Modification of the spontaneous emission of quantum dots near the surface of a three-dimensional colloidal photonic crystal*

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This paper demonstrates experimentally and numerically that a significant modification of spontaneous emission rate can be achieved near the surface of a three-dimensional photonic crystal. In experiments, semiconductor core–shell quantum dots are intentionally confined in a thin polymer film on which a three-dimensional colloidal photonic crystal is fabricated. The spontaneous emission rate of quantum dots is characterised by conventional and time-resolved photoluminescence (PL) measurements. The modification of the spontaneous emission rate, which is reflected in the change of spectral shape and PL lifetime, is clearly observed. While an obvious increase in the PL lifetime is found at most wavelengths in the band gap, a significant reduction in the PL lifetime by one order of magnitude is observed at the short-wavelength band edge. Numerical simulation reveals a periodic modulation of spontaneous emission rate with decreasing modulation strength when an emitter is moved away from the surface of the photonic crystal. It is supported by the fact that the modification of spontaneous emission rate is not pronounced for quantum dots distributed in a thick polymer film where both enhancement and suppression are present simultaneously. This finding provides a simple and effective way for improving the performance of light emitting devices.

Keywords: spontaneous emission, colloidal photonic crystal, semiconductor quantum dot, time-resolved photoluminescence

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1. Introduction

Modifying and controlling the spontaneous emission rate of micro- and nanoscale light sources such as semiconductor quantum dots (QDs) are crucial for the fabrication of sophisticated functional devices. The spontaneous emission of QDs depends not only on their own properties but also on the surrounding environment.[1] For instance, the quantum yield of colloidal CdSe QDs can be modified by partially replacing the ligands with 2-mercaptoethanol.[2] Owing to the periodic modulation of dielectric constant, photonic crystals (PCs) are expected to show great effect on the modification of the spontaneous emission of light sources. In 1987, Yablonovitch firstly introduced the idea of using a PC to control the spontaneous emission rate of atoms.[3] Since then, PCs have attracted great interest because of their potential applications in functional devices such as low threshold lasers[4−6] and single photon sources.[7,8] It is well known that the spontaneous emission rate of atoms or other light sources can be enhanced or suppressed by PCs, since the spontaneous emission rate is proportional to the local density of states of photons.[8−10] Moreover, it may exhibit an angular dependence or an asymmetry in space.[11]

So far, most research works focus on the modification of the spontaneous emission rate of emitters embedded into PCs.[4−9] Particularly, much effort has been devoted to the spontaneous emission control

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of self-assembled semiconductor QDs buried in a PC microcavity.[4−7] Although some methods have been proposed to locate a QD to a desirable position in a cavity, accurately tuning the frequency of microcavities and controlling the position of QDs remain to be a difficult task. Due to these difficulties, the enhancement factor reported so far is not so large. In other cases when a large number of emitters are randomly distributed in PCs,[12−14] the observed modification is even weaker because the enhancement is averaged over space or the enhancement and suppression are presented simultaneously. For example, Lodahl *et al.* reported on the modified emission from semiconductor QDs embedded in a PC with an inversed opal structure.[15] Both inhibited and enhanced spontaneous emission rates were observed and the control of spontaneous emission was realised by adjusting the parameters (e.g., the lattice constant) of the PC. However, the observed modification was not so significant because of the random distribution of QDs inside the PC. Similarly, Li *et al.* investigated the spontaneous emission of PbSe QDs infiltrated into a three-dimensional (3D) PC with a woodpile structure.[16] In this case, the QDs were intentionally distributed on the surfaces of polymer rods. Spectral redistribution in spontaneous emission was identified and it appeared to be significant for QDs located deeply inside the PC. The effect of photonic bandgap on the spontaneous emission of QDs was demonstrated by measuring the photoluminescence (PL) decay times of QDs at different frequencies. From the viewpoint of device applications, an accurate control of the location of light sources with respect to the PC employed to modify spontaneous emission is necessary. Thus, a simple method capable of realising efficient modulation is highly desirable. The surface of a PC has been employed to enhance the photoconductivity of a semiconductor thin film.[17,18] Very recently, manipulation of photons at the surfaces of a 3D PC was demonstrated by Ishizaki and Noda.[19] By making use of an evanescent-mode coupling technique, they demonstrated 3D PCs possessing surface states and realised localisation of light at arbitrary surface points with large Q factors. However, the spontaneous emission modification by utilising the surfaces of 3D PCs remains unexplored. For QDs on the surface of a 2D PC slab,[20] only the enhancements in the excitation and extraction efficiencies are investigated. As the terminations of periodic structures, the surfaces of PCs can support surface waves whose electric fields are strongly localised at the surfaces. Therefore, it is interesting to know whether an enhancement (or a suppression) of spontaneous emission rate can be achieved at the surfaces of PCs that implies potential applications in light emitting devices.

