Low-temperature synthesis of CdS nanocrystals in aliphatic alcohols

Lina Martinsson
Abstract

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In this report a novel low temperature synthesis approach of CdS nanocrystals is described starting from well known precursors, Cd(SA) and TOP-S, in a ligand system of aliphatic long chain alcohols. A one-pot synthesis approach is applied using a laboratory microwave heating source. The resulting CdS nanocrystals exhibit an absorbance with a pronounced fine-structure, a photoluminescence with a very high ratio between the band gap peak and the defect peak and a fluorescence quantum yield of 33%.

Different synthesis approaches have been investigated by changing heating rate, temperature, precursor concentration and chain length of the aliphatic alcohol ligand as well as chain length of the Cadmium precursor. It was found that small changes in the heating rate do not affect the reaction. Changing the reaction temperature between 200°C and 160°C has no visible effects on the quality of the resulting CdS nanocrystals. At 140°C the nanoparticles experience a significant drop in quality, probably because there is a major change in the growth mechanism of the nanocrystals at that low temperature. At 100°C and 120°C the creation of so-called CdS nanoclusters is observed, and a growth mechanism towards nanocrystals based on cluster aggregation is suggested.

For the synthesis of high quality nanoparticles it was found that a ratio of 1:25 between precursor and aliphatic alcohol is preferable as well as a ratio of 1:1 between the two precursors. If the chain length of both the precursors and the alcohol is short, the reaction rate is enhanced. If the chain length is too short the nanocrystals grow very fast and the size distribution gets broad, the photoluminescence intensity decreases and the ratio between band gap luminescence and defect luminescence decreases. The best Cd-precursor was found to be Cd-Laurate and the most suitable ligand evaluated was Tetradecanol.
Sammanfattning

Det senaste årtiondet har forskning på riktigt små partiklar tagit fart och man kan nu både syntetisera och karaktärisera partiklar som är mindre än en nanometer i en eller flera riktningar. När en partikels storlek går ner till nanometerskala, under 100 nm, får den helt plötsligt andra egenskaper än samma material i bulkform. Det beror både på att en stor andel av atomerna i partikeln finns på ytan och därför har en distorderad omgivning, och på att partikeln är mindre än många fysiska fenomen, som till exempel ljusets våglängd. I halvedade material finns ett bandgap mellan valensband och ledningsband i elektronkonfigurationen vilket ger materialet dess halvedade egenskaper. Detta fenomen blir ännu intressantare när materialets storlek kommer ner i nanoområdet för då går elektronkonfigurationen från bulkens kontinuerliga band mot molekylers diskreta elektronnivåer, vilket gör att bandgapet successivt ökar ju mindre partikeln blir. Med andra ord, partiklens egenskaper är beroende av dess storlek. I just halvedade material kan man excitera elektroner upp till ledningsbandet, som sedan när de faller till grund tillståndet igen ger upphov till en energi som tar formen av ljus. I och med att gapets storlek beror på partiklens storlek blir färgen på ljuset som sänds ut också beroende av partiklens storlek. Dessa egenskaper gör halvedade nanopartiklar intressanta i en mängd tillämpningar, som till exempel som LEDs, biologiska markörer och i solceller.


Resultatet av att variera temperaturen blev att nanopartiklar av hög kvalitet kunde syntetiseras i alkohol ner till 160°C. När reaktionsblandningen hölls vid 100°C i 6 timmar visade det sig att väldigt små kluster bildades som var stabila och behöll samma storlek över lång tid, när dessa sedan hettades upp till 200°C i 20 minuter bildades nanokristaller av samma kvalitet, form och storlek som när blandningen direkt upphettades till 200°C. Från detta drogs slutsatsen att nanopartiklarna formas från små CdS kluster som aggererar och dessa aggregat växer sedan ytterligare genom att CdS-monomorer adderas till ytan.

Variationen av de andra olika parametrarna gav slutsatserna att: små variationer i upphettningstång inte påverkar de resulterande nanopartiklarna, kort kedjelängd på kadmiumstartmaterialet ger ett mycket snabbare reaktionsförlopp medan en kortare kedjelängd på alkoholen också snabbar upp reaktionsförloppet men inte alls lika mycket som en kortare
kadmiumkälla. Vad gäller koncentrationer av de ingående ämnena ger ett överskott av kadmiumkällan mot svavelkällan större partiklar med tendens att agglomerera till lösa hopar, medan en lägre koncentration av kadmiumkällan mot svavelkällan ger mindre partiklar som växer långsammare, bäst kvalitet erhölls när lika mycket av de båda startmaterialen användes. Hur stor kvoten mellan startmaterialen och alkohol var hade mindre betydelse och inom experimentets gränser observerades inga tydliga effekter.

Av de olika kadmiumkällorna som testades gav kadmiumlaurat den högsta intensiteten i fotoluminiscens tillsammans med den lägsta spridningen av storlek hos de syntetiserade nanopartiklarna, av alkoholerna gav tetraedkanol bäst resultat och den bästa sammansättningen av de ingående ämnena var Cd:S:OH = 1:1:25(mol).
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This Master Thesis project was performed by Lina Martinsson at Freiburg Material Research Centre in Freiburg, Germany, as the finishing project in the Masters Program of Chemical Engineering with Material Science at Uppsala University, Sweden.

1. Introduction

1.1 Quantum Confinement Effect

The properties of a material are usually well described by classical and quantum mechanical theories of solid state physics, and they normally do not depend on the size of the material. This is however not longer the case when one or more dimensions of the material go down to the nanometre scale. The particles are then smaller than most characteristic lengths of physical phenomena, for example the wavelength of light (300-700 nm) and the exciton (electron – hole pair) diameter (6nm for bulk CdS). This implies that a nanoparticle cannot be described simply as a small piece of bulk material, and the different characteristics for such small particles depends mainly on the fact that a large fraction of the atoms in the particle are localized on the surface and thus have a distorted environment.\(^1\) When a particle shrinks in size somewhere between bulk and molecule it goes into a region called the quantum confinement region, where the continuous conduction band no longer exists and the energy levels starts to divide and go towards the discrete energy levels of a molecule. In this region the material cannot longer be described by classical physics, and quantum mechanics is not applicable either because periodic boundary conditions cannot be used to describe the material. In small size regimes the material properties start to change, for example semiconducting nanoparticles are an interesting class of new materials since their properties depend on their size in

![Diagram of electronic states](image-url)

*Figure 1: The electronic states, ranging from discrete levels for atoms to continuous bands for bulk material. In the nanocrystal region the band gap widens when the particle size decreases.* \(^1\)
the quantum confinement region. Bulk semiconductors have a fixed band gap between their populated and unpopulated energy levels, but when semiconducting nanoparticles shrink, their band gap starts to widen, which has the consequence that the photoluminescence behaviour depends on the particle size. CdX (X = S, Se, Te) are very interesting materials to examine quantum size effect phenomena since their photoluminescence occurs in the visible range of light. Applications for these materials are for example LEDs, laser sources, solar cells and fluorescent labels in biology.

1.2 Synthesis Methods

There are several ways to synthesize nanoparticles, for example through physical vapour deposition or inside a micelle cavity, however most methods are slow and can only handle relatively small amounts of material. So far the most convenient method to synthesize nanoparticles is through colloidal chemistry. In solution crystals can be grown by the decomposition of precursor molecules. This occurs first through a rapid nucleation followed by a slower growth period. However it is proven that the early stages of nanocrystal synthesis, especially at lower temperatures, involve simultaneous nucleation and growth.

