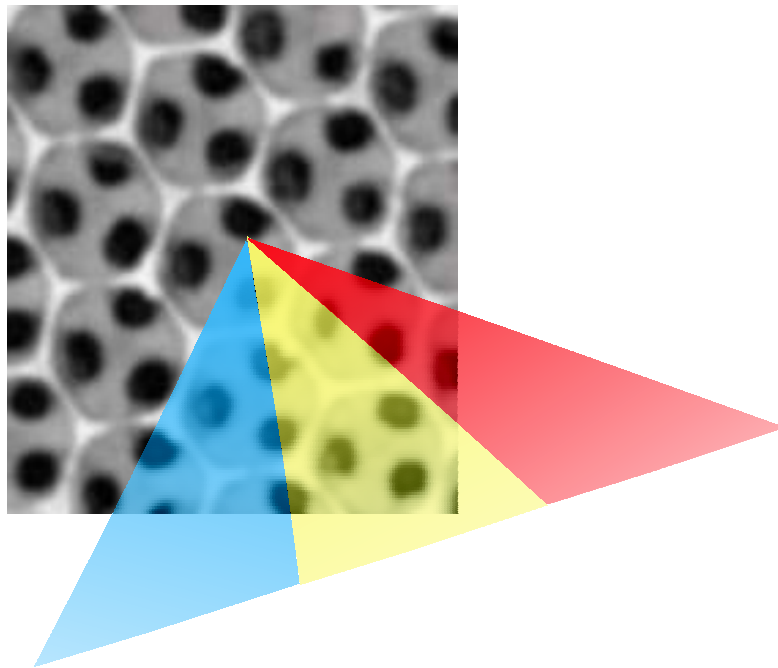


Modification of Spontaneous Emission of Quantum Dots by Photonic Crystals



Arie Irman
11 November 2003
Enschede

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Graduation Thesis
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Chapter 1

Introduction

1.1 Quantum dots

Quantum dots are semiconductor particles with diameters in the nanometer regime (1-20 nm). An example is shown in Fig. 1.1. The typical size of quantum dots results in quantum confinement, which gives unique of the electronic and optical properties. A blue shift of the absorption spectrum with decreasing dot size and a tunable emission wavelength by adjusting dot size are examples of the size dependent optical properties. These properties are distinct from those observed in the corresponding bulk semiconductor.

Quantum dots made of cadmium selenide are one of the quantum dot materials that are well understood. Advances in the synthesis method have produced extremely high quality CdSe quantum dots, as pioneered by Murray and co-workers in 1993 [1]. Furthermore, a number of theoretical approaches have been developed to analyze the phenomena observed in experimental works. The unique properties of CdSe quantum dots give rise to their potential applications in the fields of nonlinear optics, luminescence, solar energy, optoelectronic, as well as other areas. In particular, we are interested in using CdSe quantum dots as light sources to investigate the photonic properties of photonic crystals.

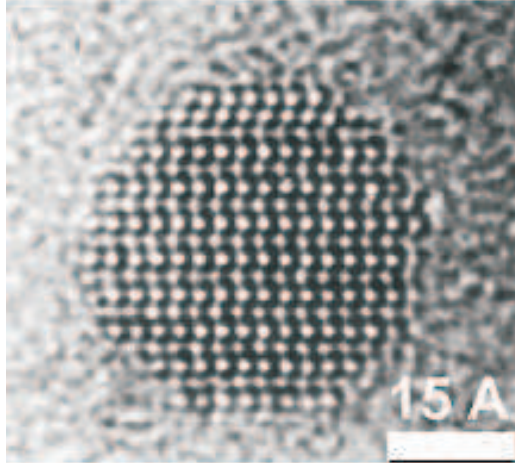


Figure 1.1: A Transmission Electron Micrograph (TEM) image of a single CdSe quantum dot. The atomic lattice is clearly seen which builds up the quantum dot. The scale bar is 15 Å. The picture is taken from reference [2].

1.2 Three dimensional photonic crystals

Three dimensional photonic crystals are dielectric composite materials in which the refractive index varies periodically in three dimensions on length scales of the order of optical wavelengths. These structures give rise to Bragg diffractions which result in forbidden frequency windows for electromagnetic modes in specific propagation directions, so called stop bands. If stop bands overlap in all directions simultaneously, the photonic band gap is formed. In such a structure no electromagnetic modes can exist at all directions and polarizations. The photonic band gap crystal will modify the density of electromagnetic modes compared to vacuum. Hence, it is expected to play an important role in tailoring atom-radiation interactions, as first put forward in 1987 by Yablonovitch [3]. One of the most important consequences is an inhibition or enhancement of decay rate of an excited atom or molecule inside the photonic band gap crystal. Experimentally this phenomenon is investigated by placing light sources inside the bulk of photonic crystals. However, the decay rate changes have not been clearly observed until this moment. In this thesis, we report for the first time both inhibition and enhancement of the decay rate of CdSe quantum dots embedded inside titania inverse opal photonic crystals.

1.3 Thesis outlook

This thesis describes experiments which concern the observation of optical properties of CdSe quantum dots and spontaneous emission of CdSe quantum dots inside titania inverse opal photonic crystals. Chapter 2 deals with the CdSe quantum dots in detail, including a theoretical overview, the synthesis method, and the optical properties. In particular, the absorption and emission spectrum, quantum efficiency, stability, and energy transfer of the quantum dots will be discussed extensively. Chapter 3 discusses the modification of spontaneous emission of CdSe quantum dots which is measured by means of angle resolved and time resolved experiments. These quantum dots are embedded inside titania inverse opal photonic crystals. Finally, conclusion and recommendations will be given in chapter 4.

Chapter 2

Quantum dots: cadmium selenide (CdSe)

2.1 Introduction

Quantum dots are semiconductor nanoparticles with a diameter range of 1-20 nm. The unique properties of these nanoparticles offer promising applications in the future for several new technologies. In this thesis, we are interested in using these nanoparticles as internal light sources to probe the photonic properties of photonic crystals. The details concerning this application will be intensively studied in chapter 3.

Quantum dots, which are made of cadmium selenide, are one of the most well understood quantum dot materials. Extremely high quality CdSe quantum dots have been produced and much new information have been obtained from this system. Furthermore, a number of theoretical approaches, e.g., the effective mass approximation [4] and the pseudopotential method [5], have been developed to explain the electronic and optical properties observed in experimental works.

In this chapter we will explore the CdSe quantum dots in details, including a theoretical overview, the synthesis process, and the optical properties. Particularly, we limit ourselves on several interesting features of the CdSe optical properties, e.g., absorption and emission spectrum, quantum efficiency, sta-

bility, and energy transfer. Since these properties become a very important issue in application on photonic crystals (see chapter 3). In the theoretical section, we will discuss the effective mass approximation method together with some limitations and assumptions which are considered. The synthesis of CdSe quantum dots is done by Drs. A. Floris van Driel and Prof. Daniël Vanmaekelbergh from the Chemistry and Condensed Matter Group in the University of Utrecht. Synthesis of quantum dots has been an intensive research area over the last past 10 years. A lot of effort and thoughts have been put into producing high quality quantum dots with high monodispersity and high quantum efficiency [1], [2], [6], [7].

2.2 Theoretical description

In semiconductor materials, an electron can be excited across the band gap into the conduction band and leave a hole in the valence band simultaneously. By the attractive coulomb interaction, an excited electron in the conduction band and the resulting hole in the valence band may approach each other. Then, they form an electron-hole pair which is called an exciton.

In case of the bulk CdSe semiconductor, an electron-hole pair forms a weakly bound exciton or the Wannier exciton [4] in which an electron-hole separation distance is larger than the lattice constant of the crystal. The characteristic distance between these two charges can be expressed as

$$a_B^{ex} = \frac{\hbar^2}{e^2} \epsilon \left[\frac{1}{m_e} + \frac{1}{m_h} \right], \quad (2.1)$$

where m_e and m_h are effective mass of electron and hole, respectively, e is the elementary charge, and ϵ represents the dielectric constant of the bulk semiconductor. This distance is also known as the Bohr radius of the bulk exciton. For the bulk CdSe semiconductor, a_B^{ex} is typically about 6 nm. When the size of this semiconductor is comparable to or smaller than the Bohr radius Eq. (2.1), the exciton will be confined spatially inside the semiconductor (dot). This results in quantum confinement, which gives a strong influence to the electronic and optical properties of the semiconductor.

Based on the effective mass approximation, Brus [4] showed for quantum dots that the energy gap between the lowest level of the conduction band (so called Lowest Unoccupied Molecular Orbital (LUMO)) and the highest level

of the valence band (so called Highest Occupied Molecular Orbital (HOMO)) can be approximately calculated by

$$\Delta E \cong \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R}, \quad (2.2)$$

where R is the radius of the quantum dot. In Eq. (2.2) the first term relates to the quantum localization which shifts the energy gap to higher energies as R^{-2} . The second term is the Coulomb term which shifts the energy to lower energies as R^{-1} . Consequently, the total energy gap (ΔE) increases in energy when decreasing the quantum dot diameter. Experimentally this effect can be observed as a blue shift of the absorption spectrum with decreasing quantum dot size. Moreover, quantum confinement causes that the valence band and the conduction band of the quantum dots consist of discrete energy levels, as shown in Fig. 2.1. These structure are often referred to as “artificial atoms”.

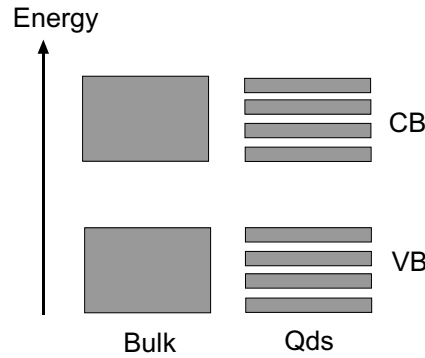


Figure 2.1: A comparison of energy levels between a bulk semiconductor and a quantum dot. The valence and conduction band in a bulk semiconductor consist of an energy continuum. On the contrary, the valence and conduction band in a quantum dot consist of discrete energy levels.

The effective mass approximation model does not consider a number of important parameters, which are observed in real quantum dots, e.g., surface structure effects and size dependent structural lattice arrangements [4]. As a consequence, this model is not valid in predicting and explaining experimental results for very small quantum dots. To overcome these problems, more sophisticated models have been invented, such as the pseudopotential model by Krishna *et al.* [5]. The explanation of this model is beyond the scope of this thesis.

