

Luminescence of CdTe nanocrystals

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Abstract

The growth of highly luminescent CdTe nanocrystals synthesized in a mixture of tri-octylphosphine and dodecylamine was investigated. The CdTe nanocrystals grow in time to a constant size which is dependent on the reaction temperature. In the initial stage of the growth particles show a broad defect emission band which is replaced by an efficient excitonic emission after a few minutes of growth. Quantum yields up to 45% were obtained. The life time of the exciton emission increases with quantum yield and reaches a constant value of about 10 ns for the most efficient particles. The life time increase is explained by the reduction of the (fast) non-radiative decay for samples with a higher quantum yield. In CdTe samples aged at room temperature sharp absorption peaks at discrete energies were observed. These were ascribed to small clusters of CdTe which form at room temperature from unreacted precursors.

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1. Introduction

In the last 20 years considerable progress has been made in both fundamental [1] and applied research (e.g. biological labeling [2,3]) of semiconductor nanocrystals (or quantum dots). Due to quantum size effects [4] the band gap can be tuned over a wide energy range without a change of chemical composition. Since the nanocrystals have a large surface to volume ratio, the passivation of the surface is important. A well passivated surface leads to excitonic emission with high quantum efficiencies. The development of the tri-octylphosphine/tri-octylphosphine oxide (TOP/TOPO)

synthesis method [5] made an important step on the way to monodispers, high quality CdSe nanocrystals with efficient excitonic emission. After this further improvement has been made to obtain highly efficient nanocrystals e.g. inorganically overcoated dots (CdSe(ZnS)) [6,7] and alkylamine coated dots (TOPO/hexadecylamine (HDA)) [8,9]. Most of this work was done on CdSe but recently also CdTe quantum dots were synthesized by the use of thiols [10]. CdTe quantum dots with both exciton and defect emission with an quantum efficiency up to 18% were obtained [11]. More recently a high temperature synthesis was developed yielding CdTe quantum dots with quantum efficiencies up to 65% in a mixture of TOP and dodecylamine (DDA) [12]. The growth of CdTe (prepared in a mixture of TOP and DDA) quantum dots is studied in this paper at three different temperatures. The growth was monitored by taking

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samples at regular intervals. Samples were examined with spectroscopic techniques like emission, absorption and luminescence life time measurements.

2. Experimental section

2.1. Materials

Dimethylcadmium (99.9%) was purchased from ARC Technologies. Dodecylamine (DDA; 98%), Tri-octylphosphine (TOP; techn. 90%) and anhydrous toluene were purchased from Aldrich. DDA was dried for several hours under vacuum at 100°C before use. Tellurium (99.999%, <250 µm) was purchased from Heraeus.

2.2. Synthesis

CdTe quantum dots were prepared via a method similar to the one described by Talapin et al. [12]. In general the reaction times, precursor concentrations and temperatures are lower [12].

In a three necked flask 10 g of dry DDA and 7 ml of TOP were heated to 50°C. To this solution 0.22 g (1.54 mmol) Cd(Me)₂ in 7 ml of TOP and 0.16 g (1.25 mmol) Te powder were added. A Cd/Te ratio of about 1.25 was used in all the syntheses performed unless a different ratio is indicated. The reaction mixture was heated to 145°C, 165°C and 180°C. To follow the particle growth in time for these temperatures, samples of about 0.5 ml were taken at regular time intervals during the growth of the quantum dots and stored in 3 ml toluene. Excess of Cd and Te was not removed during storage. The point where the reaction mixture turned from gray to green during heating (which was at about 135°C) was set as $t=0$ min. This was the point where the tellurium starts to dissolve and the TOP–Te complex was formed [13].

