# Summary

Photonic crystals are three-dimensional dielectric structures with a periodicity comparable to the wavelength of light. Due to the periodic variation of refractive index, the crystals possess unusual optical properties that affect the propagation and the emission of light. The "holy grail" of the field is the achievement of a photonic band gap: a frequency range for which light will not propagate in any direction because of Bragg diffraction. In the exciting case of a photonic band gap the emission by light sources in photonic crystals is strongly modified, resulting in inhibited emission. If emission can be controlled this way new applications can be thought of, like thresholdless miniature lasers. Interesting chemical applications are also suggested here, such as uses in solar cells and photon-induced conversion reactions. Efficiency of dye-sensitized solar cells and reaction rates of photon-induced conversions could possibly be controlled in this way. Likewise macroporous materials are interesting from a catalytic and separation chemistry point of view; the macroporous photonic crystals can act as zeolites for large molecules.

In this thesis the preparation and characterization of opal-based photonic crystals are described with the aim to control the properties of internal light sources. We also study the fluorescence of light sources embedded in such photonic crystals. Our macroporous structures, also called air-sphere crystals, are carefully synthesized and of high quality. With fluorescence measurements on these photonic crystals we probe the optical properties that lead up to the photonic band gap. The concept of the photonic band gap was already described in the late 1980s and since then many people have explored the development of photonic crystals consisting of varying structures and materials. The structure and long range order of the fabricated photonic crystals are usually characterized by means of electron microscopy. Optical experiments, such as reflectivity, transmission and emission experiments,

are performed to learn more about the interaction strength of the structure with light. Modifications in reflectivity, transmission and emission spectra result from Bragg diffraction and appear as a stop band in respectively the reflected, transmitted and emitted spectrum. Since the stop gaps are the building blocks of the photonic band gap their properties are essential.

The probability of an emission source to spontaneously decay is described by Fermi's golden rule. Fermi's golden rule can be written in a part related to the light source itself and a part related to the position dependent field. Exactly this position dependent field part, also called the local density of states (LDOS) or averaged over volume, total density of states (DOS), is strongly influenced in a photonic crystal structure (see chapter 1). In the case of a photonic band gap the DOS goes to zero. A exciting way to investigate the modified DOS, is to measure the lifetime of an embedded light source. Since the lifetime is inversely proportional to the available DOS, a change in lifetime will indicate a change in the DOS. The modification in DOS can be measured with either continuous wave (cw) or time-resolved experiments. Cw measurements were previously performed and a decrease in the total emitted power was observed which corresponded to a decrease in the DOS. A requirement to observe a DOS change with these cw measurements was a low quantum efficiency of the light source (see section 6.1).

In this thesis we want to measure the modified DOS in a dynamic way. For these time-resolved measurements, however, a high quantum efficiency is required and therefore the properties of the light source and the backbone material of the crystal should be carefully chosen. In chapter 2 we considered several emission sources and we have chosen the well-known laser dye Rhodamine 6G (R6G) as a light source. R6G exhibits a high quantum efficiency, a broad inhomogeneous and narrow homogeneous emission spectrum and is ”bleachable”. From previous experiments air-sphere crystals made of the semiconductor titania, turned out to be very effective photonic crystals, due to its high refractive index contrast and optical transparency. With these titania air-sphere crystals it was already demonstrated with cw measurements that the R6G emission, and subsequently the DOS, was strongly reduced by the photonic crystal structure. The quantum efficiency of the dye on titania in these experiments, however, was very low and therefore an observation of a lifetime effect was impossible. Titania exhibits a large electronic band gap and the adsorbed R6G dye shows electron transfer from its excited state to the conduction band of titania, which reduces the quantum efficiency drastically. This is a general feature of fluorescent light sources on semiconductor surfaces. In our research we tried to coat the titania surface with an insulating silica layer in order to preclude the electron transfer. For coated titania powders, we have demonstrated that a deposited thin silica layer indeed prevented the electron transfer, but because of the confined geometry of the air-sphere crystal itself, it was not possible to deposit a layer of silica on the titania surface of the air-sphere crystal. Therefore we explored the possibility to measure lifetimes of R6G adsorbed on other materials, as alumina, zirconia and polystyrene. When photonic crystals are made of these pure insulating materials, time-resolved measurements will provide information about the DOS since the quantum efficiency of the dye on these materials remains high. We demonstrated that R6G dye adsorbed on polystyrene does not show electron transfer and therefore this combination turned out to be an excellent candidate for time-resolved emission measurements on polystyrene opals.