2.3 Synthesis of quantum dots

The aim of the synthesis is to produce high quality quantum dots, i.e., a high monodispersity in the size distribution (standard deviation less than 5%), and high quantum efficiency (more than 50%). The first successful work in synthesizing nearly monodisperse quantum dots was done by Murray and co-workers in 1993 [1]. The synthesis process was called an organometallic synthesis. In this section, we are going to highlight that process without discussing in much details the chemical parts.

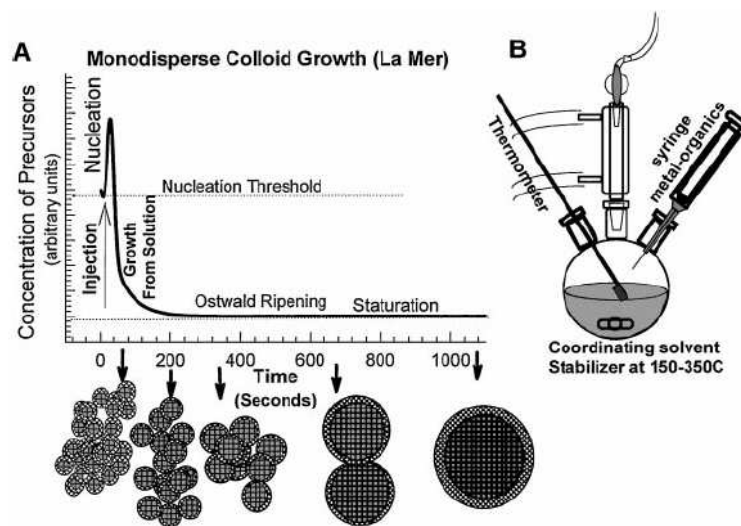


Figure 2.2: A synthesis in the framework of the La Mer model. (a) shows the stages needed to produce quantum dots. The synthesis is started with a temporally discrete nucleation event then followed by controlled growth on the existing nuclei. (b) represents an image of the apparatus where all chemical reactions for growing quantum dots take place. Reagents, i.e., TOPSe and Me_2Cd , are injected via a syringe into a coordinating solvent, i.e., TOPO and HDA, very rapidly. The picture was taken from reference [2].

A scheme of the synthesis of CdSe quantum dots is shown in Fig. 2.2. The reagents, i.e., trioctylphosphine selenide (TOPSe) and dimethylcadmium (Me_2Cd), are injected into the coordinating solvent via a syringe by means of a fast single injection. It gives rise to an increasing the precursor concentration, i.e., cadmium and selenide, exceeding its nucleation threshold. A nucleation starts after the supersaturation condition is reached in which the

precursor concentration arrives at the maximum value. Then, the concentration of the precursors decreases as the quantum dots grow. The growing process involves a second growth phase, known as Ostwald ripening. In this condition smaller CdSe quantum dots dissolve and redeposit on larger quantum dots. The size of the quantum dots is measured by performing an absorption measurement of the quantum dot solution during the growing process. Finally, the CdSe quantum dots is brought into chloroform solvent after the desired dot size is achieved.

One can improve the quality and stability of CdSe quantum dots by passivating the quantum dots surface using a larger band gap semiconductor layer, e.g., ZnSe [6]. The energy gap of ZnSe is about 0.96 eV higher than for CdSe. Moreover, this additional treatment is very important for our main research in implementing the quantum dots into photonic crystal. We would expect that the passivation layer could avoid electron transfer from quantum dots to the photonic crystals host.

2.4 Optical properties of quantum dots

Before implementing CdSe quantum dots into photonic crystals, we need to understand the optical properties of the quantum dots. In this section, we are going to discuss several optical properties of the CdSe quantum dots, such as the absorption spectrum, the photoluminescence spectrum, and the quantum efficiency.

2.4.1 Absorption spectrum

We have studied features of the absorption spectrum of CdSe quantum dots. The spectrum was obtained from an absorption experiment using a Fourier Transform spectrometer (Biorad FTS-6000) operated at a resolution of 32 cm^{-1} . As light source, we used an incandescent lamp (tungsten-halogen) which gave a very broad emission spectrum from the visible to the infrared regime. The absorption spectrum was determined by comparing the spectrum of the quantum dots in chloroform to the spectrum of a pure chloroform solution. Furthermore, the absorption spectrum can also be used to obtain the mean size of the dots. The mean size is extracted by comparing the

wavelength of the first absorption peak with the experimental results at references [1], [8], [9].

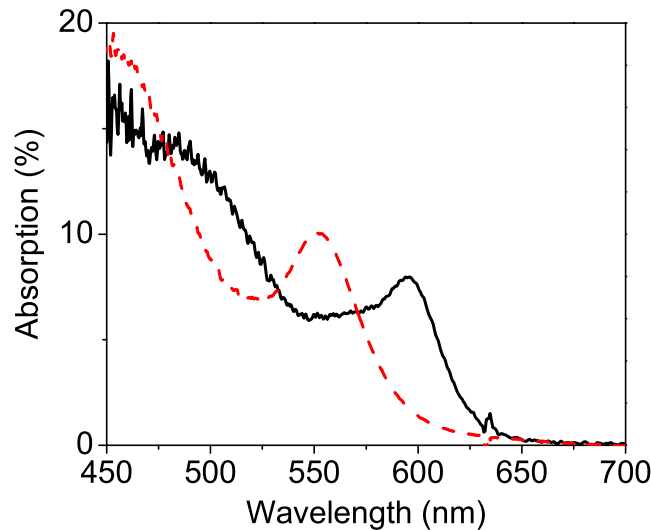


Figure 2.3: A typical absorption spectrum of CdSe quantum dots. The thick line represents the absorption spectrum of the quantum dots with mean diameter of $4.3 \text{ nm} \pm 0.4 \text{ nm}$. The dashed line shows the absorption spectrum from the $3.1 \text{ nm} \pm 0.3 \text{ nm}$ quantum dots. It is clear that the absorption spectrum shifts to shorter wavelengths for smaller quantum dots.

We performed the absorption experiment for two mean sizes of CdSe quantum dots. The results are presented in Fig. 2.3. The thick line represents the absorption spectrum for CdSe quantum dots with $4.3 \text{ nm} \pm 0.4 \text{ nm}$ in mean diameter. The first absorption peak occurs at the wavelength 595 nm. The dashed line displays the absorption spectrum for the $3.1 \text{ nm} \pm 0.3 \text{ nm}$ quantum dots in mean diameter with the first absorption peak at the wavelength 551 nm. The first absorption peak is associated with the transition energy between the LUMO and the HOMO band of quantum dots. A broadening of the absorption spectrum at the blue side as well as at the red side of the first absorption peak is due to size dispersion of quantum dots. Based on these absorption spectra, it is clear that the absorption spectrum shifts to shorter wavelengths as the mean size of the quantum dots decrease. The blue shift proves that the LUMO-HOMO energy gap for small quantum dots is wider than large quantum dots. The absorption spectrum gives information

about the efficient wavelengths to excite the quantum dots. Moreover, the absorption spectrum can also be used to determine the quantum efficiency of CdSe quantum dots.

2.4.2 Photoluminescence spectrum

The quantum confinement affects also the photoluminescence of quantum dots. That is the emission wavelength can be tuned by adjusting the size of the quantum dots. The experimental setup, which was used to measure the emission spectra of CdSe quantum dots, can be seen in Fig. 3.4. We used $\lambda = 440$ nm line for the excitation laser.

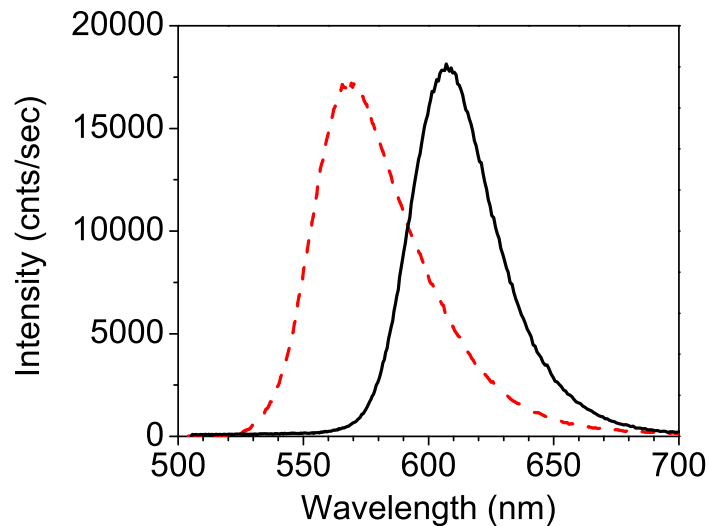


Figure 2.4: A typical photoluminescence spectrum of CdSe quantum dots. The thick line shows the emission spectrum for the $4.3 \text{ nm} \pm 0.4 \text{ nm}$ quantum dots in which the emission peak is at the wavelength 608 nm. The dashed line represents the emission spectrum for the $3.1 \text{ nm} \pm 0.3 \text{ nm}$ quantum dots. The emission peak for these quantum dots occur at the wavelength 568 nm.

We measured the photoluminescence spectrum for two mean sizes of the CdSe quantum dots. The results are displayed in Fig. 2.4. The thick line represents the emission spectrum for the $4.3 \text{ nm} \pm 0.4 \text{ nm}$ in mean diameter

which is red shifted compared to the $3.1 \text{ nm} \pm 0.3 \text{ nm}$ (the dashed line) quantum dots. The bandwidth of the quantum dot spectrum is associated with the polydispersity of the dot size. The spectral bandwidth for monodisperse quantum dots is narrower than for those observed in the polydisperse quantum dots. Moreover, a specific wavelength component in the quantum dot spectrum originates from a specific size of quantum dots, with the smaller dots emission towards the blue side of the photoluminescence spectrum and the larger dots to the red side. Since the emission linewidth of a single quantum dots is very narrow ($\sim 0.3 \text{ nm}$ at 10K [10]). The quantum dot spectrum has a narrow homogeneous linewidth and a broad inhomogeneous linewidth.