There are two main conventional routes for the colloidal synthesis of semiconducting nanoparticles, the hot-injection and the one-pot approach. Hot-injection is a method in which the organo-metallic precursor is swiftly injected into a well-stirred hot (organic) solvent, which enables a good separation between the nucleation and the growth phases. The nucleation takes place immediately after the injection, afterwards mainly growth takes place. This method is generally applied on the laboratory scale for high-quality syntheses of a variety of different semiconducting materials, such as CdS, CdSe and CdTe nanocrystals. However, this method is not suitable for large-scale industrial production and therefore so-called one-pot methods have been introduced lately. One-pot means that all chemicals are loaded together in a vessel that is heated. It is harder to get high-quality nanocrystals with this method since it is difficult to control the separation of nucleation and growth. This problem has been addressed and can be overcome by for example the addition of nucleation initiators and an accurate temperature control. In state of the art research there exist several one-pot syntheses towards nanoparticles of high quality. One example is a microwave assisted one-pot synthesis introduced by Washington et. al. where CdS homogeneous nanocrystals with quantum yield (degree of adsorbed photons that are emitted as light from the sample) of 33% were achieved.

1.3 Growth Models

There are three main growth mechanisms for nanocrystals, monomeric growth, Ostwald ripening and agglomeration.

a) Monomeric growth: The growth of a monomer on an existing nanocrystal consists of mainly two steps, first the monomer has to diffuse to the particle through the solvent matrix, and then it has to adsorb on the surface of the particle. To differentiate which of these steps is the dominating rate determining step is very difficult, and in this report these two steps will not be distinguished between. If the reaction determining step is either, the overall mechanism will be simply called “monomeric growth”. To get a well control reaction with high quality products, the monomeric growth mechanism is preferred. A common way to promote the monomeric growth in a reaction is to use ligands that act as surfactants. During
the growth period, surfactant molecules adsorb and desorb quickly on the nanocrystal allowing monomers to grow on the surface of the particle while still contributing with a large enough steric hinder to prevent agglomeration. Monomers prefer to grow on already existing particles rather than creating new nuclei, and they also grow more easily on smaller particles then bigger ones which means that this growth mechanism decreases the size distribution in a sample.\textsuperscript{6}

b) Ostwald Ripening: In so-called Ostwald ripening small solid particles, dispersed in their own saturated solution, dissolve and subsequently redeposit on the larger particles in the same solution. This means that the smaller particles disappear and the larger ones grow even larger on the expenses of the smaller ones. If no new nuclei are created Ostwald ripening should ultimately decrease the size distribution in a system by time as well as the overall number of particles. However, since in most systems nucleation can occur at any time during the reaction and other growth mechanism are present as well, Ostwald ripening usually results in a solution with a higher size distribution of particles with poor surface quality. The driving force behind Ostwald ripening is the minimization of the surface free energy of the system; small particles have a higher surface energy because of their large surface to volume ratio. This means that the dissolution of small particles and re-deposition of the material on larger particles is favourable for the system since the overall surface free energy is lowered.\textsuperscript{10}

c) Aggregation: In recent literature there has been an increasing interest in so-called magic-sized clusters (MSC) and their use as single-source precursors for the synthesis of semiconducting nanocrystals.\textsuperscript{11} MSCs refer to small clusters with a well defined number of atoms that forms out of the precursor monomers at a very early stage of the synthesis. The reason why they are called “magic sized” is that they only can grow to certain sizes containing a specific number of units. These clusters also stay the same size over longer periods of time.\textsuperscript{11} Magic-sized clusters of CdS typically give an apparent absorbance peak at a certain wavelength shorter than 350 nm\textsuperscript{11}; particles that absorb at longer wavelengths than 350 nm are considered nanocrystals in case of CdS. Once the clusters are formed they might act as nuclei to initiate the growth of nanocrystals.\textsuperscript{11} For the clusters there exist in principle two main reaction pathways, forward tunnelling and backward tunnelling. Forward tunnelling is when nanocrystals (NC) are formed by aggregation of clusters. Backward tunnelling describes the dissolution of the clusters back into monomers.\textsuperscript{11}

Figure 2. Illustration how magic-sized clusters either form nanocrystals or dissolve.\textsuperscript{11}
1.4 Sulphur precursor

There are a large number of reports on CdSe and CdTe made from chalcogenide precursors such as selenium or tellurium dissolved in trioctylphosphine (TOP) which exhibits very nice luminescent properties and a uniform particle size distribution. However, there are almost no reports on TOP-S being used as a sulphur precursor without some additives to enhance the reaction rate. The slow release of sulphur from TOP-S can be directly related to the comparably strong bond between phosphine (P) and sulphur (444±8 kJ/mol compared to 364±10kJ/mol for P-Se and 280±10kJ/mol for P-Te).9 The strong binding energy between phosphor and sulphur limits the release of sulphur into the solution which limits the possibility to stabilize the generated nuclei by further growth.9

Up to date only two different ways to solve this problem are reported. The first one is to search for a more reactive sulphur precursor which Yordanov et. al.12 did by investigating both Tributylphosphine-Sulphur and elemental sulphur. However their resulting products did not exhibit the same high QY and low size distribution as the ones that can be reached for CdSe and CdTe nanocrystals derived from TOP-Se and TOP-Te precursors. The second one is to try to selectively activate the sulphur precursor due to the relatively high dipole moment in the TOP-S using microwave radiation, which was demonstrated by Washington et. al.9 There the synthesis of high quality CdS nanocrystals with tunable optical properties and a high quantum yield (QY) of 33% was achieved by using TOP-S as a precursor in a microwave assisted synthesis approach. Normally a temperature of at least 180°C is necessary to cleave the P-S bond even by using microwave activation.9 In this publication it was already stated that the decomposition temperature of the precursor could probably be lowered by optimization of the synthesis.

1.5 Microwave assisted synthesis

Conventional heating is both inefficient and time-consuming; it also has a very big drawback in the fact that it heats the sample inhomogeneously by heating the vessel wall first and creating a temperature gradient throughout the sample. Microwave radiation on the other hand can transfer

![Figure 3. Different regions in the electromagnetic spectra are correlated with electronic, vibrational and rotational modes of molecules.](image)
energy directly to the reactive species by so-called, “molecular heating”. Microwave radiation is a form of electromagnetic energy with wavelengths between centimetres and meters. The energy-range implies that only molecular rotation is affected through the absorption of the microwave radiation and not the molecular structure itself. The microwave energy is very low relative to the typical energies needed to break molecular bonds which mean that microwaves will not affect the structure of organic molecules. Microwaves heat a sample by directly coupling to the molecules present in the sample, giving a uniform heating throughout the whole sample. The heating mechanism is either based on dipole rotation or ionic conduction. In the dipole rotation mechanism the polar molecules try to align themselves to the changing field from the microwave, but the field changes are too fast and the molecules are continuously in motion resulting in the release of heat. In the ionic conduction mechanism heat is created by the electric resistivity inside the ionic solution while the molecules try to align themselves in the changing field. ¹³

Microwaves are a reliable energy source which greatly enhances the reaction reproducibility since it can heat with a pre-programmed rate and keep the programmed temperatures with the accuracy of one degree. Microwave assisted chemistry had initially its use in organic synthesis where the first papers were published in 1986.¹³ In recent years the microwave has become more common as equipment also in nanoparticle synthesis.⁹ It has also been reported that microwave assisted syntheses are leading to a higher reaction yield and that lower temperatures are needed to overcome the activation energy compared to conventional heating systems. So far most literature regarding the microwave assisted production of inorganic nanocrystals only report on the synthesis in aqueous systems, only a few reports concentrates on common organic solvents such as diesel, octadecene and alcohol.¹⁴ Because of the uniform heating in a microwave reactor and the possibility to access fast heating rates a uniform simultaneous nucleation throughout the system and a rapid crystal growth resulting in crystallites with narrow size distribution is accessible.¹⁵ It is also stated that microwave irradiation can give the crystals the necessary energy to anneal and thus to reduce surface defect states which improves their overall photo-physical properties.⁹