2. Sample preparation and experimental setup

Recently, we have successfully fabricated high-quality PC heterostructures by introducing a planar defect layer in between the two constituent colloidal PCs.[21] The planar defect layer was a thin film of TiO_2 spin-coated on the surface of the first PC. In fact, a defect on the surface of the first PC can be easily obtained by employing the same technique without growing the second PC. We can dope the thin defect layer with QDs to study the effect of the surface defect on the spontaneous emission of QDs. However, it was found that both TiO_2 nanoparticles and QDs may infiltrate into the voids of the PC during the spin-coating process, making it difficult to accurately control the optical properties of the defect layer and the location of QDs.

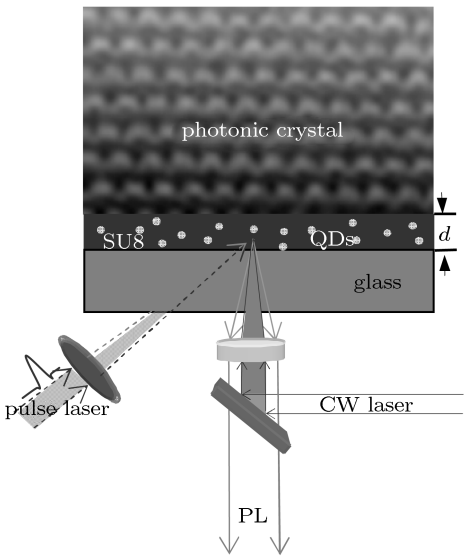


Fig. 1. Schematic showing the structure of the PC/QD samples and the experimental setup for conventional PL and time-resolved PL measurements.

The sample structure and experimental setup are schematically depicted in Fig. 1. In this paper, a simple and effective method is employed to fabricate a surface defect in which the location of QDs can be easily controlled. First, a thin polymer film (SU8, MicroChem) doped with CdSe/ZnS core-shell QDs with

a concentration ($\sim 10^{-3}$ μmol/L) was spin-coated on a glass substrate. The thickness of the film was controlled by the speed of spin coating. Then, it was baked at 90 °C for ∼40 minutes and exposed to air for ∼72 hours. Second, a colloidal PC was self-assembled on the film from the aqueous solution of polystyrene (PS) spheres with a diameter of 260 nm and a concentration of 1.0 wt% (Duke Scientific) by using the pressure controlled isothermal heating vertical deposition technique.[22] This technique has been confirmed to be an effective way to obtain high-quality colloidal PCs with deep band gaps and sharp band edges.[21]

The scanning electron microscope (SEM) image for the cross section of a colloidal PC fabricated on a glass substrate is shown in Fig. 2(a). We can clearly see well-organised PS spheres with few disorders, indicating the high quality of the PC. A set of samples with polymer films of different thicknesses were prepared. The thicknesses of the polymer films and the morphologies of the PCs were characterised by SEM. We chose to deposit the polymer films prior to the growth of the PCs because the QDs can be accurately confined in flat and smooth films which guarantee the growth of the high-quality PCs.

