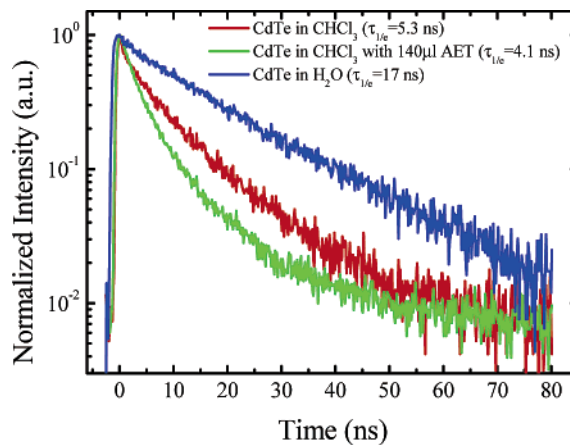
rates are reduced. This results in both a longer lifetime and a less nonexponential decay for the exciton luminescence.

Upon transferring the CdTe NCs into water using either AET (Figure 1a) or MPA (Figure 2a), the trap emission is no longer observable, indicating that surface defects, rather than lattice defects, must be responsible for trapping the exciton. Furthermore, upon transfer to water a blue shift (of about 120 meV) of the exciton emission is observed with respect to the dots in chloroform. A comparable shift is also observed in the absorption spectra (Figure 1b and Figure 2b). Talapin et al. have also reported a blue shift in the absorption and luminescence spectra when allylamine was added to TOPO-capped CdSe NCs.[8] Surface molecule exchange for TOP/DDA-capped CdTe QDs with hexanethiol in chloroform (not shown) results in a comparable blue shift in the emission and absorption spectra. This fact indicates that neither the change in solvent nor the charge of the surface molecules can be responsible for the blue shift. Also, photooxidation, which can result in a blue shift of the exciton emission of the CdTe nanocrystals due to the decrease of the particle size, is not expected since both preparation and surface exchange were performed under inert atmosphere. A possible explanation may be that the stronger bond between the thiol and the Cd atoms at the CdTe NC surface, as compared to the amine-Cd bond, induces a redistribution of electronic density and an increase in confinement energy. Further research is required to clarify the origin of the blue shift.

Figure 4 shows the decay curves of the exciton emission of TOP/DDA-capped CdTe QDs in chloroform (before and after AET addition) and of the AET-capped CdTe QDs in water. Figure 5 shows the decay curves of the exciton emission for TOP/DDA-capped CdTe QDs in chloroform and for MPA-capped CdTe QDs in water. After the AET addition, the lifetime decreases and becomes dependent on the emission wavelength, as discussed above. In contrast, transfer into water results in a longer lifetime and a monoexponential exciton decay accompanied by an increase in the PL quantum efficiencies, for both AET- and MPA-capped CdTe NCs. This implies that inter-QD energy transfer is no longer efficient, confirming that the CdTe QDs are fully
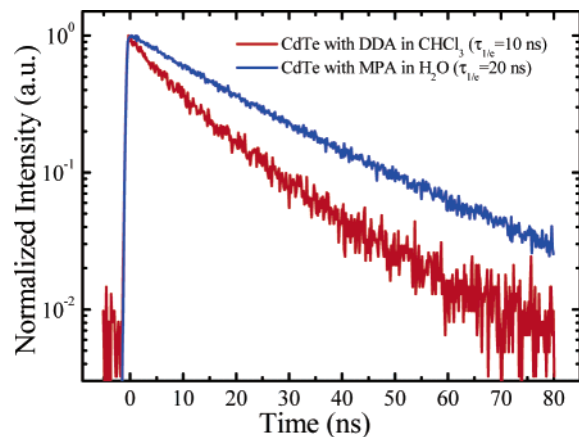
Figure 5. Luminescence decay curves (λ_{ex} = 406 nm, measured at the maximum of the exciton emission peak) of TOP/DDA-capped CdTe NCs in chloroform (red) and after transfer into water with the use of MPA (blue).

dispersed in water as individual nanocrystals rather than clusters. Furthermore, the results show that the contribution of nonradiative processes to the exciton decay is significantly reduced after transfer to water. This indicates that the concentration of surface defects is reduced and/or that the exciton trapping at surface defects is less efficient as a consequence of the new capping layer. The AET- and MPA-capped CdTe particles are stable in water under nitrogen for months, without any indication of aggregation or photodegradation. However, the samples can photodegrade within a day in air.

