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Simulation of Quantum Dots

Group project
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Chapter 1

The Quantum Dot

Quantum dots are atomic structures (usually spherical) that have a size of about 1-10nm in diameter. They are often referred to as nanocrystals, though this term is more general and includes also other shapes and morphologies, which might extend to several μm, such as rods, wires etc. Figure **??** gives some examples of possible shapes and morphologies, that are possible with nowadays technologies.

They can be made out of various materials (metals, semiconductors, compounds). According to their size and material, the can contain just a few or millions of atoms. A 10nm cube of GaAs contains for example 40,000 atoms [**SalehTeich**].

The properties of Quantum Dots (QDs) are strongly dependent on their size. Figure **??** illustrates this effect for a semiconductor QD. Under ultraviolet excitation, the QDs emit light according to their size and therefore band gap.
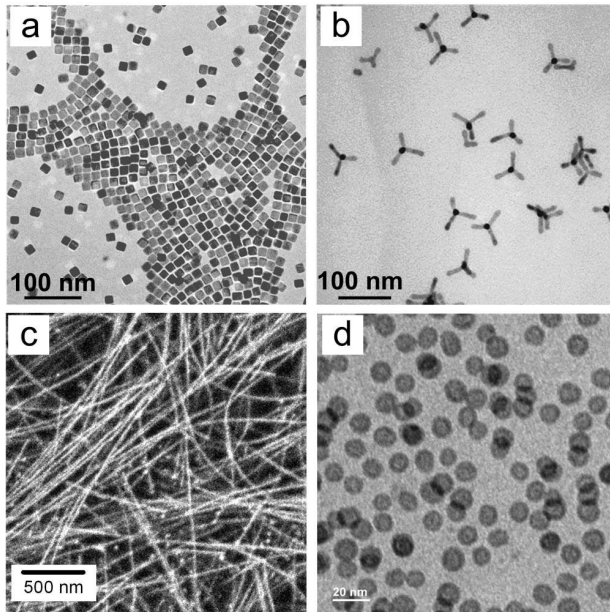

Figure 1.1: Examples of inorganic nanomaterials with different shapes and morphologies synthesized by colloidal chemistry: (a) PbSe cubes; (b) CdTe tetrapods; (c) PbSe nanowires and (d) hollow iron oxide nanoparticles. SOURCE: [**Talapin**]
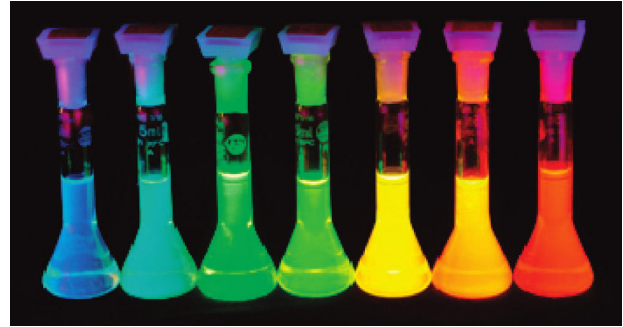
Figure 1.2: This photograph shows the size-dependent PL of the quantum dots. The particles with the smallest ($\sim$1.7nm) CdSe core emit blue and with the largest core ($\sim$5nm) emit red. SOURCE: [**Talapin**]

Basic physics of the Quantum Dot For bulk materials the band gap is a fixed parameter, that specifies the type of material. But when a particle gets smaller and reaches a size of about 10 nm this will not be the case anymore. The band gap is than depending on the size of this particle (nanocrystal). As the mobility of the charge carriers (electrons, holes) is very limited in all three dimensions in the quantum dot, the energy levels are not continuous, but instead discrete. This phenomenon is called *quantum size effect*.