1.6 Perspectives of microwave assisted synthesis of CdS nanocrystals

a) Low-Temperature synthesis of high quality CdS particles under ambient conditions

There are several reasons why a low temperature synthesis approach is preferred over a high temperature synthesis. One reason is the possibility to establish Online-Analytical investigation methods for absorption and photoluminescence measurements continuously during the growth of nanocrystals. This approach is currently developed at the Freiburg Materials Research Centre. The Online-Analytics is developed from two optical fibre based dip in probes connected to spectrometers that can measure absorbance and PL intensity in the reaction solution in real time, so the particle growth can be monitored very accurately. One limitation of these probes is their restriction to be used only under 160°C. Since most approaches for the colloidal synthesis of high quality semiconductor nanocrystals involves a reaction at much higher temperatures a new synthesis route for highly luminescent CdS nanoparticles at low temperatures has to be developed which was addressed during this master thesis project. Following the strategy of Washington et. al.⁹ the limitation due to the lack of reactivity of the TOP-S precursor will be solved by selective activation through microwave irradiation. It is reported that the synthesis of CdS nanocrystals using TOP-S as
precursor cannot be performed at temperatures below 180°C using standard ligand systems such as decane or trioctylphosphineoxid. By introducing aliphatic alcohol as novel ligands the limitation of reactivity could be overcome and high quality CdS nanocrystals were created below a reaction temperature of 160°C enabling simultaneous online analytics by using dip-in probes.

b) CdS protective shells in core-shell nanoparticles

Nanoparticles are sensitive both to chemical and physical attacks, such as oxidation\(^9\) leading to changes in their photoluminescence behaviour. Another problem in colloidal synthesis of semiconductor nanocrystals is the widely observed phenomenon of blinking. Blinking means that rather than steadily emitting light under continuous excitation the fluorescence from individual nanocrystals turns “on” and “off". \(^\text{16}\) The fluorescent blinking of nanocrystals is especially a problem in their application as biological labels on a single Quantum dot level.\(^\text{17}\) A good way to protect the nanoparticle is to surround them with a shell of another semiconductor material, preferably one with a wider band gap since this does not interfere with the original luminescent properties of the nanoparticle.\(^\text{18}\)

A problem with shelling a nanoparticle is that there has to be a low concentration of defects on the core/shell interface. This is easier achieved if the shell can be grown on the core epitaxially, therefore the lattice mismatch between the two materials have to be as little as possible. For example the lattice mismatch between CdSe/CdS is only \(\approx 4.1\%\)\(^\text{19}\) which makes CdS a very interesting protective shell material for CdSe quantum dots.\(^\text{19}\)

c) Modelsystem for defect states at room temperature

Another interesting feature to investigate in CdS quantum dots are the occurrence of defect states since they impose in case of CdS quantum dots light emission in the visible range. The quality of the surface is therefore directly correlated with an optical signal which gives an immediate and easily detectable response to changes in the surface. There are recent results that show how CdS can be used as a white light generator thanks to its different emissions in the visible range.\(^\text{20}\)

2. Material and Methods

2.1 Materials

Chloroform puriss Sigma-Aldrich, Cadmiumoxide (CdO) 99,999% ABCR, Sulphur (S) 99,5% ACROS, Steric Acid (SA) 98,5% Fluka, Succinic Acid 99,5% Fluka, Trioctylphosphine (TOP) 97% ABCR, 1-Hexadecanol (HDO) 99% Sigma Aldrich, 1-Tetradecanol (TDO) 97% Aldrich, 1-Octadecanol (ODO) 99,0% Fluka. All chemicals were used as received, without further purification.

2.2 Methods

2.2.1 Precursor Synthesis

\(\text{TOP-S (2 molar)}\)

20 mmol elemental sulphur was put in a three-neck-flask equipped with a temperature sensor in one of the necks and a septum in the other. The flask was put under a nitrogen gas flow that could be
exchanged to vacuum through a filter connected to the last neck. 10 ml TOP was taken in a syringe from the glove-box were it is stored and added to the flask through the septum. The mixture was immediately degassed by using the vacuum to empty the flask before refilling it with nitrogen gas, this was repeated three times. Then the mixture was heated to 100°C and kept there for 10 min to make sure all sulphur was dissolved, the solution was colourless during the whole time. When the solution had cooled down it was divided into air-tight 1ml vials that were labelled and stored in the glove-box before use.

**Cd-Stearate (1106g/M)**

The Cd-stearate was prepared using the same setup as for TOP-S. CdO reacts with SA and forms Cd(SA)₂ while water is released during the reaction. A 1:2 mixture of CdO and SA is not enough to let all CdO react, therefore an excess of SA was used (3.5 mol SA per 1 mol Cd) so the molar weight of the final product, Cd-stearate, was 1106g/M. 10 mmol CdO and 35 mmol SA was put together with a catalytic amount (~50mg) Succinic acid in a three-neck-flask and heated to 100°C where the flask was degassed three times. The mixture was then heated to 200°C and kept there until all red CdO had reacted, and the solution had a cloudy white colour, approximately after one hour. The succinic acid acts only as a catalyst and could be seen in the end of the reaction as small white particles in the solution. The material was white and solid when cooled down to room-temperature and was grinded in a mortar; the resulting powder was stored in a vial under ambient conditions before use.

**Cd-Laurate(810g/M) and Cd-Hexanate (517g/M)**

Cd-Laurate was already available in the lab. It was synthesized using the same protocol as described previously for Cd-Stearate only exchanging the Steric Acid to Lauric Acid. The Cd-Hexanate was also prepared in the same manner. The only difference was in the handling of hexanioc acid since it is a liquid and not a powder.

### 2.2.2 Experiment

In this report the novel approach of a microwave assisted non-injection low-temperature synthesis of CdS nanocrystals in long chain alkyl alcohols is evaluated by systematic investigation of different reaction temperatures, heating rates, concentrations and precursor- and alcohol chain lengths. It is demonstrated how these parameters affect the growth and the quality of the resulting CdS nanocrystals. The development of the nanocrystal reaction was investigated at certain stages of the reaction by taking different time- aliquots of the synthesis product which were investigated by absorption and photoluminescence spectroscopy. From every system that was examined, at the point with the highest luminescence during the reaction (so called “bright point”) a TEM picture was made to investigate the size and shape of the nanocrystals in the sample.

*Figure 4. The microwave set-up.*
2.2.2.1 Microwave assisted synthesis approach

10ml standard microwave test tubes where loaded with 2,5 mmol HDO (606 mg), 0,1 mmol Cd(SA)(111 mg) and 0,2 mmol TOP-S (0,1 ml) and closed with a snap cap, a system specially designed for the microwave which can stand high pressures up to 17 bar. The test tubes were heated in a Discover S-class microwave working at 300W, 2,455GHz (CEM, Kamp-Lintfort, Germany) to the desired temperature and kept there for different times. From the reaction products 50µl aliquot samples were taken with a syringe and then dissolved in 1 ml Chloroform for optical characterization. Since Washington et. al.\textsuperscript{9} states that the CdS growth behaviour seems to be unaffected by the presence or absence of air all experiments in this report were made in vessels that were loaded under ambient conditions and then capped without any exclusion of air.