2.3. Apparatus

Emission spectra were recorded on 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. Absorption spectra were measured using a Perkin-Elmer Lambda 16 UV/vis spectrometer. Luminescent life time measurements were performed with a Pico Quant picosecond laser ($\lambda_{\text{ex}}=406$ nm, 2.5 MHz) and monochromator (1350 lines mm⁻¹ grating, blazed at 500 nm) with a fast Hamamatsu photo-multiplier tube (H5738P-01) for light detection. Luminescence decay curves were obtained by pulse height analysis using a Time Harp 100 computer card. Quantum efficiencies were measured against commercial Rhodamine B with a known quantum efficiency of 90%. The emission spectra were corrected for reabsorption by dividing the emission spectra by the (for the path length corrected) transmission spectrum.

3. Results and discussion

Fig. 1a shows the absorption spectra (normalized to the first absorption maximum) of samples of CdTe QDs taken at different time intervals for a reaction temperature of 165°C. At the indicated times a sample was taken from the top of hot reaction mixture and diluted into 3 ml of toluene. Fig. 1b shows the emission spectra (normalized to λ_{max}) of these CdTe samples. Hardly any defect related emission is observed in the emission spectra of fresh samples. After several days a weak defect related emission was detected around 600 nm. The absorption and emission spectra show a red shift during the reaction. This indicates the particle growth with time.

In order to understand what happens during the first minutes of growth samples were taken at very short time scales after the TOP–Te complex was visibly formed. In Fig. 2a emission spectra (normalized to λ_{max}) of CdTe QDs in toluene are shown. These are samples synthesized at the same temperature as in Fig. 1 ($T=165^\circ\text{C}$) but taken on a shorter timescale. The first samples contained particles that show a broad emission peak around 600 nm. The low quantum efficiency (< 1%) and long, non-exponential luminescence lifetime ($\tau_{1/e} \sim 200$ ns, for the exponential tail, see Fig. 2b) are characteristic of a defect-related emission. This

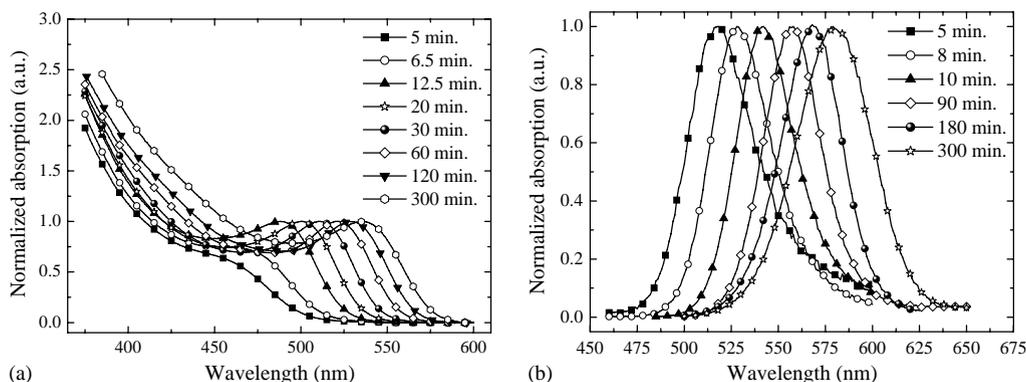


Fig. 1. (a) Absorption spectra (normalized to the first absorption maximum) and (b) emission spectra (normalized to the emission maximum, $\lambda_{\text{ex}} = 400$ nm) of CdTe QDs (diluted in anhydrous toluene) taken for a synthesis at 165°C at different time intervals (indicated in the figure).