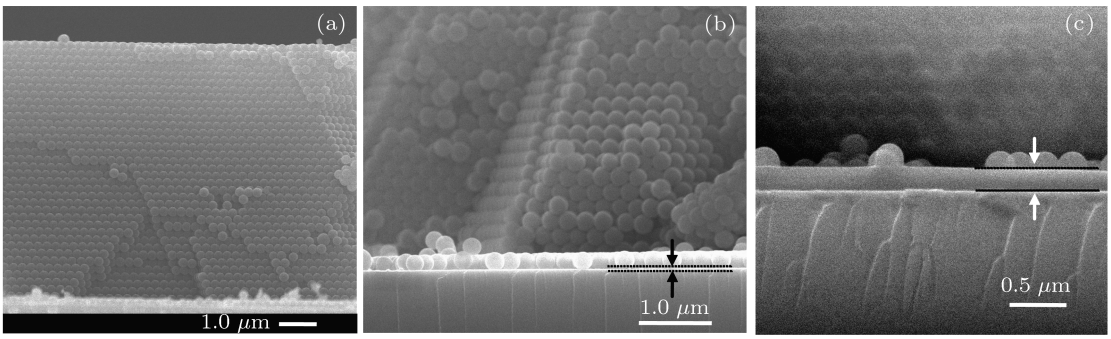


Fig. 2. The SEM images for the cross sections of (a) a colloidal PC fabricated on a glass substrate, (b) sample A in which a colloidal PC is fabricated on a thin polymer film of ∼33 nm with QDs, and (c) sample B in which a colloidal PC is fabricated on a thick polymer film of ∼210 nm with QDs.

Conventional PL and time-resolved PL (TRPL) measurements were employed to study the emission properties of the QDs. In conventional PL measurements, the 532 nm light from a solid-state laser (Coherent Verdi-5) and an inverted microscope (Zeiss Axio Observer A1) equipped with a 10× objective lens were used. For comparison, the samples were measured in two different ways in which the polymer films (or the QDs) were located below (see Fig. 1) or above the PCs (i.e., turn over the sample in Fig. 1).

In the TRPL measurements, the 532 nm light from a Nd : YAG laser (Spectra Physics 375B) with a duration of 12 ps and a repetition rate of 82 MHz was employed to excite the samples at an incident angle of 45 degree. The transient PL was collected in the [111] direction of the PC, which is normal to the surface, by using a streak camera (Hamamatsu C1587), as illustrated in Fig. 1. In this paper, we will focus on the emission properties of the QDs in two samples with the thinnest (sample A, $d = 33$ nm) and thickest (sample B, $d = 210$ nm) polymer films among all fabricated samples. Their SEM images are presented in Figs. 2(b) and 2(c) respectively where the thicknesses of the polymer films can be easily identified.

3. Conventional PL and TRPL measurement results

As a first attempt to see the effect of the PC surface on the emission properties of QDs, we have compared the PL spectra of the two samples measured in two different ways, as shown in Fig. 3. The PL spectrum of the QDs in the absence of a PC is also provided for reference. In addition, the transmission spectrum of the PC along the [111] direction is also plotted for clarity. Since we cannot accurately compare the absolute PL intensity between the two samples and the Ref. [1], the PL spectra presented in Fig. 3 have been normalised in order to find out the relative enhancement and suppression over the entire spectral range. In both samples, the PL spectral shape is modified to some extent no matter whether the QDs are located below or above the PC. Based on the change of spectral shape, one can say that the PL around the

long-wavelength edge of the band gap is enhanced or the PL near the band gap centre of the PC is suppressed. No obvious enhancement in the PL is observed at the short-wavelength edge of the band gap because a bandpass filter ranging from 575 to 640 nm was used in the measurements to block the 532 nm excitation light. Although the change in spectral shape is observed in both samples, it is noticed that the modification in sample A is more significant than that in sample B. In addition, it is remarkable that the PL spectra obtained in different ways appear to be different in sample B while they are nearly the same in sample A. Keeping in mind that the QDs in sample A are confined in a narrow region adjacent to the surface of the PC while those in sample B are distributed in a much thicker region, we suggest that the change in the PL spectral shape may originate from the modification of spontaneous emission rate near the surface of the PC rather than the blocking of the PL due to the existence of the band gap.