2.2.3 Analysis

\textit{UV-Vis Absorbance Spectroscopy}

UV-Vis Absorbance Spectroscopy is the measurement of the wavelength and intensity of absorption of light by a sample, the technique is usually applicable for light with wavelength between 200 nm and 1000 nm. The technique is applied on a cuvette containing a solution of the sample, and is very useful for quantitative as well as qualitative measurements. The spectra are obtained by scanning the wavelength and can give information on the size distribution of the particles in the sample, and it can also give some ideas on their shape and lattice structure\textsuperscript{21}. From the absorption spectra the concentration of the sample can be calculated using the Lambert-Beers law:

\[ A = \varepsilon \cdot b \cdot c \]

(1) where \( A \) is the Absorbance of the sample, \( \varepsilon \) the extinction coefficient of the sample, \( b \) is the path length, the cuvette side, and \( c \) is the sample concentration.\textsuperscript{22}

Figure 5 shows a typical absorbance spectrum of CdS QDs, the peak at the longest wavelength is called the 1\textsuperscript{st} excitonic peak and for CdS that peak is located between 400 nm and 500 nm depending on the size of the particles. If the quality of the sample is high additional peaks can be seen at shorter wavelengths and are named 2\textsuperscript{nd} excitonic peak, 3\textsuperscript{rd} excitonic peak and so forth going from right to left in the spectrum. The different excitonic peaks corresponds to energy levels which are more probable for the electrons to absorb at, with the 1\textsuperscript{st} being the most probable.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{absorbance.png}
\caption{Illustration of a typical absorbance spectrum.}
\end{figure}
The absorption spectra were recorded with a J&M TIDAS diode-array spectrometer using a halogen/deuterium combined light source (Spectralytics, Aalen, Germany) on samples dissolved in chloroform and diluted to an absorbance of ≈0.5.

**Photoluminescence (PL)**

Photoluminescence is a technique that detects the emission of fluorescent light from a sample due to an optical stimulation at a certain wavelength (excitation). The technique is sensitive, simple, and comparatively cheap. It can give both qualitative and quantitative results. The material absorbs energy by the exposure to the exciting light source. Electrons in the material are promoted from the valence band to higher energy levels in the conduction band resulting in electron-hole pairs. In luminescent materials the energy difference between the hole and the electron is released as light when the electron-hole pair recombines. From the PL spectra the size distribution of the light emitting particles can be estimated by the full width at half maximum (FWHM) of the band-gap signal. The often broader defect luminescence that can be seen at longer wavelengths in the spectra gives some information of the defect states and surface condition of the sample.\(^{23}\)

Figure 6 shows a typical Photoluminescence spectrum of CdS QDs where the highest peak is the band-edge photoluminescence peak. For CdS it usually appears between 400 nm and 500 nm. Sometimes a small peak-like feature can be seen at a shorter wavelength which directly corresponds to the used excitation wavelength, this peak is therefore called excitation peak and has nothing to do with the sample. At longer wavelengths a broad peak is often seen which corresponds to the defect states in the crystals and the ratio between the peak intensities gives an indication of the particle quality, e.g. how many defect states are present. The position of the PL band-edge peak correlates to the particle size in the sample, and the width at half intensity, FWHM, correlates to the size distribution of particles in the sample.

The emission spectra were recorded with a J&M TIDAS diode-array spectrometer (Spectralytics, Aalen, Germany) using a J&M FL 3095 monochromator (Integration time: 10s) on the same diluted samples used for the absorbance measurement. If nothing else is stated the samples were excited at 315 nm.
Transmission Electron Microscopy (TEM)

A TEM is a microscope that uses an electron beam instead of visible light for the exposure of a sample. The wavelength for an electron is typically less than an Angstrom which makes it possible to visualize objects almost in the same size-range as atoms. A TEM is constructed so that at the top there is an electron gun, and then the electron beam passes through an electromagnetic condenser lens that orders the electrons in a parallel beam hitting the sample. When the electrons are accelerated towards a sample some of them will go right through it, some will deviate a little from their path due to interaction with the specimen and some will be reflected. After the electron beam has passed the sample there are another set of electromagnetic lenses that are used for magnification. A TEM uses the electrons that are transmitted through the sample to create a picture of the sample, which is called bright-field image. The image gives information of the particle size and shape in the sample. The diffracted electrons are used to create a so called dark-field image, which can resolve the spacing between different lattice planes in the sample which correlates to the crystal structure of the sample. The TEM resolution depends on the microscope and the sample and can be less than 0.5 nm. New TEM microscopes can also be used for elemental mapping by using an additional scanning mode of the electron beam, which can reveal what kind of elements are present in the sample based on that the interaction of the beam creates element specific x-rays.

The TEM measurements were performed using a Zeiss (LEO) 912 Omega transmission electron microscope with an acceleration voltage of 120kV and zero loss filtering. Samples were prepared from one drop of reaction solution diluted in chloroform and put on a carbon coated copper grid which was then washed three times with chloroform and measured without any further treatments.

Quantum Yield

The quantum yield was evaluated with a comparative method using Quinine Sulphate in 0.5 M H₂SO₄ as reference dye based on the following equation:

\[ QY = QY_d \cdot \frac{I}{I_0} \cdot \frac{OD}{OD_0} \cdot \frac{n_d^2}{n_0^2} \quad (1) \]

Where \( QY_d \) is the known quantum yield of the dye, \( I \) and \( I_0 \) are the integrated peak areas from the sample and the dye respectively. \( OD \) and \( OD_0 \) are the absorbencies for the samples at the excitation wavelength, in our case 344 nm, and \( n \) and \( n_0 \) are the refractive indices for the solvents, namely chloroform and water.
3. Results and Discussion

In this report the effects of temperature, heating rate, concentration and ligand and precursor chain lengths on the low temperature one-pot synthesis of CdS s were investigated under ambient conditions. Starting from a microwave assisted synthesis approach using 2,5 mmol HDO, 0,1 mmol Cd(SA) and 0,2 mmol TOP-S the different parameters were varied.

The optical effects were measured with absorption and PL spectroscopy on samples with the same content only stopped after different reaction times. First, the reaction goes through a period of narrowing of the size distribution of the particles (FWHM) and their surfaces show less defects visible by the increase of the PL intensity, this phase is called “size focusing”. After that the size distribution gets broader again and the luminescence drops because the particles surfaces quality decreases. This phase is called “defocusing”. In a regular synthesis setup with a Schlenk-line different time aliquots are taken to visualise this. In the microwave reactor it was not possible to take aliquots, therefore several samples with the same content where synthesised at the same temperature but kept there for different times to give a visualisation of the reaction over time. The highest PL intensity achieved during the synthesis evolution, was reached after the size focusing regime and before the defocusing regime and is called the “bright-point” of the reaction.

