Correlation of size and photoluminescence of single CdSe/ZnS quantum dots

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Abstract

In this thesis the correlation between size and emission wavelength of single CdSe/ZnS quantum dots (QDs) has been studied. Based on the quantum confinement model QDs of different size emit light of different wavelength. In order to characterize individual QDs, experiments were carried out using a high-resolution atomic force microscope (AFM) placed on top of an inverted optical microscope. The quantum dots were exited with a high-power diode laser (405 nm) and the spectral response was recorded with a CCD camera attached to a spectrometer. Samples with two different average-sized QDs exhibiting photoluminescence maximum at 600 and 621 nm were prepared by spin-coating a highly diluted QD/toluene solution on cleaned glass cover slides. The results of this thesis verify the theoretical prediction and show on single particle level that with decreasing QD size the emission energy increases.
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Chapter 1

Introduction

Nanotechnology is a new and recent branch of the science dealing with the control of the matter at dimension less than micrometer scale, in particular typically between 1 and 100 nanometer (1 nm = 10^{-9} m).

The term "nanotechnology" generally indicates the manipulation of matter at atomic and molecular level.

Nanotechnology is a multidisciplinary field of investigation, involving several research areas like: molecular biology, chemistry, materials science, physics (both applied and basic), mechanical engineering, chemical engineering, and electronics.

The number of applications using nanotechnology are rising every year, for instance solar cells which are based on the photoelectric effect (explained by Albert Einstein in 1905 [1]), the common used Laser and recently established quantum dots (QDs). The first reference to nanotechnology (not yet using this term) dates back to the speech given by Richard Feynman in 1959, entitled “There’s plenty of room at the bottom”. [2] Feynman suggested a way to develop the ability to manipulate directly atoms and molecules, the so-called scale-down. Briefly, the method consists in designing a series of machine tools in 1:10 scale, then using them to develop and test the next generation of tools, scale 1:100, and so on.

With decreasing of the size it was necessary to redesign some tools, due to the fact that the ratio between the various forces had changed. In nanoscale dimensions, for example, the contribution of gravity becomes less and less predominant. The new physical phenomena raising up are explained by quantum mechanics. Feynman took account of all these scaling issues during his explanation.

Quantum mechanics is a physical theory describing the behaviour of the radiation, matter and their interactions, with particular regard to the phenomena typical for the (sub)atomic scales of length and energy.[3] One of the best studied material used in nanotechnology are semiconductors.

The knowledge about semiconductors has been increased very fast until today. Thanks to the intermediate characteristic between metal (no bandgap) and insulator (large bandgap)
it has been possible to engineer the width of the bandgap which is the energetic distance between valence and conduction band. With the absorption of a photon by a semiconductor material it is possible that an electron jumps from the valence band to the conduction band and let a vacancy in the valence band called hole. Afterwards, the recombination of the electron with the hole generates another photon with a wavelength depending on the bandgap.

When scaling down into the nano range quantum mechanical effects appear, which are described by the quantum confinement. The quantum confinement is explained in quantum mechanics by the quantum well theory. A quantum well is a potential well that confines charge carriers and therefore forcing their localization. The effect of quantum confinement takes place when the thickness of the well becomes comparable to the coherence length of the carriers (generally electrons and holes) and as a result the particles confined in the well can occupy a discrete number of energy levels.\cite{1}

There are many applications which are based on the quantum well effect. The first goal was to have a quantum well without applying an electric field. In this case the heterojunction is a good solution for that problem, because with the junction between different materials with different bandgap it is possible to create a quantum well in the junction. So just using a p-n junction with materials having a different bandgap in this case it is possible to create a quantum well. Applying a voltage to emit photons with a wavelength that in energy is related to the value between the first energy level in the conduction band and the first in the valence band. This is 1D confinement.

The state-of-the-art of nanotechnology is changing very fast. It can be realized having a look on the number of related publications, e.g. on nanowires (1D confinement) and QDs (0D confinement).\cite{5}

Nanowire exhibit confinement in two directions. So, there the electrons are free to move only in one direction. One of the most discussed application of nanowires are carbon nanotubes. Quantum dots show confinement in all three directions so there the charge is not free to move. They have a behaviour like a single atom that why they are called “artificial atom”, because the energy levels are discrete in all three directions.

1.1 Potential applications

The QDs studies are very recent studies. Ten years ago Bawendi et al.\cite{6} started to study monocrystalline CdSe nanostructures. The first study that has been done was very limited and the future application seemed to be low power Laser. Later on possible applications of QDs started to grow at least in theory; there were not only the low power Laser but also chemical applications and medical applications.

In biomedical research QDs were used for lighting up a cell so they can be easy visualized and localized by a microscope. QD bioconjugates can be used to identify cancer cells or tag bacteria. QDs are performing better than dye molecules used to identify cells. The
main advantage is that they have a very large absorption spectrum, instead the synthetic molecule that has a very narrow absorption spectrum. It is possible to buy QDs in solvent and they are ready for use. It is possible to get QDs with already antigen or protein integrated. So they can be injected in the body and can give the luminescent qualities. In this case it is possible to watch the moment of cell or protein in real time.\cite{7,8}

Other applications of QDs are coming from solar cell application; nowadays the solar cell efficiency is about 20-30%. Has been tested that using QDs for integrate to the silicon photovoltaic cell can improve the efficiency up to 40%.\cite{7,9} This is possible using the multi-junction cell method. It consists of having the QDs that can absorb different part of the solar spectrum (according to their size). In this case the efficiency can increase but without increasing the cost of the devices. To integrate the QDs within the devices just an additional step in the device fabrication itself is needed.

QDs are also considered for single electron transistors or single electron memories.\cite{10}

1.2 Goal of the Thesis

The material used in this thesis are CdSe/ZnS QDs. They were dispersed in toluene in low concentration and spin-coated on a cleaned glass substrate.

The main goal is the verification of the theoretical correlation between size and emission wavelength of a single QD. Depending on the QD size light of different wavelength is emitted. For example, the large ones of about 5.2 nm in diameter emit in the red spectral range and the smaller ones in the blue (about 2.2 nm). Experimentally the size of the QDs is determined using a high-resolution atomic force microscope (AFM) and the spectral characteristics of the same QDs are recorded by photoluminescence measurements.
Chapter 2

Basics and Theory

As mentioned before, small quantum dots, such as nanocrystalline semiconductors in colloidal solution, have dimensions between 2 and 10 nanometer, corresponding to about 10-50 atoms, figure 2.1 in diameter, and may reach a total of 100 - 100,000 atoms within the volume of the QD. The self-assembled QDs have a size of 10-50 nanometer and are composed in defined shapes with the use of particular technologies like electron-beam-lithography.

A QD can also be compared to atom: both have a discrete energy spectrum and retain a small number of electrons, but unlike the confinement potential of QD not necessarily show spherical symmetry. Furthermore, the electrons do not move in the free space, but within the semiconductor crystal that hosts them.

For have a efficient use of the QD properties is necessary a good control of the synthesis process, because the intrinsic characteristic are sensible to factors like: size of the dot, shape, defect or impurities in the crystal. A small variation of one of the factor mentioned before can create a large variation in the qualities of the QD.

Figure 2.1: A picture of CdSe/ZnS QD. The size of the core can be between 2-10 nm, and the shell is around 1.6 monolayer. [32]
2.1 From bulk semiconductor to quantum dot

The main characteristic of the bulk semiconductor is the distribution of possible energy levels in energy bands separated by forbidden ranges (energy gap).

In conductors usually the last band (called the conduction band) is not completely filled, so there are levels not occupied by electrons but continuous in energy to those occupied. The electrons can access these empty levels receiving energy from an external electric field and thereby induce a current density according to the field. The electrons of the lower bands, which are all filled, do not absorb energy and do not affect the conduction process. The last filled band is called valence band.

In solid state physics the electronic band structure of a solid describes the range of energies that an electron of a certain material is “allowed” or “forbidden” to own (figure 2.2). The band structure of a solid is a direct consequence of the Bloch theorem. It is used the band structure of a solid and more generally of a material to determine physical characteristics of the system.

Another direct consequence of the Bloch theorem is the fact that the energy levels $\epsilon_{nk}$ which can be filled by electrons, are characterized by two principal quantum numbers: $k$ and $n$. $n$ is an index of discrete quantum number. $k$ instead can have any value within the first Brillouin zone associated with the particular crystalline structure of the solid. Since the first Brillouin zone is described with set of $\epsilon_{nk}$ as a (continuous) function of $k$, as it is shown in the figure 2.3. In a specific set $n$, the electrons can occupy in a continuous range of energies. This creates a band of energies. The range of energies between the maximum value and the minimum value reached in a band is called bandwidth.

A solid has theoretically an infinite number of bands ($n = 1, 2, 3, ...$). However, most of the electrons lies at high energy that essentially they are free to escape from the solid. And
therefore the bands above a certain level are not taken into account. This level is located at an energy equal to the work function (vacuum level) which is the energy difference to the Fermi energy level. \[11\]

If two consecutive bands overlap may be degenerate (in this case they overlap exactly). Two bands can be non-degenerate, but have their energy intervals partially overlapped. In this case between the two bands is create a range of energies where there are not electronic levels allowed. That is the so-called bandgap.

The electrons in a solid stay at the ground state a temperature of 0 K, in consequence to their fermionic nature and the Pauli principle \[11\] which says that the fermions can not be found two in the same state. Therefore, they fill the allowed electronic states starting from the lowers energy. That occurs according to the distribution of Fermi-Dirac \[11\] calculated at 0 K. The highest occupied energy level is called the Fermi energy.