The bandgap of a spherical QD of radius R is then approximately:

$$E_g \approx E_{g,0} + \frac{\hbar^2 \pi^2}{2 m_{eh} R^2} \tag{1.1}$$

where $E_{g,0}$ denotes the bandgap of the bulk material and m_{eh} is obtained through the effective masses of electrons and holes $m_{e,p}$:
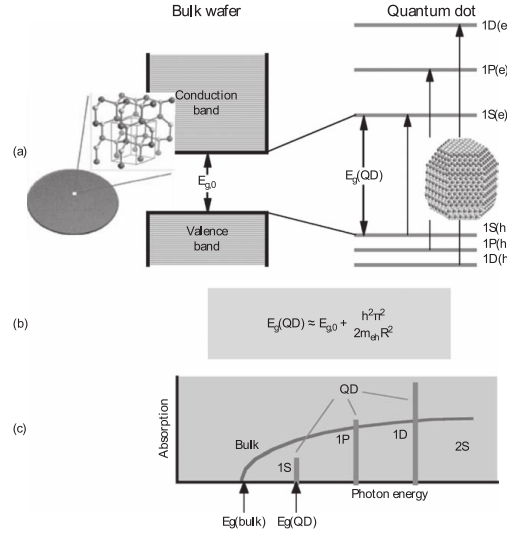
$$m_{eh} = \frac{m_e m_h}{m_e + m_h} \tag{1.2}$$

Figure 1.3: (a) The left illustration shows the band structure of a bulk semiconductor with energy band gap $E_{g,0}$, whereas the the right one illustrates the discrete energy levels of a QD and its energy gap $E_g(QD)$. (b) $1/R^2$ dependence of the band gap. (c) Theoretical absorption spectrums of a bulk material, which is continuous and a QD with discrete absorption lines. SOURCE: [**Klimov**]

We will see later in chapter **ADD** that the QD absorption spectrum as shown in figure ??(c) is not really discrete; as it is not possible to fabricate QDs that are perfectly equal in size, this results in a broadening of the spectrum. The energy gap increases for decreasing QD sizes, because more energy is required to confine the semiconductor excitation to a smaller volume. This is caused by Heisenberg's uncertainty principle, which says, that if we want to locate a particle of effective mass m (for example an electron), let's say on an x-axis within an interval Δx, we can only make an uncertain prediction of its impulse. If the spatial region gets smaller, the uncertainty of the impulse will increase.

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \tag{1.3}$$

This adds to the kinetic energy of the free particle, which is called the confinement energy, that has an significant impact, if it gets bigger than the thermal energy of the particle.

$$E_{confinement} = \frac{(\Delta p_x)^2}{2m} \sim \frac{\hbar^2}{2m(\Delta x)^2} > \frac{1}{2} k_B T \tag{1.4}$$

From this we can conclude, that the quantum size effect is relevant if

$$\Delta x < \sqrt{\frac{\hbar^2}{m k_B T}} \tag{1.5}$$

Table ?? shows the 4 possible confinement structures, which are illustrated in Figure ?? with their characteristic energy levels in the conduction band.

Table 1.1: Number of degrees of freedom tabulated against the dimensionality of the quantum confinement. The final column shoes the functional form of the density of states for free electrons. SOURCE: [**Fox**]

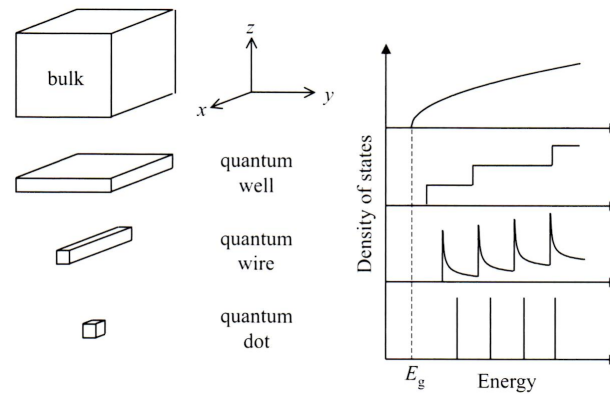| Structure	Quantum confinement	# of free dimensions	Electron density of states
Bulk	none	3	$E^{1/2}$
Quantum well/superlattice	1-D	2	E^0
Quantum wire	2-D	1	$E^{-1/2}$
Quantum dot/box	3-D	0	discrete

Figure 1.4: Schematic representation of quantum wells, wires and dots (left). The generic shape of the density of states function for electrons in the conduction band of a semiconductor with band gap E_g is shown for each type of the structure (right). SOURCE: [**Fox**]

Fabrication techniques of QD   A lot of different ways of making QDs have been developed, and a lot of research efforts are made to create more efficient QDs and new shapes and morphologies. As QDs are more and more interesting for various commercial applications, low costs play an important factor. The colloidal chemistry has made a major contribution, as it offers low energy synthesis of nanocrystals/QDs using very simple and affordable laboratory equipment. In the next chapter we will be briefly discussing the mentioned technique, by giving a short overview that avoids the use chemical terms as much as possible, rather than a detailed disquisition, as this is a research field on its own.