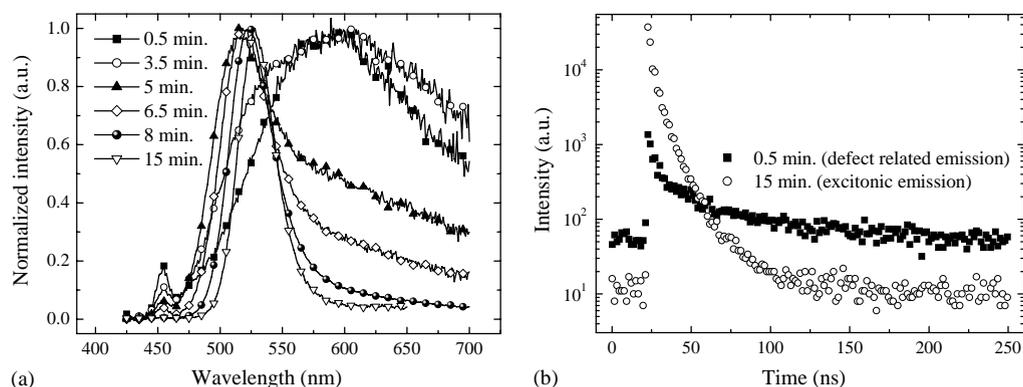


Fig. 2. (a) Emission spectra (normalized to the emission maximum, $\lambda_{\text{ex}} = 400$ nm) of CdTe QDs taken from a synthesis at 165°C and diluted in toluene at time intervals indicated in the figure. (b) Luminescence decay time curves of CdTe defect related emission ($\lambda_{\text{ex}} = 600$ nm) taken from a sample after 0.5 min and of CdTe exciton emission ($\lambda_{\text{ex}} = 525$ nm) taken from a sample after 300 min.

has been previously observed for CdS [13] and CdSe [14].

Since defect related emission often is characterized by low efficiencies this type of emission is undesired if high efficiencies are needed. Upon annealing of defects, excitonic emission may appear. The excitonic emission is clearly observed after 5 min of growth. The defect related emission has completely disappeared after 15 min and only excitonic emission is observed with a short, nearly mono-exponential life time ($\tau_{1/e} < 10$ ns, see Fig. 2b) and a quantum efficiency of about 20%.

The results presented in Fig. 2 indicate that the initially formed particles are not of good quality (imperfect lattice and/or poorly passivated surface). In time the nature of the emission changes (from defect related to excitonic emission) and the efficiency improves. The initial growth of the particles is controlled by the dissolution of Te and therefore slow (relative to methods where injection of precursors is used). This may lead to a low defect density within the nanocrystals [12] and therefore the major contribution to the improved luminescence efficiency during the synthesis is

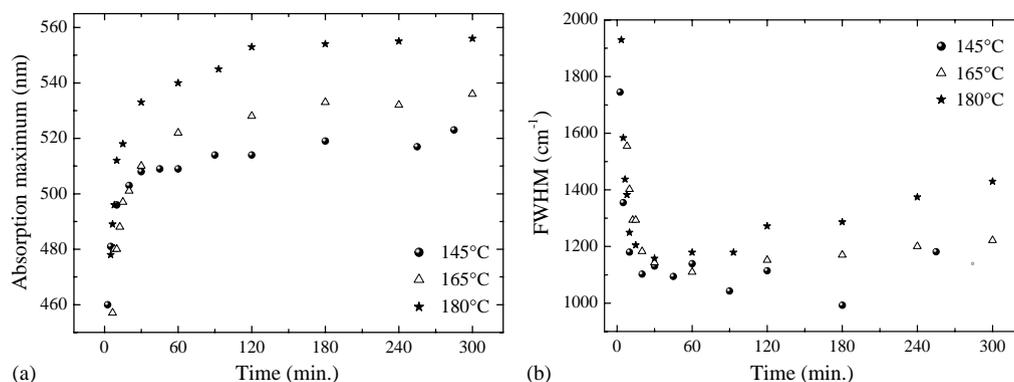


Fig. 3. (a) Absorption maximum and (b) FWHM of the emission peak as function of time for the synthesis of CdTe in TOP/DDA at three different reaction temperatures: 145°C (●); 165°C (△); and 180°C (★).

probably related to surface reconstruction and improved passivation by DDA and TOP.

