

Multilayer Photonic Crystal for Spectral Narrowing of Emission

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Multilayer colloidal crystal has been prepared by the layer-by-layer deposition of silica microspheres on a glass slide. Each layer is a slab consisting of a fcc close-packed colloidal arrays. By properly choosing the sizes of spheres, the whole spectral feature of multilayer colloidal crystal can be tuned. Here, we engineered a multilayer superlattice structure with an effective passband (380 nm) between two stop bands (366 nm and 400 nm). This gives a strong narrowing effect on emission spectrum (378 nm). With the stop bands at the shortwave and longwave edges of emission spectrum, the passband in the central wavelength region can be regarded as a strong decrease of suppression effect and enhancement of a narrow wavelength region of emission. The FWHM values of stop band modified emission spectrum were narrowed from 59 nm to 22 nm. The spectral narrowing modification effect of suitably engineered colloidal crystals shows up their importance in potential application as optical filters and lasing devices.

Keywords: photonic crystal, stop band, passband, spectral narrowing, emission spectrum.

1. INTRODUCTION

Photonic crystals have received much attention in recent years for their potential of controlling light. Their dielectric periodicities give a forbidden region for photons, analogous to the band gap in electronic crystals, i.e., semiconductor crystals. The periodic structure gives rise to Bragg diffraction, which is associated with stop bands for propagation in certain directions, similar to the bandgap of electrons in semiconductors and represents that light with a range of energies, or wavelengths, is not allowed to propagate inside photonic crystals. In this case, photonic crystals offer a complete new mechanism for the control of light. Due to their special optical properties, photonic crystals have shown the potential applications as optical reflector, filters and switches, etc [1–3]. The numerous fabrication techniques of photonic crystals can roughly be categorized into two groups: top-down and bottom-up. Compared to top-down methods, which generally use lithography to obtain three-dimensional periodicities, bottom-up methods have been proven to be easier and more cost-effective. Typically, monodisperse colloidal spheres are assembled to arrays. A number of techniques have been developed, such as gravitational sedimentation [4, 5], deposition using a specially designed cell [6, 7], electrophoretic deposition [8, 9], vertical deposition using convective self-assembly [10], and Langmuir-Blodgett technique [11, 12], etc. At the first stage of investigation, scientists' attention is mainly focused on avoiding defects during the fabrication of colloidal photonic crystals, which can diminish the band gap effect of the whole crystal. With the enhancement of the fabrication techniques of three-

dimensional photonic crystals, high-quality crystals can be obtained in large domains.

Like the heterostructures in semiconductors, some artificially introduced heterostructures in photonic crystals can also change their properties, including passband, stop band, and dispersion relation. In previous reports, different techniques were developed to introduce heterostructures into three-dimensional photonic crystals, including insertion a planar defect layer and combining slabs of spheres with different sizes [13–16].

The former involves the insertion of planar defect between two slabs of three-dimensional photonic crystals, while the defect layer has different lattice constant or refractive index comparing with the surrounding slab. Normally, for photonic crystals with this kind of heterostructures, there is a dip, also called passband, inside the stop band in transmission spectrum. The later method to fabricate heterostructures in photonic crystals is realized by layer-by-layer deposition of different opal slabs. The whole multilayer structure consists of several stacked slabs. Each slab is a close-packed array of colloidal spheres with different sizes or chemical composition [17–19]. In recent years, we have explored new methods to insert a planar defect in photonic crystals, such as direct assembly at the air/water/substrate contact line [20].

With the prime aim of light localization [21], photonic crystal structures are also studied for the manipulation of the emission of fluorophores. The periodic dielectric properties can either provide feedback for improved lasing, or result in a forbidden region, the bandgap, where emission is suppressed and the fluorescence lifetime is enhanced. These effects have been studied by use of excited atoms, quantum dots, fluorescent molecules and, thermal radiation as point sources for photons [22–25]. Since the introduction of passband inside stop band from

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heterostructures in photonic crystals, spectral narrowing of emission in colloidal photonic superlattices was reported, though the passband didn't give a clear observation in fluorescence emission spectrum [26, 27]. What's more, due to the incomplete band gaps in colloidal crystals, the band gap effect on inside omnidirectional emission is weakened, while transmission spectrum is still the most appropriate to study the spectral features of passband and stop band [28].

In this report, we use multilayer colloidal crystal to give an overall structure with strong passband and stop band. By using outside fluorophore as the emission source, we clearly observed spectral narrowing effect of photonic crystals on fluorescence.

