Synthesis and luminescence of (3-mercaptopropyl)-trimethoxysilane capped CdS quantum dots

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Abstract

A new synthesis method is presented to make CdS quantum dots in THF and MeOH with mercaptopropyl-trimethoxysilane (MPS) as silica precursor at the surface. The thiol group acts as capping agent of the CdS surface. By varying the MPS concentration, the size and thus the emission colour could be tuned. Nanocrystals with a diameter between 2 and 6 nm could be prepared this way with quantum yields up to almost 20%. The temperature dependence and the lifetime of the emission were studied and explained in terms of a recombination process in which both a trapped electron and hole are involved. The CdS nanocrystals were doped with Zn or Cu resulting in a blue shift a red shift of the emission, respectively.

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1. Introduction

Luminescing semiconductor quantum dots form a new and interesting class of luminescent materials [1]. Since their quantum size effects are understood [2], fundamental and applied research on these systems has become increasingly popular. One of the most interesting applications is the use of nanocrystals as luminescent labels for biological systems [3,4]. The development of the TOP/TOPO (tri-octylphosphine/tri-octylphosphine oxide) synthesis method for CdSe [5] provided high quality quantum dots with excitonic emission. Many publications have appeared on biological labeling using nanocrystals produced by the TOP/TOPO synthesis [3,4,6,7]. One of the major problems is to make the nanocrystals water soluble. Thiols have played an important role in solving this problem. Another problem is the release of toxic materials from the dots (e.g. Cd, Se, Zn) into the biological environment. A silica shell around the dot can reduce the release of toxic materials. It can also hamper the transfer of oxygen to the dots, making them more photo-stable in water [7,8].

In this paper, the synthesis and luminescence properties of CdS quantum dots is described. Via a relatively simple synthesis method CdS nanoparticles are synthesized in polar media (tetrahydrofuran or methanol) using MPS (3-mercaptopropyl)-trimethoxysilane as a capping molecule. In addition to providing a passivating layer around the CdS quantum dot the silane groups of MPS can also serve as a precursor for

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growth of the silica shell around the particle. Efficiently luminescing CdS particles are produced with quantum yields up to 20% at room temperature. The size of the CdS nanocrystals determines the emission color. Size control is achieved by varying the MPS concentration. In addition, the emission color can be tuned to shorter wavelengths by addition of zinc. The addition of copper red shifts the emission.

2. Experimental

2.1. Chemicals

Tetrahydrofuran (Anhydrous 99.9%, Aldrich), Methanol (Anhydrous, Merck), Cadmiumperchlorate hydrate (Aldrich), (3-mercaptopropyl)trimethoxysilane (97%, Aldrich) Hydrogen sulfide (99.5%, Aldrich), Copper chloride dihydrate (99% Aldrich), Zinc acetate (98 + %, Aldrich).

2.2. Synthesis

In a dry nitrogen atmosphere a variable amount of (3-mercaptopropyl)-trimethoxysilane (MPS) is added to $20 \, \text{ml} \, 10^{-3} \, \text{M}$ $Cd(ClO_4)_2$ in either tetrahydrofuran (THF) or methanol (MeOH). Under stirring $0.5 \, \text{ml}$ $(2.3 \times 10^{-5} \, \text{mol})$ H_2S (corresponding to an excess of $15 \, \text{mol}\%$) is added through a septum with a syringe. The final color of the solution after addition of H_2S varies from deep yellow for $40 \, \mu\text{l}$ MPS (giving a $0.01 \, \text{M}$ MPS solution) to colorless for a MPS concentration of $0.4 \, \text{M}$ $(1600 \, \mu\text{l})$. Particle sizes between 2 and 6 nm can be obtained this way. Unless mentioned otherwise copper and zinc salts were added to the $Cd(ClO_4)_2$ solution before addition of H_2S. To prevent the particles from premature flocculation, dry solvents were used. In the presence of too much water, uncontrolled polymerization of the alkoxysilane groups occurs, leading to flocculation of the quantum dots. In dry solvents the particles were stable for months.