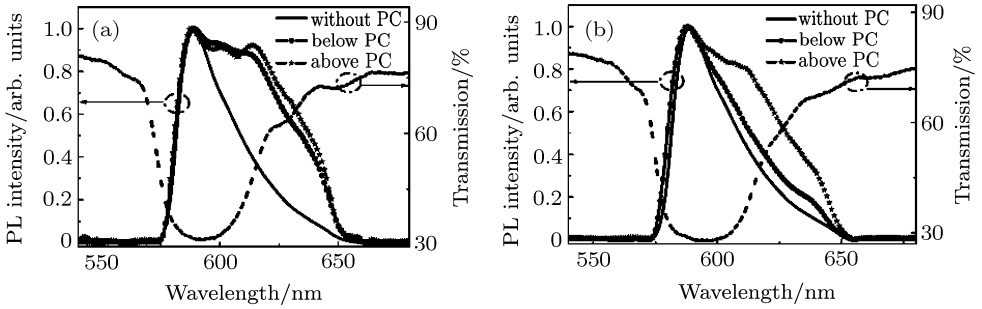


Fig. 3. Comparison of the PL spectra measured for (a) sample A and (b) sample B with the polymer films (or the QDs) below and above the PCs. The PL spectrum of QDs in the absence of the PC and the transmission spectrum (dashed curves) of the PC along the [111] direction are also provided for reference. All PL spectra are normalised in order to see the relative enhancement and suppression.

In order to confirm the above suspense, we have carried out TRPL measurements for the two samples with the polymer films (or the QDs) below the PCs. The original results for samples A and B are shown in Figs. 4(a) and 4(b), respectively. In Fig. 4(a), two bright spots (wavelengths correspond to the band edges of the PC along the [111] direction) which are indicated by arrows appeared on a relatively dark background. Thus, the PL at some wavelengths is selectively enhanced and the carrier lifetime at these wavelengths is dramatically shortened. In Figs. 4(c) and 4(d), a comparison of the PL decay traces at different wavelengths is presented for samples A and B, respectively. These specific wavelengths include the short-wavelength band edge ($\lambda = 570$ nm), the band gap center ($\lambda = 590$ nm), and the wavelength far from the band gap ($\lambda = 650$ nm). In sample A, it is found that the carrier lifetime in the QDs is increased slightly to 437 ps at the band gap center and decreased dramatically to 46 ps at the short-wavelength band edge with respect to that far from the band gap (393 ps). In comparison, a monotonous increase of the carrier lifetime from 290 to 421 ps is observed in sample B. The dramatic reduction of the carrier lifetime in sample A indicates that a significant modification of spontaneous emission has been achieved near the surface of the PC.

Similar to conventional defect modes, surface modes or leaky modes usually appear in the bandgap of a PC due to the destroying of the periodically modulated structure at the surface of the PC.[20,23] The leaky nature of the surface modes could be exploited in the development of light-emitting diodes (LEDs) and biosensors with improved performance. The external excitation of surface states leads to the creation of high-intensity near fields which efficiently excite QDs placed on the surface.[20] The emission intensity of QD can be greatly enhanced by placing them in proximity to regions where the surface states concentrate most of their energy. Additionally, the coupling of QDs to surface modes may enhance the QD emission in some preferred directions. In our case, we found that the modification of spontaneous emission appears to be stronger for QDs close to the surface of the PC, as shown in Figs. 3 and 4. This behaviour can be ascribed to the exponential decay of the amplitude of the surface states away from the surface.[23] The significant modification in spontaneous emission achieved for QDs near the surface of a PC offers us an opportunity for further improving the performance of various functional devices such as LEDs and biosensors.