So, there is the possibility to find three different band diagram:

- There is a band, or more than one of the last filled by electrons, which is partially filled and some states remain empty. In this case it has to do with a metal, then the last electrons have the possibility to move to energy levels very close but also infinitesimally higher in energy to the one it is, and therefore have the possibility of a high mobility that leads the system to be a good conductor of electricity, as it is shown on figure 2.4 le image on the left.

- The last band has been completely filled in such a way that the next electronic state is allowed on the next band, and between this band and the band completely filled there is a forbidden band (band gap) of energies. In this case the solid is an insulator figure 2.4

- Finally, there is the semiconductor which consist in an insulator with the band gap so small that at room temperature there is a certain probability that the electrons are found to skip the band gap for thermal agitation. Therefore, the system is in a situation close to that of a metal, with values of electrical conductivity not null, as it is shown on figure 2.4 le image on the right.

Figure 2.3: Bloch function. The wavefunction of an electron inside a crystal structure. In this graph the interaction with the atoms nucleus is evident. \[33\]
The bandgap in a semiconductor can be of two type: direct and indirect. The direct bandgap is called when the maximum value of energy in the valence band is exactly in the same position to the lower energy level of the conduction band in the k space.

So, indirect is a bandgap in which the minimum of conduction band is shifted by a vector k relative to the maximum energy level in the valence band. The difference of vector k represents the momentum.

The semiconductor having a indirect bandgap are inefficient in the emission of light, because from the figure 2.5 it is possible to see that for the transition in this case we need the interaction with a phonon as well. This happens because each electron present in the conduction band move quickly to the energy minimum of the band. The electrons require a minimum source of momentum that allows them to exceed the threshold and to fall in the valence band. The photons possess small momentum in comparison to the k vector. The change of k value of a photon emitted or absorbed is negligible and the direct transitions are mostly “vertical” in k space.

Since the electron can not reach the valence band with by radiated recombination. Therefore, electrons in the conduction band stay a long time before recombining in less efficient ways. The time that an electrons spend in the conduction band is called life time. Silicon, for example, is an indirect band gap semiconductor, so it is not generally useful in LED (“light-emitting diodes”) or diode lasers.

The behaviour of the charge carriers within a bulk crystal can be described by the model of the “free electron gas”. As a first approximation, it is assumed that these electrons do not interact with the internal potential of the crystal. In addition, we consider the solid of infinite dimensions, in order to disregard the contribution of the surface atoms. This approximation is no valid in the case of a nanocrystal, in which the fraction of the surface atoms with respect to the total number is high. This introduces a significant contribution
Figure 2.5: Direct and indirect bandgap. In the direct interband transition the phenomena is affected only from the energy of the photon for the transition from valence band to the conduction band and vice versa from the bandgap, in the indirect transition the phonon have a important part, as it is shown on the figure, their interaction is fundamental for the transition.[35]

to the total potential of the solid.

2.1.1 Quantum confinement

When the size of the crystal becomes comparable to the de Broglie wavelength associated to the particles that interact with it, the motion of the charge carriers is strongly confined within that structure. The description of their behaviour, therefore, has similarities with the problem of the quantum “particle in a box” based on the solution of the Schrodinger equation.[12]

For a nanocrystal, this approach allows to derive a discretization of the energy levels in the vicinity of the bands. This is a distinguishing feature compared to the continuous energy levels associated with the corresponding bulk solid. This phenomenon, found experimentally, is commonly called to the “quantum confinement”. The density of the quantum states can be derived as a function of energy depending on whether the “box” of potential is limited in one, two or three dimensions.[13]
In a solid bulk, there is almost a continuous energy and the density of electron states, \( N(E) \), is a function of \( E^2 \). In a two-dimensional system ("quantum well"), (b) picture in figure 2.6 that is infinitely extended in the directions \( x \) and \( y \), the quantization effects are due to the confinement of charge carriers along the \( z \) direction only. In this case \( N(E) \) has a "step" like behaviour, for which the density of states is quasi-continuous with respect to \( k_z \) (\( k \) is the wave vector associated with a possible electronic state), but it takes only a few independent values from energy \( E \). These features allow, for example, the use of "quantum wells" of semiconductors in the LEDs or as laser sources for reading disks.\[13\]

In a one-dimensional system ("quantum wire"), (C) picture in figure 2.6, it has confinement in two directions, for example along \( y \) and \( z \). In this case the density of states depends from \( E^{-\frac{1}{2}} \). Each branch of the hyperbola describes a continuous distribution of states \( k_x \) and a discrete distribution of \( k_y \) and \( k_z \). Quantization in two dimensions has important consequences on the charge transport. The electrons can move freely along the \( x \) axis, but may occupy discrete states along \( y \) and \( z \). They therefore act as channels of discrete conduction. To this end, for example, are studied the well-known carbon nanotubes as electron emitters or as single electron transistor.\[13\]

In zero-dimensional systems ("quantum dots"),(d) picture in figure 2.6, where the quantum confinement exists in three dimensions, the distribution of states \( N(E) \) will be a delta function \( \delta \) very similar to that of an atomic system. The smaller number of quantum states allowed in a "quantum dot" than a "quantum well" or a "quantum wire" allows greater modulation of the radiation emitted by luminescent nanocrystals, and electromagnetic properties.\[13\]

For each material there exists a critical size below which the effects of quantum confinement become noticeable. Since the discretization of the of the bands edges and the increase of the band-gap resulting in a substantial differentiate of electrical and optical

![Figure 2.6: Electronic density of states versus energy profile in semiconductor material.](image)

a) bulk, b) quantum well, c) quantum wires and d) quantum dots.\[36\]
properties of the nanocrystal compared to its bulk counterpart. This happens when the energy $\Delta E$ that separates two successive quantum levels exceeds the thermal energy to the temperature $T$:

$$k_B T << \Delta E = \frac{4E_F}{3N}$$  \hspace{1cm} (2.1)

where $E_F$ is the Fermi level of the crystal and $N$ is the number of free electrons in the conduction band. From (2.1) it is evident that the observation of new properties are related to the quantum confinement in a nanocrystal. Linked to the intrinsic nature of the material (through $E_F$ and $N$).

For example, in the metal $N$ is generally large and then the separation between the two bands is minimal. The increase of energy gap will be detectable only in $T$ of a few Kelvin and for very small nanocrystals (2-3 nm). On the contrary, for a semiconductor $N$ is small and the Fermi level lies in the bandgap. In this case, the energy gap tends to increase dramatically already at room temperature and for relatively large size of the nanocrystals (5-50 nm).

2.1.2 CdSe/ZnS QDs

Cadmium selenide (CdSe) is a semiconductor compound by cadmium and selenium. This material is transparent to IR light. Application of CdSe as bulk material is not widespread but on the contrary, studies as nanostructured material have been raised very quickly in the last fifteen years.

Major part of research was devoted to the improvement of the synthesis and its application. The main problem dealing with CdSe in biomedical area is the toxicity of cadmium for the human body. Selenium is toxic too but only large quantity. So, the most interesting and practicable area for that type of semiconductor is in solar cells and thin-film transistors.

CdSe is a semiconductor made by materials from group II and group VI which form in standard configuration a direct bandgap material. Due to that fact the material has very good photoluminescence qualities. The bandgap is 1.74 eV, that means this material in bulk form has a spectral emission to the near IR range. But the most important characteristic of the material comes out when it is used like a nanomaterial, because there, with the quantum confinement effect, the spectral range moves to the visible light, as it is shown in the figure in each bottle there are QDs with a range of size that permit to have light emission from red to blue colour.

The fabrication of the QDs is made by synthesis of nanocrystals by thermal decomposition of the precursor in a hot solvent. The goal of the controlled chemical synthesis is to obtain monodispersed crystals. In fact, the final distribution is related both to the size distribution of the cores in the initial states and the subsequent growing of them. It is necessary to establish conditions that permit the separation in time between the creation
of the core(nucleation) and the stage of growth.

The rate of the nucleation is extremely more sensitive to the temperature then the rate of growth. It means that ideally a way to suppress the nucleation and allow only growth is to constrain the system to a strong decrease in temperature after reaching the threshold of supersaturation.

The synthesis of nanocrystals is carried out in a flask containing a solvent and one or more precursors, figure 2.8. In this case they are alkylcadmium and trioctylphosphine selenide \[ \text{TOPSe} \] and the reaction is:

\[
\text{Me}_2\text{Cd} + \text{TOPSe} \rightarrow \text{CdSe} + (\text{byproducts}).
\]

After setting the mixture to a suitable temperature, the precursors are injected whose reaction triggers the nucleation of the nanocrystals. One way to separate the creation of the core from the growth is to use a injection of the hot precursor (hot injection technique). In a first moment in the solvent mixture is added to the surfactants at 100-350 °C and then is quickly injected a solution of cold precursors (usually at room temperature). The abrupt lowering of temperature (20-50 °C) ensures a relatively short period of creation of the cores, which follows the growth of the cores, therefore, the main condition is to focus on the variation in size.

After cooling the reaction mixture, the extraction of the nanocrystals is made by using a solvent of opposite polarity to that of the reaction mixture. That makes possible the interaction between the particles, inducing aggregation and, therefore, the precipitation is made by spin coating.