2.4.3 Quantum efficiency

In general, quantum efficiency of quantum dots is defined as a ratio of the total emitted photons to the total absorbed photons. Experimentally this quantity can be extracted by calculating the ratio of the total luminescence to absorption data, then compare that ratio with the quantum efficiency of a standard reference sample. For a reference, we used laser dyes Rhodamine 6G (R6G) in ethanol which has quantum efficiency $\eta_{R6G} = 95\% \pm 5\%$ [11]. Calculations of the quantum efficiency of quantum dots can be expressed as follows [7]

$$\eta_{QD} = \left[\frac{1 - T_{R6G}}{1 - T_{QD}} \right] \left[\frac{\Delta\Phi_{QD}}{\Delta\Phi_{R6G}} \right] \eta_{R6G}, \quad (2.3)$$

where $1 - T_{R6G}$ and $1 - T_{QDs}$ are the absorption values of R6G and quantum dots, respectively, which are obtained from the absorption measurements. $\Delta\Phi_{QDs}$ represents the total luminescence intensity of quantum dots extracted by integrating the emission intensity over the whole spectrum ($\Delta\Phi_{QDs} = \int I(\lambda) d\lambda$). $\Delta\Phi_{R6G}$ is obtained using the same calculation for R6G. It is important to note that the wavelength used to get the absorption should be the same as the wavelength used to excite the quantum dots and R6G. For CdSe quantum dots studied here, we obtained the quantum efficiency $\eta_{QDs} = 50\% \pm 5\%$.

2.5 Stability and energy transfer of quantum dots

In the following section, we are going to discuss two main issues of quantum dots before they are placed in photonic crystals, i.e., the stability and the energy transfer of quantum dots. These issues are of crucial importance since they can obscure observations of the stop bands as well as the lifetime effect on photonic crystals.

2.5.1 Stability of quantum dots

We did a stability measurement for CdSe quantum dots in two difference circumstances, i.e., in air and nitrogen atmospheres. We put a drop of the quantum dot solution on two glass plates, separately. Then, they were dried under a nitrogen flow. After that, the first glass plate was stored in nitrogen atmosphere and the second was kept in air. The 440 nm line of a pulsed laser was used for excitation. The experimental setup can be seen in Fig. 3.4. We recorded the intensity at the spectrum peak as a function of time. The results are displayed in Fig. 2.5. The thick line represents the stability of CdSe quantum dots in nitrogen. It shows that the intensity of the quantum dots remains constant over 20 minutes. On the other hand, the intensity of the quantum dots in air decreases over $\sim 20\%$ within the same period. The quantum dots in air are photooxidation during illumination.

The photooxidation of CdSe quantum dots can be illustrated as follows. When oxygen comes in contact with the quantum dots, it can penetrate through the ZnSe passivating layer and reach the CdSe core. An inactive layer is created in the core as a result of chemical reaction between oxygen and CdSe. The photooxidation causes a shrinkage of the active CdSe core. Experimentally this effect can be investigated by recording the emission spectrum of quantum dots as a function of time. Wilfried *et al.* [13] observed that a blue shift of the overall spectrum of quantum dots in air. To avoid these effects, it is very important to keep the quantum dots in an oxygen free atmosphere, such as inside a nitrogen chamber, during the optical experiments.

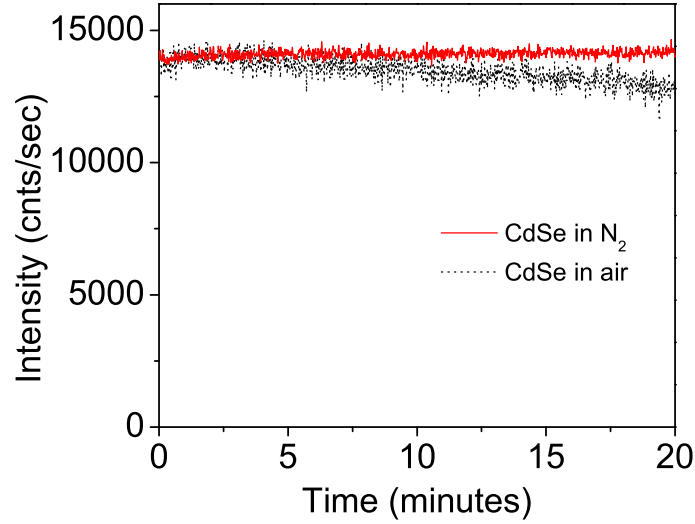


Figure 2.5: The thick line represents the stability curve for the quantum dots placed in nitrogen atmosphere. It shows a stable intensity over a range of time, in this case about 20 minutes. On the contrary, the quantum dots placed in the air atmosphere show a decrease in intensity within the same range, represented as the dotted line (multiply by a factor 6).

2.5.2 Energy transfer between quantum dots

One CdSe quantum dot can give its energy to other CdSe dots via energy transfer. In this case, the dipole moment of an exciton in a donor quantum dot couples with an absorbing transition of a nearby acceptor. The rate energy transfer depend strongly on separation distances between the donor and the acceptor, in which the rate is faster for short distances [14].

We have studied the energy transfer for high density of CdSe quantum dots. This condition can be achieved by evaporating the chloroform from a 10^{-6} M CdSe solution on the same way as in the previous stability measurement. The sample was store inside a nitrogen chamber during optical characterizations. To evaluate the energy transfer on this sample, we performed spectral measurements and time resolved experiments using the setup presented in Fig. 3.4 and Fig. 3.9, respectively. We used 440 nm light for excitation from

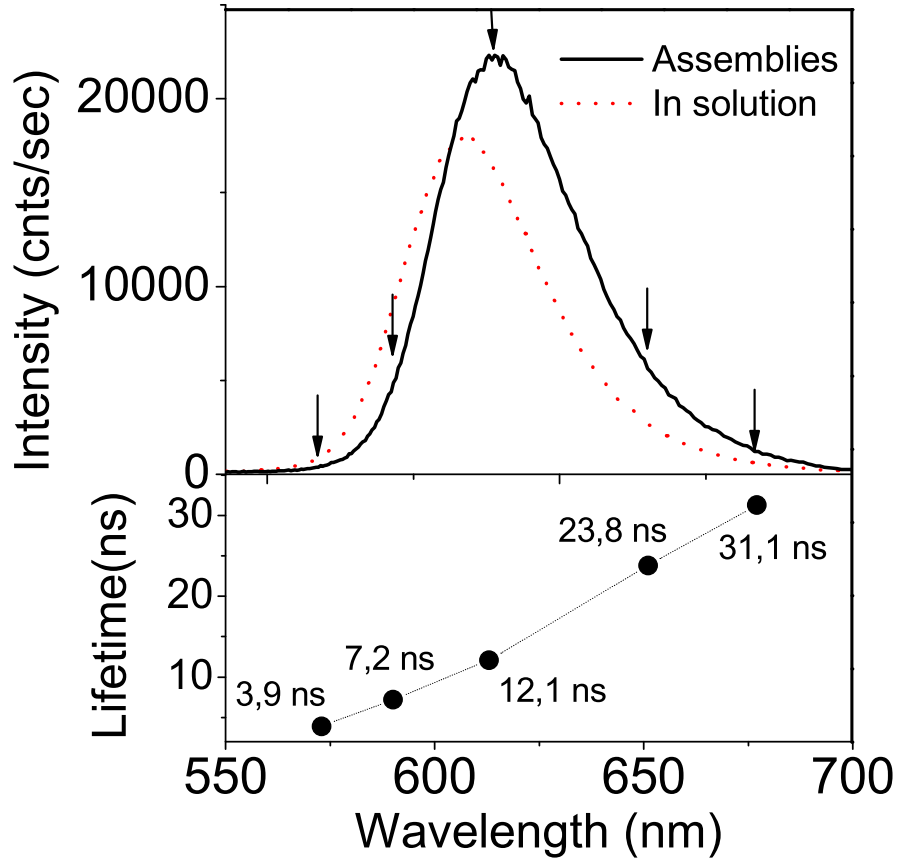


Figure 2.6: Due to the energy transfer, the emission spectrum for assemblies quantum dots is redshifted in comparison to the spectrum of quantum dots in solution. The arrows represent wavelengths for measuring the lifetime of CdSe quantum dots (see figure 2.7). The bottom figure shows the measured lifetimes on the corresponding wavelength. The lifetime increases as the wavelength increase.

a pulsed diode laser with pulsed intervals of 50 ns. All the measurements were performed at room temperature.

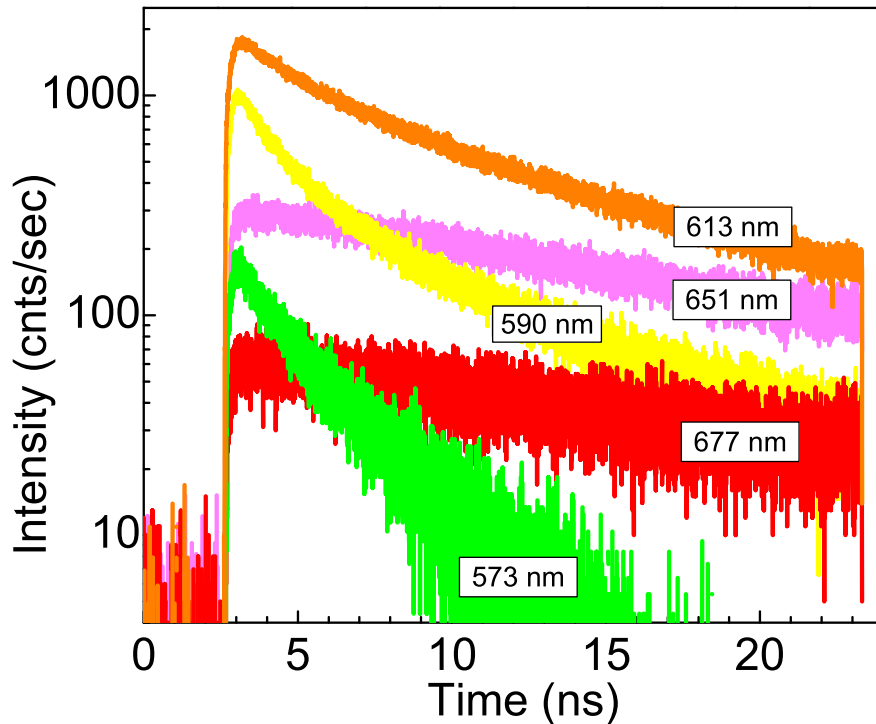


Figure 2.7: Direct observation of the energy transfer can be obtained by the time resolved experiment. The lifetimes in the red side of photoluminescence spectrum enhance compared to the blue side.

Based on the spectral measurements, the energy transfer is observed as a red shift of the assembly spectrum in comparison to the spectrum obtained in solution, see Fig. 2.6. Smaller quantum dots emitting at the blue side of the photoluminescence spectrum feed their energy to larger quantum dots at the red side by means of energy transfer. This mechanism produces an enhancement of the emission intensity for larger quantum dots and, at the same time, inhibits the emission intensity for smaller dots. In our experiment, the emission peak shifted about 5 nm to the red.

