



Laser-induced fluorescence measurements on CdSe quantum dots[#]

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Abstract

In this paper, we report on photoluminescence decay measurements on CdSe quantum dots (QDs) as a function of size in the diameter range of 2.1 to 3.5 nm. The nanoparticles were synthesized by the kinetic growth method from CdO and elemental Se precursors. We studied the effects of growth time on the diameter, emission spectrum and the fluorescence lifetime of the synthesized QDs. The decay time measurements were performed using single shot time-resolved laser-induced fluorescence techniques using a Nd:YAG laser system. Two different decay times were measured on each CdSe sample, a fast one and a relatively slow one. The slow decay was found to be size dependent whereas the fast one was independent of the QD diameter.

Keywords: CdSe, quantum dot, laser-induced fluorescence spectroscopy

I. Introduction

Quantum dots are semiconductor fluorescent nanocrystals. Their properties are between those of bulk semiconductors and discrete atoms because of their unique optical and electronic characteristics. QDs are also known as zero-dimensional materials because their charge carriers are confined in all three spatial dimensions. This quantum confinement is responsible for the size dependent properties. Their diameters are typically in the range of 1–10 nm and they are often composed of atoms from groups II-VI, III-V or IV-VI elements of the periodical table. One of the most important properties of these nanocrystals is the size-tunable fluorescent emission wavelength. The most extensively studied QDs are the CdSe nanocrystals because their emission spectra are in the visible range and the emission wavelength can be tuned easily by changing the crystal size. The emission of CdSe QDs is varying in color from blue to orange-red and in visible range from yellow to red depending on crystal size. The size-depen-

dent optical properties render them ideal materials for many technical applications [1]. It is possible to produce light-emitting diodes [2,3], lasers [4], photovoltaic cells [5] from QDs and they are also applicable as single-photon sources [6] or probes in biological imaging [7]. In these applications the exciton dynamics play an important role. QDs receive considerable attention from the ceramics research community as well. They are important components in a number of current glass-based optical devices and filters. There are many efforts in the literature on embedding luminescent nanoparticles in silica by sol-gel process to make “QD-glasses” [8–10].

II. Experimental

The synthesis of CdSe nanocrystals is based on the kinetic growth method in which crystal size depends on reaction time. Two methods were applied to synthesize the QDs. The first is directly open to air and the other is a standard air-free procedure using inert atmosphere. This method under N₂ atmosphere yields slightly larger dots at the same growth time than the previous method because of the higher applied temperature. In both methods CdO is used as cadmium precursor instead of other pyrophoric and unstable materials such as dimethylcadmium [11,12]. In the first, open to air method oleic

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acid (OA) was used as Cd ligand and trioctylphosphine (TOP) as Se ligand. The non-coordinating solvent is the extensively used octadecene (ODE) in both methods. The synthesis is similar to that reported previously by Dai et al. [13] with minor changes. In a typical synthesis 16.3 mg of CdO (99.5% Aldrich), 0.75 ml of OA (90% Aldrich) and 12 ml of ODE (90% Aldrich) were loaded into a round-bottom flask containing a magnetic stirrer bar and heated directly open to air with a heating mantle until the temperature reached at least 230°C. The reddish CdO solution became clear at 180°C when Cd-oleate was formed. The Se stock solution contains 7.5 mg of Se (99.99% Aldrich) and 0.1 ml of TOP in 2 ml of ODE. In a 5 ml round bottom flask the Se was dissolved under gentle heating and the clear Se solution was allowed to cool to room temperature. When the temperature of the Cd-oleate solution reached 230°C the room-temperature Se solution was introduced by a syringe as quickly as possible. The injection of room temperature selenium stock solution into the Cd-oleate solution at 230°C results in a short burst of nucleation and a temperature drop which quenches further nucleation and commences crystal growth. After the nucleation CdSe QDs samples were taken from the reaction solution at different intervals and the nanocrystals were precipitated by adding acetone or methanol. After the precipitation the synthesized QDs were redissolved in toluene.