After washing, the nanocrystals can then be stabilized in a wide range of solvents (of similar polarity to that of the reaction mixture in which they were prepared), depending on the hydrophobic or hydrophilic character conferred by the surfactants bound to their surface.

![Figure 2.7: Evident CdSe/ZnS QDs. The colour of the bottle is light emitted from the QDs and their colour indicate the size of the QDs as well.](image)
Figure 2.8: Chemical fabrication of CdSe QDs. The flask has inside the solvent used to grow the QDs and inside are also the dots after the chemical reaction.

**Shape**

The shape of CdSe crystal depends on the fact if the material is bulk or nanocrystal.

Typically, the CdSe crystal structure for bulk is hexagonal wurtzite or rock-salt structure and the bandgap is direct or indirect, respectively, figure 2.9.[18] The variation of those characteristic depends on the pressure which the material is subjected. In fact, above the pressure of 3GPa the crystal bulk type pass from hexagonal wurtzite to rock-salt. For QDs structure remain those qualities but the pressure affecting the variation of the crystal increases.

The parameters of the synthesis are optimized in each case with an appropriate choice of precursors, surfactants, temperature and reaction time. The average size of the nanocrystals are established by the balance between the stage of nucleation and the growth, determined by the actual concentration of the reactive species, monomers, and the temperature.[16]

As in the size, the properties of the nanocrystals depend on the shape as well. Therefore, it is important to examine the experimental parameters which influence that. At the current state of the art, there are numerous examples of nanocrystals of various materials in different forms, such as spheres, rods, tetrapods, prisms, cubes and stars.

Generally, isotropic forms (cubic or spheres) assume symmetric crystal structure (cubic zinc-blende or rock-salt, etc.), while anisotropic objects (rods, discs) have crystal asymmetrical structures (eg. hexagonal wurtzite, tetragonal anatase). However, it may happen that the creation of the cores and growth occur at different stages, causing the formation of
nanocrystals with a coexistence of phases and with new morphologies. This fact is clearly illustrated by the case of tetrapods, in which the faces equivalents (111) of a core tetrahedral zinc-blende can grow wurtzite stretch sections of rod-like shape along the direction (001).[17]

**Surface properties**

With the extremely small dimension of the QDs the surface properties become very important for their characterization. In fact, the number of atoms which cover the surface are between 15 % to 30 % depending on the size of the QD. The height of the surface-to-volume ratio influences the QD optical absorption, quantum efficiency, luminescence intensity and spectrum.

The emission efficiency of a QD is generally low because of the non-radiative relaxation processes due to the “trap states” present on the surface of the QD. These trap states are electronic states with different energy of surface atoms that arise from non bounded atoms. To avoid the recombination of the electrons only in the form of heat, and instead obtain a extremely high fluorescence quantum yields of 70-80 % it is necessary to delete these trap states with a surface passivation.

**Shell passivation**

The surface passivation is made by another type of material, called shell material, with the same crystal properties of the core. In the core/shell systems, the core interior is formed by a pair of atoms not bounded, while the outer shell you choose another pair of atoms to generate the same crystal structure, so, as to complete the bonds of atoms surface of the inner core. Furthermore, the bandgap of the material of which it is done the shell must have a larger bandgap then that one of the core, figure 2.10. So, the electrons is “Trapped” in the core and cannot recombine non radiative.

It is necessary to keep the size distribution of the shell during the growth:

![Figure 2.9: CdSe different lattice view.](image-url)
• Delete the homogeneous nucleation of the material of the shell, or eliminate the formation of core made only with the material of the shell.

• Must be a homogeneous growth of monolayers precursor of the shell material over the core. Thus leading to the formation of shell with uniform thickness around the core.

For this reason, the conditions, like addition of the precursors, temperature control, cycles heating and cooling in the process of colloidal synthesis, must be controlled very accurate.

2.2 Photoluminescence in semiconductor QDs

Semiconductor nanocrystals have in the dominating effect of quantum confinement a systematic variation of the density of electron states and energy bandgap. With decreasing size, the enlargement of the bandgap is accompanied by the development of discrete energy levels close to the edge of the bands.

The minimum energy required to create an electron-hole pair (an “exciton”, figure 2.12) in a quantum dot is defined precisely by energy the bandgap. Radiation with energy less than the bandgap cannot be absorbed by QDs. Since the energy bandgap depends on the size of the QD, the threshold for the absorption will consequently be related to them. The absorption spectra of nanocrystals are characterized by the presence of some bands, which correspond to possible transitions induced by the discretisation of them. As the size increases, the absorption bands are moving to energies lower and become progressively less resolved due to the reduced quantum confinement effect. Usually, the exciton peak is better defined at lower energy.

Figure 2.10: CdSe/ZnS core/shell, the shell made in ZnS is often used like a shell for the larger energy gap so that increase the probability that a exited electron remain in the core. [37]
In some materials, excitons tend to relax radiately with high quantum yield. The emission bands arising from electron-hole recombination from the band are on border, so, they are directly related to the bandgap. The broadening of peaks of absorption and luminescence strongly depends also on the size distribution of the nanocrystals. This fact allows, for example, to monitor the growth of nanocrystals in a colloidal solution with a conventional spectrometer.

The quantum confinement in the QD can be explained by the “particle in a box”-theory, figure 2.11, and the energy levels inside the dot are given by:

\[ E_n = \frac{n^2 \hbar^2 \pi^2}{2mR^2}. \tag{2.3} \]

where \( n \) is the quantum number and indicates the level, \( R \) is the diameter of the well (QD diameter).

The total amount of energy is given from by energy gap of the bulk material and the quantum confinement energy of the first level for both electron and hole:

\[ E_{\text{confinement}} = \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) = \frac{\hbar^2 \pi^2}{2\mu^* R^2}, \tag{2.4} \]

where \( m_e \) and \( m_h \) are respectively the effective mass of electron and hole and \( \mu^* \) is the effective reduced mass of the electron-hole pair (\( \mu^* = \frac{m_e m_h}{m_e + m_h} \)).

### 2.2.1 Excitons

In a nanocrystal, in which the dimensions are greater than the lattice constant of the material, the electronic properties are determined by the periodicity of the crystal and the motion of charge carriers is restricted to the volume of the nanocrystal. This leads to quantum confinement effect and the increase of energy of the transitions between the conduction band and valence band. In order to explain the nanocrystal energy behaviour it is necessary to follow some approximation model. In the case of CdSe nanocrystal they
are given from the study of Brus: [27] [28]

- The nanocrystal is spherical and the radius is R.
- The inner part of the nanocrystal is a uniform, so, there are no point charges or occupied spaces other than the excited electron and hole (i.e., nuclei or bound electrons).
- The potential energy outside the nanocrystal is infinite, thus the electron and hole are always found within the nanocrystal (i.e., the surface of the nanocrystal defines the walls of the “box”).

The Hamiltonian of the system for a non-interacting hole-electron pair is given by:

\[
\hat{H} = -\frac{\hbar^2}{4\pi^2 \varepsilon_e} \nabla^2_e - \frac{\hbar^2}{4\pi^2 \varepsilon_h} \nabla^2_h + V_{e,h}
\]  

(2.5)

with the confinement potential:

\[
V_{e,h} = \begin{cases} 
0 & \text{per } r_{e,h} < R \\
\infty & \text{per } r_{e,h} > R 
\end{cases}
\]

where \(m^*_e, m^*_h\) are the effective mass of electron and hole(0, 13m_o and 0, 45m_o), \(r_e, r_h\) are their respective radial coordinates. In this system the wave function of the electron-hole pair is expressed by two independent contributions due to the two charge carriers. Applying the boundary conditions to the narrow limits \(\psi(R) = 0\). The solution to the Schrödinger equation in this case is the particle-in-a-box solution to the Schrödinger equation, modified for the case of a sphere:

\[
\psi(R)_n = \frac{1}{R\sqrt{2\pi R}} \sin \left(\frac{n\pi r}{R}\right)
\]  

(2.6)

Figure 2.12: The electron-hole pair is also defined by the name of exciton.
where $\chi_{nl}^2$ is the $n^{th}$ root of the Bessel function of order $l$ [23]. The energy of a particle in a spherical potential well features discrete values and it is inversely proportional to the radius $R$. Considering the ground state the following formula is obtained:

$$E_{nl}^{e,h} = \frac{\hbar^2 \chi_{nl}^2}{2m_{e,h} R^2} \quad (2.7)$$

With respect to the bandgap of the bulk semiconductor, the energy of the transition of the lowest state of the electron-hole pair ($1S_h \rightarrow 1S_e$) undergoes an increase of:

$$\Delta E = \frac{\hbar^2 \pi^2}{2\mu^* R^2} \quad (2.9)$$

where $\mu^*$ is the effective reduced mass of the electron-hole pair ($\mu^* = \frac{m_e m_h}{m_e + m_h}$).

The next step towards a discussion of the problem is the inclusion of the Coulomb interaction between the hole and the electron inside the quantum dot. The Hamiltonian corresponds to the following expression:

$$\hat{H} = -\frac{\hbar^2}{4\pi^2m_e^2}\nabla_e^2 - \frac{\hbar^2}{4\pi^2m_h^2}\nabla_h^2 + \hat{V}(\vec{S}_e, \vec{S}_h) \quad (2.10)$$

where $\vec{S}_e, \vec{S}_h$ are the positions of the electron and hole, respectively, within the nanocrystal, and $\epsilon$ is the dielectric constant of the nanocrystal.