Direct investigation on the energy transfer phenomena can be done by the

time resolved experiment. In this experiment one can measure the decay rate of a specific size quantum dot, see Fig. 2.7. We obtained that the decay time of the quantum dots increased gradually with increasing dot size. At the blue side of the photoluminescence spectrum (due to smaller dots), the measured lifetime was about 3.9 ns. On the other hand, the measured lifetime for the larger dots (at the red side) was about 31.3 ns. This shows the energy transfer mechanism in which smaller dots transfer their energy to larger dots, so that the lifetime of the larger dots is enhanced. Finally, the energy transfer stops when the largest dots can not find even larger dots that can accept exciton. To avoid the energy transfer, one can use a sufficiently low concentration of quantum dots, so that the average distance between the dots are long.

2.6 Conclusion

We have studied intensively the CdSe quantum dots. Particularly, the optical properties of the quantum dots, which are mainly needed to investigate the photonic properties of a titania inverse opal crystal. Adjusting the dot size can tune the emission wavelengths of the quantum dots, hence it can be tailored to a specific titania inverse opals lattice parameter. The CdSe quantum dots coated by ZnSe layer have high quantum efficiency (more than 50% in solution). Furthermore, we found that the quantum dots placed in air atmosphere tend to be unstable, i.e., photooxidation. In this case the quality of the quantum dots decreases rapidly in minutes. Hence, in order to maintain the quality of the quantum dots, it is very important to store the quantum dots in a nitrogen chamber during the optical characterizations. Finally, the energy transfer between quantum dots occurs for a high density of the dots where the distance between them are short. The energy transfer occurs from smaller dots (donor dots) to larger dots (acceptor dots). Hence, the lifetime of the acceptors is larger than the donor dots. To minimize the energy transfer, a sufficient low concentration of the quantum dots is needed.

Chapter 3

Quantum dots in photonic crystals

3.1 Introduction

Photonic crystals are dielectric composite materials in which the refractive index varies periodically on length scales of the order of optical wavelengths. This periodic structure can generate Bragg diffractions which result in forbidden frequency windows for electromagnetic modes in specific propagation directions, so called stop bands. In three dimensional periodic dielectrics, stop bands can overlap in all directions simultaneously and create a photonic band gap. In such a structure no electromagnetic modes can exist at all directions and polarizations.

Photonic crystals are expected to play an important role in tailoring atom-radiation interactions, as proposed for the first time by Yablonovitch in 1987 [3]. These types of crystals are predicted to be able to modify the density of electromagnetic modes in comparison to those in vacuum. In vacuum the density of electromagnetic modes is proportional to the square of the frequency, which is shown as the dotted line in Fig. 3.1. However, a photonic band gap crystal forms a range of frequencies where the density of electromagnetic modes vanishes, represented as the gap in Fig. 3.1.

One of the important consequences is an inhibition or enhancement of the

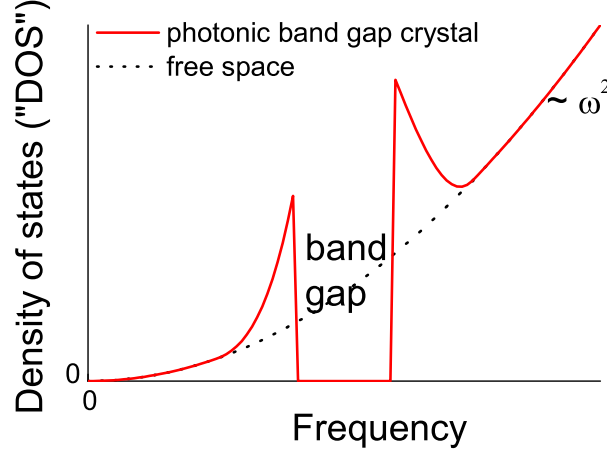


Figure 3.1: A scheme of the density of electromagnetic modes in a photonic band crystal in comparison to vacuum. In a photonic band gap crystal, the band gap appears in the density of electromagnetic modes. The dotted line displays the density of electromagnetic modes in vacuum which is proportional to the square of the frequency.

decay rate of an excited atom or molecule placed inside the photonic band gap, as stated by the Fermi's golden rule Eq.(3.1) [15]

$$\Gamma(\mathbf{r}) = \frac{\pi\omega_{ab}}{3\hbar\epsilon_0} |\langle a | \hat{\mu} | b \rangle|^2 \rho(\mathbf{r}, \mathbf{d}, \omega_{ab}), \quad (3.1)$$

where $|\langle a | \hat{\mu} | b \rangle|^2$ is the transition dipole moment, $|a\rangle$ and $|b\rangle$ are the excited state and the ground state of the atom, respectively. $\rho(\mathbf{r}, \mathbf{d}, \omega_{ab})$ represents the local density of electromagnetic modes and depends on the position $\mathbf{r}$, dipole orientation $\mathbf{d}$, and transition frequency ω_{ab} of the emitters. The complete inhibition occurs if the atom has the transition frequencies inside the band gap, which means that the atom can not emit photons at all. In contrast, the decay rate is enhanced if the emission frequency tuned to the edge of band gap where the density of electromagnetic modes is larger than in vacuum, see Fig. 3.1.

Although proposed already in 1987, an influence of the density of electromagnetic modes on the decay rate has not been clearly observed. Martorell *et al.* in 1990 [16] reported an inhibition of the lifetime of dye molecules embedded in an ordered aqueous suspension of polystyrene spheres. However, the

observed inhibition was due to the electronic interactions of dye with the surrounding structures, as clarified by Tong *et al.* [17]. In 1998 Petrov *et al.* [18] reported the photonic effect on the spontaneous emission of organic molecules placed inside a photonic crystal. Later, Megens *et al.* [19] showed both theoretically and experimentally that the modification reported by Petrov *et al.* could not be attributed to photonic effects. Recently, Zhang *et al.* [20] addressed the angular dependence of the spontaneous emission of CdTe quantum dots inside a silica air spheres crystal. In their Letter they misinterpreted the lifetime data, which are principally angle independent. In this chapter we report for the first time both inhibition and enhancement of the decay rate of CdSe quantum dots embedded in titania inverse opal crystals.

Placing light sources, such as quantum dots or laser dyes, inside photonic crystals provides a powerful tool to explore the fundamental properties of the corresponding photonic crystal. Essentially, the emitted light from the internal sources will experience two effects: (i) modification of the emission spectra due to the existence of stop bands at specific propagation directions (ii) a change of the radiative lifetime caused by modification of the density of electromagnetic modes. Modification on the density of electromagnetic modes can also be measured by recording the total emitted power from the internal light sources [21], [22]. However, this technique is less direct and sensitive. Experimentally the first effect can be investigated by means of an angle resolved experiment, and the second is examined by a time resolved experiment.

In this chapter measurements on the modification of spontaneous emission from CdSe quantum dots, which are imbedded inside an inverse opal photonic crystal, will be discussed. We have performed both angle resolved and time resolved experiments. Quantum dots are promising light sources because they can overcome limitations possessed by laser dyes. They offer a number of advantages such as a high quantum efficiency and tuneable emission wavelength over the range of interest. Most importantly, they have a narrow homogenous linewidth and a broad inhomogeneous linewidth (see previous chapter). Hence, quantum dots are expected to be able to probe the changes in the density of electromagnetic modes. Furthermore, by covering the surface of the quantum dots with an insulating layer, e.g., ZnSe, one may avoid the electron transfer from the quantum dots to the host photonic crystal, as appears to be a major problem for laser dyes [21], [22], [23].

The photonic crystals studied here are made of closed packed air spheres in anatase titania (refractive index 2.7 ± 0.4 in the visible regime [24]) forming an

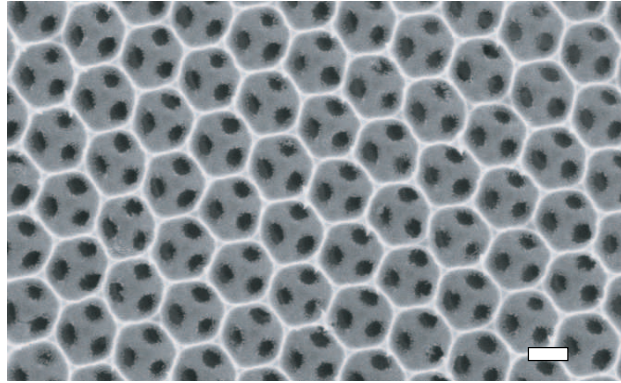


Figure 3.2: Scanning Electron Micrograph (SEM) image of a $[111]$ plane of a titania inverse opal with lattice parameter $a=496$ nm. The scale bar represents 200 nm. The black dots are connecting windows to the next lattice plane.

fcc crystal structure. These crystals are produced by filling the voids of latex opals with a precursor of tetra-propoxy-titane and subsequently removing the latex opal by calcination, then followed by a drying process. It yields a highly ordered and strongly interacting photonic crystals with high refractive index contrast. The details can be read in references [24], [25]. Figure. 3.2 shows an image of a titania inverse opal photonic crystal with lattice constant 496 nm. The hexagonal pattern indicates that the lattice plane orientation is $[111]$ for the fcc crystal structure.

3.2 Infiltration of quantum dots in titania inverse opals

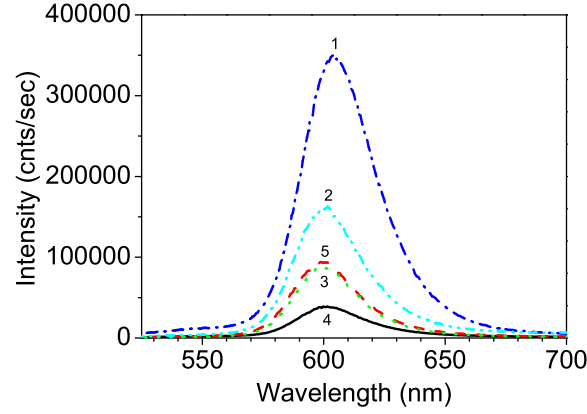
Before being able to perform the emission experiments, a technique to place CdSe quantum dots in a well-controlled way into titania inverse opal crystals had to be invented. Different from the organic laser dye Rhodamine 6G (R6G), which dissolves well in polar solvents such as ethanol, the CdSe quantum dots are favorable dissolved in non-polar solvents like chloroform. This is due to fact that the quantum dots are covered with uncharged organic capping molecules on the outer surface, as e.g., trioctylphosphine oxide (TOPO) molecules. These molecules are also crucial in maintaining stability of the quantum dots since they prevent precipitation of the quantum dots [1].