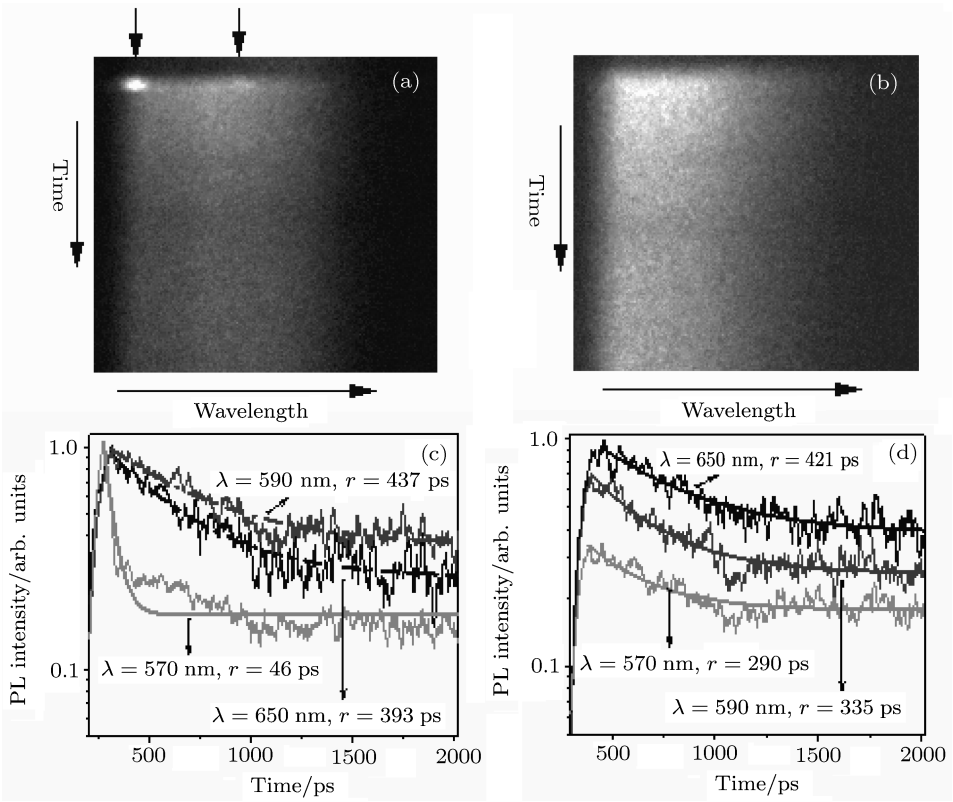


Fig. 4. Transient PL from (a) sample A and (b) sample B obtained in TRPL measurements. The PL decay traces at some specific wavelengths are compared in (c) and (d) for samples A and B, respectively.

4. Numerical simulations based on finite difference time domain (FDTD) technique

To further confirm the modification near the surface, we have performed FDTD simulations for a 3D structure similar to the samples used in the experiments.[24] In the numerical simulations, a point source is inserted into a polymer film ($n = 1.60$) which is brought into contact with the PC containing 22 layers of PS spheres. A detector with a finite size ($s = 0.265\ \mu\text{m}^2$) is placed 1 μm away from the point source to detect the emitting power of the point source which reflects the integrated spontaneous emission rate of the point source within a solid angle. The evolution of the spontaneous emission spectrum with the separation between the point source and the surface of the PC (denoted as z) is shown in Fig. 5(a). The spectra are shifted vertically for clarity. Apparently, the spectral shape exhibits a clear dependence on z. When the point source is close to the surface (e.g., $z = 20$ nm), a pronounced enhancement is observed at the short-wavelength band edge while a suppression is found in the band gap. This is in good agreement with what we observed in sample A. When the point source is moved away from the surface, it seems that the correlation between the spontaneous emission rate and the density of states of photons along the [111] direction is lost. It is noticed, however, that the spectral shape is recovered when z is increased to 200 nm. If we examine the dependence of the spontaneous emission rate on z, it is found that it varies periodically with increasing z, as shown in Fig. 5(b). Similar phenomenon has been observed in a Si/SiO_2 structure.[25] A rigorous quantum-mechanical calculation for erbium ions near an interface found that the local density of optical modes exhibits a damped oscillatory dependence on the distance from the interface.[26] Similarly, the dependence of the spontaneous emission rate on z in our work may be ascribed to the damped periodical oscillation of the surface states.

We think that the superposition of the spontaneous emission spectra from multiple sources over the thickness of the polymer film should reflect roughly the spontaneous emission spectrum in the two samples although a single point source is used in the simulations. The increase in the number of point sources does not change the general features of the spectra.