In the confined volume of the bulk the influence of Coulomb potential is essential and is the reason for the existence of excitons (observable only at cryogenic temperatures, because their binding energy is comparable with the thermal $kT$). The absence of the confinement potential allows to separate the Hamiltonian in the motions of the center of mass and relative to the center of mass of the electron-hole pair. In quantum dots this separation is not possible. An analytical solution of the problem is very complex. The simplest approach that takes into account the Coulomb potential is inversely proportional to the electron-hole distance ($\propto \frac{1}{R}$), while the kinetic energy is inversely proportional to the square of the radius ($\propto \frac{1}{R^2}$).

A possible description of nanocrystals is based on the Bohr radius $a_0$:

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e \varepsilon^2} \quad (2.11)$$

In the strong confinement regime ($R \ll a_0$) the Coulomb interaction can be neglected, and the solution of the problem reduces to the discussion above, a non-interacting electron-hole system, but this explanation cannot be enough prices. Similarly, for QDs with radius ($R \gg a_0$) (weak confinement), the problem can be solved considering the entire exciton confinement as a single particle in a potential well. In semiconductors with a high exciton
binding energy, this approach represents a good approximation.

The potential energy \[ V(S_e, S_h) \] consists in two parts, one the Coulomb attraction between the carriers and second the polarization energy. For \( r < R \) the first part is the Coulomb attraction between the negatively charged electron and the positively charged hole:

\[
\hat{V}_{\text{Coul}}(S_e, S_h) = -\frac{e^2}{4\pi\epsilon_{\text{CdSe}}\epsilon_0 | S_e - S_h |}.
\]

(2.12)

Where the dielectric constant for CdSe is 10.6. The second component of the potential energy is the polarization energy. Essentially, a point charge inside a nanocrystal polarizes the crystal. This polarization affects the energy of the second charge. The polarization term is given by:

\[
\hat{V}_{\text{Pol}}(S_e, S_h) = \frac{e^2}{2} \sum_{k=1}^{\infty} \alpha_k \frac{S_e^{2k} + S_h^{2k}}{R^{2k+1}}
\]

(2.13)

where

\[
\alpha_k = \frac{(\epsilon - 1)(k + 1)}{4\pi\epsilon_{\text{CdSe}}\epsilon_0 (\epsilon k + k + 1)}; \epsilon = \frac{\epsilon_{\text{CdSe}}}{\epsilon_{\text{out}}}
\]

(2.14)

where \( \epsilon_{\text{out}} \) is the dielectric constant of the medium surrounding the nanocrystal.

Writing the eqs. 2.12, 2.13 together it is possible to write the Hamiltonian:

\[
\hat{H} = -\frac{\hbar^2}{4\pi^2 m_e} \nabla_e^2 - \frac{\hbar^2}{4\pi^2 m_h} \nabla_h^2 - \frac{e^2}{4\pi\epsilon_{\text{CdSe}}\epsilon_0 | S_e - S_h |} + \frac{e^2}{2} \sum_{k=1}^{\infty} \alpha_k \frac{S_e^{2k} + S_h^{2k}}{R^{2k+1}}
\]

(2.15)

From this equation, it is clear that as \( R \to \infty \), the polarization term \( \hat{V}_{\text{Pol}}(S_e, S_h \to 0) \), and the Hamiltonian in eq 4.4 becomes the hydrogen-like Hamiltonian of the bulk.

In the electron-hole system in order to determine the wave function \( \Phi(\bar{S}_e, \bar{S}_h) \), it is necessary that the function are studied at the lowest-energy wave functions of the individual charges, so, to get the \( \Psi(\bar{S}_e) \) and \( \Psi(\bar{S}_h) \) As a first-order approximation we can use the uncorrelated wave function:

\[
\Phi(\bar{S}_e, \bar{S}_h) = \Psi(\bar{S}_e)\Psi(\bar{S}_h)
\]

(2.16)

So, solving now the Schrödinger equation, the calculated internal energy of the exciton is

\[
E_{\text{ex}} = \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_{\text{CdSe}}\epsilon_0 R} + \frac{e^2}{R} \sum_{k=1}^{\infty} \alpha_k \left( \frac{S}{R} \right)^{2k}
\]

(2.17)
As energy of polarization is small compared to the kinetic and Coulomb energies, a good understanding of the lowest-energy excitonic state may be made by omitting this term. So, considering also the bandgap energy, the total amount of energy needed for a transition between the lowest energy level in the valence band and the lowest energy level in the conduction band is calculated by:

$$\frac{hc}{\lambda} = E_{tot} = E_g + \frac{\hbar^2}{8R^2}(\frac{1}{m_e} + \frac{1}{m_h}) - \frac{1.8e^2}{4\pi\epsilon_{CdSe}\epsilon_0 R}$$ (2.18)

These equations are valid for nanocrystals in the regime of strong confinement, or in systems which show a substantial absence of hole-electron correlation. It has been amply demonstrated [21] that this case is not limited only to clusters with radius $R \ll a_0$, but extends to $R = 2a_0$. These expressions are, therefore, the simple relations, which allow the calculation of the ground state energy of the electron-hole pair in the region where they are most observed effects of quantum confinement (the Bohr radius for CdSe is approximately 49 Å, it is then possible to calculate the energy of the transitions for crystals of CdSe up to 10 nm).

With the (2.18) it is possible to correlate the light wavelength emitted from a QD with the size of this one, for example if the light wavelength of a QD is 600 nm it should have, according to the (2.18), a size of the core of 2.7 nm.

In conclusion, the theoretical approach to the problem of quantum confinement allows to understand the phenomenon and to know what are the different contributions that affect the energy diagram of a nanodimensional solid.

### 2.2.2 Blinking

One of the drawbacks of the QDs luminescence is the emission intermittency. This phenomenon, is called also blinking, features in a non continuous emission of light when the dot is exited. The quantum dot, generally, change between a “on” state (light emission) and “off” (no light emission). The changing between these two states is random and differs from QD to QD. Observing a bunch of QDs, several QDs exhibit continuous emission whereas up to 20-30 % are “off” for the time of observation [26].

The QD blinking is change with the changing of the environment, temperature, pressure, laser intensity and size of the QDs [22]. The blinking rate of them is non constant in time, this means that the QD will have never the same blinking behaviour, so, the changing between “on” and “off” state will be always the same.

A simple explanation of blinking is based on the three-level model [22]. This model has three states: the ground state (“a” in figure 2.13), the light-emitting state and the “dark” trap state in which the QD undergoes to the “off” state (“b” in figure 2.13). Lets suppose that the system is exited by a laser with sufficient hight energy to excite an electron from the ground state to the light-emitting state. Now, this electron will relax radiately to the ground state and emit a photon. But, not in the case of blinking, because the electron will
Figure 2.13: QD blinking model: a, ON states contain a photoexcited electron ($e^-$) and hole ($h^+$) and emit efficiently. b, In an A-type blinking event, the OFF state contains an additional electron in an excited state and is dark due to an increased non-radiative relaxation rate. c, In a B-type event, “hot electrons” are trapped by surface states immediately following photoexcitation, and combine non-radiatively with the remaining hole. d, Addition of external charges in the trap states deactivates the trapping pathway, and causes B-type blinking suppression.\[26\]

relax, actually, non radiately to the “dark” state and the system it going to be in the “off” state. Let suppose, now, that a new electron is exited to the light-emitting state. In a first approach we can say it will do the same of the one before, but it is not, because the “dark” level is already occupied by the first one, so, then the electron is going to relax radiately.

This behaviour explains the blinking phenomenon in a easy way, but the physics of the “dark” state are not complicity understood yet. There existent a large number of theories about the “dark” state due to the fact that there are many types of trap states and all of them can affect the blinking behaviour. The trap state can be created for a not bound of the interface atom of the core with the shell. In this case the lifetime of the electron in this trap depends on the core material. Another type is the tunnelling of the electron outside the shell, so, in this case the blinking depends of the probability of the electron to pass through that one. Therefore, it depends on the thickness of the shell.
Chapter 3

Experimental

All the work for this thesis has been done in the Electrum Laboratory in Kista at KTH. For accomplishing the tasks of the thesis advanced microscopes, clean room techniques, and a diversity of chemicals were used. All relevant processes were carried out with complete respect to the safety rules. None solution, cleaning process or measurement has been done without an approbation of a supervisor.

The material and instruments involved in this thesis are several. The QDs made by Evident Technologies are of the type Core Shell EviDots (EB-C11-TDL-0600 and EB-C11-TDL-0621). Toluene and chloroform are used as a solvent for dispersing and diluting the QDs, “7up” solution for the cleaning process of the glass cover slides serving as substrate, and a spin-coating machine to distribute the solution over the cover glass. Atomic force

Figure 3.1: Scheme of the instrumentation setup. The AFM is provided by JPK company, the XY scanning stage and the microscope objective lenses are provided by Zeiss and the CCD detector as well as the spectrometer are from Andor company.
3.1 Sample preparation

The substrate used for the measurements are glass cover slides of 23.5 mm diameter and 130 µm thickness. The sample has to be made on glass in order to use both AFM and PL at the same time. Since the substrates are provided by JPK company, they suit perfectly with the instrumentation.

In order to clean the substrate and to reduce the surface roughness cleaning in “7up” solution (a mixture of sulphuric acid ($H_2SO_4$) and hydrogen peroxide ($H_2O_2$)) has been done for 10 minutes at 110 °C. Afterwards, to wash out the acid the substrates were flushed in distilled water followed by isopropanol and drying with an air gun.

