Engineering a light-emitting planar defect within three-dimensional photonic crystals

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Abstract
Sandwich structures, constructed from a planar defect of rhodamine-B (RhB)-doped titania (TiO$_2$) and two photonic crystals, were synthesized via the self-assembly method combined with spin-coating. The modification of the spontaneous emission of RhB molecules in such structures was investigated experimentally. The spontaneous emission of RhB-doped TiO$_2$ film with photonic crystals was reduced by a factor of 5.5 over a large bandwidth of 13% of the first-order Bragg diffraction frequency when compared with that of RhB-doped TiO$_2$ film without photonic crystals. The angular dependence of the modification and the photoluminescence lifetime of RhB molecules demonstrate that the strong and wide suppression of the spontaneous emission of the RhB molecules is due to the presence of the photonic band gap.

Keywords: photonic crystals, photoluminescence, planar defect, self-assembly

1. Introduction
Ordering materials at the nanoscale can modify their fundamental properties. This powerful route can also be used to combine different materials and explore new properties of the resultant heterostructures. In particular, using nanostructured light-emitting materials, one can modify their emission properties for new optical applications. Photonic crystals are materials with a periodic dielectric structure, and have a forbidden region for electromagnetic waves, and attract much interest for their potential applications [1, 2]. In 1987, Yablonovitch first investigated the inhibition of spontaneous emission in the photonic band gaps of photonic crystals [1]. Since then, the modification of spontaneous emission by utilizing photonic crystal structures has been studied theoretically and experimentally [3–8]. Lasing from photonic crystals has been extensively studied by infiltrating the solutions containing dye molecules or semiconductors into them [9–13]. To date, numerous reports have confirmed optical modifications using two-dimensional (2D) and 3D photonic crystals [3–13].

Among 3D photonic crystals, those comprising self-assembled polystyrene nanospheres are very attractive. This is because of their ease of fabrication and tunable photonic band gaps in a wide wavelength range from ultraviolet to near-infrared through the control of the size of the polystyrene nanospheres. Although self-assembled 3D photonic crystals only possess a directional band gap along the [111] direction (L gap), they can also be utilized to manipulate the spontaneous emission of light emitters [3, 8]. Complete suppression of vacuum fluctuations, expected in the case of a photonic band gap, is difficult to realize [14]. In previous experiments on 3D photonic crystals, the inhibition was limited to a few percent by the small dielectric constants [15], and was confined to less than 45% by fabricating strongly interacting photonic
crystals with high dielectric contrasts [16]. Recently, sandwich structures with superior optical properties were constructed by engineering a planar defect between two photonic crystals [17–20], which may contribute to the modification of the spontaneous emission from dye molecules or semiconductor quantum dots embedded inside the planar defect. It was well known that high-intensity excitation is very important for the enhancement of spontaneous and stimulated emission. Surprisingly, the thickness of the planar defect doped with fluorescent molecules in the sandwich structure is also important for the enhancement of the emission. A thick planar defect doped with fluorescence materials contributes to the stimulation of re-emission and the lowering of the threshold excitation energy. The enhancement of emission [21] and lasing from a dye-doped polymer film thicker than 2 µm, sandwiched by two photonic crystals, was observed experimentally [22, 23] and found to provide a possibility for engineering a low-threshold laser. However, there has been little investigation on the inhibition of emission from such structures.

In this work, we investigated the inhibition of the spontaneous emission of the above sandwich structures. Uniform and large photonic crystals were synthesized through the self-assembly of monodisperse polystyrene spheres. A rhodamine-B (RhB)-doped titania (TiO$_2$) light-emitting planar defect was engineered between a pair of photonic crystals via the spin-coating method [17, 20]. The thickness of each photonic crystal was chosen to be about 10 µm to enable the strong localization of light. To reduce re-emission, the thickness of the planar defect in this work was controlled to ~100 nm and the power density of excitation was ~30 mW cm$^{-2}$. The emission properties were examined in conjunction with transmission and reflection spectra. A strong and wide inhibition of spontaneous emission was achieved, which opens up new research opportunities for studies of quantum optical phenomena in condensed matter.