2.3. Apparatus

Emission and excitation 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. Time-dependent measurements were performed using the third harmonic (355 nm) of a Quanta-ray DCR Nd^{3+}:YAG laser as an excitation source. The emission light was guided through a fiber optic cable to a monochromator (Acton SP-300i, 0.3 m, 150 lines mm^{-1} grating, blazed at 500 nm). The signals were recorded using a thermoelectrically cooled photo multiplier tube in combination with a Tektronix 2430 oscilloscope. Temperature-dependent PL emission and lifetime measurements were recorded using a liquid helium flow-cryostat equipped with a sample heater to stabilize the temperature at different temperatures between 4 K and room temperature. Samples were first cooled to 4 K and slowly heated to room temperature.

3. Results and discussion

CdS nanocrystals were prepared using different MPS concentrations. The thiol concentration has a large influence on the size of the nanocrystals. In Fig. 1a, the absorption spectra are shown for nanocrystals prepared with MPS concentrations varying between 0.01 and 0.4 M. The onset of the absorption shifts to higher energy upon increasing the thiol concentration. The particle size (see Table 1) increases from 2.2 nm for the smallest dots to 4.6 nm for the largest dots (for the lowest thiol concentration) in MeOH. In THF larger sizes were obtained for the same MPS concentration. The sizes were determined using the well-established relation between particle size and absorption onset [9]. A higher MPS concentration also leads to a more monodispers particle size distribution.

To obtain semiconductor nanocrystals the choice of the capping molecules is critical. The bonding between the capping molecules (here the thiol) and the precursors (Cd^{2+}) needs to be neither too weak nor too strong. If the bonding between capping molecule and nanocrystal precursor is too weak, particle growth is fast and
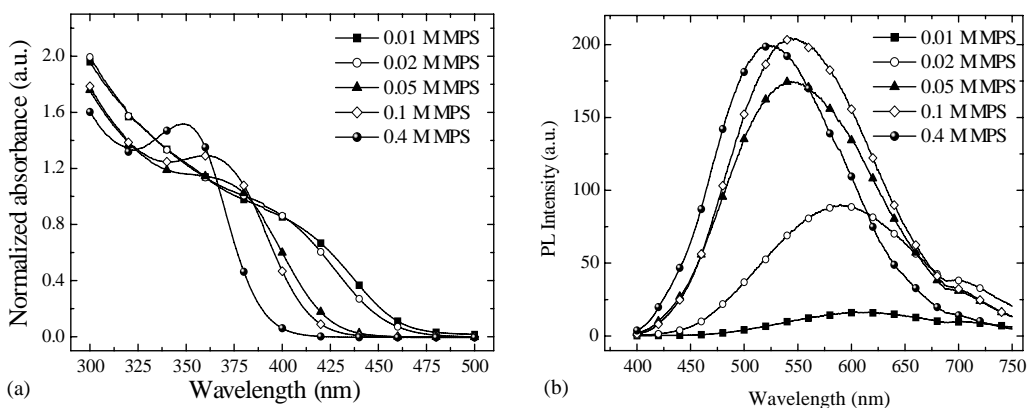
Fig. 1. (a) Absorption spectra and (b) emission spectra ($\lambda_{ex} = 400\,\text{nm}$) of CdS NCs synthesized in methanol with different concentrations of MPS (between $0.01\,\text{M}$ ($40\,\mu\text{l}$) and $0.4\,\text{M}$ ($1600\,\mu\text{l}$)).

Table 1
Quantum efficiencies and particle sizes of CdS NCs for synthesis in MeOH and THF for different concentrations of MPS

[MPS] (mol/l)	MeOH		THF	
	QE (%)	Size (nm)	QE (%)	Size (nm)
0.01	1.9	4.6	0.7	6.5
0.02	4.7	4.4	0.8	6.2
0.05	10.5	3.2	15.9	4.8
0.1	9.9	2.8	15.6	4.6
0.4	9.5	2.3	18.9	4.1

bigger crystallites are formed. If the binding is too strong, the nanocrystals will not be formed. The rate at which the capping molecules attach and de-attach to the surface influences the growth rate and thus final size of the particles. By the choice of the type and concentration of capping molecules and the temperature, the dynamics of attaching and de-attaching can be influenced and the particle size can be tuned. At lower capping molecule concentrations, the concentration of the cation-capping molecule complex is lower resulting in a faster particle growth. At higher capping molecule concentrations the reaction is slower yielding well passivated and more monodispers particles.