2. EXPERIMENTAL

2.1. Materials

All solvents and chemicals are of reagent quality and used without further purification except the water was of Milli-Q quality (Millipore, USA). Tetraethoxysilane (TEOS, 98 %, Acros) and 28 % (w/w) ammonium hydroxide was purchased from Alfa Aesar. Ethanol (a.p.) was obtained from Beijing Chemical works. Microslides (75 x 25 x 1 mm, Fisher) are cut into four smaller pieces with the size of 19 x 25 x 1 mm. The fluorophore, recrystallized β -naphthalene methylformate was kindly provided by Prof. Li-Zhu Wu (Beijing, China).

2.2. Preparation of monodisperse silica spheres

Monodisperse silica spheres were synthesized following the Stöber-Fink-Bohn method through strict control of the reaction condition. In our case, reaction temperature was changed to adjust the size of obtained silica spheres, with fixed amounts of reagents (typically, 6 mL TEOS, 6.6 mL H₂O, 4.4 mL NH₃ · H₂O and 100 mL EtOH). Under vigorous stirring, TEOS was quickly added to the mixture of deionized water, NH₃ · H₂O and ethanol in a 250 mL round bottom flask and react for at least 12 h.

All the glass reaction vessels were extensively cleaned with hydrofluoric acid (2 %) and rinsed with water and ethanol prior to use. In order to study the band gap effect on emission of fluorophore, the proper size of silica spheres was chosen to match the stop bands with the emission of fluorophore. In a certain range, we found that the size of prepared silica spheres could be easily adjusted by slightly changing the reaction temperature. Also there was a good relation curve reaction temperature and the final size. With the decreasing of temperature, the spheres got larger. The two kinds of silica spheres we used in this study were prepared under 32 °C and 30 °C separately, with the final sizes as 168 nm and 184 nm.

2.3. Fabrication of multilayer colloidal crystals

After being purified by repeated centrifugation, the obtained monodisperse silica spheres were deposited onto the glass slides which were previously cleaned with piranha acid (1/3(v/v) sulfuric acid, 2/3(v/v) hydrogen peroxide as oxidant), to fabricate colloidal crystals in the method of convective self-assembly [10]. The final multilayer structure was obtained by repeated the

deposition of colloidal crystal slab on a prepared one. Since the different sizes of silica spheres result in dimensional defects between two slabs of colloidal crystals, we deposited the slab of bigger spheres on the surface of the slab of smaller spheres. The thickness of each slab can be easily controlled by adjusting the concentration of colloidal suspension. In order to get the diffraction peaks of each slab of colloidal crystals with the similar intensities, the concentration of each colloidal suspension was carefully controlled.

2.4. Characterization

Spheres and the superlattice of colloidal crystal were observed by scanning electron microscopy (SEM, S-4300, Hitachi, Japan). Transmission spectra were recorded by UV-vis spectrometer (Lambda 35, Perkin Elmer), and taken along the [111] crystallographic axis which is normal to the direction of the glass slide.

To investigate the effect of stop band/pass band on the emission (spectral narrowing), β -naphthalene methyl formate has been chosen as the fluorophore. It's a solution in mixed solvents (the volume ratio of ethanol and water is 1:9) gives emission in the wavelength range between 335 nm–450 nm, overlapping the stop band of our fabricated photonic crystals.

Emission spectra were measured by an F-4500 fluorescence spectrophotometer (Hitachi, Japan). We excited the dye with a beam of 280 nm. The experimental setup is shown in Fig. 1.

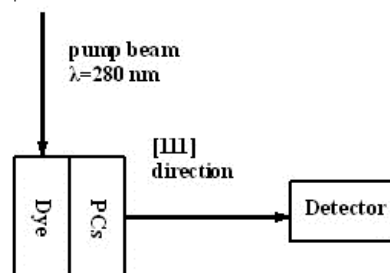


Fig. 1. Scheme of the optical setup. Using light of wavelength 280 nm as the excitation beam, the emitted light was detected under 90° direction by spectrometer. The slide with colloidal crystal was carefully attached on the cell supporter, with the slab face to the spectrometer. Emitted light is collected normal and detected normal to the glass slide, of course, also to the (111) lattice plane of colloidal crystal

A slab of colloidal crystal on glass slide was placed between the detector and the quartz cell containing fluorophore solution. The glass slide was attached on the cell supporter, and perpendicular to the detecting direction. In this case, we can make sure that all the detected emitted light pass through the colloidal crystal and experience the strongest stop band/passband effects.

3. RESULTS AND DISCUSSION

3.1. Morphology of photonic crystals and photonic superlattices

Fig. 2 shows the typical scanning electron microscopy (SEM) top-view images of the photonic crystals films

mentioned above and a cross-sectional micrograph of photonic crystal superlattice. These top-view images clearly indicate that colloidal spheres are in a FCC arrangement with the close-packed (111) plane oriented parallel to the substrates, with each sphere touching six others in one layer. The close-packed arrangement could extend over a large area (several square centimeters) [28]. The diameters of two kinds of silica spheres are A: 168 nm and B: 184 nm. Their corresponding single crystals gave stop bands at the wavelength of 366 nm and 400 nm, respectively.