## 2. Experimental details

In the previous study [17], we demonstrated sandwich structures constructed from a planar defect and two photonic crystals with different lattice constants. In this work, the sandwich structures were composed of a light-emitting planar defect and two photonic crystals with the same lattice constants. Sandwich structures in this work were also prepared by the self-assembly method and the spin-coating method. First, an aqueous suspension of polystyrene spheres (0.5 wt.%) with a diameter of 260 nm (purchased from Duke Scientific Corporation, California, USA) was directly deposited on the glass substrate to form a high-quality photonic crystal, as reported elsewhere [24]. The refractive index ($n$) of the polystyrene spheres is 1.59 at wavelength $\lambda = 589$ nm. The sample was then placed in a vacuum chamber for drying at room temperature for 20 h—to increase the stability as well as the mechanical strength of the fabricated samples. Then, the light-emitting material was prepared by mixing TiO$_2$ spheres (diameter 37 nm, Solaronix HT) and RhB molecules. The concentration of RhB molecules was about $10^{-6}$ M and that of TiO$_2$ suspension was 3.0 wt.%. The mixture of RhB and TiO$_2$ was then spin-coated onto the surface of the photonic crystal fabricated in the first step to form a thin film, i.e. a light-emitting planar defect. The sample was baked at 90 °C in the oven for about 30 min and then air-cooled for about 36 h to enhance the mechanical stability of the structures. Finally, the next photonic crystal was self-assembled on the surface of the film doped with RhB molecules from the same aqueous suspension of polystyrene spheres. A sandwich structure was thus formed.

Transmission and reflection spectra of photonic crystals were measured using a spectrophotometer with a halogen lamp as the light source. The incidence light emitted from the halogen lamp was dispersed into the wavelength range of 350–1200 nm. A photodetector was used to detect the light transmitted/reflected from a 7.5 × 3 mm$^2$ circular region of the sample, along the [111] orientation. Spontaneous emission was excited with an Nd:YAG picosecond laser (Spectra Physics, Model 375B) operating at the wavelength of 532 nm and repetition rate of 82 MHz and having a pulse duration of 12 ps. The photoluminescence (PL) spectra were measured using an inverted microscope (Zeiss Observer A1) connected to a spectrometer. The inverted microscope is equipped with objective lenses having different numerical apertures (NAs) that allowed us to study the angular dependence of the PL. The time-resolved PL was measured along the [111] direction of the photonic crystal using a streak camera (Hamamatsu, C1587) with a time resolution of 2 ps. The schematic configuration of the sandwich structure is shown in figure 1.
3. Experimental results and discussions

3.1. Characteristics of photonic crystal and RhB-doped TiO$_2$ film without photonic crystals

Figure 2 shows a typical cross-sectional scanning electron microscope (SEM) image of the sandwich structure. The inset in the upper left corner was viewed from the top of the sample. As shown in figure 2, photonic crystals at both sides of the planar defect are self-assembled in 3D face-centered cubic (fcc) close-packed arrangements, and only a few intrinsic defects (vacancies, particle polydispersity and site randomness) are present in this sample. The two crystal regions in the sandwich structure remain distinct, and the particles of both crystals are stacked layer by layer, demonstrating a high degree of order along the [111] orientation. In the outermost close-packed (111) plane of the photonic crystal, there are many voids, each surrounded by three spheres; such voids are denoted as ‘entrance windows’ [17, 20]. The size of the entrance windows (z) is estimated as the diameter of the sphere that exactly fits the voids, as shown schematically in the inset in the bottom left corner in figure 2; this corresponds to $z = 0.1547D$ (in our case, $z \approx 55$ nm), where $D$ is the diameter of the polystyrene spheres. As analyzed previously [17, 20], we can deduce that the solution of RhB and TiO$_2$ did not form the opal structure through the external pores because $z$ is close to the diameter of the TiO$_2$ spheres. Consequently, a smooth and highly uniform planar defect with controllable thickness was formed on photonic crystals (see figure 2).

