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Research Letter

Angular Dependence of Fluorescence Emission from Quantum Dots inside a Photonic Crystal

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The fluorescence of emitters embedded in a photonic crystal is known to be inhibited by the presence of an incomplete photonic band gap or pseudogap acting in their emission range. Here, we present a study of the angular dependence of the fluorescence emission of emitters embedded in a photonic crystal. Our results clearly show an angular dependence of the fluorescence emission, which is caused by the presence of an incomplete 3D band gap.

1. INTRODUCTION

Photonic crystals (PCs), often also called photonic band gap materials, are the optical analogues of electronic crystals, that is, semiconductor crystals, which form the basis of all modern electronics applications [1, 2]. While the periodicity in the materials' properties is on the ångström scale in electronic (ionic) crystals, it is on the optical wavelength scale in photonic crystals. In electronic crystals, the periodic potential results in a band gap, that is, a forbidden range of energies for the electrons. In photonic crystals, the periodic refractive index results in an optical band gap, that is, a forbidden spectral range for the photons. These periodic changes of refractive index radically alter the local density of optical states (LDOS), which governs the interaction between the emitter and the electric field in the structure. A simple way of producing three-dimensional (3D) photonic crystals consists of ordering, through convective self-assembly [3], Langmuir-Blodgett deposition [4], sedimentation [5], or spin coating [6] monodisperse, colloidal spheres. The self-assembly results in the thermodynamically most stable face-centered cubic (fcc) crystal structure or in the (random) hexagonal closed packing (Rhcp) crystal structure, both with a packing efficiency of 74%. The type of packing, the size, and the refractive index of the colloidal spheres determine the spectral position of the band gap. The combination of these dense crystal structures (fcc or Rhcp) with the low-refractive index of most monodisperse spherical colloidal particles (latex, silica) results in an incomplete band gap (pseudogap or stop band) [7], that is, a gap with properties depending on the incidence angle of the impinging light. In this study, we present the angular dependence of the fluorescence emission of emitters embedded in PCs. Our investigations show that the angular dependence of the pseudogap causes a shift in both the maximum of fluorescence intensity as well as in the reduced emission of the embedded emitters. These findings can be used to optimize maximal tuning of the spontaneous emission from inside a PC.

2. EXPERIMENTAL PART

The Stöber method [8] was used to obtain monodisperse silica spheres of both 185 and 260 nm for, respectively, the reference (PC1) and the active (PC2) PCs. Silica colloids were chosen because they allowed for monodispersity better than 3% which is essential to produce good quality photonic crystals. Colloidal photonic crystals were then fabricated from these particles using the self-assembly protocol developed

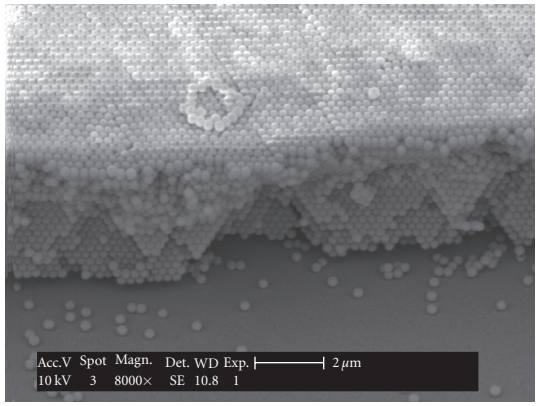

Figure 1: Transverse view obtained by scanning electron microscopy of PC2, produced by convective self-assembly from a colloidal suspension (size of the particles: 265 nm).

by Jiang et al. [3]. Figure 1 shows a transversal view of a colloidal crystal PC2 obtained by use of a scanning electron microscope (Philips XL30ESEM FEG). The figure allows one to judge the good quality of the approximately 4.5 μm thick crystal consisting of 18 layers of colloidal particles. CdSe/ZnS core/shell quantum dots of ~2.6 nm with an excitation maximum at 540 nm and an emission maximum around 565 nm were purchased from Evident USA. The infiltration was performed by placing the crystals in a 0.1 μM solution of quantum dots followed by overnight drying. Optical extinction spectra were performed on large areas (millimeter sized) to ascertain the quality and spectral features of the samples using a Perkin-Elmer Lambda 900 UV-VIS-NIR spectrophotometer. Fluorescence emission spectra of CdSe/ZnS in toluene were measured using a FluoroMax-3 (SPEX Instruments, Edison, NJ, USA).

Angle-dependent photoluminescence spectra were recorded using a home built setup. The third harmonic output of an Nd:YAG laser (GCR-11-2, *Spectra Physics*) yields pulses at a wavelength of 355 nm, a duration of 10 nanoseconds and a repetition rate of 10 Hz. The fluorescence from the samples was directed to the entrance slit of a 60 cm focal length monochromator (HR 640, *Jobin Yvon*). For detection, at the output slit a photomultiplier tube (C3531, *Hamamatsu*) photocurrent was preamplified and recorded/digitized using a 500 MHz bandwidth oscilloscope (TDS5052, *Tektronix*). All signals were averaged 20 times, all spectra were recorded with a wavelength increment of 4 nm. In the front-face excitation geometry, the light (50 mW) and the luminescence collection are both oriented at the same angle with respect to the sample surface. The sample was rotated at different angles which were measured with an accuracy of 3 degrees.