The air-free procedure was based on the previously reported work of Peng et al. [14] with some modifications. In a typical synthesis 12.7 mg of CdO, 114 mg stearic acid (95% Aldrich) and 2 ml of ODE were loaded into a three-neck flask and heated to 150°C under N₂ flow. After the CdO formed Cd-stearate with the stearic acid the solution became optically clear and the mixture was allowed to cool to room temperature. Then 1.94 g of TOPO and 1.94 g of hexadecylamine were added to the reaction flask and this reaction mixture was heated to at least 310°C under N₂ flow. The mixture became optically clear and the selenium stock solution was swiftly inject-

ed into the hot reaction pot. The selenium solution contained 80 mg of Se in 2 ml TOP and was allowed to cool to room temperature after dissolution as in the previous case. After the injection of Se solution the temperature dropped to approx. 285°C and this temperature was maintained for crystal growth during which QD samples were taken at regular intervals. The QD samples were allowed to cool to 30–40°C and after the addition of several mL of chloroform the nanocrystals were precipitated with acetone and subsequent centrifugation. The resulted nanocrystals were redissolved in toluene.

For size determination of nanocrystals we used transmission electron microscopy measurements (TEM) and size-determination methods based on the UV-VIS spectra of CdSe suspensions [15]. A Philips CM10 TEM microscope was used with ultra thin carbon film covered copper grids. The other size determination method is based on the UV-VIS spectra of CdSe nanocrystals suspended in toluene. The first absorption peak of the spectra is proportional with the size of nanocrystals so by analyzing the curves the mean size of the QDs can be determined with rather good accuracy [16]. For the UV-VIS measurements a Perkin-Elmer Lambda 15 spectrometer was used. The photoluminescence measurements were performed on a Hitachi F-2000 spectrofluorometer at 390 nm excitation wavelength. The crystal structure of the synthesized CdSe nanocrystals was analyzed by XRD (X-ray Diffraction) on a Rigaku MiniFlex II system utilizing Cu K α radiation. The samples were prepared from toluene suspensions by precipitation with acetone.

In fluorescence lifetime measurements a short pulse of light excites the sample and the subsequent fluorescent emission is recorded as a function of time. In our system we used a third harmonic generated pulsed Nd:YAG laser system which has a wavelength of 355 nm, 30 ps pulse duration, 10 Hz repetition rate and 60 μ J pulse energy. The CdSe QDs feature longer radiative lifetimes than bulk CdSe (typically 1 ns). In general, their lifetimes are in the range of several to tens of nanoseconds.

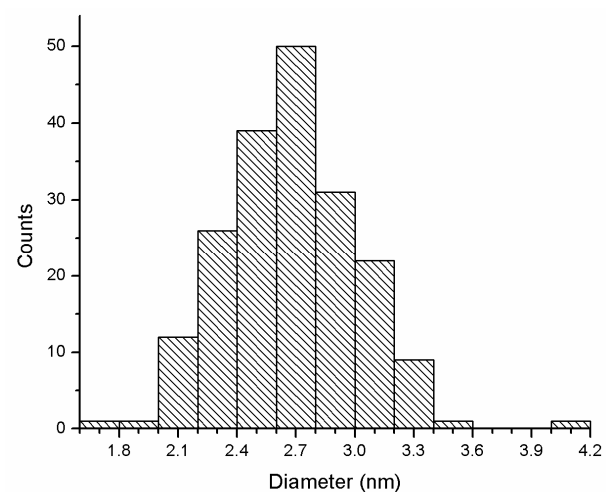
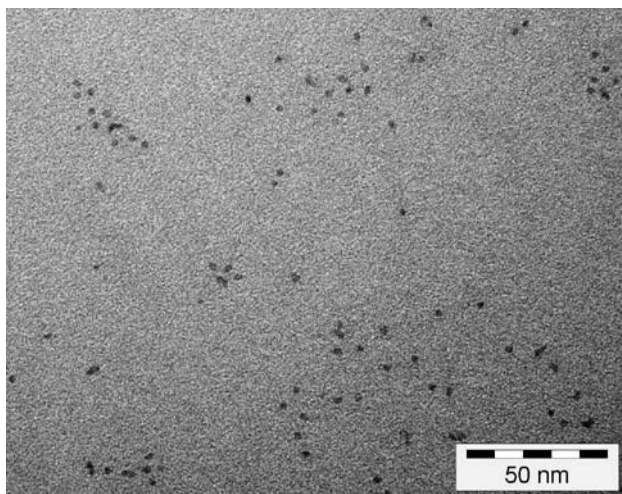