Some other methods are listed below.

Physical methods	Characterization
Molecular-beam-epitaxy (MBE)	High-energy-input, expensive apparatus, used for QDs
Metalorganic-chemical-vapor-decomposition (MOCVD)	High-energy-input, used for QDs
Vapor-liquid-solid (VLS)	High-energy-input, used for quantum wires
Electron-beam lithography	

Chemical methods	Characterization
Colloidal chemical synthesis of crystalline semiconductor nanoparticles	Low-energy-input, wet chemistry, used for various structures

Applications   In biology and chemistry QDs are used as spectral tags that are attached to molecules making their position visible for identification under optical illumination. In the past one used organic dyes, but compared to QDs the sharpness of emission lines is not as good.

In electronics, QDs are used to increase the efficiency of lasers [**SemiconductorCD**], every day light sources and solar cells. Furthermore they are used in broadband Light-emitting diode (LED), memory elements, flexible displays, photodetectors.

We have to add, that a lot of these applications are still developed in research institutions and not yet available for commercial use.

Although the applications seem impressive and are probably motivate new technologies, there are reasonable concerns about these nanoscale particles. Some of the material are toxic and through the small sizes it is unclear what might happen if the particles end up in living organisms or generally speaking into the the environment. For those that are interested, we recommend the following paper for further reading: **Hardman Hardman [Hardman**].

Chapter 2

Colloidal Nanocrystal Synthesis

The colloidal chemistry has offered a remarkable amount of tools for creating nanostructures. In the past growing simple spherical monodisperse nanoscrystals were the starting point of this research area, whereas nowadays various shapes, such as spheres, cubes, tetrapods, wires or rods can be engineered. The main advantages of the colloidal synthesis are:

- High precision shape control of the crystal and Multicomponent structures are possible
- Good size adjustability, trough which the optical properties of the material are determined
- Monodispersity of the nanocrystals
- Low energy and low cost fabrication with simple experimental setup
- Broad range of materials, including metals, semiconductors and magnetic materials can be synthesized at sub-20nm range

Due to the listed advantages, the colloidal nanocrystal synthesis is the best candidate for commercial applications so far.

2.1   The synthesis

The colloidal nanocrystal synthesis is a wet chemical method to create nanostrucures. Its basic idea is the controlled growth of a nanocrystal, which is mainly depending on time.

In figure **??**, a reaction flask with thermometer and injection in form of a syringe is sketched. In praxis a heater is installed around the lower part of the flask, to keep the solvent at a desired constant temperature.

The procedure itself starts with the heating of a solvent funneled into the flask. The thermometer will indicate the temperature of the solvent, which is a key variable for a good growth process. Therefore it is important to control, as the reaction will have an influence on the temperature as well.

Once the solvent has reached the desired temperature, the growing of the nanocrystals is initiated, with the injection of precursors. From now on the duration of reaction determines the size of the final nanocrystal. The longer the reaction, the more the crystals will grow. The time to reach a desired size, are empirical values.

As soon as the final size is reached, the reaction is stopped, by switching of the heating and cooling down the compound.

After the reaction was stopped, the nanocrystals get washed in a last step to remove impurities from the reaction.

Once the nucleation process is stared, the size of the nanocrystal is determined by the time, i.e. the longer the reaction, the larger the crystals can grow. Figure **??** illustrates the stages of the traditional LaMer model by the U.S.-American chemist Victor LaMer. Unfortunately, the process is more complicated, as the model predicts. It does not hold for hot-injection schemes for instance, because nucleation, ripening and growth may almost occur concurrently [**Klimov**]. Furthermore the nucleation process does not have to start immediately after injection, but it is usually a single discrete event in time

three-component system composed of precursors, organic surfactants, and solvents
temperature high enough, precursors turn into monomers
if the concentration of the monomers in the reaction medium is high enough, crystal growth starts with nucleation process.