In chapter 3 we have described the synthesis and characterization of air-sphere crystals, also called inverse opals, one of the most effective photonic crystals. The general synthesis of our air-sphere crystals consists of three steps. First a template is formed via a self-organizing system consisting of colloidal particles. This template is also called artificial opal because of its beautiful opalescence. Second the interstitial holes in the template are infiltrated with a liquid precursor of a metaloxide, which reacts to yield solid material. In the final step the infiltrated template is heated during which the template is calcined and the infiltrated material, the metaloxide, becomes crystalline. The resulting obtained air-sphere crystal is a replica of the artificial opal and therefore often called inverse opal. We have synthesized air-sphere crystals consisting of several backbone materials. The best known material used for air-sphere crystals in the visible range is titania, which has a high refractive index, and is transparent at optical wavelengths. The air-sphere crystals, as well as the templates, were well-characterized by optical and electron microscopy. To characterize the optical properties we performed reflectivity measurements. The relative width of the reflectivity peak, or the stop band, was investigated since it is a building block for the photonic band gap. We concluded from the characterization that our air-sphere crystals are of high quality and exhibit long range order. Since the photonic band gap is expected to occur at the second order Bragg diffraction, and this second order Bragg is much more sensitive to disorder, a long range order is essential.

In chapter 4 we take a closer look at the process of air-sphere crystal formation. By applying two different materials during the synthesis of the air-sphere crystal, the distribution of both materials in the structure can be investigated. The homogeneity was examined from mm to 100 nm scale by means of energy dispersive X-ray spectroscopy and by examination with the naked eye. To our knowledge we are the first that report on spatial distributions in air-sphere crystals. We observed extreme spatial compositional inhomogeneities on mm, 100 $\mu$m and 100 nm scale. The technique of successive infiltrations was originally developed for spherically layered air-sphere crystals, in order to create an environment with a shielded semiconductor surface to prevent electron transfer. The inhomogeneous infiltration discussed in chapter 4, however, explains why this technique will not result in air-sphere crystals with a homogeneous layer of insulating material on the inner surface. Another important consequence of the inhomogeneous distribution of the oxides can be the spatial variation of the average refractive index, which might be important for optical applications. When applying only one material, however, this seems to be no issue since the inhomogeneities average out.

In chapter 3 the stop band was already measured in reflectivity experiments and the relative width of the stop band was analyzed. In chapter 5 the stop band was investigated with emission experiments. In these emission experiments the light is probed from inside instead of externally as is done in reflectivity experiments. We measured directional fluorescence spectra of R6G dye in polystyrene opals and alumina air-sphere crystals and investigated quantities as spectral position, spectral width and amount of attenuation. The measured stop bands were compared with calculated stop gaps and they showed good agreement. Since both direct (opals) and indirect (inverse opals) structures were measured, attenuations observed in the spectra were compared with each other. The attenuations were explained in terms of mean free paths and Bragg lengths. We observed, as expected, that the alumina inverse opal exhibits a longer mean free path and a shorter Bragg attenuation length compared to the mean free path and the attenuation length of polystyrene opals. An intriguing feature that happens at both the direct and indirect structures is an enhancement of emission at the blue side of the stop band. We explained this enhancement with a model of the so-called escape function of diffuse light. Emission that is limited to propagate in certain directions due to internal Bragg diffraction, escapes in other existing angles and appears as enhanced emission. Since the enhancements at the blue side of the stop band are both present for the direct and the indirect structure, the explanation of the enhancement with standing wave effects was ruled out. In chapter 5 we reported on the first emission measurements on photonic crystals with second order Bragg diffraction. A strong attenuation of R6G emission was observed and although the shape and the position of the second order stop band is much more complicated than the first order stop band, we were able to compare the second order stop band with reflectivity measurements on a similar sample. The positions and the intensity of the features agreed very well. Since the DOS at this second order Bragg is expected to vary much more our pioneering research is of utmost importance and stresses the need for further theoretical interpretation.