Figure 1. TEM image with adherent histogram of a CdSe QDs sample synthesized under air atmosphere

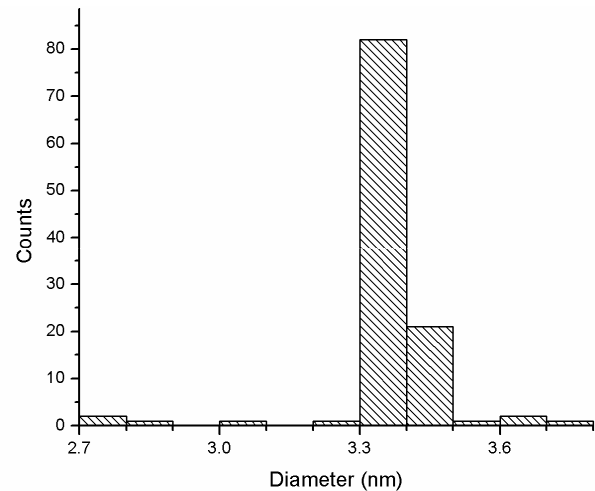
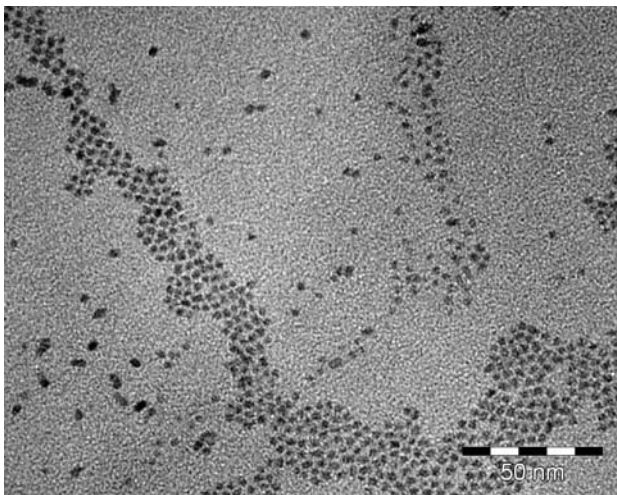


Figure 2. TEM image with adherent histogram of a CdSe QDs sample synthesized under N_2 atmosphere

The laser-induced fluorescence (LIF) measurements were performed at ambient temperature and the QD samples were suspended in toluene. The measured points were fitted with biexponential curves with errors smaller than 3%. Therefore, with biexponential fit we were able to determine two lifetime components for each sample: a fast and a relatively slow decay. The fast one was measured by a streak camera while the slow one by a PIN diode and oscilloscope.