For the deposition of the QDs on the substrate, a highly diluted solution is needed. Thus, starting with the original solution given from the company, the desired QD concentration is obtained by dilution in toluene (or chloroform). After having the QD solution ready, ultrasonic treatment in a water bath is done for 30 minutes. This reduces the number of the QD agglomerates in the solution.

The final step of the sample preparation is the spin coating. Typical parameters for injecting 5 µl of solution are 10,000 rpm and 40 s rotation time. In this way a thin layer of QDs on the glass substrate is yielded.
3.2 AFM

The atomic force microscope (AFM) has been used to study the surface of the samples and to analyse the size of the QDs. With the AFM it is possible to obtain the topography of a sample on a scale that ranges between 10 nm and 100 microns. In the frame of this work a NanoWizard III AFM from JPK company was used in tapping mode.

General applications of the AFM are related to studies in the scale of atomic dimensions of surfaces composed of various kinds: thick or thin films of ceramic materials, amorphous materials, glass, synthetic or biological membranes, metals, polymers and semiconductors. An atomic force microscope is able to operate in air, in UHV and liquid (biological samples) and to analyse both conductive materials as well as insulating.

The basis of an atomic force microscope is the cantilever to the end of which is a sharp tip (point like), typically composed of silicon or silicon nitride, which has a tip radius of several nanometers. The tip is placed in close proximity to the sample surface. Van der Waals forces acting between the tip and the sample cause a deflection of the cantilever (whose spring constant is known). Typically, the deflection is measured using a laser reflected from the top side of the cantilever to a matrix of photodiodes.

If the tip is scanned at constant height, there is a risk that it may collide with the surface, causing damage. Consequently, in most cases a feedback mechanism is used to adjust the distance between the tip and the sample in order to maintain a constant force acting between them. Generally, the sample is placed on a piezoelectric tube, which can move in a direction perpendicular (z direction) to maintain a constant force and in the plane (x and y directions) in order to scan the surface. The resulting image represents the topography of the sample surface. It can reach a resolution of 10-20 nm along the x-, y-, and of 0.01 nm along the z-axis.

3.2.1 Scanning modes

Over the years have developed different ways of working with the atomic force microscope. The main modes of operation are:

- contact mode (the tip touches the sample and the distance between the tip and the sample is less than the average size of an atomic radius)
- non-contact mode (while being close to the surface of the sample, the tip does not touch it)
- tapping mode (in the case where the tip scans the specimen so as to have a contact discontinuous determined by a regular succession of oscillating movements (that consist in a continually passing from the condition that no contact to contact)).

In the AFM different types of forces interact between the sample and the tip. Those can be used to produce images. In the non-contact mode images are produced by forces of Van
der Waals, or electrostatic forces, magnetic forces and capillaries forces. The contact mode is dominated by ionic repulsion forces. In addition to these forces particularly important for the purposes of a complete analysis and detailed view of the sample is the frictional force acting between the tip and the surface. Besides being an indicator of the properties of the sample, the friction or “lateral force” or “lateral deflection” provides information on the rules of interaction between tip and surface.

### 3.2.2 Tip properties

In atomic force microscopy are, in general, used three types of tips:

- the normal tip, consisting of a flattened pyramid high \( \sim 3 \, \mu m \) with radius of curvature of \( \sim 30 \, \text{nm} \), figure 3.3 image (a);

- the supertip, produced by electron bombardment of a normal tip, resulting in deposition of carbonaceous material. The supertip is longer and thinner than a normal tip and also has a better radius of curvature, figure 3.3 image (b);

- the Super-Sharp, produced by AppNano and made through a photolithographic process. The Super-Sharp tip are 14 - 16 \( \mu m \) long and can have radii down to \( \sim 6 \, \text{nm} \). The most common are the standard tip of silicon nitride \( Si_3N_4 \) and the tips of silicon, figure 3.3 image (c) [38].

The properties and dimensions of the tip have an important role in determining the resolution and the sensitivity of the measurements carried out with the AFM. For the observation of samples with sensitive surfaces or only slightly adhering to the sample holder use of a probe with low spring constant value is optimal considering the fact that a minimal lateral force during the scan is applied.

The radius of curvature (generally between 20 to 60 nm) and the angle (between 60 to 75°, depending on the orientation of the tip with respect to the sample surface) of the tip is the main factor determining the resolution. The limitations imposed by the structural
characteristics of the tips should be properly considered taking into account that they may have caused artefacts. A typical example of convolution of the tip is where the AFM image is nothing more than an artefact that is produced when the surfaces of the particles under observation are more inclined than the angle of the tip. The image reflects the design of the pyramidal tip rather than the topography of the particles under observation.

The tips of silicon are normally used for observations in tapping mode. The silicon tip has a radius of curvature between 5 and 10 nm, and an angle of between 20° and 50°, smaller than the silicon nitride. For this reason the use of this tip is recommended in applications that require a high degree of stability of the tip. This reduces the formation of artifacts (see figure 3.4).

Recently, with the use of focused ion beam, silicon tips were made even thinner and have a higher degree of stability. These tips have, in addition, an improved length to thickness ratio (high aspect ratio) which allows to use them on surfaces inclined (at angles close to 90°). They, however, are very delicate and have a limited use in time.

3.3 PL spectrometer

The term spectrometer refers to any instrument that allows to measure the intensity of light as a function of its wavelength. The majority of spectrometer uses the principle of interference to decompose the light radiation in its wavelengths and measuring its intensity with a CCD camera. Within this thesis an inverted optical microscope (Zeiss, Observer.Z1m) equipped with two CCD cameras (Axio CamMRC & Andor iXon3 888) and a spectrometer (Andor Shamrock303i, gratings: 150 1/mm, blaze 800; 1200 1/mm, blaze 500) was used.

The spectrometers have a wide range of applications that reflect the diversity of types and characteristics of these instruments. Applications ranging from cosmology to physics to engineering materials. Normally the spectrometers are divided according to their resolution and the section of the light spectrum that can be measured (visible, UV, X-rays,
microwaves, etc.).

3.3.1 Optical resolution

To have a PL image of individual QDs a microscope with very high optical resolution is needed, because very small light sources have to be magnified. The resolution of a microscope is defined by the minimum distance at which two points are distinct (see figure 3.5). If the instrument is based on the use of radiation with a wavelength associated with their own, such as conventional optical microscopes, resolution and wavelength are parameters which are closely related.

In first approximation we consider the relation between the resolution $d$ (distance between two points which still can be resolved), the numerical aperture $AN$ of an optical system and the wavelength $\lambda$:

$$d = \frac{\lambda}{2AN}$$

(3.1)

This relationship is generally known as the Abbe principle.

For an optical microscope working in visible light, $d$ reaches 0.2 $\mu$m; in contrast a SEM goes down to 0.1 nm. For imaging the CdSe/ZnS QDs an objective lens with a numerical aperture of 0.75 has been used. The emitted wavelength of the QDs is about 600 nm. Therefore, the resolving power is 0.4 $\mu$m. Knowing the resolving power it is possible to determine the density of QDs on the substrate. With a resolving power of 0.4 $\mu$m, the density has to be 0.16 particles per $\mu m^2$.

This result is done without considering the optical aberration. The aberration of an

![Figure 3.5: The resolution problem of two light sources occurs when the distance between the points is smaller than the wavelength.](image)

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optical system has a very important effect on the imaging because it is the difference between the actual image, real or virtual, formed by the system and the image that was desired. The aberrations can give (usually more on the periphery of the image at its centre) poor sharpness, image deformation, differences between the images corresponding to different colours, non-uniformity of brightness.

In particular, the differences are called aberrations of an image than that provided in the paraxial approximation. They are distinguished aberrations polychromatic (due to the dependence of the refractive index on the wavelength of light) from those monochrome. In addition to imperfections of the components or materials which constitute the optical system, the aberrations may be due to the fact that the system moves away from the paraxial optics conditions, when it collects rays at angles larger or diverges them to much. This can be reduced, sometimes almost completely eliminated, using the finest materials, working in a particular optical coupling many components, etc.. In general, the correction involves an increase in production costs.

An element influencing the development of aberration is the thickness of the optical medium traversed by the light, from the decomposition of the latter related to the phenomenon of refraction and the distribution in the different wavelengths of the colours visible in the visible.

An phenomenon that influence the development of aberration is the diffraction, figure 3.6. The diffraction effects are significant when the wavelength is comparable with the size of the obstacle. In particular for visible light (wavelength around 0.5 µm) diffraction phenomena will occur when it interacts with objects of µm size. Taking into account all those effects the resolving power of the QDs increase. The density of QD per area commonly used is 1 particle per µm².

Figure 3.6: Optical diffraction effect.
Chapter 4

Results

The purpose of this work is to investigate experimentally the correlation between size and emission wavelength of single CdSe/ZnS QDs. The QDs under investigation are provided by the company Evident Technologies. As described in the experimental section, two different average-sized QDs were studied. According to the data given by the company they show photoluminescence maxima at 600 and 621 nm, in the following termed as “orange” and “red” QDs, respectively.