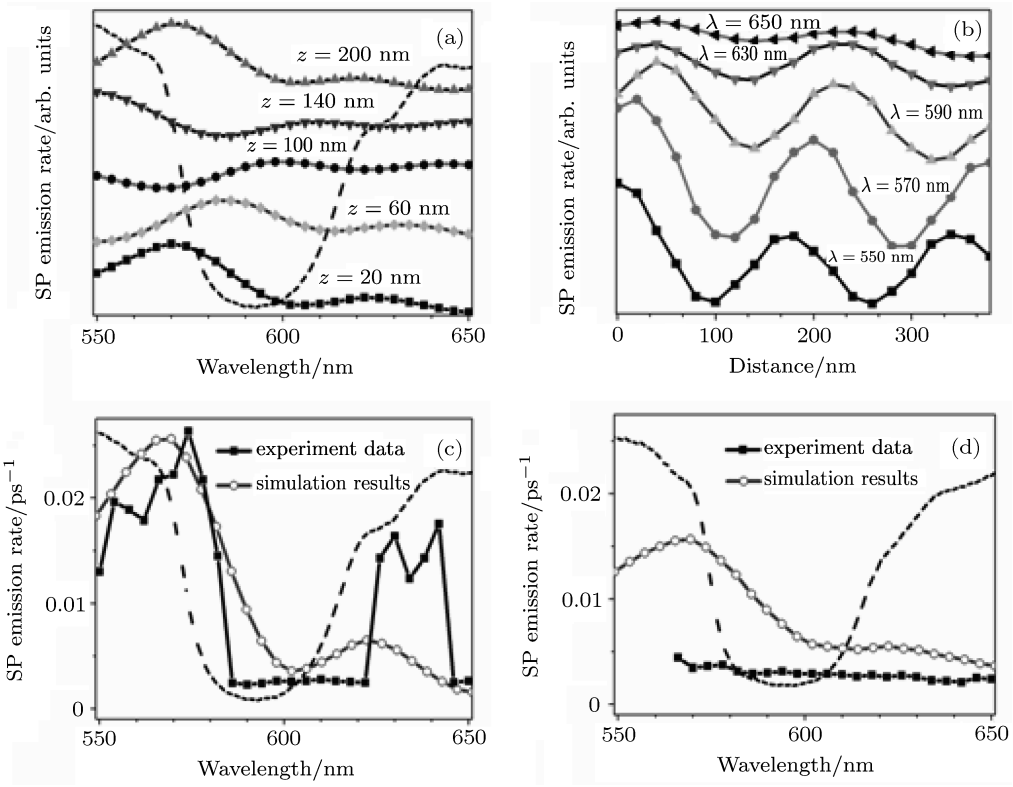


Fig. 5. Dependence of the spontaneous emission spectrum (a) and the spontaneous emission rate (b) on the separation between the point source and the surface of the PC obtained in FDTD simulations. The spontaneous emission rates obtained in experiments and simulations are compared in (c) and (d) for samples A and B, respectively.

The averaged spontaneous emission spectra for samples A and B are shown in Figs. 5(c) and 5(d), respectively. While the enhancement at the band edges and the suppression in the band gap are pronounced in sample A, they become smeared in sample B. In Figs. 5(c) and 5(d), we also provide the experimental data for the spontaneous emission spectra where the spontaneous emission rates are derived from the measured carrier lifetimes. A qualitative agreement between the experimental data and the simulation results is observed in sample A. It verifies that significant modification in spontaneous emission can be achieved near the surface of a PC. In sample B, an obvious discrepancy is found because the simple superposition mentioned above is not sufficient to describe the contribution of QDs located at different places.

5. Conclusion

In summary, we have demonstrated experimentally and numerically that significant modification of spontaneous emission can be achieved near the surfaces of 3D PCs. For QDs confined in a thin polymer film adjacent to a 3D colloidal PC, a dramatic reduction in the carrier lifetime was observed at the short-wavelength band edge of the PC while an increase in the carrier lifetime was found at the band gap of the PC. It is also revealed that the spontaneous emission rate varies periodically when an emitter is moved away from the surface of a PC. Our finding may be employed to improve the performance of light emitting devices.

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