Manipulating emission of CdSe/ZnS nanocrystals embedded in synthetic opals

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\textbf{Abstract.} Photonic crystals (PCs) are the object of great interest due to the possibility, for appropriate PCs, to modify and control light propagation and even to influence the emission properties of an emitter, such as its emission diagram and its life time. One of the most common approaches to prepare 3D PCs takes advantage of the spontaneous self-organisation of spherical colloidal particles. Various self-assembly techniques such as sedimentation, convective or Langmuir-Blodgett ones have been studied as they provide a low cost and relatively easy protocol to obtain artificial opals. SiO\textsubscript{2} opals exhibit a pseudo-band gap. Nevertheless the coupling of II-VI nanocrystal emitters in such PCs allows one to recognize and study some basic problems. Large opals have been prepared by the sedimentation method and the size of the balls has been adjusted so that the pseudo-band gap of those PCs lies in the same region as the emission band of CdSe/ZnS nanocrystals. Diagrams of radiation and the modification of the spontaneous life time of the embedded nanocrystals will be presented and discussed. Introducing well-defined defects in PCs which are necessary to guide the photons through the crystal remains a hard technological challenge. Several top-down methods have been investigated. We will present different bottom-up routes proposed by different groups to engineer planar defects into colloidal PCs.

\textbf{Keywords:} Photonic crystal, opal, quantum dots, decay rate, planar defect.

1. Introduction
Photonic crystals (PCs) in the visible and near infra-red ranges are characterized by a periodic dielectric constant at wavelength scale. As a consequence, the emission of light sources embedded inside PCs can be strongly affected by the band gap such as its propagation with minimal losses, its emission diagram and its life time [1]. Many approaches have been proposed to fabricate 3-D periodically modulated dielectric materials. Some of them come from more or less well established
microelectronic industry processes such as semiconductor layer-by-layer nanomachining [2], layer-by-layer direct laser writing [3–5], interference lithography using a single diffraction mask [6], holographic lithography with at least 4 laser beams [7, 8] or two-beam only but with multi-exposure [9]. Alternatively to these methods which have known different sophisticated modifications proposed by several groups, bottom–up techniques taking advantage of the spontaneous self-organisation of spherical colloidal particles have been investigated. Various self-assembly techniques have been studied as they provide a low cost and relatively easy protocol to obtain artificial opals. Each one has received large attention and several groups have proposed for each technique modifications and improvements. Well orientated fcc crystals have been formed by gravity [10–12] or controlled sedimentation onto patterned substrate [13]. Different convective methods, vertical evaporation [14], induced by a temperature gradient [15] or by isothermal heating evaporation-induced self assembly (IHEISA) at a heating temperature of the solvent very close to its boiling point, method indicated for large balls [16] have provided large mono-domain opals. Langmuir-Blodgett (LB) technique is a layer-by-layer procedure for the preparation of large area synthetic opals. Solid films of particles are transferred from the water surface onto supports. The results suggest that a successful synthesis of ordered monolayers of monodisperse silica with the LB technique critically depends on the hydrophilic/hydrophobic balance [17, 18]. Silica spheres opals have been the object of a large number of papers even if these opals do not present a complete photonic bandgap due to the low index contrast between silica and air. Nevertheless the pseudo photonic band gap affects the propagation of light through the opal and causes transmission dip or reflectance peaks in the sample spectra depending with direction. Experimental studies on quantum dots [19–24] or molecules [25–28] embedded in such opals have been reported. However, the corresponding measured modification of the decay rate is limited since the refractive index contrast is low (below 5% for an index contrast of 1.2) [29]. A way to obtain larger effects is to use inverted opals as they present high refractive contrast and complete photonic bandgap [25, 30, 31]. As an example, lifetime reductions up to 30% have been measured for CdSe Qdots infiltrated in titania inverted opals [1]. But the production of good quality inverted opals over large scale is not yet totally mastered.

2. Opals characterization

![Figure 1](image)

Figure 1. (a) Reflectivity spectra of an opal for various incidence angles. Dashed line: nanocrystals luminescence spectrum. (b) Comparison of the experimental results with the Bragg’s law (D=269 nm, n_{eff}=1.34).

The opals characterized and then infiltrated with nanocrystals were prepared by sedimentation of 270 nm diameter silica balls in suspension in water. They were optically characterized by specular reflection. Details on the experimental set-up are given in ref. [32].
The figure 1a shows spectra corresponding to specular reflection for non polarized light at different incidence angles. The maxima are obtained for wavelengths linked to the incidence angles $\phi$ by the Bragg’s law:

$$\lambda_{\text{max}} = \frac{1}{2} \sqrt{\frac{2}{3}} D (n_{\text{eff}} - \sin \phi)$$