4.1 Sample preparation

The first step was to disperse the solution containing the QDs on a substrate with a low surface roughness. In this work two different substrates, silicon wafer and glass cover slides, were used. The first one was used in principle because easy to find and to clean. The cleaning of the silicon wafer has been done by dipping in a HF bath. In this way the

![SEM and AFM images of QDs deposited on silicon wafer](image.png)

(a) SEM microscope  (b) AFM microscope

Figure 4.1: Images of QDs deposited on silicon wafer: (a) SEM micrograph and (b) AFM height image.
silicon oxide present on the substrate was removed. Once the samples were cleaned QDs were deposited using the spin coating technique.

This first type of QDs used for the characterization were the “orange” QDs. As it is shown in figure 4.1a by SEM and in figure 4.1b by AFM the initial QD concentration is very high since the as-provided solution ($21,8nMol/\mu l$) given by the company was used.

Whereas silicon wafer is adequate in order to obtain SEM images, it cannot be used for combined AFM/PL measurements. Since an inverted microscope is used a transparent substrate is necessary in order to let the light emitted from the dots passing the substrate to be collected by the objective lens. All AFM measurements were done in tapping mode using a standard tip (type ACTA from AppNano, see Appendix A). Tapping mode was chosen because scanning in contact mode would move the dots from their initial position and therefore hindering to determine the exact size of the QDs.

In reason of that the substrate for the QDs has been changed from silicon wafer to glass cover slip provided by the company JPK. An AFM height image of the untreated glass cover slip surface is shown in figure 4.2. Although the cover slides exhibit already a quite flat surface, cleaning must be done, since a difference of 1 nm can lead to a large variation in the QD size, directly affecting the correlation between size and emission wavelength.
To improve the flatness of the glass cover slip cleaning in 7 up solution for 10 minutes at 110 °C has been done. Figure 4.3 reveals the cleaned surface. The amount of dust has been decreased significantly.

After cleaning the sample and storing them in a box an interesting phenomenon was observed. Undetermined dust has grown, ranging in the size of the QDs. The problem was solved by successive cleaning with isopropanol. This treatment has removed the dust fully, as can be seen in figure 4.4. So, to utilize the glass substrate a further cleaning has been needed.

After the cleaning process has been optimized, the CdSe/ZnS QDs were deposited. As it was found for the silicon wafer samples that the initial QDs concentration was too high for doing single dot spectroscopy, a highly diluted solution has been used in order to reduce the QD concentration over the sample. In the beginning a concentration of $10^{-n} Mol/l$ has been used. As it is shown in figure 4.5, the dispersion of the QDs was not done in an acceptable
way. The existence of agglomerates on the surface shows that the QD concentration is still too high for detecting single QD PL. In figure 4.5 large QD agglomerates but also small agglomerates in the size range of QDs can be figured out. To verify that the small agglomerates are indeed single QDs PL spectroscopy must be carried out. Here, typical blinking behaviour (switching between ON and OFF state) proves that single QDs are under investigation.

The residue of toluene over the substrate was a big issue for the purpose of this thesis, because the residue can affect the size of the single QDs. In some cases the measurement can give a size of the QD bigger than actually it really is or in some other cases just the size of the toluene can reach value in the range of the QDs. To solve this problem the solvent was changed. Chloroform has been used as alternative to toluene. The choice was made in order to have a non-polar solvent because the CdSe/ZnS QDs have a TOPO coating (hydrophobic behaviour). An interaction with other polar solvents like acetone, isopropanol

Figure 4.4: AFM height image of a glass cover slip before (the left image) and after isopropanol treatment.

Figure 4.5: AFM height image of QDs deposited on the glass substrate. The high concentration of QDs in the solvent (toluene) leads to the creation of big QD agglomerates.
or ethanol makes the dots to interact with each other and form bigger agglomerates.

Chloroform was chosen because of its boiling point (61 °C) that is in comparison with toluene (111 °C) lower. The idea of using the new solvent was to achieve a faster evaporation of the solvent leading to less solvent residue on the sample. The solution was treated in an ultrasonic bath for 30 minutes and then a small quantity of the solution was spreaded over a cleaned glass substrate.

As we can see in figure 4.6, the result of QDs in chloroform is comparable to the results obtained from the toluene samples. The concentration and the height of the agglomerates is the same like for the sample prepared with QDs solved in toluene. Therefore and regarding the fact that chloroform is highly toxic toluene has been used for further sample preparation.

4.2 Identifying single quantum dots

The results presented in the following paragraphs were obtained by using toluene as solvent. In order to have a layer of single QDs in low concentration several dilution steps (decreasing by two decade of concentration) were done. This was achieved by taking with a pipette 10µL of the initial solution and to add this one to 1 ml of toluene. After each dilution step a sample was prepared in order to check the concentration and the agglomerate size. Once a concentration of 10 pMol/l was reached, it was possible to observe small-sized QD agglomerates going down to the size of single CdSe/ZnS QDs.

Due to applying spin coating particular rings of QD agglomerates appeared. In the inner part of these rings relatively empty regions were found containing single quantum dots. The study of this sample was very interesting because the creation of the rings enabled an ease orientation on the sample. In figure 4.7 a part of such a ring is shown. In the center an almost empty area can be observed containing a few small agglomerates. Cross section measurements reveal that the height of these dots is close to the expected size of a single CdSe/ZnS QD.
Figure 4.7: AFM height images of CdSe/ZnS QDs. On the left the maximum scan range of 100 x 100 µm is plotted. The border of the rings resulting from spin coating can be seen clearly. Outside are agglomerates located whereas inside single dots are supposed. On the right a smaller area of 20 x 20 µm is investigated giving a better height resolution for finding single dots.

With the acquisition of high-resolution images by AFM it was possible to determine the height of the particles/agglomerates more precise. In figure 4.8 a histogram of the height of each agglomerate present in figure 4.7 is shown. As one can see the main part is located in a size range between 4 and 10 nm. Larger sizes can be ascribed to agglomerates.

However, the size distribution is too broad in order to have a reasonable result for

Figure 4.8: Histogram on the quantum dot size distribution obtained from the height image on the right in figure 4.7. The size varies between single dots (less then 10 nm) and agglomerates (larger then 10 nm).
the emission wavelength. As a matter of fact, small variation of the size around 1-2 nm correspond to a very large variation on the emission wavelength of the QDs (between 30 to 70 nm).

### 4.3 PL measurements

Photoluminescence measurements were carried out using an inverted microscope equipped with two CCD cameras and a spectrometer. The objective lens has a 63 times magnification and inside it has also a correction lense. The correction lens is necessary because the microscope is an inverted microscope. This does mean that the lens is going to collect the light coming through the glass of the substrate. The Andor CCD camera has the possibility to be cooled down to -75 °C. A comparison between the PL images obtained by the two different cameras is given in figure 4.9. The spectral detection range of the Andor CCD camera covers 300 to 1000 nm to 300 nm (see Appendix B), this means wavelength from infra-red to ultraviolet can be detected.

#### 4.3.1 The background issue

The samples were exited using a diode laser with a emission wavelength at 405 nm. A drawback of this system was that the final images have always a green background, seen in figure 4.10 on the left. The image on the right in figure 4.10 shows the same area but using a bandpass filter in front of the camera with central wavelength at 600 nm and 30 nm bandwidth. The background is due to PL arising from defects in the dioxide structure.

![Figure 4.9: Photoluminescence image of CdSe/ZnS QDs. The photo on the left has been taken with the colour camera and the one on the right was obtained using the high-resolution Andor camera.](image-url)

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of the substrate as well as from the optical components in the microscope itself. This conclusion has been drawn after checking the background also with other substrates like pure silicon wafer and suprasil glass. The main issue of the green background PL is that the intensity is comparable to the single dot PL intensity. This leads to the point that the single dot PL is hidden under the background signal until the data processing is done.

Figure 4.11: PL image (left) with the area pointed out with the black rectangle indicates where the slit was positioned. The spectral image (right) shows the PL intensity as a function of the wavelength of the light coming from the slit.
4.3.2 Tracking spectra of single quantum dots

Once the PL camera was adjusted images with a very low noise level and well focused quantum dots were recorded. In the PL image shown in figure 4.11 the wide luminescence spots are ascribed to large QD agglomerates and the smaller ones are arising from single QDs. In order to visualize a single QD luminescence it is necessary to take a photo with very long exposure time. The camera can accumulate enough light from the tiny light source. This process is not that easy, because a large amount of light is coming from the big agglomerates and saturates the CCD camera. Therefore, it is advisable to select an

Figure 4.13: Histogram in which has been counted for a range of 5 nm wavelength how many single spectra have the central wavelength into that range.
area where no big agglomerates are located.

In order to record spectra on part of the PL image is selected by placing a slit into the optical path. In figure 4.11 a PL image is shown where the slit is marked by a black rectangle. The width of the slit can be defined between the maximum range of the image down to a minimum opening of $10\mu m$. Since single QDs are in the focus of investigation the minimum width was chosen in order to avoid detection of further and unnecessary light coming form the background.

The resulting image, shown in the right side of figure 4.11 shows in the x-axis the wavelength and in y-axis the spacial resolution of the sample area been chosen to investigate. Selecting one line of the image, a PL spectrum (of one agglomerate or single dot) can be extracted. This is shown in figure 4.12.

Once a certain amount of spectra is taken it is possible to start the study of QDs emittance behaviour. A histogram with all the PL maxima of each spectrum is done.
Here it is possible to check if the investigated QDs follow the nominal value given by the company. In figure 4.13 the histogram of several single “orange” QD spectra is plotted. The most often measured value of the PL maximum is around 580 nm.