The emission spectra of the particles from Fig. 1a are shown in Fig. 1b. The emission spectra are broad band emissions that cover a large part of the visible spectrum, even for the monodispers particles obtained at high MPS concentrations. The shift of the emission maximum between the lowest (0.01 M) and the highest (0.4 M) MPS concentration ($\sim 3000\,\text{cm}^{-1}$) is smaller than the shift of the absorption onset ($\sim 4000\,\text{cm}^{-1}$). Also the emission maximum lies at lower energy than expected for an excitonic emission. Therefore, it is concluded that trap related emission takes place where the hole, the electron or both are trapped. As the wave function of trapped charge carriers is less extended than for free charge carriers, the quantum size effects are smaller for trapped charge carriers than for the band edges. The large spectral width of the emission band is caused by both inhomogeneous broadening (due to a variation in particle size) and broadening due to electron–phonon coupling.

Quantum efficiencies have been determined using Coumarine 153 (a commercial laser dye with a 90% quantum yield) as a reference. The quantum efficiencies (up to almost 20%, see Table 1) are among the highest reported for trap related emission of CdS quantum dots [10]. As the thiol concentration increases, the quantum efficiency also increases due to better surface passivation. Above 0.05 M, the quantum efficiency is at a constant level, indicating that at a 0.05 M MPS concentration is sufficient to passivate the surface. The high quantum efficiencies show that the mercapto group of MPS is able to serve as a
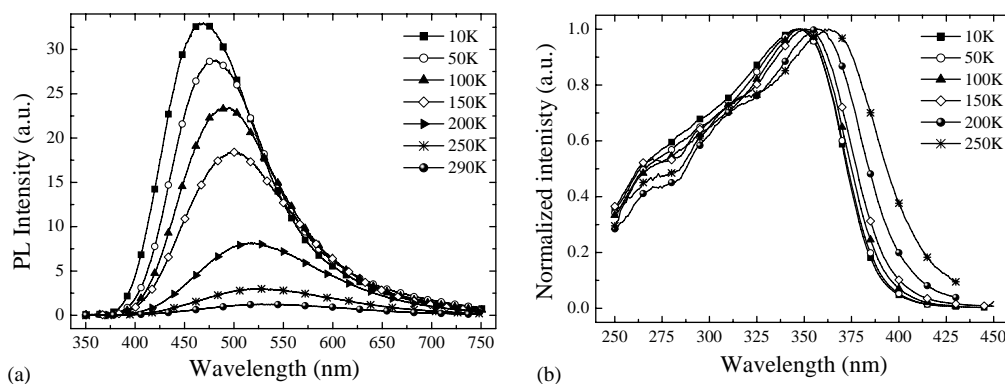
Fig. 2. (a) Temperature-dependent emission spectra ($\lambda_{ex} = 400$ nm) and (b) excitation spectra (measured for the emission maximum) of CdS QDs synthesized in methanol with 0.4 M MPS.

good capping to passivate the surface of CdS particles. The tri-methoxysilane group can be used to grow a thin silica layer on the CdS nanoparticles.

Fig. 2a shows the temperature-dependent emission spectra. Upon increasing the temperature from 4 to 300 K the emission shows a shift to longer wavelength corresponding to about 300 meV. This shift is larger than the shift of the band gap determined from the temperature-dependent excitation spectra (180 meV, Fig. 2b). A shift of the band gap to lower energies is commonly observed for (nanocrystalline) semiconductors [11,12]. The larger red shift of the emission spectra may be explained by detrapping of shallower trapped holes or electrons. A redistribution over (deeper trapped) donor–acceptor pairs at higher temperatures may explain the additional red shift of the maximum emission. Due to a solid–liquid phase transition of the solvent (at 176 K for methanol and at 165 K for THF), it is hard to determine the luminescence quantum efficiency at 4 K. However the strong increase in the luminescence signal at 4 K in comparison to RT is obvious and the low temperature quantum yield may very well be close to 100%.