Since the spectra measurements in chapter 5 demonstrated that the polystyrene opals strongly influence the angle-dependent emission of R6G, we performed in chapter 6 time-resolved angle-independent measurements; a lifetime change will be independent on angle. From chapter 2 we already learned that R6G dye on polystyrene does not exhibit electron transfer but remains its high efficiency and therefore the polystyrene opals are very promising to use in time-resolved measurements. Due to large variations in the DOS of photonic crystals, it was expected to see enhanced or inhibited spontaneous emission, appearing in shorter or longer lifetimes. From the angle-independent lifetime measurements discussed in chapter 6 we conclude, however, that it is very difficult to observe a lifetime change caused by the photonic structure, as is discussed below.

We have measured lifetimes as a function of wavelength and although a $\lambda^3$ behavior should be expected (from Fermi's golden rule), a wavelength independent behavior was observed. This was explained in terms of the homogeneous linewidth. Formerly it was assumed, based on literature, that the homogeneous linewidth was as small as 5 % of the complete emission spectrum. It turned out that the homogeneous linewidth of dye molecules adsorbed on polystyrene however, is much broader, possibly as wide as the emission spectrum. If the homogeneous linewidth of the dye is broader than the width of the stop gap, the spontaneous emission can not be modified and therefore no changes in lifetime will be observed.

We also observed that reabsorption of dye emission is a major issue in photonic crystals. Due to multiple scattering of the light by defects in the photonic crystal, the light path of emitted light is strongly folded up and has typical length scales of ~ 1 cm. This light path is clearly much longer than the sample thickness, and therefore the chance for reabsorption by dye molecules, especially at high dye-concentrations, can be increased. As a consequence the lifetime is considerably lengthened but not as a result of the photonic structure. We have calculated for our samples that it is very likely that $10^{-5}$ Molar R6G doped samples exhibit reabsorption and indeed these samples show longer lifetimes compared to samples doped with $10^{-6}$ Molar R6G.

Both effects, the unexpected broad homogeneous linewidth of the dye and an increasing chance for reabsorption with increasing dye concentration, are very important since many groups nowadays try to investigate modified spontaneous emission with the use of fluorescent dyes. The effects discussed in this thesis, possibly precludes people to observe any lifetime change with dyes and should be carefully considered in the future.

A very remarkable feature that was observed in the lifetime data in chapter 6, was a radius dependent lifetime behavior. For R6G in opals with smaller sphere radii a shorter lifetime was obtained while opals with larger sphere radii displayed a longer lifetime. We proposed a hypothesis that describes a relation between the lifetime and the local DOS at the sphere surface of single spheres. The remnants of this single sphere behavior, i.e., an increased LDOS nearby the sphere surface are proposed to account for the variations observed in the lifetimes.

This thesis clearly demonstrated that photonic crystals, opals as well as inverse opals, are in many ways an interesting subject of research. While chemists put a lot of effort in synthesizing photonic crystals, like varying crystal structures and materials, physicists concentrate more on optical and fundamental properties such as photonic band gaps. This thesis was written from a chemist point of view, but a lot of physics was involved. Exactly this combination makes this thesis interesting for both disciplines, and in the future this will probably become visible in applications in both fields; macroporous materials in optical chips as well as in for instance catalysis.