Temperature critical factor for determining optimal crystal growth
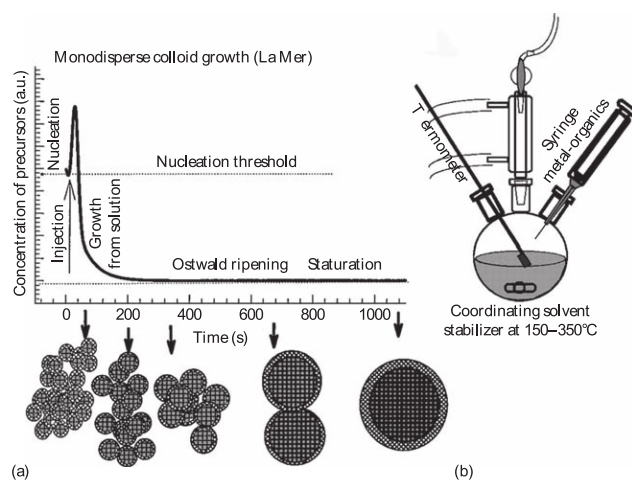Lower temperatures support growth process

Figure 2.1: (a) Stages of the monodisperse nanocrystal synthesis according to La Mer. (b) Basic apparatus used in the synthesis. SOURCE: [**Klimov**]

Higher temperature causes annealing and rearrangement of atoms
Critical factors: monomer concentration
    The growth process of nanocrystals can occur in two different regimes, "focusing" and "defocusing"

    at high monomer concentrations, small critical sizes (size of nanocrystals stays the same) -> growth of nearly all particles (smaller particles grow faster than large ones) (since larger crystals need more atoms to grow than small crystals). optimal when the monomer concentration is kept in a way, that present average nanocrystal size is always slightly larger than the critical size
When the monomer concentration is depleted during growth, the critical size becomes larger than the average size present, and the distribution "defocuses" as a result of Ostwald ripening.
    beaker (Messbecher)

Glossary

Annealing . 7

Colloid Colloids are particles or droplets with a diameter of about 1-1000nm, that are dispersed in another medium, which can be a solid, gas or liquid. 7

Colloidal Quantum Dot Quantum Dots that have been created by a chemical solution process (see chapter **??**). 7

Monodispersity A collection of particles with same size, shape or mass is called monodisperse. 7

Monomer Monomers are molecules that can take part in chemical reactions. They can connect themselves and form molecular chains, or Polymers.. 7

Nucleation Nucleation is the process of strongly localized phase changes in a substrate around focal points (nuclei). The nucleus often grows exponentially with time. Speaking in terms of crystal formation, this means, that atoms, ions or molecules in a solvent respectively liquid form a solid crystal.. 7

Ostwald rippening Is an autonomous running process in disperse matter (for example liquid sols) with inhomogeneous particles. Here smaller particles dissolve and get attached to bigger ones. 7

Phase The term phase as understood in material sciences, thermodynamics and physical chemistry is a region, where the chemical composition of matter is homogeneous under certain circumstances. Often, the phase is related to the state of matter, i.e water is of a constant phase for temperatures below the freezing point. 7

Precursor Precursor is a compound that is used for a chemical reaction during a synthesis.. 7

Transmission electron microscopy A transmission electron microscope is a high resolution microscope, that uses an electron beam to produce an enlarged image of a sample. The beam impacts the ultra-thin specimen and the transmitted electrons form an image that gets enlarged to make it visible for the human eye. Usually the samples have to be prepared very carefully, as the electrons interact with the specimen. 7

Acronyms

CQD Colloidal Quantum Dot. 7, *Glossary:* Colloidal Quantum Dot

EDO Experimental Data Object. 7

GUI Graphical User Interface. 7

LED Light-emitting diode. 3, 7

PbS Lead sulfide. 7

PL Photoluminescence. 1, 7

QD Quantum Dot. 1–3, 7

QDO Quantum Dot Object. 7

TEM Transmission electron microscopy. 7, *Glossary:* Transmission electron microscopy

TOM Toolbox for OMEN in MATLAB. 7

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