3. RESULTS

As was mentioned above, the CdSe/ZnS were infiltrated in photonic crystals with a pseudogap (i) outside the spectral range of the fluorescence emission (PC1: reference, λ_{max} = 406 nm) and (ii) in the spectral range of the fluorescence emission (PC2: active sample λ_{max} = 573 nm) of the embed-

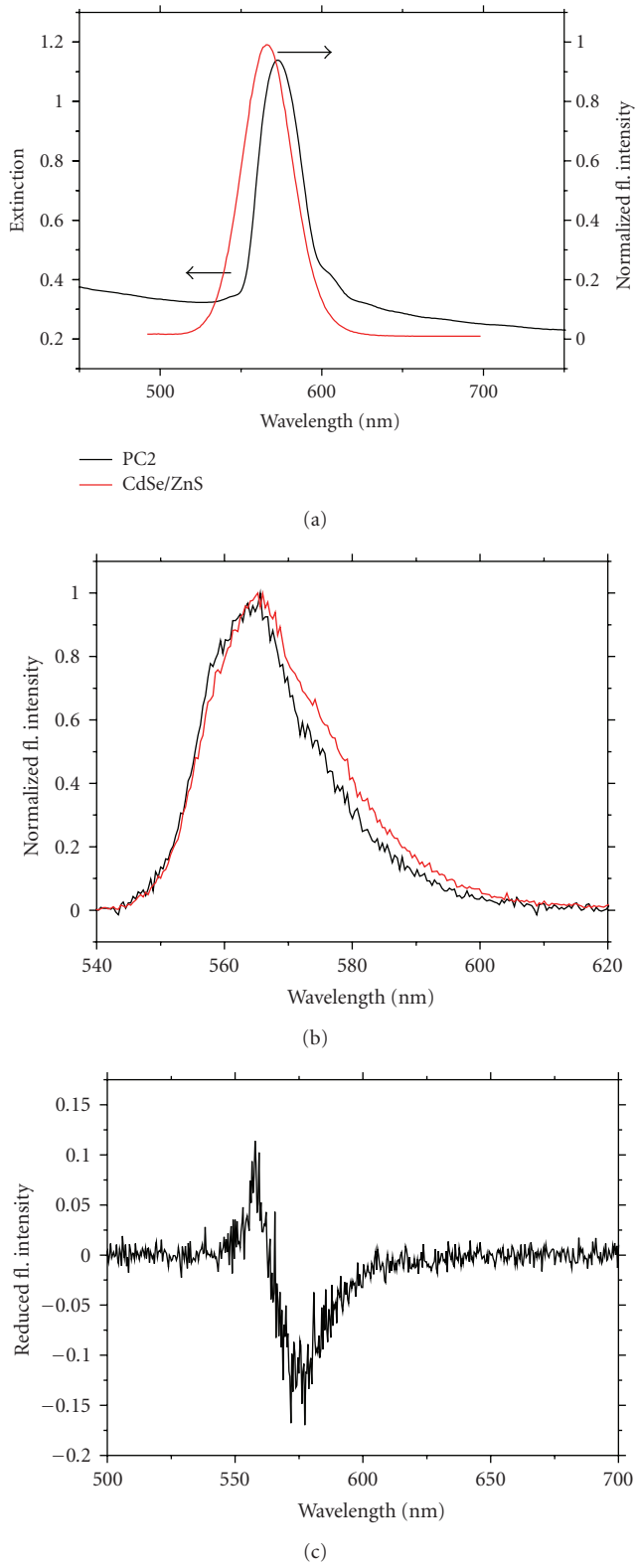

Figure 2: (a) Extinction spectrum of PC2 (black, left axis); normalized emission spectrum of the CdSe/ZnS core/shell quantum dots (0.1 μM) in toluene (red, right axis), (b) normalized emission spectrum of CdSe/ZnS quantum dots infiltrated in PC1 (black) and PC2 (red), (c) normalized fluorescence spectrum of CdSe/ZnS (right) embedded in PC2 subtracted by the normalized fluorescence spectrum of the respective emitters embedded in PC1.