The influence of the reaction temperature on the final particle size was studied by synthesizing CdTe quantum dots at a higher temperature (180°C) and at a lower temperature (145°C). Fig. 3a shows the energy of the first absorption peak maximum of the samples in toluene taken from the solution at various times for all three temperatures ($T=145^{\circ}\text{C}$, 165°C and 180°C). For all three temperature series a strong increase in the position of the first absorption maximum is observed in the first 30 min indicating a fast growth of the particles. Probably the Te dissolves in the first half hour in the TOP/DDA mixture leading to fast growth from precursors. In the next hours only a slight shift of the absorption maximum is observed that may be caused by Ostwald ripening of the quantum dots. Finally, the absorption maximum remains at constant value for all three temperatures indicating a constant particle size has been reached. The particles grown at higher temperatures show an absorption maximum that is more red-shifted than the particles grown at a lower temperature. This reflects that at higher temperatures larger particles are obtained. A good control over particle sizes between 2 and 3 nm (determined from the relationship between the maximum of the first absorption peak and the particle size reported in Ref. [10]) can be obtained by changing the temperature between 145°C and 180°C.

Fig. 3b shows the FWHM of the emission peak as function of reaction time. The FWHM decreases rapidly within the first 15–30 min. This is due to the decrease of the broad defect related emission that was present in the initially formed particles. The FWHM of the excitonic peak reaches a minimum after about 30 min. The size distribution increases upon further heating and this increase is more pronounced for the higher synthesis temperature. This so-called ‘defocusing’ of the particle size has been assigned to Ostwald ripening [15].

The quantum efficiency is one of the most important properties of luminescing quantum dots. Therefore the dependence of the quantum efficiency on reaction time is studied for samples from the synthesis at 165°C. Only very fresh samples were measured as the CdTe quantum dots are sensitive to oxidation leading to a lowering of the quantum yield over time. The results are shown in Fig. 4a. The quantum efficiency increases during the first 2 h of the reaction from a few percent to constant value of $\sim 40\%$. As discussed above this increase is mostly due to better passivation of the nanocrystals by DDA and TOP. The quantum efficiency is lowered by non-radiative decay. Since the non-radiative decay shortens the life time of the exciton state, the luminescent life time contains information about the quantum efficiency. In Fig. 4b the luminescence lifetime of the exciton emission is plotted

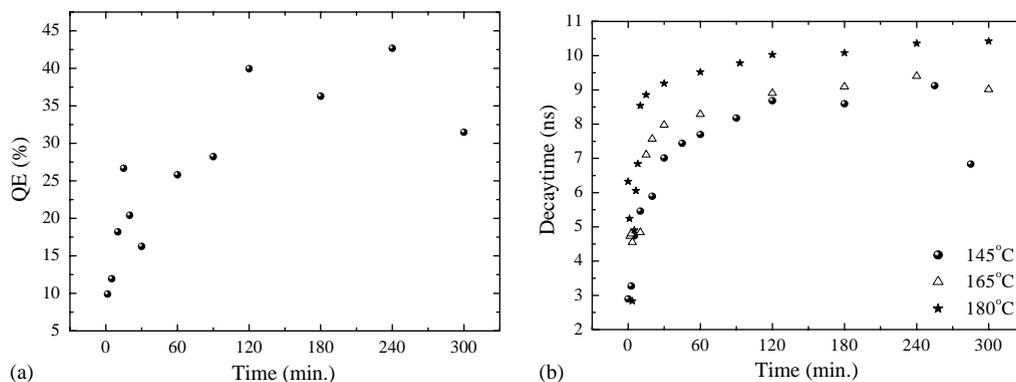


Fig. 4. (a) Quantum efficiency (measured against commercial Rhodamine B, $\lambda_{\text{ex}} = 400$ nm) as function of time for CdTe synthesis at 165°C. (b) Luminescence life time ($\lambda_{\text{ex}} = 406$ nm) measured for the emission maximum as function of reaction time for three different temperatures: 145°C (●); 165°C (△); and 180°C (★).

against the reaction time for particles prepared at the three different temperatures. The decay time strongly increases in the first minutes of the reaction until it levels off at a constant value after about 2 h. For the synthesis at 165°C this increase of the luminescence decay time follows the increase in quantum efficiency closely, indicating that the luminescence life time may be used to estimate the quantum efficiency. At higher reaction temperatures a longer decay time is measured indicating a higher quantum yield that can be explained by a faster surface reorganization (leading to a better capping) and higher crystallinity.