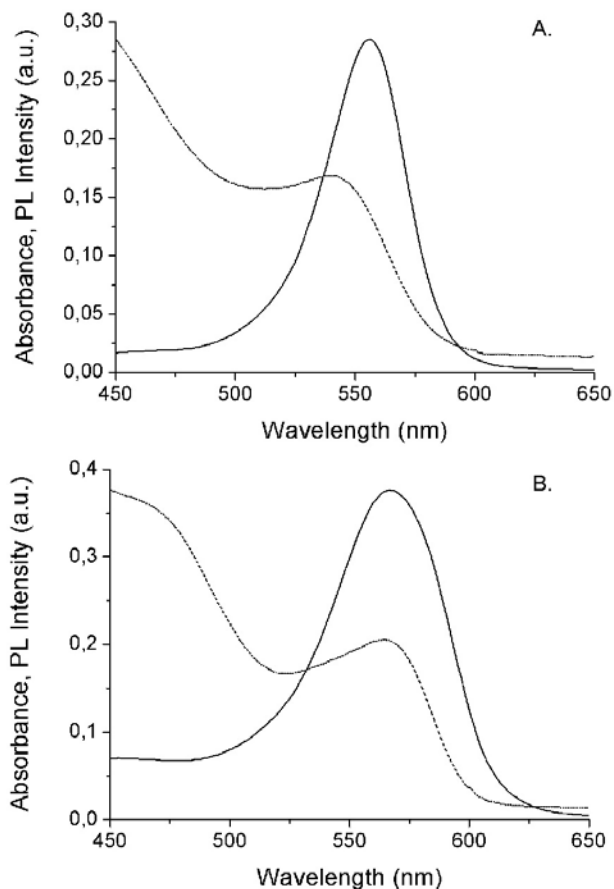


Figure 3. Absorption and PL spectra of the CdSe QDs seen in the TEM pictures. Part A: synthesized under air, Part B: synthesized under N_2 atmosphere

III. Results and discussion

The first method of CdSe synthesis (directly open to air) yields smaller nanocrystals in the first few minutes of crystal growth. Typical QD diameters fall in the range from 2.2 to 3.0 nm while the synthesis under inert atmosphere yields slightly larger nanocrystals up to 3.4 nm in the same first few minutes of the synthesis. In the beginning of crystal growth we obtained samples with narrower size distribution than at later stages that are characterized by depleted monomer concentration and Ostwald ripening [17]. Thus, in the first several minutes (usually up to 20 minutes) of the crystal growth we were able to synthesize samples with mean particle diameter standard deviation values less than 10 %. Both methods resulted in dot shaped nanocrystals of good size uniformity and narrow size distribution. The size distribution was almost equal in the two methods but the synthesis in inert atmosphere sometimes resulted in samples with slightly narrower size distribution than the synthesis directly open to air. In Fig. 1 and 2 the TEM images of two representative samples of the two synthesis methods with adherent histograms are presented. A sample synthesized under air can be seen in Fig. 1. The mean diameter of the sample is 2.6 nm with standard deviation of 9.9 %. These crystals grew for 16 minutes at 220°C before sampling. In Fig. 2 the nanocrystals derived by the air-free procedure are depicted. The diameter of the nanocrystals is 3.4 nm with standard deviation of 5.4 %. The crystal growth time was 3 minutes at 335°C in this case. The standard deviation did not exceed the value of 15 % and the FWHM (Full Width at Half Maximum) of photoluminescence curves was in the range from 20 to 30 nm for both methods. The adherent UV-VIS and PL spectra of these two samples can be seen in Fig. 3. A 390 nm UV light was used for the excitation of the samples and the nanocrystals were suspended in toluene.

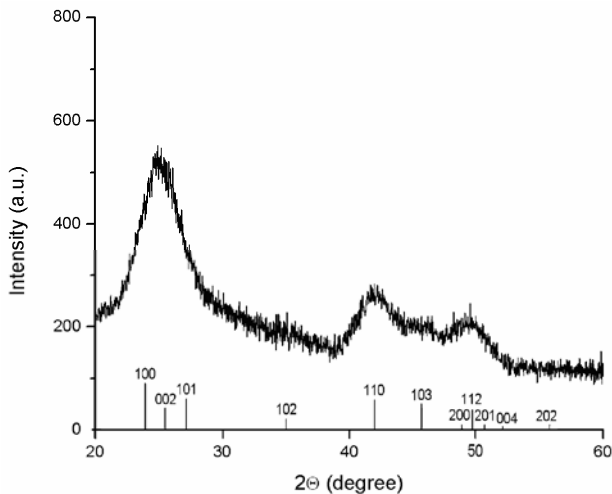


Figure 4. XRD pattern of a representative CdSe QD sample (synthesized under N_2 atmosphere). The vertical bars represent the positions of the diffraction peaks for bulk wurtzite structure and their lengths are proportional with their intensity