Trying to infiltrate titania inverse opals with the quantum dots in chloroform turned out not to be successful. This is probably due to the polarity of the titania surface. The quantum dots do not have enough affinity to attach onto the titania surface which is more polar. Hence, most of the quantum dots were observed to be on the outer surface of the crystal.

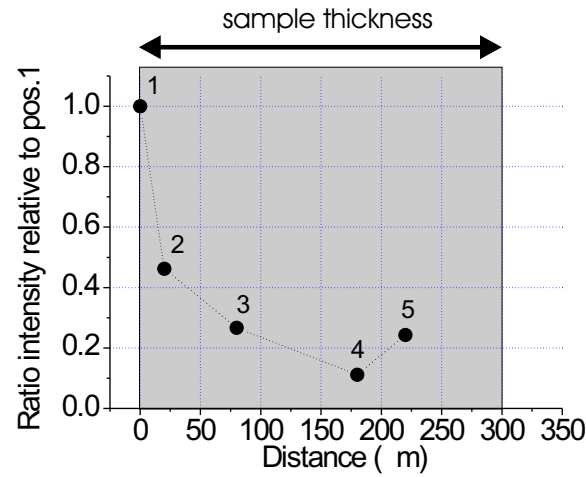
To solve this problem, we have studied extensively the possibility of suspending the CdSe quantum dots in polar solvents. We chose butanol for several reasons. First, butanol may provide chemical chains to bind the quantum dots onto the titania surface. Second, the CdSe quantum dots were found to be stable within a mixture of chloroform and butanol. Hence, the color of the quantum dot solution looked the same and no agglomeration was observed for a week observation time.

Infiltration was performed for three sizes of lattice constants of the titania inverse opal, they were $a=496$ nm, 419 nm, and 370 nm. These crystals were immersed within a CdSe quantum dot suspension, which consists of 1:1 chloroform and butanol, for 24 hours. Subsequently, they were rinsed with pure chloroform for about 1 minute and then dried for a night. The concentration of the CdSe suspension was $1 \cdot 10^{-7}$ M.

Probing the cross section of a sliced doped titania sample was performed to ensure that quantum dots were present in the middle of the crystal. The crystal was cut into two and we recorded the quantum dot spectra at several positions on the broken side of the sample. The experimental setup is represented in Fig. 3.4. For excitation, we used a continuous wave (cw) argon laser at the wavelength 497 nm and focused the beam to $70 \mu\text{m}$ in diameter by a lens ($f=10$ cm) onto the crystal cross section. The emitted light from the crystal cross section was dispersed by a Carl Leiss spectrometer (resolution 2 nm) and detected by a photomultiplier tube (PMT). The results for a sample that was doped 30 minutes can be seen in Fig. 3.3. The thickness of the crystal was about $300 \mu\text{m}$. Position 1 was a measurement which was done on the crystal surface. Position 2, 3, 4, and 5 were measured at 20, 80, 180, and $220 \mu\text{m}$ inside the sample, respectively. The x-axis in Fig. 3.3(b) represents the position of each measurement point relative to one of the crystal surfaces. On the y-axis we have plotted the normalized peak intensity relative to the peak intensity at position 1. It is clear that even for this relative short doping time, we have at least 10% of quantum dots in the middle of the crystal. Accordingly, for 24 hours doping time we would expect to have even higher concentration of quantum dots inside the bulk of the crystal. The sample preparation and optical measurements were done



(a)



(b)

Figure 3.3: Distribution of CdSe quantum dots inside a titania inverse opal after cutting the sample and measuring at the broken crystal's cross section. Position 1 was on the crystal surface. Position 2, 3, 4, and 5 were recorded at 20, 80, 180 and 220 μm inside the sample, respectively. The peak intensity for each point was normalized to the peak intensity at the surface. Fig. 3.3(a) shows the emission spectra of the quantum dots at those positions and Fig. 3.3(b) displays the normalized peak intensity relative to the position 1 as a function of depth.

inside a nitrogen atmosphere to avoid photooxidation of the quantum dots (see chapter 2). These results are encouraging and very important. Since we can show and prove that the quantum dots are present inside the bulk of titania crystal. Therefore, we are ready to do the emission experiments on the doped titania samples. The emission experiments are studied intensively in the following sections.

3.3 Spectral measurements

It is important to study the optical properties of stop bands since they are known as the building blocks of the photonic band gap. Stop bands are caused by the Bragg diffractions of light by lattice planes during the transport through a photonic crystals. If the stop bands overlap in all directions simultaneously, the photonic band gap is formed. The photonic band gap is a range of frequencies where there are no possible modes for all directions and polarizations.

In the angle resolved experiment, the features of the stop bands can be studied by comparing the spectra of the internal sources inside the photonic crystal with those in a reference crystal. The reference crystal is a chemically identical crystal with smaller lattice constant than the photonic samples. Hence, this sample is photonic at shorter wavelengths, where the internal sources do not emit.

3.3.1 Experimental setup

We applied a newly constructed setup for an angle resolved experiment on doped titania inverse opal with CdSe quantum dots, see Fig. 3.4. We placed the doped sample inside an evacuated chamber to avoid photooxidation of the quantum dots during the experiment. In order to ensure that the emitted light originated solely from the quantum dots inside the bulk of crystal, we excited the doped sample through the back surface, i.e., the side of the sample away from the detector. The emitted light was collected from the front surface of the sample. This construction was necessary since the quantum dots located on the crystal surfaces could not be bleached despite using highly intense beams.

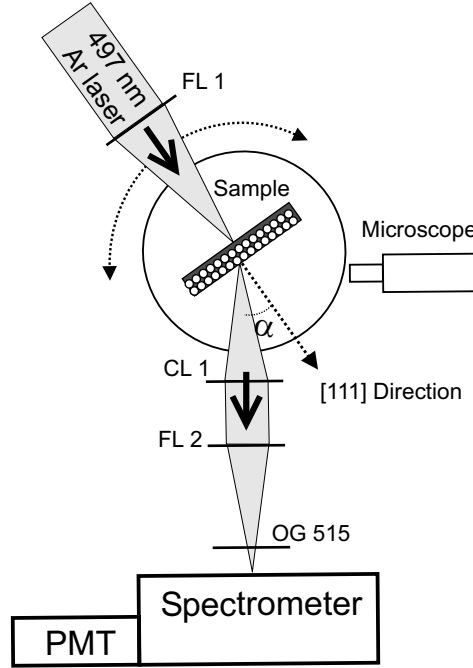


Figure 3.4: A scheme of the angle resolved experimental setup. The Argon laser ($\lambda = 497 \text{ nm}$) coupled through a singlemode fiber was focussed by an objective lens FL1 ($f=7 \text{ cm}$) onto the back surface of the sample. The emitted light from the front surface was collected by a lens CL1 ($f=12 \text{ cm}$) at an angle α relative to the normal of the $[111]$ lattice planes of the sample. A focussing lens FL2 ($f=12 \text{ cm}$) imaged this light onto a spectrometer equipped with a photomultiplier tube.

We have performed angle resolved emission experiments for three sizes of lattice constants of doped titania inverse opal, i.e., $a=496 \text{ nm}$, 419 nm , and 370 nm . An Argon laser at wavelength 497 nm was coupled into a single-mode fiber and focused by an objective lens FL1 ($f=7 \text{ cm}$) onto the back side of the sample, called the excitation area. The titania crystal was glued on a needle and placed inside a chamber that was evacuated to a pressure of 0.7 mbar nitrogen. We mounted the fiber holder and the chamber on the same goniometer plate so that the excitation area was always the same for every measurement angle. We detected the emission from the front side of the sample, called the detection area. The position of the excitation and the detection area were monitored by a microscope. The emitted photons were collected by a lens CL1 ($f=12 \text{ cm}$) at an angle α relative to the normal of the $[111]$ lattice plane of the titania crystal, and imaged onto a Carl

Leiss spectrometer by a focussing lens FL2 ($f=12$ cm). The input slit of the spectrometer was $200\text{ }\mu\text{m}$ which provided a spectral resolution of 2 nm . A photomultiplier tube (PMT) was connected at the end of the spectrometer for detecting the photons. Finally, an OG 515 long pass filter, which filters out wavelengths below 515 nm , was placed in front of the spectrometer to protect the PMT from direct reflections from the excitation laser.

3.3.2 Emission spectra on photonic and non-photonic samples

We have performed angle resolved experiments of the quantum dot emission spectra on the three doped samples with lattice parameter $a=496\text{ nm}$, 419 nm , and 370 nm . The experiments were done at various detection angles (α) between 0° and 60° . Detector dark-counts were subtracted for each spectrum. The dark-counts were calculated by averaging the detected counts at wavelengths below $\lambda = 515\text{ nm}$ for each spectrum separately

The measured spectra on each sample are displayed in Fig. 3.5, 3.6, and 3.7. Apparently, the spectrum exhibits the same shape at every measurement angle. Furthermore, the overall intensity of each spectrum varies with angle. A possible explanation for these observations will be described in the following. Based on a reflectivity experiment [26] on these samples, we found that a full width at half maximum (FWHM) of the stop band about 100 nm . On the contrary, the quantum dots showed the emission bandwidth only about 40 nm at FWHM. Hence, the spectrum of the quantum dots would not be modified partially but the whole spectrum would be inhibited by the stop band. These results are definitely difference in comparison to those observed for dye molecules on titania inverse opals in previous work by Schriemer *et al.* [27]. In this case, a suppression in the emission spectrum due to stop band was observed directly in the spectra.