where $D$ is the diameter of the balls, $\phi$ is the incidence angle relative to the normal to the (111) plane and $n_{\text{eff}}$ the effective refractive index of the medium. The high measured reflectivity (about 20% in spite of the fact that we illuminate a large area of the sample because of our large spot size) demonstrates the good quality of the samples. In figure 1b the values of $\lambda_{\text{max}}$ deduced from the above spectra are plotted according to the incidence angle. An adjustment with the Bragg’s law yields to a diameter of the balls $D = 269$ nm with a precision of 5% and to an effective refractive index of the medium $n_{\text{eff}} = 1.34$, corresponding to an index of silica $n_{\text{silica}} = 1.44$ (deduced from the expression

$$n_{\text{eff}} = \sqrt{\alpha n_{\text{silica}} + (1 - \alpha) n_0}$$

where $\alpha = 0.74$ represents the filling factor for closed packed structures). This diameter is in good agreement with the measurements performed with an atomic force microscope.

3. Modification of nanocrystals spontaneous emission diagram

![Figure 2](image)

Figure 2. (a) Luminescence spectra of infiltrated nanocrystals in an opal sample at different collection angles. (b) Diagrams of emission of infiltrated nanocrystals at different wavelengths. (c) Diagrams of emission at 560 nm in opal (green plain line) compared to nanocrystals in opal infiltrated with decane (dashed black line).

We first study the emission diagram modification of nanocrystals embedded in the opal. We infiltrate 1 µl of a nanomolar solution of CdSe/ZnS nanocrystals (Qdot Invitrogen 565 ITK) diluted in decane. Briefly, the nanocrystals are excited by a pulsed nitrogen laser at 337.1 nm, their luminescence is collected by an optical fiber mounted on a rotary stage and analyzed with a spectrometer coupled with a nitrogen-cooled Si CCD detector (see [32] for experimental details). Depending on the angle of collection, the central wavelength of the luminescence spectra is shifted
from 556 nm to 566 nm and the linewidth is reduced from 30 to 25 nm (see figure 2a). In figure 2b, the radiation diagrams are plotted according to the angle of detection for different wavelengths. For each wavelength, a strong reduction of luminescence is observed for specific angles, demonstrating the modification of the nanocrystals emission diagram by the photonic bandgap of the opal. In order to confirm the role played by the photonic crystal, the opal is filled with decane (n_{decane} = 1.41). The decane infiltrated opal can be considered as a homogeneous medium. In this case, the dip in the emission diagram disappears (see figure 2c). In figure 3, the wavelengths for which the luminescence is reduced are plotted as a function of the external angle. The curve is well fitted by the Bragg’s law, like the central wavelengths of the specular reflection spectra previously measured (see figure 1).

![Figure 3. Comparison of the experimental results with Bragg’s law.](image)

4. Modification of the decay time
We now consider the influence of the opal on the nanocrystals decay time. We experimentally compare the lifetime of the nanocrystals embedded in an opal and in the same opal infiltrated with a solution of decane which provides a uniform medium used as a reference. The experimental set-up is the same as the one used for the luminescence study. The emission at 560 nm is selected by a spectrometer and the lifetime measurement is provided by a photomultiplier. The resolution of our setup is equal to one nanosecond. As shown on figure 4, the self-luminescence of the silica balls influence on the decay rate becomes negligible after 40 ns.

We experimentally demonstrate an increase of the lifetime of 16% (28 ns ±1 ns for quantum dots embedded in the opal, 24 ns ±1 ns for quantum dots embedded in the opal filled with decane). The same experiment performed with similar nanocrystals infiltrated in a 320 nm balls diameter opal gives the same result.