Figure 3 shows the reflection spectra for the photonic crystals before (unbaked) and after (baked) spin-coating of the solution containing RhB molecules and TiO$_2$ spheres. The optical properties of these two samples are almost the same, except for a minor red-shift and a minor change in the lowest reflectance in the latter sample. This indicates that the presence of the planar defect in the middle does not introduce optical disorder into the periodic dielectric medium.

A high baking temperature can enhance the mechanical stability of photonic crystals, but it may destroy the crystalline structure of polystyrene because of the low glass-transition temperature of polystyrene. Once the crystalline structure is destroyed, the band gap corresponding to the polystyrene photonic crystals disappears [25]. The similarity of these two spectra demonstrates that the crystalline structure of the polystyrene photonic crystals was not destroyed at $\sim 90{^\circ}$ C, as can also be seen from the SEM images in figure 2.

The constituent photonic crystals show a clear orange color under sunlight; the color did not vary with the viewing angle but changed with the incident angle owing to the Bragg diffraction from the (111) plane. The transmission spectrum of the photonic crystals is shown in figure 4. A deep band gap with a full-width at half-maximum (FWHM) of 41 nm is seen at the wavelength of 595 nm. The lowest transmission in this transmission spectrum is about 8%, and the transmission in the pass band exceeds 80%, indicating a low volume density of imperfection. The transmission minimum can be ascribed
to the $L$ gap of the fcc structure, as verified by calculations of the corresponding band structure (see figure 5) using a plane wave expansion method [26–28]. The transmission spectrum is slightly shifted to shorter wavelengths, which may be attributed to the shrinkage of the polystyrene spheres during the drying process. The shape of the band gap is sharp, narrow, and almost symmetric, and may be attributed to the highly ordered photonic crystal structures containing only a few defects [24].

In order to elucidate whether the emission behavior of the RhB molecules is modified in the sandwich structures, the mixture of RhB molecules and TiO$_2$ spheres was spin-coated onto a glass substrate to form a reference light-emitting film with a thickness of $\sim 100$ nm. The PL spectrum of this film is also shown in figure 4. The PL emission of the film exhibits a peak at 590 nm with a FWHM of 27 nm under 532 nm excitation. Obviously, the pronounced attenuation and the overlapped $L$ gap of photonic crystals coincides with the emission band of RhB molecules. The overlap between the $L$ gap of photonic crystals and the emission band of dye emitters is necessary for the excitation of stimulated emission [29].

3.2. PL spectrum of RhB-doped TiO$_2$ film with photonic crystals

An RhB-doped TiO$_2$ film with a thickness of $\sim 100$ nm was sandwiched by a pair of photonic crystals of about 20 $\mu$m thickness to form a sandwich structure (see figure 2). The $L$ gap of the photonic crystals was utilized to modify the spontaneous emission of the RhB-doped TiO$_2$ film in such a structure. These two constituent photonic crystals significantly alter the emission spectrum of RhB-doped TiO$_2$ film as compared with that of RhB-doped TiO$_2$ film without photonic crystals. Figure 6 shows the PL spectra of RhB-doped TiO$_2$ film with and without photonic crystals, and the transmission spectrum of the constituent photonic crystals measured at normal incidence. The PL signals were collected at a direction normal to the (111) planes of photonic crystals. The single broad PL band of RhB-doped TiO$_2$ film without photonic crystals, which coincides with the dip in the transmission spectrum of photonic crystals, was divided into two sub-bands in the PL of RhB-doped TiO$_2$ film with photonic crystals. Interestingly, the intensity of PL from RhB molecules was attenuated 5.5 times. The TiO$_2$ planar defect introduced inside the photonic crystals should not affect the main features of the photonic band gaps of the constituent photonic crystals because of their finite thickness compared with that of the photonic crystals [17, 18]. The strong inhibition of light emission from the RhB molecules is mainly due to the low density of photonic states in the band gap or $L$ gap of photonic crystals. There is a very weak (less than 45%) inhibition of the emission of dye molecules infiltrated into individual photonic crystals, which were composed of materials with small or high dielectric constants [15, 16]. Compared with the sandwich structures studied here, a weaker inhibition was obtained by infiltrating dye molecules into the inverse opals in TiO$_2$ [30]. The strong inhibition of emission in this work may be ascribed to the strong modification provided simultaneously by the two constituent photonic crystals at both sides of the planar defect. In figure 6, we also find that the emission rate of light emitters in the sandwich structure is clearly reduced for frequencies from the blue edge to the red edge of the $L$ gap, over a bandwidth of 13% of the $L$ gap center frequency, which also attests to the strongly photonic character of the photonic crystals over a larger wavelength range. This strong and broadband inhibition of spontaneous emission in sandwich structures opens up new research opportunities for studying quantum optical phenomena in condensed matter.