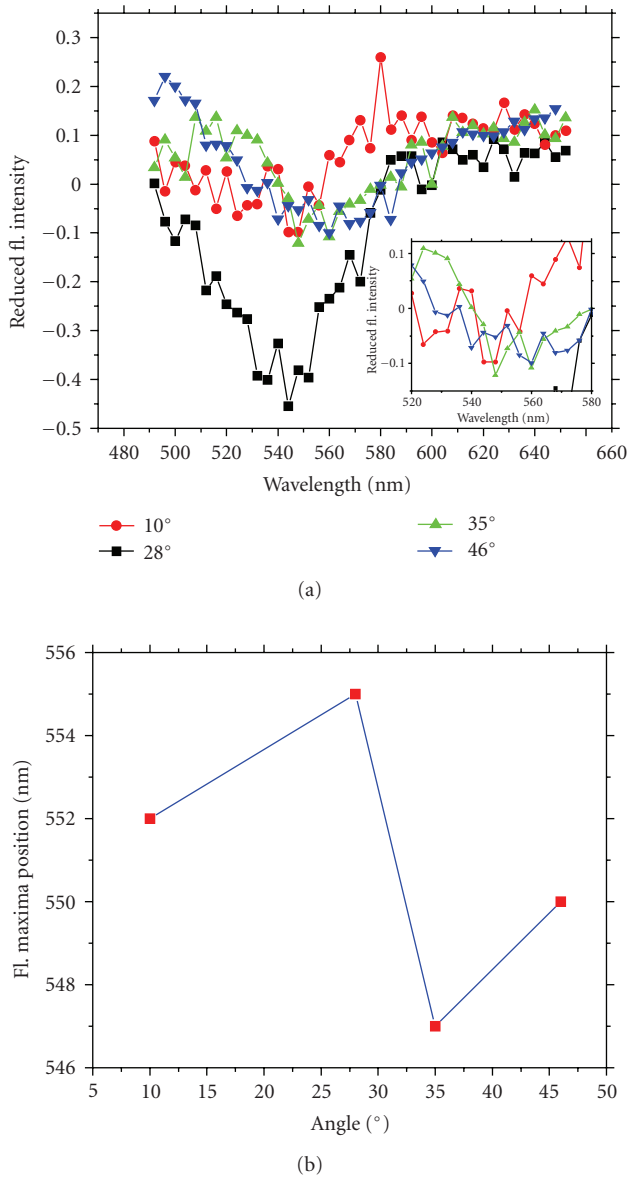

FIGURE 3: (a) Reduced fluorescence intensity of CdSe/ZnS embedded in a PC at different collection angles, the inset shows a zoom of the graph; (b) maxima of fluorescence intensity as fitted with a lorentzian function, of CdSe/ZnS embedded in a PC as a function of collection angle.

ded emitters, in order to investigate the alterations of their fluorescence characteristics. Figure 2(a) shows the steady-state emission spectrum taken from a solution of the CdSe/ZnS quantum dots in toluene and the extinction spectrum of PC2 engineered to overlap with it.

The effect caused by the pseudogap on the steady state spectra of the quantum dots infiltrated in the photonic crystals is presented in Figure 2(c). These (reduced) spectra are obtained by: (i) normalizing with respect to their maxima the steady-state emission spectra of CdSe/ZnS in both the reference (PC1) and active (PC2) photonic crystals these spectra are shown in Figure 2(b); (ii) subtracting the normalized spectra obtained for emitters embedded in PC1 from the normalized spectra pertaining to the corresponding emitters in PC2. This is done to allow for clear observation of the shape modification of the fluorescence spectra. Figure 3(a) presents the reduced emission of the quantum dots embedded in a photonic crystal at different collection angles, as the effect became small for some angles these are shown as an inset. Figure 3(b) shows the angular dependence of the spectral position of the fluorescence maximum of the quantum dots embedded in the active sample (PC2).

4. DISCUSSION

In our investigations, we used CdSe/ZnS quantum dots due to their photophysical stability and because these quantum dots are a very well-investigated system [9–12]. Figure 2 clearly shows that we succeeded in engineering a photonic crystal PC2 with a pseudogap in the spectral range 561–615 nm that covers a substantial part of the fluorescence emission of the chosen emitters. Because of the low-refractive index contrast between silica particles and air, the photonic band gap is incomplete and hence fluorescence emission was not inhibited completely and in all directions in this spectral range. Accordingly only a decrease of fluorescence emission in PC2 as compared to PC1 was observed [13, 14]. This suppression of emission was expected due to the decrease of the number of available photonic states in the pseudogap for PC2 [14–16]. Figure 3(a) shows the pseudogap which can be seen in the reduced fluorescence spectra for different incidence angles. In Figure 3(b), we show how the maximum of fluorescence intensity shifts with collection angle. This is attributed to the angular dependence of the pseudogap, which shifts to shorter wavelengths at higher incidence angles. Note that the angular dependence of the intensity of light scattering from a periodic structure or colloidal suspension was also observed before and it is not a unique property of the photonic crystal [17]. A unique property of the photonic crystal is a shift of the fluorescence maxima as a function of the angle. The observed shift is a consequence of the shift of the pseudogap at a different incidence angle [18] which changes the overlap of the fluorescence emission and pseudogap. Since the fluorescence emission is not completely covered by the pseudogap, at some angles more photonic states are available for emission of the quantum dots and spontaneous emission is less suppressed.

5. CONCLUSION

We observed a shift of the fluorescence maximum for CdSe/ZnS quantum dots infiltrated in a photonic crystal engineered to have a pseudogap which covers a substantial part of the CdSe/ZnS emission. We attribute this angular dependence to the angular dependence of the spectral range covered by the pseudogap.

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