As previously mentioned, two different nominal sizes of CdSe/ZnS QDs have been investigated. The studies of the “red” QDs followed the same procedure as discussed before for the “orange” QDs. In contrast to the “orange” QDs which show main emittance peak around 580 nm, the “red” QDs are expected to emit at longer wavelength, shifted by 15-20 nm. However, a sum of all spectra is shown in figure 4.15 in order to compare the two type of dots. The graphs are normalized, whereas the orange line represents the “orange” QDs emittance and the red line the red dots. The wavelength with the highest intensity corresponds to the main wavelength of the QDs type. So, comparing the PL maximum of the two type of QDs a difference of 15-20 nm is found, but the PL maxima are found to peak at shorter wavelength as the given nominal values of 600 and 621 nm.

The variation of single PL spectra is shown in figure 4.14. The top four single spectra are from the orange QDs and the other two from the red type. The range of central wavelength varies between 575 nm and 612 nm. The FWHM of those spectra is between 15 to 20 nm and this result is resonable with other works also.

4.4 Correlation between AFM and PL measurements

The main focus of this thesis is put on the correlation between the AFM measurements and the PL ones. The passage described in this paragraph was the most important within
this thesis. This part was also the one in which has been spent more time in measurement
and data processing.

In order to scan with the AFM the same area which is shown also in the PL image the
following steps were done. First of all, the position of the AFM tip was aligned with the
optical axis of the microscope, in particular over an area pointed out from the objective
lense. The lense, as is it shown in figure [3.2], is below the glass substrate. Ones the tip is
positioned over the objective lense it was possible to see it with the PL camera but only if
the camera is in focus with the tip.

In figure [4.16] are some images shown recorded using the Zeiss colour camera (left
image), the Andor camera (middle image) and the AFM (right image). One can see that
the three images correspond to each other even the measurements have been done with
different acquisition methods.

The size of the AFM image in figure [4.16] is 100µm². According to this one can
derive that, being one fourth of the whole PL image, the PL image is about 400µm². Unfortu-
nately, the PL image is subjected to optical aberration because of the objective
lense. This causes some distortions on the edge and the image dimensions do not correspond
anymore to the AFM image proportions. The AFM image should correspond to the real
space distribution of the sample. The PL image is not matching exactly with the AFM,
which is shown for example figure [4.17].

![Figure 4.16: Three different images of the same sample area. On the left: image taken
with the colour camera of the Zeiss microscope, in the center: image taken with the high-
resolution Andor camera, and on the right: AFM height image corresponding with the
center part of the PL images.](image)

50
Comparing the PL image and the AFM scans it is found that not all the "points" match with each other. Quantum dots appearing in the AFM height images do not always appear in the correlated PL image. This can be explained by the fact that not all the QDs are emitting light. Some QDs are dark (OFF state), which means that they are not going to emit any light because the recombination between the electron and the hole is non-radiative. Reasons are some intermediate energy level caused by dust or not regular crystal shape. Those levels are located inside the energy bandgap of the QDs and the recombination of the electron pass through those levels. In this case the energy released by the electron-hole recombination is emitted in form of phonons and not any more as photon.

In the course of single particle spectroscopy the blinking phenomenon, explained in the theory chapter, was observed. Setting the PL camera for fast acquisition, it has been possible to visualize in a series of PL images the fluorescence intermittency. An example of such a time trace featuring a two level PL intensity is shown in figure 4.18. This facts proves that indeed single CdSe/ZnS QDs were investigated and not agglomerates, because the blinking phenomenon in a single QD has a clear intermittent light between two states.

Once that the different measurements of the same area were accomplished, it was possible to proceed with analyzing the correlation. In figure 4.19 is shown on the left image and on the middle one the same environment measured by AFM and PL, respectively.

Figure 4.17: Correlation between the PL image and the AFM scanning image. The large image represents the PL and the redish ones were recorded by AFM. The AFM images are different because different areas were scanned. As can be seen that the AFM images match very good with the PL one.
Figure 4.18: The intensity of the light coming from a single CdSe/ZnS QD switches between two distinct levels.

There it is possible to determine the height of the quantum dot. The dashed line indicates the position of the cross section shown below the micrographs. Once an particle is found which corresponds to the height range of a single QD it was necessary to check then the PL image if this one appears also there. The second step of the measurement was to place

Figure 4.19: Correlation between AFM measurements, PL images and PL spectra. On the left the AFM height image is shown, in the middle the related PL image and on the right the spectral images that correspond to the area between the two vertical lines indicated on the PL image. Below the images the respective cross sections are plotted (dashed line).
Figure 4.20: The graph shows the correlation of emission energy and size for different individual QDs. In orange the “orange” QDs and the same for the red dots. With decreasing QD size the emission energy increases.

The procedure shown in figure 4.19 to measure single QDs has been done for several individual dots of both type (orange and red). A graph of the final result is plotted in figure 4.20. The dots over the graph show the correlation between emission energy and QD size. It is found that with decreasing QD size the emission energy increases. The graph in figure 4.20 indicates some single size-emittance wavelength correlation of CdSe/ZnS QDs. The first characteristic has been notice from the graph is that the variation of the size between the maxima and the minima value is larger than what has been found in earlier
Figure 4.21: The graph shows the correlation of emission energy and size for different QDs in comparison with theory. The black line shows the theoretical size-to-energy correlation.

Such a large variation in size has also been not expected from theoretical calculations. The expected variation of the size has to be in the range of the square variation of the energy according to the theory \[2.18\]. From this graph has been pointed out that the size measurements have a significant error. Actually, the measurement by tapping mode made by AFM have an intrinsic error of 4-5 Å. This is due to the oscillation of the tip over the sample. An error of 4-5 Å is a significant error because it can affect the value of the expected wavelength from the QDs up to 30-40 nm.

However, in the graph also a difference between the orange type of QDs and the red type is observed. It can be seen that the energy relativity to the red type is in a small quantity lower than the orange type. This behaviour was expected from the theory and as well from the data given by the company.

In order to compare between the data measured and the data expected from the theory has been done a study by taking the value of the size measured. It has been used the formula \[2.18\] and then calculated the expected emission energy using the size measured of each QD. From the value of the QD size has been subtracted also a value that correspond to the shell value and the organic coating because is not needed in the calculated emission energy. The value of the size of the shell, unfortunately, has not been given from the
company. So, it were taken into account reasonable values of previous work \[29\] \[31\], saying a shell size of 3 atomic monolayer. The result is shown in figure 4.21 where the black line is the derived theoretical curve. The graph shows that, in the experimental results, the emission energy does not follow very well the theoretical data. However, this result confirms previous studies \[30\].
Chapter 5

Conclusion

The correlation between size and emission wavelength of single CdSe/ZnS quantum dots (QDs) was investigated in this thesis. In order to measure and analyse the size and photoluminescence (PL) of individual CdSe/ZnS QDs optical spectroscopy and high-resolution atomic force microscopy (AFM) were carried out at the same time. For this purpose the AFM was placed on top of an inverted optical microscope. The quantum dots were exited with a high-power diode laser (405 nm) and the spectral response was recorded with a CCD camera attached to a spectrometer. Samples with two different average-sized QDs exhibiting photoluminescence maxima at 600 and 621 nm were studied.

The nanocrystals were provided by the company Evident Technology and deposited on cleaned quartz cover slides. In order to obtain samples with a very low coverage of density of QDs sufficient for single particle spectroscopy a highly diluted QD/toluene solution was prepared. The as-provided CdSe/ZnS QDs were dispersed in toluene followed by successively dilution. Initial agglomerates of QDs were reduced by applying ultrasonic treatment. Spin coating was used to disperse a small droplet (5 µl) of the QD solution on the substrate. Additionally, chloroform was tested as alternative solvent but no improvement in the sample quality was observed.

In the beginning two different kind of substrates were considered for dispersing the QD solution, silicon wafer and standard glass cover slides. However, disregarding the drawback of background luminescence arising from the substrate itself and overlapping partly with the spectral emission range of CdSe/ZnS QDs, glass cover slides were used since they are suitable to do AFM and PL measurements in parallel.

The substrates were cleaned using a mixture of sulphuric acid ($H_2SO_4$) and hydrogen peroxide ($H_2O_2$). A reasonable decrease of the dust over the substrate was observed and confirmed by AFM measurements. Furthermore, occurring as a side-effect of the treatment in acid, the surface roughness was decreased leading to an increase of the accuracy of AFM measurements.

The AFM and PL results confirm the data given by the company. The standard variation of the emission wavelength is in the range of 20-30 nm, and the wavelength
variation was between 575 and 612 nm with a FWHM of 15 to 20 nm. Blinking, being a phenomenon characteristic for single QD spectroscopy, was observed and proves the fact that in deed single CdSe/ZnS QDs were investigated. In order to correlate size and emission energy a certain number of dots was chosen from each type and analysed in detail. The obtained results, showing that with decreasing QD size the emission energy increases, were discussed in terms of theoretical expectations based on the quantum confinement model. The results have reasonable numbers and they are in the range reported in other works [30].

Further studies on the blinking phenomenon of CdSe/ZnS QDs are going to be investigated. The different behaviour of the blinking under low and high excitation will be studied.
Bibliography


[33] Lecture noted from nanoelectronic class at KTH


APPNANO probes are compatible with most commercially available SPMs. These probes are nanofabricated using highly doped single crystal silicon with unparalleled reproducibility, robustness and sharpness for consistent high resolution imaging capabilities.