To further investigate the effect of the $L$ gap on RhB emission, time-resolved PL measurements were carried out. Figure 7 shows the PL lifetime data of RhB-doped TiO$_2$ film with and without photonic crystals. A nonexponential decay behavior of the dye ensemble is revealed, which can be well described by two wavelength-independent decay components; their lifetimes were determined using a multieponential least-squares fitting procedure [31]. The biexponential nature of the emission decay is attributed to different subensembles of RhB molecules, which have different nonradiative decay.
The longer decay component, originating from RhB molecules, is affected by the presence of the photonic crystals, while the shorter component is attributed to intermolecular interaction. The longer PL lifetime at 590 nm for dye-doped TiO$_2$ film with photonic crystals is 464 ps, which is much longer than that of dye-doped TiO$_2$ film without photonic crystals (225 ps). The decay rate is reduced owing to the lower local density of states in the $L$ gap. PL lifetime measurements further confirm that the inhibition of the dye emission is due to the presence of the photonic band gap.

3.3. Angular dependence of PL spectra

We also measured the PL spectra of the sandwich structure with a luminescent RhB-doped TiO$_2$ light-emitting planar defect between two photonic crystals. Figure 8 shows the results obtained using objective lenses with different NAs ($5 \times /NA = 0.12$, $10 \times /NA = 0.25$, and $20 \times /NA = 0.45$). Apparently, the PL spectra are modified in all cases as a result of the existence of the photonic crystals that alter the photon density of states of the RhB molecules. The emission spectra at low excitation intensities show a sharp peak at about 586 nm with a broader shoulder centered at about 624 nm, which is about 34 nm red-shifted compared with that of RhB-doped TiO$_2$ film without photonic crystals. When the $5 \times$ objective lens was used, the NA was small and only the PL within a small solid angle along the [111] direction was collected. In this case, a significant attenuation of the PL spectrum is observed at around 595 nm, which corresponds to the center of the $L$ gap. Such attenuation becomes less significant at longer wavelengths, and the broader shoulder peak at $\sim$624 nm shifted to shorter wavelengths with increasing NA. This phenomenon can be explained by considering the band structure of the photonic crystals. With increasing NA or collection solid angle, more and more PL signals along the other directions, for example [200], will be collected, and the PL spectrum along the [111] direction will no longer be dominant. Since the $L$ gap of the photonic crystals shifts to shorter wavelengths with increasing angle with respect to the [111] direction, the blue shift of the PL spectrum is easily understood.

4. Conclusions

We have experimentally investigated the modification of the spontaneous emission of RhB molecules located in the planar defect in the sandwich structures. The experimental results clearly revealed a significant modification of spontaneous emission in the wavelength range corresponding to the $L$ gap of photonic crystals. Compared with RhB-doped TiO$_2$ film without photonic crystals, the spontaneous emission in the RhB-doped TiO$_2$ film with photonic crystals was reduced by a factor of $\sim$5.5 over a large bandwidth of 13% of the first-order Bragg diffraction frequency. The PL lifetime at 590 nm for the RhB-doped TiO$_2$ film with photonic crystals is doubled compared with that of RhB-doped TiO$_2$ film without photonic crystals. The strong and wide inhibition of RhB emission is caused by the presence of the photonic band gap, and can be employed to study the quantum optical phenomena in condensed matter.