In Fig. 3.5 spectra of the $a=370\text{ nm}$ reference sample are displayed. The stop bands for this sample appear on the blue side of the quantum dot emission. This means that the emission spectra of the quantum dots would not be affected by the stop bands. We observed that the spectrum intensity decreased gradually, starting from $\alpha = 0^\circ$ and reached a minimum value when $\alpha = 60^\circ$. The decrease likely followed cosines of the detection angle (Lambertian behavior). This Lambertian behavior is caused by the diffusion of emitted light

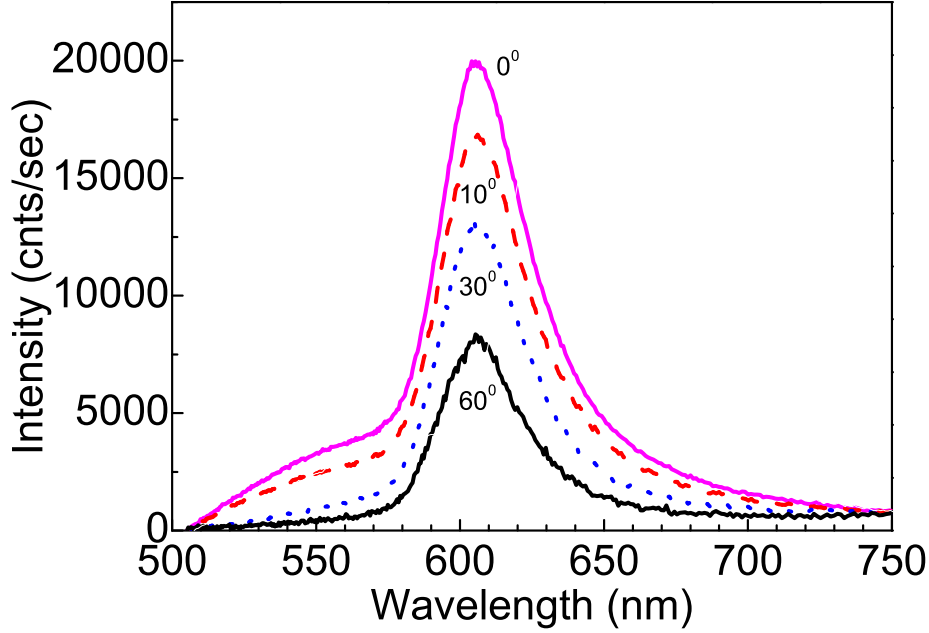


Figure 3.5: The spectra on the $a=370$ nm reference sample in which the intensity of each spectrum decreases gradually with decreasing the detection angle. These spectra are unaffected by the stop bands since the stop bands appear at the blue side of the quantum dot emission.

inside the crystal [21].

Figure 3.6 shows the spectra on the $a=496$ nm photonic sample at $\alpha = 0^\circ$, 10° , 25° , and 50° . Each spectrum appears to have the same shape and the emission peak occurs at $\lambda = 630$ nm. We observed that the intensity dropped gradually and acquired a minimum value at $\alpha = 25^\circ$. For α larger than 25° , the emission increased again until $\alpha = 50^\circ$ where the spectrum dropped further. To interpret these data, we plotted the result from a reflectivity experiment at the same figure. The details about reflectivity experiment can be found in reference [26]. The reflectivity was measured at the same sample on the same detection area. This reflectivity experiment was performed at

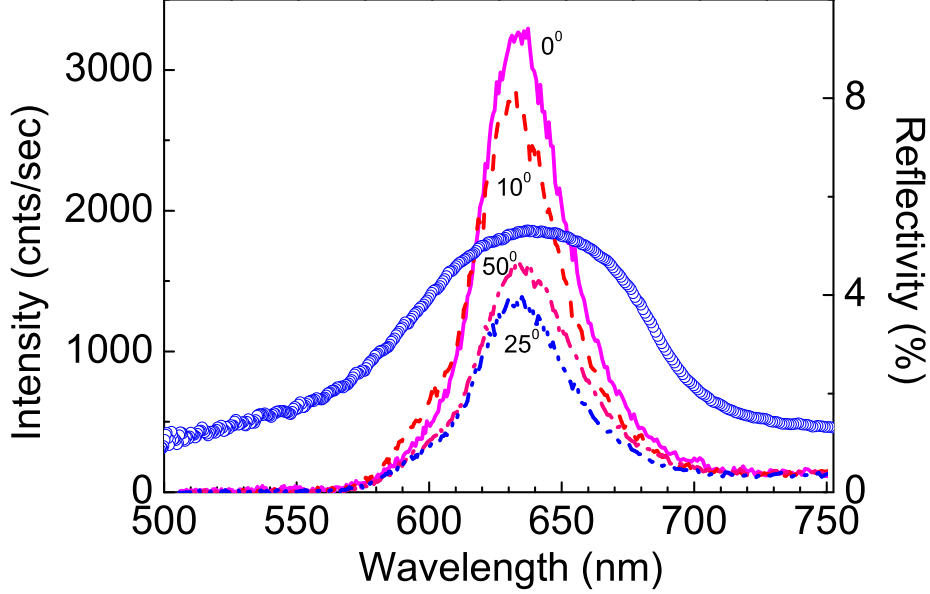


Figure 3.6: The spectra on the $a=496$ nm photonic sample in which the entire spectrum is strongly suppressed at $\alpha = 25^\circ$. The suppression is due to the stop band covering the whole quantum dot spectrum. This is confirmed by result from a reflectivity experiment which the reflectivity is shifted with $\cos(\alpha = 25^\circ)$ (shown as the open circles)

the normal of the [111] lattice plane of the sample. The central wavelength of the measured stop band was about 680 nm and the reflectivity was about 5 %. When the detection angle was increased, the stop band shifted to shorter wavelengths as $\cos(\alpha)$. Here, we assumed that the shift of stop band followed the Bragg's law for the [111] lattice plane. The stop band moved inside to the quantum dot emission region, and shifted away for larger angles. At $\alpha = 25^\circ$, the emission spectrum was exactly inside the stop band bandwidth (represented as the open circles in Fig. 3.6). Hence, we had a strong suppression on the quantum dot emission, as we can see on the 25° spectrum. Furthermore, the stop band shifted away from the quantum dot emission when increasing the angle further. Therefore, we observed an increase of the intensity.

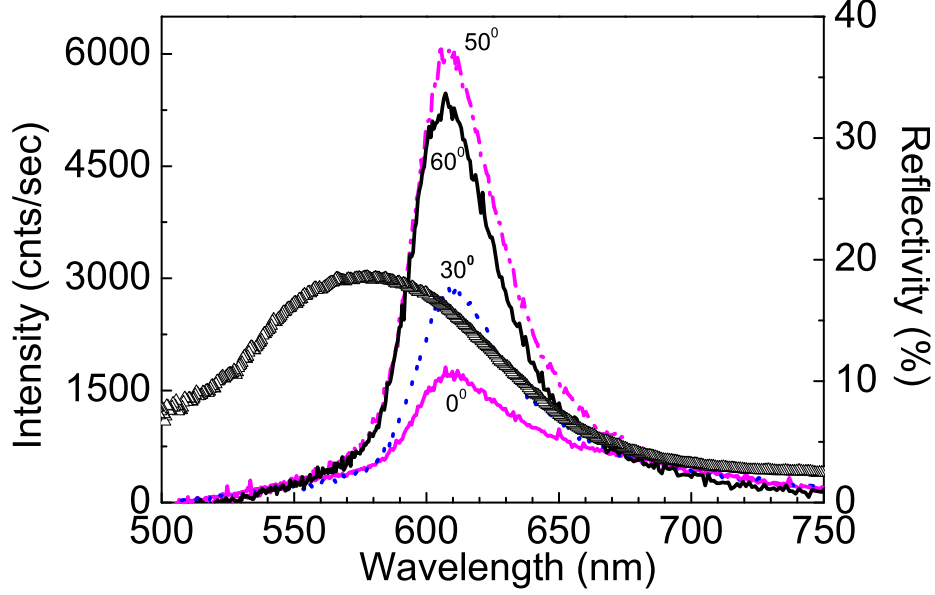


Figure 3.7: The spectra on the $a=419$ nm photonic sample in which a suppression occurs at $\alpha = 0^\circ$. The suppression has a good agreement with the reflectivity result at $\alpha = 0^\circ$ (shown as the open triangles).

We also observed similar behavior for spectra on the $a=419$ nm photonic sample. The spectra are plotted in Fig. 3.7. Based on the reflectivity experiment at 0° on this sample (displayed as the open triangles), we obtained the center wavelength of the stop band about 578 nm. The peak reflectivity attained was 17 %. At $\alpha = 0^\circ$, the emission spectrum was lying inside the stop band bandwidth. Hence, we observed the lowest spectrum intensity. As the stop band moved to shorter wavelengths by increasing the detection angle, the emission was enhanced. We observed an increase in the intensity for $\alpha = 30^\circ, 50^\circ$, and a decrease for $\alpha = 60^\circ$.

To conclude the results from the angle resolved experiment, we plotted the normalized peak intensities, relative to the corresponding peak at $\alpha = 60^\circ$, as a function of the detection angle, see Fig. 3.8. At $\alpha = 60^\circ$ the emission of the quantum dots is independent of the stop bands. Hence, it is used as a reference on each sample. The closed circles show a pronounced minimum at

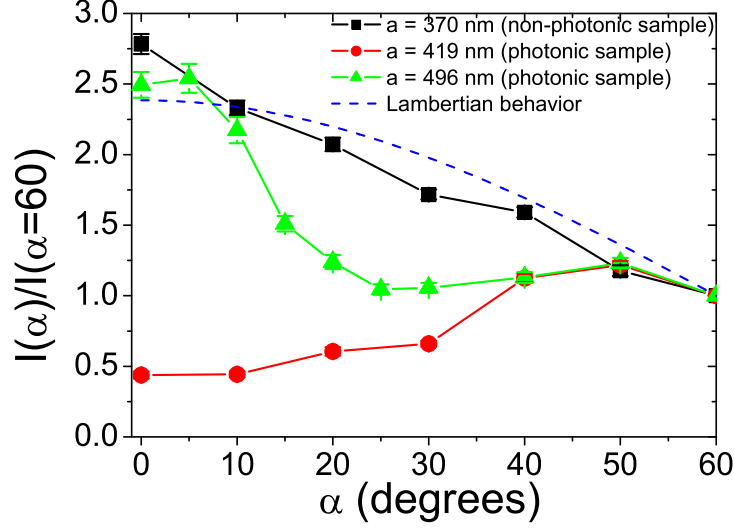


Figure 3.8: Plot of the peak intensities relative to the corresponding intensities at $\alpha = 60^\circ$. The closed squares represent the normalized peak intensity on the $a=370$ nm sample. The intensity decreased as a function of the detection angle. The closed triangles show the normalized peak intensities on the $a=496$ nm sample. We observed strong suppression due to the stop band at $\alpha = 25^\circ$. The closed circles, related to the $a=419$ nm sample, were suppressed at $\alpha = 0^\circ$. The dashed line represents the escape function calculated for the reference sample.