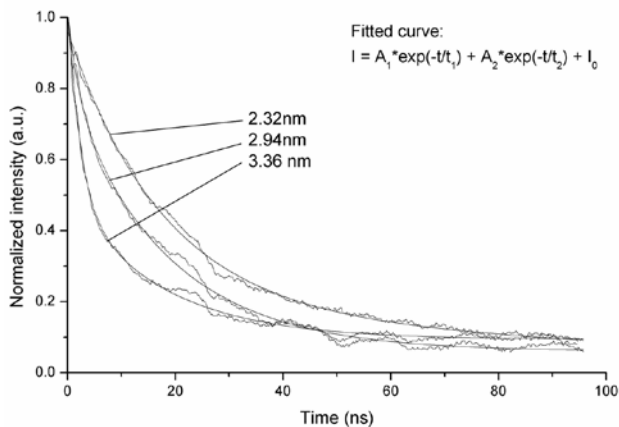


Figure 5. Three representative fluorescence decay spectra (excited at 355 nm) fitted with biexponential curves for QDs with mean diameter of 2.3 nm, 2.9 nm and 3.3 nm, respectively

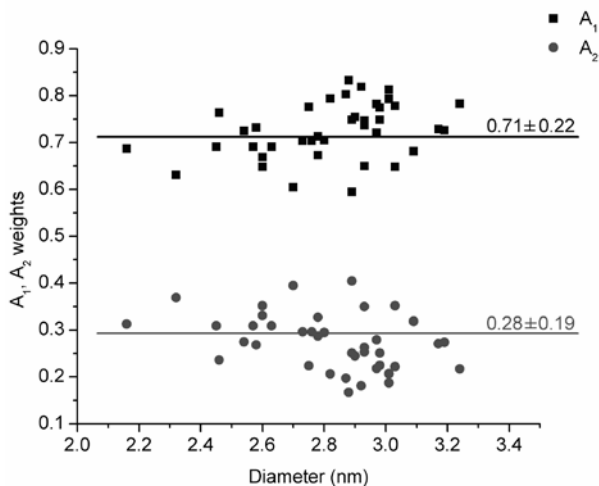


Figure 6. Amplitude values of the shorter- (A_1) and longer-lifetime (A_2) components

The XRD measurements provide results averaged from a large number of crystallites. As can be seen in a representative CdSe sample (Fig. 4) the crystal structure of the product CdSe QDs is a wurtzite lattice structure regardless of the synthesis method chosen.