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References

[1] Yablonovitch E 1987 Phys. Rev. Lett. 58 2059
[2] John S 1987 Phys. Rev. Lett. 58 2486
[3] Li J, Jia B, Zhou G and Gu M 2007 Appl. Phys. Lett. 91 254101
[4] Jiayu Z, Xiaoyong W and Min X 2003 Opt. Lett. 28 1430
[5] Shen C, Michielsen K and Raedt H D 2006 Phys. Rev. Lett. 96 120401
[6] Zhou J, Zhou Y, Buddhudu S, Ng S L, Lam Y L and Kam C H 2000 Appl. Phys. Lett. 76 3513
[7] Lin Y, Zhang J, Sargent E H and Kumacheva E 2002 Appl. Phys. Lett. 81 3134
[8] Barth M, Schuster R, Gruber A and Cichos T 2006 Phys. Rev. Lett. 96 243902
[9] Frolov S, Vardeny Z, Zakhidov A and Baughman R 1999 Opt. Commun. 162 241
[10] Shkunov M N, DeLong M C, Raikh M E, Vardeny Z V, Zakhidov A and Baughman R H 2001 Synth. Met. 116 485
[11] Polson R, Chipouline A and Vardeny Z 2001 Adv. Mater. 13 760
[12] Nishijima Y, Ueno K, Juodkazis S, Mizeikis V, Misawa H, Mitsuru M and Masashi M 2008 Opt. Express 16 13676
[13] Nishijima Y, Ueno K, Juodkazis S, Mizeikis V, Fujiwara H, Sasaki K and Misawa H 2009 Opt. Express 17 2976
[14] Bourdon G, Robert I, Adams R, Nelep K, Sagnes I, Moison J and Abram I 2000 Appl. Phys. Lett. 77 1345
[15] Li Z Y and Zhang Z Q 2001 Phys. Rev. B 63 125106
[16] Thijssen M S, Sprik R, Wijnhoven J E G J, Megen M, Narayanan T, Lagendijk A and Vos W L 1999 Phys. Rev. Lett. 83 2730
[17] Liu G Q, Wang Z S, Liao Y B, Chen Y, Hu H H and Liu Z M 2009 J Opt. A: Pure Appl. Opt. 11 085104
[18] Palacios-Lidón E, Galisteo-López J E, Juárez B H and López C 2004 Adv. Mater. 16 341
[19] Tétreault N, Mihi A, Miguez H, Rodríguez I and Ozin G A 2004 Adv. Mater. 16 346
[20] Pozas R, Mihi A, Ocaña M and Miguez H 2006 Adv. Mater. 18 1183
[21] Jin F, Song Y, Dong X Z, Chen W Q and Duan X M 2007 Appl. Phys. Lett. 91 031109
[22] Jin F, Li C F, Dong X Z, Chen W Q and Duan X M 2006 Appl. Phys. Lett. 89 241101
[23] Furumi S, Fudouzi H, Miyazaki H T and Sakka Y 2007 Adv. Mater. 19 2067
[24] Liu G Q, Liao Y B, Liu Z M and Chen Y 2008 J Opt. A: Pure Appl. Opt. 10 115202
[25] Yan Q, Zhou Z and Zhao X S 2005 Langmuir 21 3158
[26] Shen L and He S 2002 J. Opt. Soc. Am. A 19 1021
[27] Shi S, Chen C and Prather D W 2004 J. Opt. Soc. Am. A 21 1769
[28] Cao Y, Hou Z and Liu Y 2004 Phys. Lett. A 327 247
[29] Lodahl P, Driel F, Nikolaev I S, Irman A, Overgaag K, Vanmaekelbergh D and Vos W L 2004 Nature 430 654
[30] Koenderink A F, Bechger L, Schriemer H P, Lagendijk A and Vos W L 2002 Phys. Rev. Lett. 88 143903
[31] Enderlein J and Erdmann R 1997 Opt. Commun. 134 371