The lifetime of the donor–acceptor emission was studied as function of temperature, particle size and emission wavelength (see Fig. 3). At 4 K, the decay curves are almost single exponential with a lifetime of 5 μs for the lowest and 20 μs for the highest MPS concentration. The particles prepared
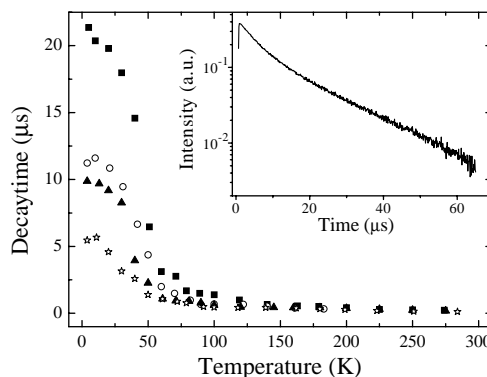

Fig. 3. Temperature dependence of the decay time of the CdS emission ($\lambda_{ex} = 355$ nm) for four different MPS concentrations (☆: 0.01M, ▲: 0.05M, ○: 0.1M, ■: 0.4M) in THF. The inset shows a decay curve for 4.1 nm CdS particles at 4 K. Lifetimes were determined from the linear tail of the logarithmic decay curve.

in the highest MPS concentration also have the highest quantum yield. Therefore, the non-radiative decay is most suppressed in these particles, resulting in a longer luminescence lifetime. The lifetime decreases considerably (from microseconds to nanoseconds) between 20 and 100 K. To explain the temperature dependence a multiphonon relaxation model was proposed in Ref. [13]. Upon increased temperatures thermal occupation of phonon modes enhances the nonradiative decay rate as described in, for example, Refs. [14,15]. Even though the fit to the model for
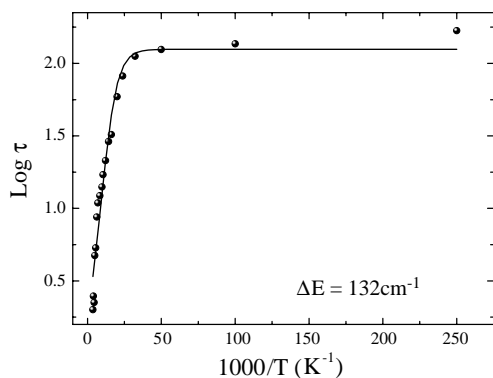
Fig. 4. Arrhenius plot of the decay time of the emission from for CdS particles synthesized in a 0.1 M MPS solution in THF. The logarithm of the decay time is plotted against the $1000/T$. The drawn line is a fit to the Arrhenius equation for an activation energy of $132\,\mathrm{cm}^{-1}$.

Fig. 5. Emission spectra $(\lambda_{ex} = 400\,\mathrm{nm})$ of $Cd_{(1-x)}Zn_xS$ $(0 \leqslant x \leqslant 0.3)$ made with a MPS concentration of 0.1 M in THF. The Zn-precursor was added before particle formation.

multi-phonon relaxation gave a reasonably good agreement with the measured temperature dependence for the lifetime, there are several reasons why it is not likely that this type of thermal quenching is responsible for the temperature dependence of the lifetime. Firstly, the Huang-Rhys coupling parameter S that was determined from the fits in Ref. [13] is 110. This is an unrealistically high value. Secondly, the temperature dependence of the emission intensity does not show a large drop between 20 and 100 K (see Fig. 2a). If increased non-radiative relaxation would be responsible, the intensity has to drop at the same rate as the decay time.