In the lifetime measurements of CdSe QD samples the photoluminescence decay curve took a biexponential form of $I = A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2) + I_0$, where the time constants t_1 and t_2 fell in the range of 3 ns to 5 ns and 20 ns to 60 ns, respectively. Fig. 5 shows PL decay spectra of three differently sized samples together with the fitted biexponential curves. The photoluminescence amplitude values of the shorter- (A_1) and the longer-lifetime (A_2) components are roughly size-independent with mean values of 0.71 ± 0.11 for A_1 and 0.28 ± 0.12 for A_2 as seen in Fig. 6. The ratio of the A_1 and A_2 amplitudes depends on the quality of QD surfaces. The larger the value of A_2 (related to the longer-lifetime component), the better the surface condition (fewer the surface defects), and the larger the role of surface-related emission is [18]. The values of the shorter lifetime component (t_1) as a function of diameter can be seen in Fig. 7. The t_1 component does not exhibit any characteristic size dependence and its spread is also noticeable, however, its values mostly fall between 3 ns and 5 ns (the mean error value for this lifetime component is 0.2 %). This short lifetime component can be attributed to the intrinsic recombination of initially populated core states [14]. The longer lifetime component (t_2) was attributed to the involvement of surface states in the carrier recombination process [14]. The t_2 components were in the range of 20 ns to 60 ns for most samples (the fit values for this t_2 had 1.9 % mean error). Fig. 8 shows the t_2 slow decays as a function of diameter. The spread is also noticeable but an exponentially decreasing tendency can be noticed. So as a consequence of quantum confinement, larger QDs have lesser t_2 lifetime components. Our measurements for t_1 and t_2 lifetime components confirm those reported in the literature earlier by Wang et al. [18] and Javier et al. [19]. Their measurements were also performed under ambient conditions. The shorter lifetime components with 3–5 ns are in good agreement with Wang et al.'s 2–5 ns (in the range of 3.5 nm to 5.0 nm) and Javier et al.'s 1–3 ns (in the range of 1.6 to 2.8 nm). However, the longer lifetime component had larger values in our measurements (20–60 ns) than in those performed by others (15–25 ns [14] and 20–30 ns [15]).

The size dependence of the longer lifetime component was observed by Javier et al [19] as well. In their report, the slower decay decreased almost linearly with the size in the range of 1.6 nm to 2.8 nm whereas we found an exponentially decrease in the 2.4 nm to 3.5 nm diameter range.

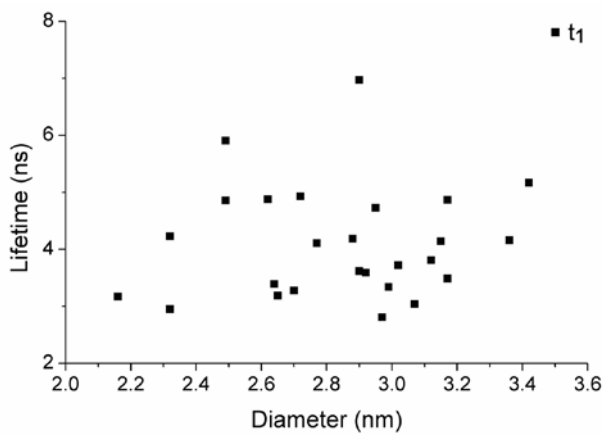


Figure 7. Fast decay components (t_1) as a function of QD diameter

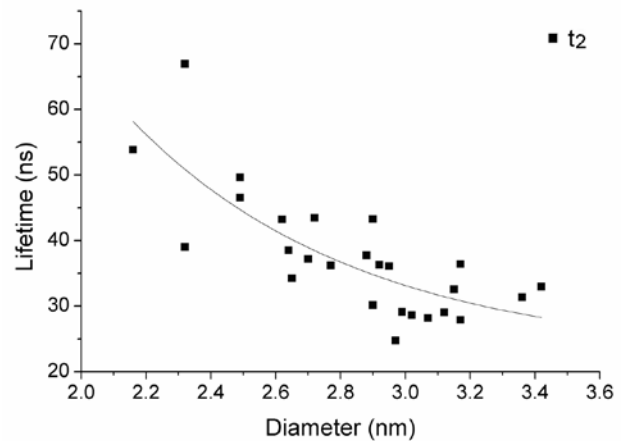


Figure 8. Slow decay components (t_2) as a function of QD diameter

IV. Conclusions

We studied the size dependence of CdSe QD fluorescence lifetimes under ambient conditions in the size range of 2.2 nm to 3.5 nm. We found that a biexponential fit can describe the PL decay spectra with good results (minimal fitting errors).

The biexponential fit revealed that neither the decay amplitudes nor the fast decay time constant are size dependent in the studied systems. On the other hand, the slower decay component exhibited a characteristic size-dependent feature that appears to be exponential. This finding complements previous literature results where a strictly linear character was assigned to the size dependence phenomenon.

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