The exciton decay behavior observed in the present work for CdTe NCs differs markedly from the results reported by Kapitonov et al.[25] for 1-thiolglycerol-capped CdTe nanoparticles. The exciton decay curves of the TOP/DDA-capped CdTe NCs observed in the present work are slightly nonexponential, while Kapitonov et al.[25] reported a strongly nonexponential decay, that was analyzed assuming an extremely broad distribution in lifetimes. The difference in the decay kinetics can be explained by the fact that the PL QE of the 1-thiolglycerol-capped CdTe nanoparticles investigated by Kapitonov et al. is much lower ($\sim$3%)[25] than that of the TOP/DDA-capped CdTe QDs prepared in this work (up to 45%). The contribution of the nonradiative decay is thus larger for the CdTe QDs capped with 1-thiolglycerol than for those capped with TOP/DDA.

The PL QE increases from 48% for the TOP/DDA-capped CdTe NCs in chloroform to 59% for the AET-capped nanoparticles in water. The PL QE of the MPA-capped nanoparticles increased from 9% to 22%. The relative increase of the PL QE for TOP/DDA-capped CdTe samples with a low initial QE is larger than for samples with a high initial QE. The efficiency of the water-soluble QDs is dependent on the quality and PL QE of the original TOP/DDA-capped CdTe QDs, but an increase in QE upon transfer to water is observed for both AET- and MPA-capped NCs. The increase in PL QE is consistent with the increase of the exciton lifetime discussed above. The fact that even samples with a PL QE of 22% present a monoexponential exciton decay suggests that the emitting NCs in the ensemble have

a very high QE. Since the total QE is only 22%, the rest of the ensemble must consist of weakly luminescent ("dark") NCs. This is consistent with the observations reported by Ebenstein et al.[26] from the investigation of CdSe(ZnS) NCs with an ensemble QE of 48% by correlated atomic force and fluorescence microscopy. The results revealed that the ensembles consisted of highly luminescent (QE close to 100%) and "dark" CdSe(ZnS) QDs.

Talapin et al.[10] recently reported the transfer of TOP/DDA-capped CdTe NCs into water by using *N,N*-dimethyl-2-mercaptoethylammonium chloride. In contrast to the results reported here, the PL QE was observed to decrease from 30 to 65% to 13−18% after transfer into water.[10] Their method differs from ours in two key aspects. First, we used an aminothiol with a primary amine instead of a tertiary amine. This might affect both the ligand exchange efficiency and the packing density at the NC surface. Second, in the present method the TOP/DDA-capped CdTe NCs were not directly transferred into water but were first flocculated with an aminothiol in the absence of water. The aggregated nanoparticles were subsequently transferred to water with the aminothiol ligands already attached to the CdTe NCs surface, thus strongly reducing the interaction between the water molecules and the CdTe surface. The NC surface might be particularly vulnerable during the ligand exchange itself, since some of the coordinating surface sites might be temporarily accessible to water molecules competing with the new ligand. This might, together with a lower crystallinity,[17] be the reason for the low initial QE for CdTe nanocrystals prepared directly in water by arrested precipitation, since in this case a strong competition between the thiol and the water molecules for the CdTe surface sites can be expected.