The results of the optical investigation were visualized by Evolution curves (PL intensity as a function of time), Growth curves (PL wavelength as function of time), Absorbance curves (Absorbance as a function of corresponding PL wavelength, corresponds to the concentration of the product at a certain size) and by absorbance and PL data as a function of wavelength from a chosen point during the reaction. Additionally a TEM image was taken from the sample were the absorbance and PL spectra are shown as a function of wavelength, to investigate the shapes and the size distribution of the particles. The Evolution curves show the PL intensity for the samples at different times and also their FWHM. The intensity is taken as quality criteria of the particles and their surface constitution. Highly luminescent particles have well protected surfaces and a limited amount of surface trap states. The FWHM is the width of the PL peak at half of its maximum intensity value, giving a good indication of the size distribution of the particles in the sample. A broad size distribution is reflected in broad peaks (larger FWHM values). The growth curves show the PL peak position, which directly correlates to the particle size since the particle band gap in the quantum confinement region changes with size, and is plotted against the reaction time. This curves show how fast the particles grow in a sample up to a certain size. Finally the absorbance curves display the absorbance intensity as a function of PL peak position. The Absorbance correlates to the particle concentration via the Lambert-Beers law (equation 1), assuming that the particles do not grow at that stage in the reaction. The PL peak position correlates to the particle size in the sample and therefore the absorbance curves gives a visualization of the concentration of particles in a sample when the particles are of a certain size. All the conclusions derived from the different graphs are only valid if the particles are spherical in shape; therefore the TEM pictures are an important supplement to the optical measurements in order to extract valid conclusions.
3.1 Pre experiment using a conventional synthesis setup

In a pre-experiment a conventional synthesis set-up using a Schlenk-line and a heating mantel was used. The solution quickly and surprisingly turned grey as soon as the temperature rose over 200°C. This can be attributed to the decomposition of Cd-Stearate to CdO. In a conventional synthesis approach with ligands protecting the Cd-stearate precursor, it is possible to synthesize CdS nanoparticles at higher temperature. However, the alcohol seems to promote the decomposition of Cd-stearate and some investigations had to be made before the system was usable. In a conventional synthesis set-up using standard heating-systems accurate temperature control was hard to achieve. When the temperature was measured inside the solution it could be as much as 20°C higher than the temperature measured by the controlling sensor through the sensor glass, whereas the microwave equipment in the laboratory allows controlling the reaction temperature with an accuracy of one degree Celsius. Therefore the microwave was used to study the “grey-point” problem in order to avoid the formation of CdO during the synthesis of CdS nanoparticles. Different synthesis temperatures were used. It was found that Cd-Stearate does not decompose in HDO below 210°C during reasonably long reaction times (up to two hours). It is obvious that there is time-temperature correlations that make Cd-Stearate decompose at longer reaction times (several hours) even if the temperature is below 210°C. The grey CdO particles are formed immediately when the temperature reaches 210° or higher. Because of this limitation only reaction temperatures between 100°C and 200°C will be investigated for the synthesis of CdS nanoparticles in this report.
3.2 Influence of the heating rate on the CdS nanoparticle growth

The heating rate is the time that was needed to heat the samples from room temperature to 200°C. Different heating rates are compared: Fast = 1 min 30s, Medium = 3 min, Slow = 5 min. The resulting absorption and photoluminescence spectra taken when the PL intensity reached a maximum (bright point) are imaged in Figure 4 together with a corresponding TEM image revealing the shape and size of the CdS particles.

The absorbance and PL measurements (figure 4) indicate that all of the samples consist out of high quality crystals with a narrow size-distribution. TEM imaging confirmed that the particles are spherical. The expected sizes can be calculated from the absorbance peak positions\textsuperscript{26} and results in 4,0 nm (fast heating rate), 4,1 nm (medium heating rate) and 3,9 nm (slow heating rate), which correlates to the particle sizes seen in the TEM pictures, ≈4,0 nm (fast heating rate), ≈4,1 nm (medium heating rate) and ≈3,8 nm (slow heating rate).

There is no significant difference observed when comparing the different heating rates. This leads to the conclusion that small changes in the heat-up time of the samples do not affect the quality of the particles. This is a very promising feature for up-scaling of the synthesis since larger volumes are more difficult to heat up quickly, even with microwave heating, and a larger heating rate is the consequence.

*Figure 7* (left) illustrates the Absorbance, PL Intensity and TEMs for the bright-point samples from the different heating rates.
3.3 Influence of the reaction temperature on the CdS nanoparticles

![Absorbance and PL Intensity curves](image)

Figure 8 (above) Shows the Absorbance, PL Intensity curves and corresponding TEM images at the bright-point for each reaction temperature (left), as well as the Evolution curve for the whole reaction at each temperature (right).
From the fine-structure of the absorbance and the narrow PL peaks (figure 8) the CdS nanocrystals seem to be of very high quality. From the TEM it is clear that they are spherical and the sizes calculated from the absorbance peak position are $200^\circ C = 4.0 \text{ nm, } 180^\circ C = 4.3 \text{ nm, } 160^\circ C = 4.3 \text{ nm}$ which correlates nicely with what can be seen in the TEMs. The TEM pictures are of bad quality, probably because of the lack of proper purification before the sample was put on the grid; therefore the TEMs are mainly to control the particle shape. Such things as statistics and mean value of the particle size could not be calculated from the TEMs. However, it is possible to see from the scale bars in the pictures that the sizes of the particles at least lie in the right size-range to correlate to the calculated values.

During the reaction there is first a rise and then a drop in PL intensity. This is a common effect observed in all 3 reactions at different temperatures and can be attributed to a monomeric growth mechanism. Afterwards a drop of the PL intensity is observed which might originate from Ostwald ripening of the particles. The monomeric growth is faster for smaller particles, thus decreasing the FWHM and making the fluorescence stronger, which can be seen in the decrease in the FWHM curve in the beginning of the reaction (Figure 8 b, d, f) while the PL intensity is rising. However during Ostwald ripening the luminescence intensity is supposed to decrease and the FWHM should increase since larger particles get larger while smaller get smaller and the size-distribution gets broader. This is seen in the graph in 8d and 8e; however, in 8b the FWHM goes down and then stays down. This could be because the precursors are not that reactive, so when the Ostwald ripening starts there is still a slow release of monomers which induces the growth of the smaller particles thus keeping the size-distribution and the FWHM down. After Ostwald ripening the particles surface is usually less protected leading to a decrease of their luminescence.

The most significant difference between the three reaction temperatures is the time-scale. It takes longer time to reach the bright-point at lower temperature. From the growth curve (figure 9a), it can also be seen that it takes longer time to reach the same particle sizes for the reaction at lower temperature. The absorbance (figure 9b) correlates to the concentration of particles in the solution. Taking into account that the extinction coefficient is strongly dependent on the size of the particles.
and that the absorbance values were normalized by dividing all of them with either the lowest or highest absorbance in that certain reaction the absorbance values are not completely linearly correlating to the concentration. Based on this, and due to the lack of duplicates of the experiments, the values in the graph contain some uncertainty in them and it can be concluded that there is nearly no concentration difference between the different temperatures.

These results suggest that the initial reaction mechanism is similar for all three syntheses temperatures and that it is monomeric growth. Afterwards Ostwald ripening becomes more and more apparent at later stages of the syntheses. They also show that the temperature mainly affect the time-scale of the reaction.

In common synthesis routes the usage of a sulphur activity enhancer compound is one way to subdue the sulphur reactivity problem. Dithiolbenzothiazole can be used as sulphur activity enhancer and can together with elemental sulphur and cadmium acetate dehydrate lead to high quality CdS nanoparticles in octadecane. In a publication of Washington et al. it is mentioned that TOP-S is very rarely used as S-precursor since it has comparable high bond strength between the phospine and the sulphur, and how the reactivity of the precursor can be enhanced by using microwave radiation. It is also stated that a temperature of at least 180°C is necessary to cleave the phospine sulphur bond, even by using microwave radiation for activation. Here TOP-S has been used successfully as an S-precursor at temperatures far below 180°C using a commercially available microwave synthesis reactor. In a different publication by Pan et. al the effects of the binding strength of the ligands on the nucleation and growth of the CdS nanoparticles is discussed. It is stated that a weakly coordinating ligand enhances both nucleation and growth, while a strong ligand can totally impede the nucleation and growth. Therefore it is here concluded that although TOP-S may be a comparatively unreactive precursor the activation by microwave irradiation together with a weakly coordinating ligand, in our case long-chain alkylalcohol, is sufficient to make TOP-S a useful S-precursor reactive even at lower temperatures.
3.3.1 Low-temperature synthesis of CdS nanoparticles

![Graph](image1)

Figure 10 (above) Shows the absorbance and PL spectra for three different low-temperature syntheses performed at 100°C, 120°C and 140°C respectively.