A more plausible explanation for the shortening of the lifetime is a thermal detrapping of one of the charge carriers. As discussed above, the broad band luminescence is most likely to originate from recombination of donor–acceptor pairs with shallowly trapped electrons and holes. As the temperature increases the charge carrier in the shallowest trap becomes detrapped and more delocalized. The wave function overlap for recombination with the trapped charge carrier will increase, thus shortening the luminescence lifetime. The detrapping energy of the shallowest trapped charge carrier can be calculated if the $\ln\tau$ is plotted against $1/T$. By fitting with an Arrhenius type model the energy trap depth is estimated at $132\,\mathrm{cm}^{-1}$ (Fig. 4).
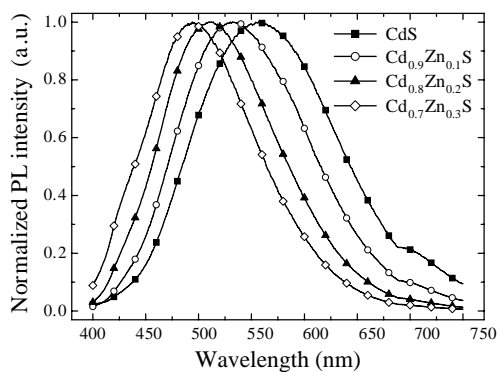
Besides changing the band gap through quantum size effects (particle size) the band gap can also be varied by co-doping the CdS nanocrystals with Zn [16]. The band gap of CdS increases upon adding Zn as the band gap of ZnS is larger than CdS. Zn was incorporated in the CdS nanocrystals using the same synthesis method with MPS as a capping agent (0.05 M) and using 5, 10 or 15 mol% of Zn instead of Cd. In Fig. 5, the emission spectra are shown. The donor–acceptor emission band shifts to shorter wavelengths as more Zn is incorporated. The luminescence quantum efficiency remains high ($\sim 15\%$) for the synthesis with Zn. While incorporation of Zn causes a blue shift of the emission spectra, a red shift may be obtained if Cu is used [12,17]. The addition of Cu does not strongly influence the band gap but Cu serves as a recombination center situated in the band gap resulting in a red-shifted emission. In Fig. 6, the emission spectra are depicted for samples synthesized with various Cu concentration. The concentrations indicated are concentrations present in the reaction mixture, in mol% relative to Cd. The actual concentrations of Cu incorporated in the CdS nanocrystals will be much lower [17]. The emission spectra show that incorporation of Cu causes a red shift of the emission. For the lower Cu concentrations the emission spectrum is broadened since emission from both doped and undoped CdS quantum dots
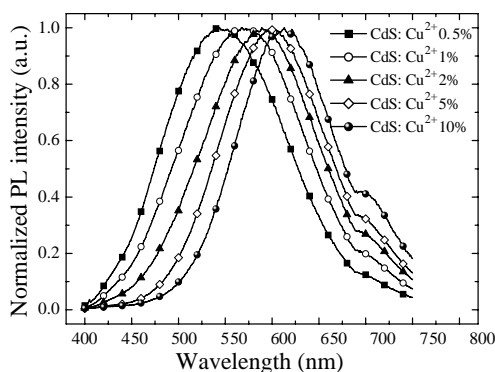
Fig. 6. Emission spectra ($\lambda_{ex} = 400$ nm) of CdS:Cu (0.5–10% Cu added to the solution before particle formation) synthesized in methanol with a MPS concentration of 0.1 M.

is observed. For the sample with 10% Cu in the reaction mixture, the emission consists almost exclusively of the red Cu-related emission. The decay time of this emission is 2 μs at 4 K and decreases to about 200 ns at room temperature. The luminescence lifetime behavior of the Cu related emission is similar to that has previously been observed for ZnSe:Cu [12]. The quantum efficiency of the CdS:Cu nanocrystals decreases with increasing Cu concentration and is low at room temperature (about 1%). This makes the red shifted emission less useful for applications where a high quantum yield is required.

4. Conclusions

A simple synthesis method has been reported for efficiently luminescing CdS quantum dots using MPS as a capping molecule. The particle size can be controlled by varying the MPS concentration. The size and temperature dependence of the luminescence and the luminescence lifetime are reported and explained by a model based on a donor–acceptor type luminescence. Tuning of the emission color is possible via particle size (MPS concentration) or by doping with Zn or Cu. The use of MPS as capping molecule provides the quantum dots with a precursor for growth of silica at the surface which is useful to incorporate the quantum dots in a silica shell or silica matrix.

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