The FORT-SS Probe is a Super Sharp probe designed for Force Modulation applications. These probes have a medium frequency and spring constant making them ideal for Force Modulations.

### Handle Chip Specifications
- **L x W x T**: 3.4 mm x 1.6 mm x 300 µm
- **Alignment Grooves**: YES

### Tip Specifications
- **Shape**: Pyramidal
- **Height (µm)**: 14 - 16
- **ROC (nm)**: 2
- **Coating**: None

### Cantilever Specifications
- **Material**: Si
- **Shape**: Rectangular
- **Front Coating**: None
- **Reflex Side Coating**: None

### Parameter | Value
--- | ---
**Spring Constant (N/m)** | Nominal: 3.0, Minimum: 1.2, Maximum: 6.4
**Frequency (kHz)** | Nominal: 62, Minimum: 47, Maximum: 76
**Length (µm)** | Nominal: 225, Minimum: 215, Maximum: 235
**Width (µm)** | Nominal: 30, Minimum: 25, Maximum: 35
**Thickness (µm)** | Nominal: 3, Minimum: 2.5, Maximum: 3.5

### Ordering Information
| Part Number | Probes |
--- | ---
FORT-SS-10 | 10 |
FORT-SS-20 | 20 |
FORT-SS-50 | 50 |
FORT-SS-200 | 200 |
FORT-SS-W | 410 – 424 |

**NOTES:**
1. The specification range is guaranteed. The values of spring constant and frequency are calculated using mathematical formulation.
2. These probes feature alignment grooves compatible with all alignment chips available in the market.
3. Please contact our distributor in your area to order the probes.
4. For more technical information, please contact either our distributor in your area or e-mail us directly at info@appnano.com.
Andor's iXon3 888 is megapixel back-illuminated EMCCD, combining large field of view, single photon detection capability and > 90% QE. The 1024 x 1024 frame transfer format offers unequalled thermoelectric cooling down to -95°C and industry-lowest clock induced charge noise. EMCCD and conventional CCD readout modes provide heightened application flexibility. New EX2 technology offers extended Quantum Efficiency performance.

The iXon3 888 benefits from an advanced set of user-requested features, including OptAcquire, Count Convert, Spurious Noise Filters, Cropped Sensor Mode, Signal Averaging and enhanced Photon Counting capability. Patented EMCAL™ and RealGain™ provide sustained quantitative EM gain calibration.

### Specifications Summary

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
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<tbody>
<tr>
<td>Active pixels</td>
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<tr>
<td>Pixel size (W x H)</td>
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<tr>
<td>Active area pixel well depth</td>
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<tr>
<td>Gain register pixel well depth</td>
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<td>Maximum readout rate</td>
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<td>Frame rate</td>
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<td>Read noise</td>
<td>&lt; 1e⁻ with EM gain</td>
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<td>Maximum cooling</td>
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### System Specifications

<table>
<thead>
<tr>
<th>Model number</th>
<th>888</th>
</tr>
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</table>
| Sensor options | EX2: Back illuminated, dual AR coated  
BV: Back Illuminated, standard AR coated  
UVB: Back Illuminated, standard AR with additional lumogen coating |
| Active pixels | 1024 x 1024 |
| Pixel size | 13 x 13 μm |
| Image area | 13.3 x 13.3 mm with 100% fill factor |
| Minimum temperature air cooled | -80°C |
| coolant recirculator | -90°C |
| coolant chiller, coolant @ 10°C, 0.75/min | -95°C |
| Digitization | True 14 bit @ 10, 5, 3 & 1 MHz readout rate (16 bit available @ 1 MHz) |
| Triggering | Internal, External, External Start, External Exposure, Software Trigger |
| System window type | Single window - AR coated or uncoated available |
| Blemish specification | Grade 1 sensor (CCD201-20), as defined by the sensor manufacturer e2V  
For further details see [www.e2v.com](http://www.e2v.com) |

### Advanced Performance Specifications

| Dark current and background events | 0.001  
Spurious background (events/pix) @ 1000x gain / -95°C | 0.01 |
| Active area pixel well depth | 90,000 e⁻ |
| Gain register pixel well depth | 730,000 e⁻ |
| Pixel readout rates | Electron Multiplying Amplifier  
10, 5, 3, 1 MHz | Conventional Amplifier  
3 & 1 MHz |
| Read noise (e⁻) | 10 MHz through EMCCD amplifier  
47  
5 MHz through EMCCD amplifier  
35  
3 MHz through EMCCD amplifier  
27  
1 MHz through EMCCD amplifier  
18  
1 MHz through conventional amplifier  
6 |
| With Electron Multiplication | < 1  
< 1  
< 1  
< 1 - |
| Linear absolute Electron Multiplier gain | 1 - 1000 times via RealGain™ (calibration stable at all cooling temperatures) |
| Linearity | Better than 99% |
| Vertical clock speed | 0.9 to 6.5 μs (variable) |

### Frame Rates (Standard Mode)

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### Frame Rates (Cropped Mode)

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<tr>
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</tr>
<tr>
<td>2 x 2</td>
<td>34</td>
</tr>
<tr>
<td>4 x 4</td>
<td>64</td>
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<tr>
<td>8 x 8</td>
<td>117</td>
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</tbody>
</table>
Quantum Efficiency Curves

QE v Fluorophores Curve

Deep Cooling

Field of View Comparison

Images of extremely dim LED signal (signal intensity typical of weak luminescence experiments) acquired with iXon3 888 at cooling temperatures -70°C and -95°C (water cooling to achieve latter), 120 sec exposure times, sub-region show. The need to push to such deeper cooling temperatures can be readily observed under such extreme low light conditions.

Field of View Comparison between iXon3 models. The 888 model has a x2.6 greater sensitive area than 897 and 885 models.
Chapter 8

Appendix C
Features and Benefits

- **Pre-aligned, pre-calibrated detector & spectrograph**
  Motorized, individually factory-calibrated systems – out-of-the-box operation and seamless integration to experimental set-ups

- **Image astigmatism correction**
  Optimised toroidal optics enabling high density multi-track capabilities

- **USB 2.0 interface**
  Plug and play connectivity, ideal for laptop operation alongside Andor USB cameras

- **Motorized, indexed triple grating turret**
  Easily upgradeable in-the-field

- **Dual detector outputs**
  For extended wavelength coverage when combining Andor UV-Visible CCD and InGaAs cameras.
  Compatible with Andor’s range of CCD, ICCD & EMCCD cameras

- **Wide range of accessories available**
  The ultimate in modular set-up and in-field upgradability, including:
  - Motorized slits & filter wheel
  - Microscope interfaces
  - Shutters
  - Fibre-optic & lens couplers
  - Multi-way fibre-optic bundles
  - Light sources and optics

- **Silver-protected coated optics option**
  Most efficient for Near-Infrared detection when used in conjunction with Andor InGaAs cameras

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Research-grade high performance spectrograph

The Shamrock 303i spectrograph is a research-grade, high performance and rugged platform designed for working with demanding low-light applications, but equally suited to day-to-day routine measurements. It is a highly versatile platform configurable seamlessly with a wide range of light coupling interfaces and gratings upgradeable in-the-field. The Shamrock 303i can be seamlessly integrated with Andor’s world-class range of CCDs, Electron-Multiplying CCDs, InGaAs and Intensified CCDs to offer a versatile, yet most sensitive modular solutions on the market. Andor Solis software offers the most user-friendly and state-of-the-art real-time control of detectors, spectrograph and motorized accessories at the touch of a button.

---

Specifications Summary

<table>
<thead>
<tr>
<th>Resolution with Newton DU940 CCD</th>
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</thead>
<tbody>
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<td>1200 l/mm @ 500 nm</td>
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<tr>
<td>2400 l/mm @ 300 nm</td>
</tr>
<tr>
<td>Aperture</td>
</tr>
<tr>
<td>Focal length</td>
</tr>
<tr>
<td>Magnification @ centre of CCD</td>
</tr>
<tr>
<td>Vertical, spectral flange</td>
</tr>
<tr>
<td>Vertical, multi-track flange</td>
</tr>
<tr>
<td>Gratings</td>
</tr>
<tr>
<td>Slit width range (input/output)</td>
</tr>
<tr>
<td>Communication</td>
</tr>
<tr>
<td>Wavelength accuracy</td>
</tr>
<tr>
<td>Wavelength repeatability</td>
</tr>
<tr>
<td>Stray light</td>
</tr>
</tbody>
</table>
Step-by-Step System Configuration

How to customize the Shamrock 303i:

Step 1. - Chassis configuration
a) Select either a single output port (A) or dual output port (B) option.
b) Select type of optics coating required (aluminium + MgF₂ is standard, protected silver coated optics available on request for NIR detection).
c) Select purge port option (for extended detection below 180 nm), or shutter for background acquisition and detectors protection.

Step 2. - Resolution & band-pass
a) Select the appropriate Shamrock spectrograph platform, giving due consideration to bandpass and spectral range requirement.
b) Select gratings and detector to fulfill resolution requirements.
c) Select gratings for suitable wavelength coverage.

Step 3. - Input light coupling interface
Refer to accessory tree for available configurations (direct coupling, fibre coupling or 3rd party hardware connectivity).

Step 4. - 2nd exit port configuration
Refer to accessory tree for available configurations, including camera flanges.

Step 5. - Software interface
Select either state-of-the-art Solis software or Software Development Kit (SDK) option – please refer to appropriate section for further information.