Compared to the high-temperature synthesis approaches the low-temperature approaches performed at 140°C shows a significant increase in the ratio between defect luminescence and band gap luminescence. This demonstrates that the optical properties of the nanocrystals were of lower quality than those made at higher temperatures. This can also be seen in the absorbance spectrum where a lack of fine structure is observed. The corresponding TEM confirms the decrease of particle quality and it is seen that the particles form loose assemblies. This decrease of quality seems to be a consequence of the lower reaction temperature, due to the fact that the nucleation and growth are not clearly separated leading to a broader particle size distribution. The decomposition of monomers at the particle surface is more difficult and slower, leading to an increase of surface defect states which is visible by the pronounced broad PL signals between 550 and 600 nm (Fig. 10b).

![Graph](image2)

Figure 11. The emission spectra at short wavelengths.

In the low-temperature reactions performed at 100°C and 120°C, sharp and well pronounced peaks occur at 332 nm and 337 nm in the absorption spectra respectively. In a recent publication by Yu and Liu\textsuperscript{11} similar peaks in the absorption spectra for low temperature reactions of CdS nanoparticles as have been attributed
to so-called magic sized clusters with sizes less than 2 nm in the solution. Additionally a theory for clusters aggregation to form stable nanocrystals was introduced. The theory states that clusters stay stable at the same size for longer periods, e. g. their peak position does not shift and then when they aggregate to form nanoparticles a new peak appear with a shift towards longer wavelengths. The way the two cluster peaks from the 100°C and 120°C spectra (figure 10a) evolve into the to peak-like features that can be seen in the 140°C curve (figure 10a) when temperature is changed accord well with the theory that the nanocrystals actually form from CdS clusters that aggregate.

In the publication of Yu et al.\textsuperscript{11} it is additionally stated that at higher reaction temperature, in their case over 150°C, the creation of clusters and their aggregation into nanocrystals is so fast that there is a clear separation of the nucleation and growth phase even for one-pot reactions. That could be also in our case a reasonable explanation for the nice optical properties of the nanoparticles synthesized at 160°C and above. From figure 10 and figure 11 it can be concluded that the CdS-clusters are not luminescent. The broad peak that can be seen results from the few nanocrystals that exists in the sample and absorb from 370 nm and towards longer wavelengths in the absorbance spectra (figure10b). From the same figures it can be noted that for the reaction at 140°C there is a clear PL peak from the band edge of the nanocrystals visible at 430 nm which means that there are more nanocrystals in the solution even though the comparably low band gap luminescence and the large defect luminescence suggest the particles are containing a significant amount of defects.

For the reactions at higher temperatures (160°C, 180°C and 200°C) the sharp absorbance peak between 330 and 340 cannot be detected but this is probably due to the fact that at higher temperatures the creation of clusters and their evolution to nanocrystals is very rapid, which means that they already formed nanocrystals when the first aliquot was taken. All these results suggest that early in the reaction nanoclusters with very specific sizes are created, which might act as nuclei and form nanocrystals by aggregation or sequential growth, which then can further grow by monomeric growth, continuous growth.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{TEM pictures from the low temperature reactions performed at, a) = 100°C b) = 120°C and c) = 140°C.}
\end{figure}

Figure 12 shows the TEM pictures from the low-temperature synthesis; they show that nanocrystals are present at both 100°C and 120°C; however, they seem to be smaller than the nanocrystals seen
previously in higher temperature synthesis. In the TEM image of the product synthesized at 140°C it is clear that the nanocrystals are bigger and that they agglomerate and form loose assemblies.

![Graph showing optical spectra](image)

Figure 13. The optical spectra for nanocrystals that form when CdS nanoclusters are heated to 200°C for 20 minutes.

Figure 13 shows the resulting nanocrystals based on heating-up of clusters to 200°C for 20 minutes. The clusters were originally synthesized at 100°C for 6 hours. Since the optical properties are very similar to the optical properties of the CdS nanoparticle synthesis performed at 200°C it is concluded that the initial nanocrystal formation is most likely based on the aggregation of clusters.

The TEM picture from the same sample (figure 14) also confirms this theory since the nanocrystals in the sample have the same shape and mean size, ≈4nm, as the earlier seen nanocrystals synthesized at 200°C.

![TEM image](image)

Figure 14. TEM picture from clusters created at 100°C for 6h and then reheated to 200°C where they were kept for 20 min.
3.4 Effect of the concentration on the growth of CdS nanoparticles

3.4.1 Precursor concentration

The alcohol to precursor ratio was varied while keeping the concentration ratio of the Cd and S-precursors 1:1. The precursor to alcohol ratio was the following: 1:50 = (0,05 mmol Precursor to 2,5 mmol HDO, 1: 25 = (0,1 mmol Precursor to 2,5 mmol HDO) and 1:12,5 = (0,2 mmol Precursor to 2,5 mmol OH).

From the Absorbance and PL spectra it can be concluded that the particles are of similar high quality as presented in chapter 4.2 and 4.3.

In table 1 some key-parameters from samples synthesized at 200°C for 60 min with different precursor to alcohol concentrations are highlighted. The parameters are extracted from the spectroscopic data.

With increasing precursor concentration the absorption signal rises. This is expected since more precursor material is directly resulting in a higher particle concentration. It can be also clearly seen that the particles are smaller in the Cd:OH = 1:50 concentration compared to the samples with a higher precursor concentration (1:12,5), and that they at the same time have a slightly larger FWHM (see table 1).

From this the conclusion can be drawn that at low concentration of precursor material the slow release of the precursor results in a slower growth.

Figure 15. Absorbance, PL intensity and TEM pictures for the synthesis of CdS nanoparticles at 200°C with different precursor to alcohol ratios. The reaction was stopped after 60 min.
which leads to particles with a broader size distribution (see table 1). The maximum PL intensity is also smaller for the 1:50 sample having a maximum for the 1:25 sample. When the concentration is increased to Cd:OH = 1:25 the FWHM is decreased at the same time as the PL Intensity is increased, which means that the particles have less surface defects, probably because there is enough precursor to let them have a controlled monomeric growth. In the sample with the highest precursor concentration (1:12.5) a decrease in PL Intensity can be seen while the FWHM still stays low, this is probably because of the effect called concentration quenching which occur in high concentration samples where the proximity to other nanoparticles quenches their luminescence.

Table 1. Some different key values for the samples synthesized at 200°C for 60min with different precursor to alcohol concentrations.