$\alpha = 0^\circ$ as well as the closed triangles at $\alpha = 25^\circ$. These strong suppressions are due to the occurrence of a stop band at those angles. As a comparison, we plotted the normalized peak intensities for the reference sample (shown as the closed squares) in which no depth was observed. The dashed line represents the escape function of the emitted light calculated for the reference sample. The escape function describes a redistribution of photons, which come out from the crystal, over the available escape angles. This model considers that the emitted light is diffuse inside the crystal. The diffusion of light is caused by unavoidable structural disorder in photonic crystals. Generally, the escape function is proportional to $\cos(\alpha)$ (Lambertian) times a correction term which is due to the internal reflection at the crystal interface [21]. This model fits the results from the reference sample quite nicely. The shift of the suppression to larger detection angles with larger lattice constants, confirms

that the spectral variations are due to the photonic crystal properties. This is the first clear stop bands effect observed in quantum dot emission in photonic crystals [20], [28], [29], [30].

3.4 Lifetime measurements

The rate of spontaneous emission of an excited emitter does not depend only on the emitter properties, but is also influenced by the electromagnetic photon density of states around the emitter (LDOS) [3]. In the quantum dot, electrons in the excited state may decay to the ground state with emission of photons if there are electromagnetic modes available. On the other hand, in the case where no electromagnetic modes exist, the electrons will remain trapped in the excited state. Since photonic crystals can modify the electromagnetic density of state (DOS) compared to in vacuum, it is interesting to investigate the lifetime of light embedded in the crystal.

In order to investigate a large lifetime effect inside photonic crystals, one needs emitters with high quantum efficiency [21]. Furthermore, the emitters should have a narrow homogeneous linewidth which is smaller than the variations of the electromagnetic density of state. Finally, one needs to have a highly ordered and strongly interacting photonic crystals to manipulate the DOS.

3.4.1 Experimental setup

We studied the radiative lifetime of CdSe quantum dots embedded in strongly photonic titania inverse opals. The lifetime is measured by means of a time-correlated single-photon counting technique [31]. It measures statistically the time delay between a time related to the excitation pulse (the started time) and a time of arrival of a photon onto detector (the stopped time). By accumulating many of these events and representing in a histogram, the lifetime value of the quantum dots can be extracted.

The time resolved experiment setup is displayed in Fig. 3.9. The CdSe quantum dots inside a titania inverse opal were excited by a pulsed laser of wavelength 440 nm. The laser was triggered by a pulsed diode laser driver (PDL).

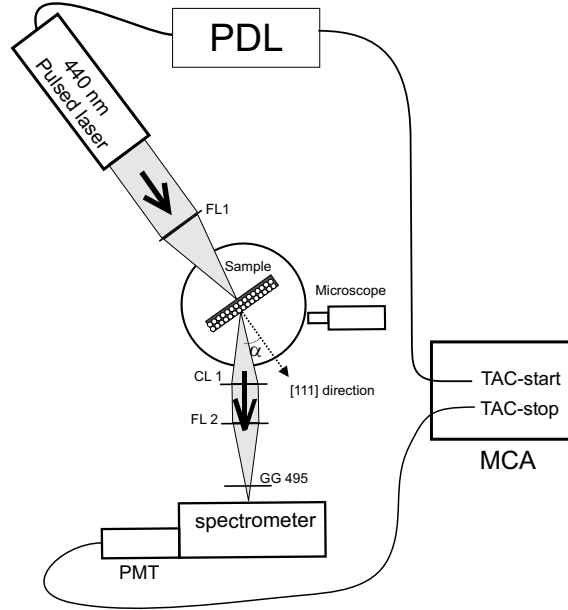
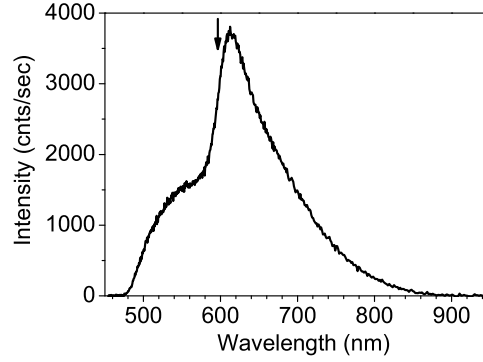
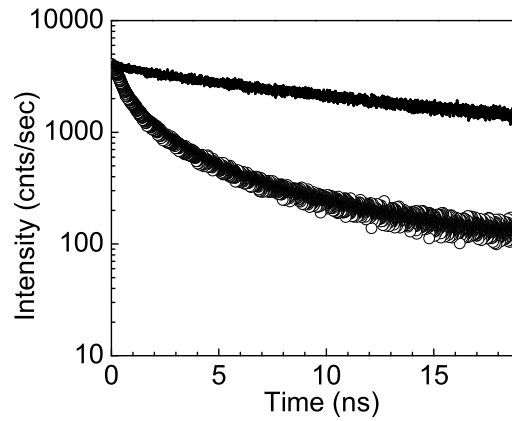


Figure 3.9: Schematic of a time resolved experimental setup. Excitation pulses ($\lambda = 440$ nm) were triggered by a pulsed diode laser driver (PDL). The pulse train of 50 ns in intervals were focussed onto the back surface of a doped sample by a lens FL1 ($f=10$ cm). The sample was stored inside a chamber of pressure 1.7 mbar. The emitted light from the front surface was filtered by the GG 495 cut-off filter before entering a spectrometer. A photomultiplier tube (PMT) used to detect the emitted light was connected to the spectrometer. The detected signal from the PMT and a triggered pulse from the PDL were fed into a TAC (time-amplitude converter) and multi channel analyzer (MCA), where the delay time was recorded.

The pulses of duration 100 ps and intervals 50 ns were focussed by a lens FL1 ($f=10$ cm) onto the back surface of the sample. The emitted light was detected by the photomultiplier tube (PMT), i.e., the stopped time. This detected signal was an input to time-amplitude converter (TAC). A multi Channel Analyzer (MCA) recorded the delay time between the started time from the PDL and the stopped time from the PMT. The time-correlated single-photon counting technique gives a resolution about 55 ps [31]. The detected signal was collected in 8192 bins in a 23 ns time window, hence the resolution for each bin was 2.89 ps. The total dark counts were calculated by multiplying the detected counts when the PMT was closed with the time needed for recording the signal.



(a)



(b)

Figure 3.10: Spontaneous emission of CdSe quantum dots inside a titania inverse opal, which is pumped by a 440 nm pulsed laser. 3.10(a) displays the spectrum obtained from the $a=419$ nm sample. The additional emission on the quantum dot spectrum at the blue and red side is due to luminescence of the titania. The open circles in 3.10(b) show a typical decay curve of the quantum dots on the same sample, measured at $\lambda = 598$ nm (indicated by the arrow on 3.10(a)). The decay curve has two different decay components, i.e., a short lifetime due to the titania and a long lifetime for the quantum dots. As a comparison, the thick line shows the typical decay curve of the quantum dots in solution.

3.4.2 Lifetime on photonic and non-photonic samples

The time resolved experiment was performed on three doped samples, i.e., $a=496$ nm, 419 nm, and 370 nm. These samples were the same samples as we used in the angle resolved experiment presented previously. The lifetime was recorded at several wavelengths inside the quantum dot spectrum. A typical decay curve of the CdSe quantum dots can be seen as the open circles in Fig. 3.10(b). This decay curve was measured on the $a=419$ nm sample at wavelength 598 nm. In this case, the decay curve shows a different shape compared to the decay curve observed in solution (see the thick line in Fig. 3.10(b)). The decay time on this doped sample shows two typical lifetime values, i.e., a very short lifetime at the beginning of the curve then followed by a longer lifetime. Moreover, result from the spectrum measurement shown in Fig. 3.10(a) exhibits additional emission at the blue side as well as the red side of the quantum dot emission. These effects are due to an influence of spontaneous emission from the titania. It is possible since we excited the quantum dots with a laser of wavelength $\lambda = 440$ nm, which was near the edge of the band gap of the titania (~ 415 nm).

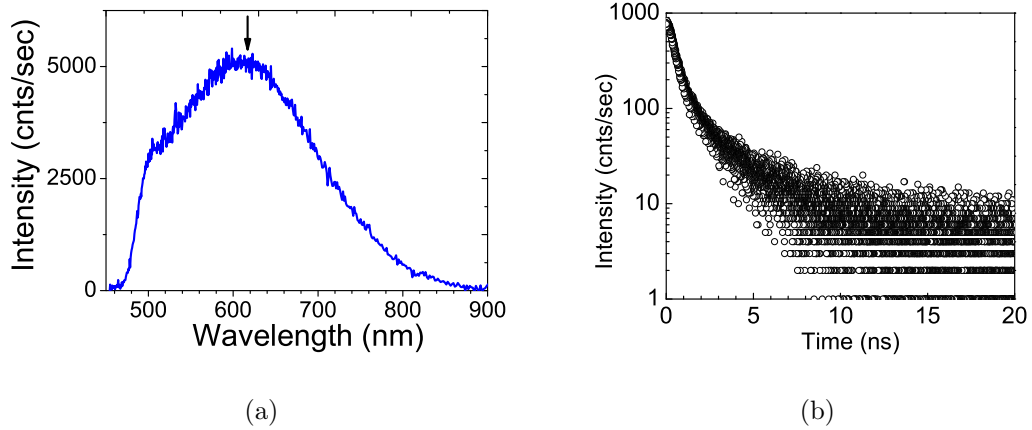


Figure 3.11: 3.11(a) displays the spectrum of titania pumped by a 440 nm pulsed laser. The spectrum extends from around $\lambda = 500$ nm to $\lambda = 800$ nm. 3.11(b) shows a typical decay curve of the titania. This lifetime was measured at wavelength $\lambda = 617$ nm, indicated by the arrow in Fig. 3.11(a). The decay curve decreases over 1.5 decade in 5 ns.

In order to investigate the influence of titania to the characteristic lifetime of quantum dots, we did both angle and time resolved experiments of the

undoped titania pumped by a 440 nm pulsed laser. The results are presented in Fig. 3.11. We observed that the spectrum of the titania was broad ($\lambda = 500 \text{ nm} - 800 \text{ nm}$). Fig. 3.11(b) displays the decay curve of the titania host obtained by the time resolved experiment. We found that the titania host decayed rapidly with more than 1.5 decade in the first 5 ns. This decay rate is much shorter than the typical decay rate of CdSe quantum dots.