In order to explain these lifetime modifications, we have performed a calculation of the variation of the local density of states (LDOS) at the emitters position [32]. The 16% increase of the lifetime observed for the 320 nm balls diameter opals is in good agreement with the LDOS calculations, whereas, for the 269 nm balls diameter opals, no decay time modification is predicted. These results prove that the observed lifetime variation is due to an effect not fully taken into account in the LDOS calculation. In the previous calculations, we have assumed that the dipole moment is randomly oriented and that its value is kept constant whatever the environment is. Our experimental results suggest that this assumption is too restrictive and that the variations of the dipole moment due to the local electromagnetic field may play a key role, which can hide the effect of the photonic bandgap on the radiative lifetime.
5. Planar defects
The behavior of nano-emitters in PCs is somehow well understood. To go further in controlling the light emission, one has to introduce defects in the photonic structure. This leads to the occurrence of localized states in the forbidden region of the band gap [33]. The defect results in the observation of a pass band in the photonic band gap. The appearance of the defect mode changes with the thickness of the crystal, the dip decreasing as the thickness increases. The position of the pass band is a function of the size (thickness, diameter of the balls) of the defect. A point-like defect could serve as a microcavity to localize light: a high-Q single mode cavity could be created by the introduction of a local defect in a PC, leading to a thresholdless laser. Linear defects offer great technological appeal as they can serve as optical linear waveguides. As it adds an extra dimension, the introduction of planar defects in PCs is a way to strongly increase the electromagnetic field confinement and leads to planar waveguides [34]. Introducing well-defined defects in PCs which are necessary to guide the photons through the crystal remains a hard technological challenge. In synthetic opals, several top-down methods have been investigated like multi-photon polymerization and laser micro-annealing introducing defects like points and lines [35, 36] or photolithography allowing linear defect [37]. These methods are precise and allow design flexibility; but they are time consuming and seem to be limited to small area. We will present different bottom-up routes proposed by different groups to engineer planar defects into colloidal PCs. Planar defects have been fabricated by combining convective colloidal self-assembly and chemical vapour deposition to introduce a silica thin layer between two opal PCs [38, 39]. While these defects are passive, the Ozin group has also proposed active and tunable planar defects by incorporating polyelectrolyte multilayers having refractive index and thickness tuned by exposure to different solvent vapour pressures [40], UV-exposure as well as temperature. In this latter case, they obtain a full reversibility [41]. Another way to introduce a planar defect has been proposed by incorporating a monolayer of microspheres prepared by the Langmuir-Blodgett technique between two opal films with spheres of different diameters prepared by convective self-assembly. The LB technique supplies a well-defined single layer when it is difficult to realize such objective by using other self-assembly methods [42, 43]. Recently, the whole structure, the planar defect between two opals, has been prepared by the same LB technique, providing good quality samples [44]. The kind of defect introduced in the PC depends on the size of the spheres: when the size of the middle layers spheres is larger /lower than that of the lower and upper spheres it is a donor/acceptor like impurity peak which is relatively closer to the high-energy edge/low energy edge (low/high wavelength) of the optical stop band [45]. The technologies developed to engineer planar defects are now mastered. The next step consists in introducing emitters such as nanocrystals in such defects. As the LDOS scales like the square of the field, strong effects on the emission and particularly on the lifetime are expected.

Figure 4. Luminescence decay of nanocrystals embedded in an opal (green line), dissolved in decane (black line), in the opal infiltrated with decane (blue line) Self-luminescence of the opal (red line).
References

[1] Lodahl P, Driel F van, Nikolaev I S, Irman A, Overgaag K, Vanmaekelbergh D and Vos W L 2004 Nature 430 654
[2] Fleming J G and Lin Shawn-Yu 1999 Optics letters 24 49
[3] H B Sun, S Matsuo and H Misawa 1999 App. Phys. Lett. 74 786
[4] Deubel M, Freymann G Von, Wegener M, Pereira S, Bush K and Soukoulis C M 2004 Nature Materials 3 444
[5] Mizeikis V, Seet Khuen, Juodkazis S and Mizawa H 2004 Optics Letters 29 2061
[6] Deubel M, Freymann G Von, Wegener M, Pereira S, Bush K, Koch W, Enkrich C, Deubel M and Wegener M 2003 App. Phys. Lett. 82 1284
[7] Lai N D, Wen P L, Jian H L, Chia C H and Cheng H L 2005 Optics Express 13 9605
[8] Astratov V N, Vlasov Yu A, Karimov O Z, Kaplyanskii A A, Musikhin Y U G, Bert N A, Bolomolv V N, Prokofieff A V 1996 Physics Letters A 222 349
[9] Miguez H, Lopez C, Meseguer F, Blanco A, Freymann G von, Bush K, Koch W, Enkrich C, Deubel M and Wegener M 2003 App. Phys. Lett. 82 1284
[10] Astrovsky Y A, Xiang-Zheng Bo, Sturm J C and Norris D J 2001 Nature 414 289
[11] Megens M Wijnhoven, J E G, Lagendijk A and Vos W L 1999 Phys. Rev. A 59 4727
Adv. Mater. 17 1269

[38] Palacios-Lidon E, Galisteo-Lopez J F, Juarez B H and Lopez C 2004 Adv. Mater. 16 341
[39] Tétreault N, Mihi A, Miguez H, Rodriguez I, Ozin G A, Meseguer F and Kitaev V 2004 Adv. Mater. 16 346
[40] Tétreault N, Arsenault A C, Mihi A, Wong S, Kitaev V, Manners I, Miguez H and Ozin G A 2005 Adv. Mater. 17 1912
[41] Fleischhaker F, Arsenault A C, Kitaev V, Peiris F C, Freymann G von, Manners I, Zentel R and Ozin G A 2005 J. Am. Chem. Soc. 127 9318
[42] Zhao Y, Wostyn K, Schuetzen G de, Clays K, Hellemans L, Persoons A, Szekeres M, Schoonheydt R A 2003, App. Phys. Lett. 82 3764
[43] Wostyn K, Zhao Y, Schuetzen G de, Hellemans L, Matsuda N, Clays K and Persoons A 2003 Langmuir 19 4465
[44] Masse P, Reculusa S, Clays K, Ravaine S 2006 Chemi. Phys. Lett. 422 251
[45] Pradhan R D, Tarhan I Inanç and Watson G H 1996 Phys. Rev B 54 13721