<table>
<thead>
<tr>
<th>Cd:OH</th>
<th>Abs Wave (nm)</th>
<th>Conc. (a.u. at PL wave, 430 nm)</th>
<th>PL Wave (nm)</th>
<th>PL Intensity (a.u.)</th>
<th>FWHM (nm)</th>
<th>Calculated size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:50</td>
<td>413</td>
<td>0,02</td>
<td>430</td>
<td>15300</td>
<td>19</td>
<td>3,8</td>
</tr>
<tr>
<td>1:25</td>
<td>422</td>
<td>0,50</td>
<td>437</td>
<td>22700</td>
<td>16</td>
<td>4,2</td>
</tr>
<tr>
<td>1:12.5</td>
<td>422</td>
<td>1,20</td>
<td>438</td>
<td>17700</td>
<td>16</td>
<td>4,2</td>
</tr>
</tbody>
</table>

From the growth curves (figure 16) it can be seen that a higher precursor concentration leads to larger particles, demonstrating that the precursor concentration affects the kinetics of the reaction. It is also seen that the decomposition of the precursor follows the Arrhenius equation:

\[ V = c^*e^{(\Delta G/kT)} \]  (2)

Where \( V \) is the release of monomers from the precursor, \( c \) is the concentration of precursor, \( \Delta G \) is the activation energy and \( k \) is Boltzmann’s constant. 29

Simply, when the concentration is increased the release of precursor is increased as well, which result in a faster growth to larger nanoparticles.
3.4.2 Influence of the Cd:S ratio on the synthesis of CdS nanoparticles

The concentrations used in the experiments were: Cd:S = 2:1 (0.2 mmol Cd to 0.1 mmol S), Cd:S = 1:1 (0.1 mmol Cd to 0.1 mmol S), Cd:S = 1:2 (0.1 mmol Cd to 0.2 mmol S). In all cases 2.5 mmol HDO was used as ligand. The reactions for the CdS nanoparticle synthesis were performed at 200°C and stopped after 60 min of reaction time.

The absorption and PL graphs are imaged in figure 17 together with corresponding TEM images. The TEMs shows that the particles are spherical, and altogether the graphs suggest the nucleation and growth mechanics is monomeric growth on particles nucleated by cluster aggregation as stated earlier in chapter 4.3.

In table 2 (below) the spectroscopic details are summarized for the CdS nanoparticle synthesis at 200°C by varying the Cd:S ratio. The reaction was stopped when the PL signal reached its maximum (bright point). It can be seen that the concentration of particles in the samples are the same, considering errors and the extinction coefficient not being linearly dependent when converting absorbance to concentration. However the particle sizes in the Cd-rich samples seems to be larger. This is probably because the precursor TOP-S can act as a surface ligand as well, while Cd(SA) only acts as precursor. If there is enough TOP-S present which can act as surface ligand and protect the surface of the particle the particle surface is protected in a very

Figure 17. Absorbance, PL intensity and TEMs from the 60 min sample at 200°C for different precursor ratios.
initial stage and it is harder for monomers to grow onto the initial particle. At the same time the ligands also protect the particles from aggregation. In the Cd-rich samples the particles grow faster and larger, and from the TEM it can also be seen that they form loose assemblies. This might be attributed to the fact that there are not enough ligands in the mixture to protect the surface, so the growth is considerably easy and aggregation can occur more easily. From Table 2 it can also be seen that the FWHM stays almost the same value independent of the precursor ratio, while the PL Intensity drops down both for Cd-rich and S-rich particles. In case of the Cd-rich particles this can be explained by the formation of assemblies which make the local particle concentration very high, thus quenching the luminescence. In case of the S-rich particles it is known that S-based compounds are quenching the PL of Cd-based nanocrystals.

Table 2. Some key-values for the 60 min samples at 200°C from different precursor ratios.

<table>
<thead>
<tr>
<th>Cd:S</th>
<th>Abs Wave (nm)</th>
<th>Conc. (a.u. at PL wave 436 nm)</th>
<th>PL Wave (nm)</th>
<th>PL Intensity (a.u.)</th>
<th>FWHM (nm)</th>
<th>Calc. Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>428</td>
<td>0,75</td>
<td>440</td>
<td>16200</td>
<td>15</td>
<td>4,37</td>
</tr>
<tr>
<td>1:1</td>
<td>422</td>
<td>0,67</td>
<td>437</td>
<td>22700</td>
<td>16</td>
<td>4,15</td>
</tr>
<tr>
<td>1:2</td>
<td>422</td>
<td>0,55</td>
<td>437</td>
<td>17100</td>
<td>16</td>
<td>4,15</td>
</tr>
</tbody>
</table>

From the growth-curve it can be concluded that the Cd-rich particles grow larger and faster, which is an effect of a less protected surface since there is less TOP-S in the mixture which might additionally act as surface ligand both during the nucleation phase and the growth phase of the reaction.

Figure 18. Growth-curves of CdS nanoparticles for different precursor-ratios.
3.5 Influence of the compound chain lengths on the resulting CdS nanoparticles

3.5.1 Cd-precursor

Figure 19. (above) Absorbance and PL Spectra for CdS nanoparticle syntheses performed at 200°C with different Cd-precursors a) and b) = Cadmium Stearate, c) and d) = Cadmium Laurate and e) and f) = Cadmium Hexanate. The reaction was stopped after 90 min and 30 min respectively after reaching the bright point. The corresponding TEM are displayed as well.
The Cd-precursors were prepared from three acids with different chain length. Cd(SA) from Steric Acid (18 carbon atoms), Cd(LA) from Lauric acid (12 carbon atoms) and Cd(HA) from Hexanoic acid (6 carbon atoms).

The calculated sizes of the particles were 4.5 nm for Cd(SA) and 5.0 nm for Cd(LA), because of the lack of fine structure or even a clear absorbance peak for the Cd(HA) that particle size was not calculated. The mean sizes from the TEMs were ≈ 4.5 nm for Cd(SA), ≈ 5 nm for Cd(LA) and ≈ 7 nm for Cd(HA).

Here, the evolution curves are shown (figure 19 b, d and f) since the curves for the particles made from Cd(HA) show significantly different results. The absorption spectra for the Cd(SA) and Cd(LA) particles show pronounced fine structure features. As stated earlier these results points towards a monomeric growth on nanoparticles created from cluster aggregation. However, the absorption spectrum for the Cd(HA) particles does not exhibit any fine structure, and a broad FWHM values as well as a rapidly decreasing PL intensity demonstrates a lower particle quality. Also the TEM picture for the Cd(HA) sample shows a large size-distribution. This suggests that aggregation might be the dominant growth mechanism in this case. This also suggests that the particle growth occurs quite rapidly and that even if the initial growth is leading to steep growth curves indicating a well separation between nucleation and growth is leading to a considerable particle size distribution and a low PL intensity. Once again the release rate of monomers from the precursor is the answer, from Arrhenius equation (equation 2) it can be seen that the activation energy also affects the release rate. Here the activation energy of the precursor depends greatly on its chain length, and the very short chain length in Cd(HA) results in an almost explosive release of monomers. The fast growth results in particles with bad luminescent properties which is directly seen in the low PL intensity for the particles created from Cd(HA).
3.5.2 Influence of the chain length of the alkyl-alcohol ligand

Figure 21 (above) Shows Absorbance, PL Intensity and TEM pictures for the different alkyl-alcohol chain lengths, as well as evolution curves for the three reactions. The reactions were made at 200°C and kept there for 90 min.
For all three different chain lengths the absorbance spectra show a resolved fine-structure as well as narrow PL peaks indicating a high quality of the particles. (figure 21) The PL intensity and the FWHM also still follow the same behaviour as earlier reactions where the PL intensity first increases and then decreases while the FWHM goes down and then stays down. From the growth-curves (figure 22) it can be concluded that the particles grow larger when the ligand is shorter. This is confirmed by the calculated particles sizes. Ouyang et. al.27 showed the same results in a very similar reaction approach. They explained the phenomenon by the effect of sterical hindrance from the ligand chain influencing the reactivity of the precursors. They demonstrate that longer ligand chain lengths are leading to smaller particle sizes. This also occurs in our synthesis approach.