The absorption spectra of samples taken from the syntheses at 165°C and 180°C were measured after 1 week of aging. In samples taken at an early stage during the synthesis discrete peaks at about ~ 420 and ~ 450 nm were observed to appear. Fig. 5 shows the absorption spectra of CdTe samples from the synthesis at 165°C (taken after 1.5 min) and at 180°C (taken after 3.5 min) after 1 week of aging. The sharp absorption peaks are observed at relative high energy and seem to be at discrete energies. It is known that in the small size regime clusters of certain sizes are favored [16, 17]. These have been prepared and reported for CdS [16] and CdSe [18, 19] and CdTe [10]. For these small clusters not all sizes can be obtained but only those that are thermodynamically stable. Therefore, very monodispers particles can be expected

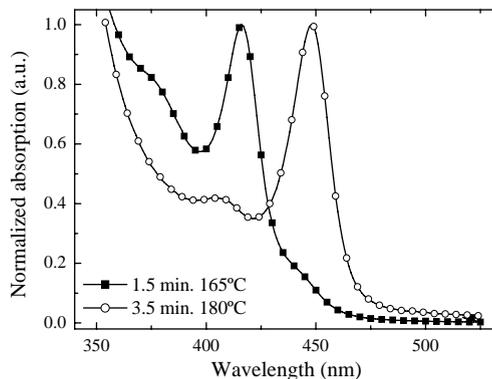


Fig. 5. Absorption spectra (normalized to the first absorption maximum) of CdTe samples after 1 week of aging taken after 1.5 min from the reaction mixture at 165°C (■) and after 3.5 min from the reaction mixture at 180°C (○).

since only certain clusters are thermodynamically stable. The clusters may be slowly formed at room temperature from unreacted Cd and Te precursors. To verify this hypothesis Cd(Me)₂ in TOP was added to a mixture of TOP–Te complex (made by dissolving Te overnight in TOP at 180°C) with DDA that was kept 40°C (just above the melting point of DDA). After 1 h a sample was taken from this mixture and was dissolved into toluene. The absorption spectra obtained for different ratios of Cd:Te are shown in Fig. 6a. The ratio Cd:Te determines the size of the clusters. If excess Te is used (Cd:Te=1:4) an absorption peak at ~ 420 nm

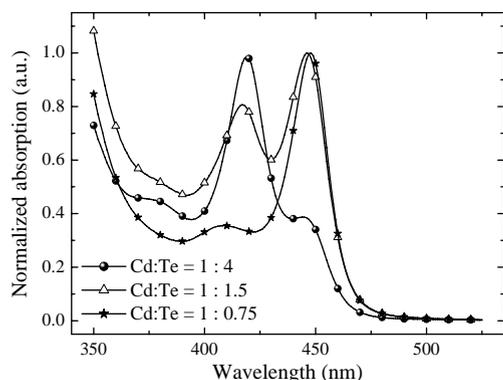


Fig. 6. Absorption spectra (normalized to the first absorption maximum) of CdTe samples prepared at 40°C for Cd:Te ratios of: 1:4 (●); 1:1.5 (△); and 1:0.75 (★).

is observed, indicating that smaller clusters are formed. If excess Cd is used (Cd:Te=1:0.75) the peak at ~450 nm is prominent.

4. Conclusions

The growth of highly luminescent CdTe quantum dots via a TOP/DDA synthesis is followed in time for different synthesis temperatures. After the initial formation mainly defect related emission is observed. Due to a better surface passivation excitonic emission is observed after about 5 min of reaction time. The quantum yield increases from a few percent up to 45% after several hours. Particle growth is fast in the first 30 min. The final size of the particles is reached after 3 h and is determined by the reaction temperature. A good correlation between the luminescence life time of the excitonic emission and the quantum efficiency is observed. For higher reaction temperatures the increase in luminescence life time is faster. Evidence is presented for the formation of thermodynamically stable small clusters from the reaction of pre-

cursors at temperatures close to room temperature.

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