Water-soluble CdTe QDs (positively and negatively charged) with a monoexponential exciton emission decay ($\tau_{1/e}\sim$ 20 ns) and a high PL QE (up to 60%) have been reported in this paper. QDs with a monoexponential decay offer advantages in studies of QDs in photonic crystals and in energy transfer processes in biological systems where QDs can act as donors. If energy transfer takes place, the decay time of the coupled donor decreases and can be used to accurately determine the energy transfer rate between the QD and an acceptor (viz. another QD or dye). The method reported here is also very attractive for its simplicity compared to other methods for producing water-soluble semiconductor QDs.[12,13,27,28] It also yields water-soluble NCs with photophysical properties superior to those presented by NCs prepared directly in water via arrested precipitation[17,18] (viz. a higher QE associated with a monoexponential exciton decay and no defect-related luminescence).

References

(1) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226−13239.

(2) Brus, L. E. J. *Chem. Phys.* **1986**, *90*, 2555−2560.

(3) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354−357.

(4) 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*, 314−317.

(5) Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; A. Alivisatos, A. P.; *Science* **1998**, *281*, 2013−2016.

(6) Chan W. C. W.; Nie, S. *Science* **1998**, *281*, 2016−2018.

(7) Murray, C. B.; Norris, D. B.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(8) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1*, 207−211.

(9) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333−337.

(10) Talapin, D. V.; Rogach, A. L.; Mekis, I.; Haubold, S.; Kornowski, A.; Haase, M.; Weller, H. *Colloids Surf. A* **2002**, *202*, 145−154.

(11) Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142−12150.

(12) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. *J. Phys. Chem. B* **2001**, *105*, 8861−8871.

(13) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759−1762.

(14) Sondi, I.; Siiman, O.; Koester, S.; Matijevic, E. *Langmuir* **2000**, *16*, 3107−3118.

(15) Winter, J. O.; Liu, T. Y.; Korgel, B. A. Schmidt, C. E. *Adv. Mater.* **2001**, *13*, 1673−1677.

(16) Rogach, A. L.; Kornowski, A.; Gao, M.; Eychmueller, A.; Weller, H. *J. Phys. Chem. B* **1999**, *103*, 3065−3069.

(17) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Hoppe, K.; Shevchenko, E. V.; Kornowski, A.; Eychmueller, A.; Weller, H. *J Phys. Chem. B* **2002***, 106*, 7177−7185.

(18) Wang, S.; Mamedova, N.; Kotov, N. A.; Chen, W.; Studer, J. *Nano Lett.* **2002**, *2*, 817−822.

(19) Talapin, D. V.; Haubold, S.; Rogach, A. L.; Kornowski, A.; Haase M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 2260−2263.

(20) Wuister, S. F.; Driel van F.; Meijerink A. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1253−1258.

(21) de Mello Donega, C.; Hickey, S. G.; Wuister, S. F.; Vanmaekelbergh, D.; Meijerink, A. *J. Phys. Chem. B* **2003**, *107*, 489−496.

(22) Kagan, C. R.; Murray, C. B.; Nirmal, M.; Bawendi, M. G. *Phys. Rev. Lett.* **1996**, *76*, 1517−1520.

(23) Crooker, S. A.; Hollingsworth, J. A.; Tretiak, S.; Klimov, V. I. *Phys. Rev. Lett.* **2002**, *89*, 186802/1−4.

(24) Henderson, B.; Imbusch, G. F. Optical Spectroscopy of Inorganic Solids, Clarendon Press: Oxford, 1989, 448.

(25) Kapitonov, A. M.; Stupak, A. P.; Gaponenko, S. V.; Petrov, E. P.; Rogach, A. L. Eychmüeller, A. *J. Phys. Chem. B* **1999**, *103*, 10109−10113.

(26) Ebenstein, Y.; Mokari, T.; Banin U. *Appl. Phys. Lett.* **2002**, *80*, 4033−4035.

(27) Schroedter, A.; Weller, H.; Eritja, R.; Fordand, W. E.; Wessels, J. M. *Nano Lett* **2002**, *2*, 1363−1367.

(28) Pathak, S.; Choi, S. K.; Arnheim, N.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4103−4104.