The reaction with TDO as ligand exhibits the highest value for the fluorescent intensity compared to all reactions performed during this master thesis. The relative photoluminescent quantum yield (QY) was measured using Quinine Sulphate, and resulted in a QY of 33%. In a recent publication by Ouyang et. al.27 they measured the QY of CdS nanoparticles based on a similar procedure. Their product based on a one-pot synthesis of CdS using the traditional non-coordinating ligand octadecene resulted in a QY value of 30% which is only a little bit lower than presented here. Compared to literature results which usually shows QY of less than 30%9 this novel synthesis route under ambient conditions results in high quality CdS nanoparticles with a fluorescent QY at the same level as the state of art experiments. One explanation for the considerably high luminescence from the particles in TDO could be that the ligand is able to create well protective ligand spheres around the particles leading to an enhancement of the luminescence.
3.6 CdS clusters as a shelling material

The fact that the very small magic sized clusters can form CdS nanocrystals at higher temperatures opens the possibility to use them as single source precursors for the nanocrystal synthesis (refer to previous results shown in Fig. 14) as well as for using them as protection/shelling material.

A "proof of principle" experiment was conducted to demonstrate that CdS clusters can be used to protect CdSe nanocrystals from oxidation. It was observed that pre-made CdSe nanocrystals heated in HDO at 200°C for 20min can be completely photo-oxidized resulting in a shift of the PL peak to shorter wavelengths because the CdSe reacts with the oxygen in air. This makes CdSe in HDO a good system to study protective effects such as a protective shell which prevents photo-oxidation of the CdS nanocrystals. CdS clusters made from a mixture of 2,5 mmol HDO, 0,1 mmol Cd(SA) and 0,2 mmol TOP-S was kept at 100°C for six hours. Then CdSe nanocrystals were added and the mixture was heated to 200°C where it was kept for 20 minutes. The PL measurements this time showed a clear CdSe peak at a constant wavelength together with a much smaller peak at shorter wavelengths (figure 23b). This result clearly demonstrates that the CdS nanoclusters protect the CdSe nanocrystals from photo-oxidation to some extend and slows down the photo-oxidation in general. That some CdSe still photo-oxidizes can be a concentration effect and the proof of principle experiment has to be modified. However with the performed characterisation methods alone it is impossible to say whether the CdS clusters form a shell around the existing CdSe or not, but that the presence of CdS clusters protect CdSe from oxidation is obvious.

![Graphs showing absorbance and PL intensity](image_url)

*Figure 23. Shows the absorbance (left) and the PL Intensity (right) for the shelling system.*

Worth to mention is also the fact that CdSe because of charge transfer quenches the PL characteristics from CdS nanocrystals (figure 24a) which makes it impossible to determine if there is co-nucleation in the mixture or not. More detailed investigations have to be performed to clarify this issue. However the possibility to grow a protective CdS shell in the same ligand system as the CdSe nanocrystals opens interesting new possibilities towards core shell materials.
Figure 24. a) CdSe PL intensity in the presence of CdS nanocluster b) TEM picture from the CdSe particles in the presence of CdS nanocluster after 20 min at 200°C.
4. Conclusions

In this report a new low temperature synthesis approach of CdS nanoparticles out of TOP-S and Cd(SA) in a novel ligand system based on long-chain alkyl alcohols is reported. The ligand together with the use of microwave irradiation enhances the reactivity of the TOP-S precursor so that it can be efficiently used as S-precursor at low temperatures. The system was thoroughly investigated in aspect of the influence of different synthesis parameters such as heating rate, reaction temperature, precursor concentrations and ligand chain lengths. It was found that small changes in heating rate do not affect the system or the PL quality of the resulting particles.

The reaction temperature only affects the reaction time; longer reaction times are needed to reach the bright point at lower temperatures. This is due to a slower release of monomers from the precursors at lower temperatures. Between 200°C and 160°C there is no difference in the wavelength, FWHM and intensity of the PL peak from the particles. But at 140°C there is suddenly a great increase of defect states which can be detected by fluorescence spectroscopy. At lower temperature the precursor’s reactivity is also significantly decreased and particle aggregation as an alternative growth mechanism is observed rather than particle growth by monomeric growth. At lower temperatures, down to 100°C, a sharp absorbance peaks at 332 or 337 nm are observed which can be attributed to recently identified “magic sized clusters”, approximately 1.8 nm in diameter, of CdS reported in literature.\(^\text{11}\) It has been also reported that these clusters can aggregate to nanocrystals.\(^\text{11}\) Similar results were found as well for CdSe magic sized clusters\(^\text{30}\).

This fact might be also the explanation why the particles observed in the beginning of the reaction are never smaller than approximately 4 nm, regardless which parameters are changed. The clusters simply aggregate to a certain size and then they grow further by monomeric growth. A decrease of the PL intensity can be seen in all reactions with increasing reaction times due to Ostwald ripening. One explanation why the FWHM stays low could be because the precursors are so un-reactive that they release monomers slowly during the whole reaction time which gives a competition between further growth and Ostwald ripening, this could result in Ostwald ripening giving the particle surface problems thus decreasing the luminescence while the particles still grow by monomeric growth keeping the FWHM down.

A low precursor concentration results in a slower growth and the formation of smaller particles. From the Arrhenius equation this is expected, a lower precursor concentration results in a slower release of monomers. If the concentration is too high the PL intensity decreases probably due to concentration quenching.

A high TOPS concentration also results in a slow growth and the formation of smaller particles since the precursor TOPS can act as a surface ligand and protects the particles from aggregation. An excess of ligand also slows down the growth rate since it is more difficult for the monomers to reach the particles and grow onto them.

Changing the Cd-precursor chain lengths gives the largest effect influencing the CdS nanoparticle formation. A short chain length vastly enhances the precursor reactivity which results in a fast growth of nanoparticles with lower quality. The fast growth is probably due to particle aggregation of
small CdS clusters, while nanoparticles grown from precursors with longer chain lengths seem to obey more the monomeric growth mechanism.

Changing the alkylalcohol chain length results in a less pronounced effect, however it is shown that a shorter ligand also enhances the precursor reactivity and results in slightly larger particles. It is also found that the crystals synthesized in a shorter ligand exhibit the best luminescence properties and the highest QY.

Overall the new reaction is leading to high quality particles, the best were found to be the ones synthesized with Cd(LA) and TOP-S in HDO. Additionally from the results of the alcohol chain length it is assumed that the particles might be even better if synthesized with Cd(LA) and TOP-S in TDO. CdS clusters formed at low temperature were found to protect CdSe from photo-oxidation in a HDO ligand system heated together at higher temperature which opens the door for new approaches towards core shell materials in a microwave reactor.
5. Outlook

Online analytics with BWeLabs

BWeLabs is a research project focused on the possibility to develop a “virtual” or “remote controlled” lab environment to make raw material and equipment more accessible. As a part of this project an online analytic system is currently constructed in the Freiburg Material Research Centre. The system is based on two dip in probes that can measure absorbance and PL intensity continuously during the reaction which will make the time aliquot approach unnecessary and also give insight into the very early stages of synthesis when it is hard to make aliquots fast enough by hand. However, these probes can only be used at a temperature up to 160°C. By optimizing the synthesis of CdS in alkyl alcohol it is possible to make nanoparticles at 160°C and therefore this system is very adaptable as a model system during the optimization of the online analytic system.

Up-scaling

The up-scaling of this synthesis is also very promising since the system is not that sensitive to small changes, especially in heating rate and also since the reaction is very repeatable. Furthermore, microwave heating is also a promising avenue for up-scaling of chemical reactions.

Defect states

There was no time to research the defect states of CdS during this project; however it is still an interesting investigation to do and the results in this report shows how to create or avoid defect states in CdS made in an alcohol based ligand systems.
References


24 A.S. Sologubenko *Novel carbon nanosheets as supporting foils for ultrahigh resolution TEM studies of nanoobjects* EMC 14th European Microscopy Congress 1-5 September (2008) Aachen, Germany