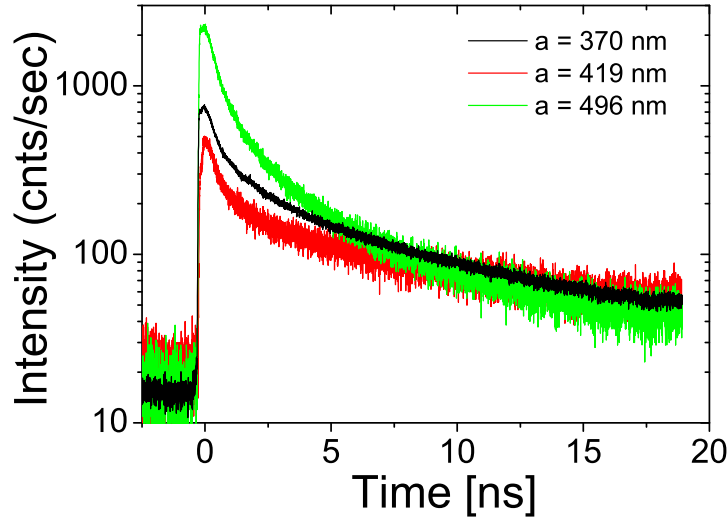


Figure 3.12: Raw data of CdSe quantum dot decay rate on the $a=370 \text{ nm}$ (the black line), the $a=419 \text{ nm}$ (the red line), and the $a=496 \text{ nm}$ (the green line). These decay curves were measured at the frequency 15700 cm^{-1} . The green line shows smaller decay rate than the black line, and the red line is the largest.

Based on the previous investigations on the undoped titania, we extracted the lifetime of the quantum dots by cutting out the first 5 ns of the decay curve and fitting the rest using a monoexponential model ($y(t) = a \exp^{-t/\tau}$), where τ is the lifetime value. Reduced χ^2 is used to determine the quality of the fit. The reduced χ^2 value obtained from this fitting procedure was about 2, indicating that this model was reasonable to use. The error bars were obtained from the fit. The results are shown in Fig. 3.13. We plotted the decay rate (the inverse of the lifetime) of the quantum dots as a function of frequency ($1/\lambda$). The connected dots show the decay rates observed on the reference sample ($a=370 \text{ nm}$). These decay rates increase as the cubic

of frequency in which the smallest decay rate (or $\Gamma = 0.081 \text{ ns}^{-1}$) occurs at frequency 15600 cm^{-1} and the largest decay rate (or $\Gamma = 0.105 \text{ ns}^{-1}$) at frequency 16900 cm^{-1} . The measured decay rates on the $a=419 \text{ nm}$ photonic sample display a very strong deviation from those on the reference sample, indicated by the connected squares. The decay rates are found to be larger at 15100 cm^{-1} and smaller at 16200 cm^{-1} compared to the corresponding frequency of reference sample. Moreover, the connected triangles represent the measured decay rates of the $a=496 \text{ nm}$ photonic sample. These decay rates are systematically smaller compared to the decay rates on the reference sample.

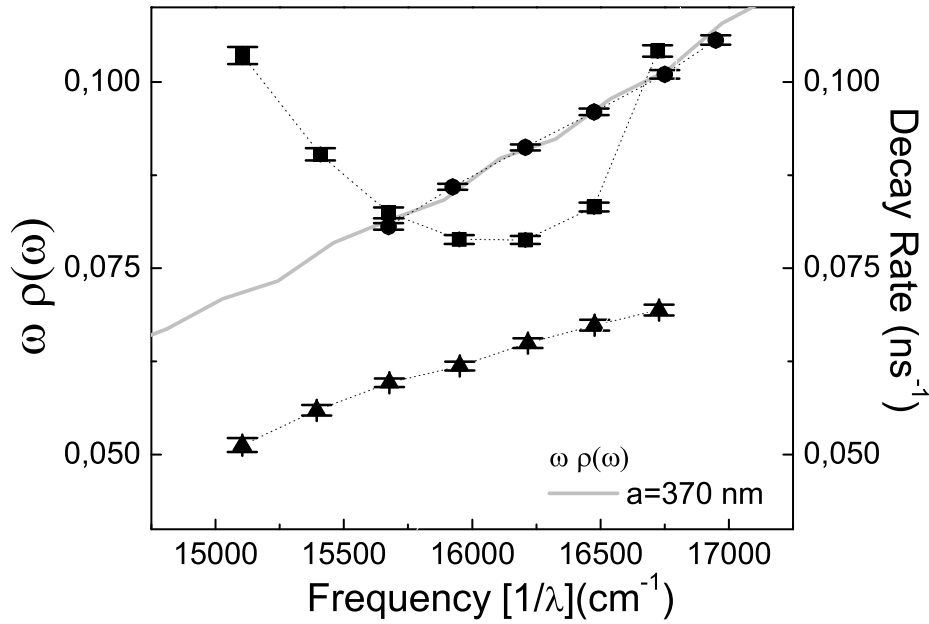


Figure 3.13: Plot of the observed decay rates on three doped samples as a function of frequency. The connected dots show the observed decay rates for the reference sample ($a=370 \text{ nm}$), the squares for the $a=419 \text{ nm}$ photonic sample, and the triangles for the $a=496 \text{ nm}$ photonic sample. As a comparison, the calculation of $\omega \rho(\omega)$ for the reference sample is plotted (displayed as the gray line). It can be seen that a trend of the measured decay rates for the reference sample has an excellent agreement with the theoretical calculation.

In order to make a comparison to the theory, we plotted $\omega\rho(\omega)$ as a function of frequency in the same figure, where $\rho(\omega)$ is the total density of states. This relation follows the Fermi's golden rule Eq.(3.1). The calculation of the total DOS for an fcc titania inverse opals was made by Femius Koenderink [21]. The gray line represents $\omega\rho(\omega)$ for the reference sample. We found that the measured decay rates for the reference sample followed the theoretical curve of $\omega\rho(\omega)$ very nicely. These results show that the LDOS, which is probed by the quantum dots, is equal to the DOS. Furthermore, these results revealed that the quantum dots had very high quantum efficiency (more than 90%). This can be illustrated with the following argument. The quantum efficiency can be expressed as $\eta = \Gamma_{rad}/\Gamma_{total}$, where Γ_{rad} is the radiative decay rate which is proportional to the LDOS. Γ_{total} is the measured total decay rate which is a sum of the radiative decay rate and non radiative decay rate ($\Gamma_{total} = \Gamma_{rad} + \Gamma_{nonrad}$). Γ_{nonrad} results from accumulation of all possible non-radiative decay channels. $\Gamma_{nonrad}=0$ gives a quantum efficiency equal to unity ($\eta = 1$) and results the total decay rate only depends on Γ_{rad} ($\Gamma_{total} = \Gamma_{rad}$). Hence, the total decay rate follows the theoretical calculation of the $\omega\rho(\omega)$.

The measured decay rates for the a=419 nm photonic sample show an inhibition at frequency 16200 cm^{-1} and enhancement at 15100 cm^{-1} . These results reveal that the LDOS is smaller at frequency 16200 cm^{-1} and larger at frequency 15100 cm^{-1} in comparison to the LDOS at the corresponding frequencies of reference sample. The very sharp deviation indicates that the LDOS varies very rapidly. For the a=496 nm photonic sample, we measured that the decay rates were inhibited over a very broad bandwidth ($\omega \sim 15100\text{ cm}^{-1}$ - 16700 cm^{-1}) compared to the reference sample. These indicate that the LDOS are smaller compared to the reference sample in this range. Here, we have observed for the first time both inhibition and enhancement of the decay rate of CdSe quantum dots embedded in titania inverse opal photonic crystal.

It is important to understand that the time resolved experiment basically measures the LDOS. Since the LDOS determines the radiative lifetime of the quantum dots inside a titania inverse opal. However, until now only theoretical calculations on the total DOS are available. The total DOS is the unit cell average of the LDOS. Therefore, a theoretical calculation of the LDOS is crucial in order to make an appropriate comparison to the time resolved experimental data.

3.5 Conclusions

In this project, we showed that quantum dots made of cadmium selenide can be used as internal light sources to probe the photonic properties on a titania inverse opal crystal. The quantum dots have to be placed in a well-controlled way into the bulk of the titania inverse opal. We found that CdSe quantum dot solution mixed with butanol can infiltrate titania inverse opals very well. We observed the presence of the quantum dots at the middle of the crystal (at least 10%) after it was doped for 30 minutes. Furthermore, we have discovered, for the first time, clear and convincing stop bands from the emission of quantum dots placed inside titania inverse opal photonic crystals. The width of the emission spectrum of quantum dots is narrower than the stop band bandwidth, and hence required a very careful data analysis to conclude the presence of stop bands. In particular, a good understanding of the diffusion of light inside the crystal is required to help interpreting the experimentally obtained spectra. The shift of the suppression to larger detection angles with larger lattice constants, confirms that the spectral variations are due to the photonic crystal properties. Moreover, our results from the time resolved experiment showed for the first time the photonic effect on the decay rate of CdSe quantum dots. We have found both inhibition and enhancement of the decay rates of the quantum dots. The decay rates of the quantum dots are clearly changed and attributed to a variation on the local density of states in the crystal.

Chapter 4

Conclusions and recommendations

Cadmium selenide quantum dots were used to investigate the photonic properties of a titania inverse opal crystal. New experimental setups for angle resolved and time resolved spectroscopy have been developed in order to measure those properties. We observed for the first time clear stop bands in the emission of quantum dots in titania. Moreover, both inhibition and enhancement of the decay rate of quantum dots were discovered.

The main issue in infiltration of CdSe quantum dots into titania inverse opal is the polarity of the titania surface. The titania surface is more polar than the quantum dots. Hence, it decreases the affinity of quantum dots to stick onto the titania surface. The affinity probably can be raised by replacing the TOPO with a kind of charge capping molecules, as reported by Kuno *et al.* [12].

The time resolved experiment on the doped titania sample has shown both enhancement and inhibition of the decay rates of CdSe quantum dots. In order to improve the statistic of lifetime data, a large detection time window and a lower repetition rate of pulsed laser are needed. Furthermore, signal to noise ratio can be increased by measuring the lifetime for longer time.

For the future research CdSe quantum dots can be used to investigate the photonic properties of higher order band gap, where the modification of the density of states is stronger. It will give an opportunity to observe the full

photonic band gap in which the emitted light from the quantum dots is totally inhibited. Furthermore, the emission decay rate of CdSe quantum dots can be switched from an acceleration decay to a complete inhibition, or vice versa, on ultra fast timescales. It can be done by switch the local density of states of the photonic crystal, as proposed by Johnson *et al.* [32].

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