Photonic superlattices were made by successive deposition of photonic crystal slabs composed of colloidal particles of the different sizes A and B. The slabs were deposited out of an ethanolic suspension of approximately 0.4 vol %. From the cross-sectional views (Fig. 2 c), it can be observed that the colloidal superlattice exhibit a highly ordered structure. We deposited the slab of smaller spheres firstly on glass slide, in order to give upper slab with bigger spheres a relative flat bottom. And in Fig. 2, with

the crystals of bigger spheres (diameter 184 nm) as the top slab which grow on the surface of the bottom slab of smaller ones (diameter 168 nm), the interface between the compositional colloidal crystal films was flat. The total thickness of the photonic crystal is about 3 μm and consists of 20 layers of colloidal spheres.

The multilayer photonic superlattice exhibits dual photonic band gaps resulting from the linear combination of stop bands of the individual stacks (A at 366 nm and B at 400 nm, respectively). Since the FWHM (full width at half maximum) of photonic stop band is proportional to the wavelength of stop band, with certain quality, here, we chose smaller silica spheres as building blocks to give sharper stop bands, and sequentially, deeper passband.

To study the effect of the stop band/passband on the emission properties (spectral narrowing) of fluorophore, different photonic crystal samples were made. Sample 1 is single slab photonic crystal of A; sample 2 is single slab photonic crystal of B; and sample 3 is AB photonic crystal superlattice. Their extinction spectra are shown in Fig. 3.

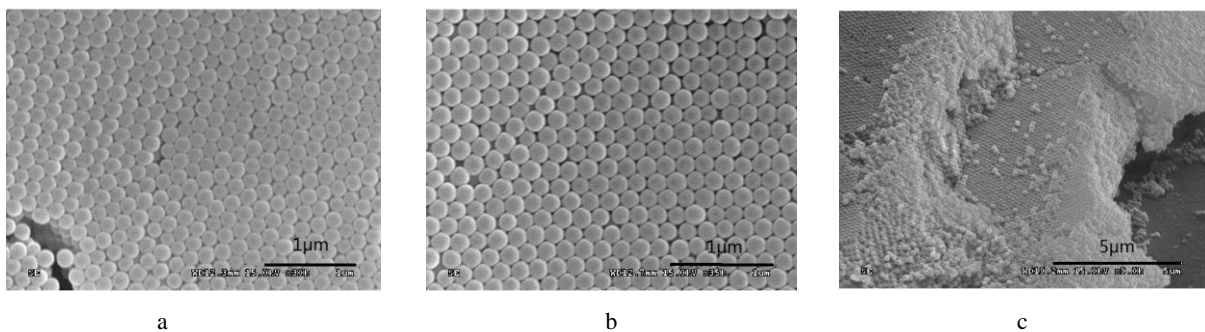


Fig. 2. SEM top-view images of silica colloid spheres with average diameter: a–168 nm; b–184 nm; c–cross-section views of photonic superlattices of silica colloidal spheres with two different diameters (about 20 layers)

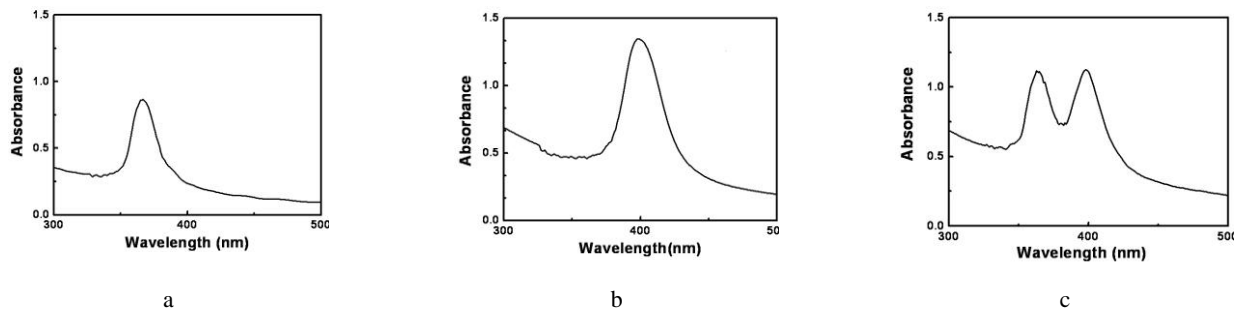


Fig. 3. Optical reflection spectrum of photonic: a–crystal sample 1; b–sample 2; c–AB superlattice sample 3

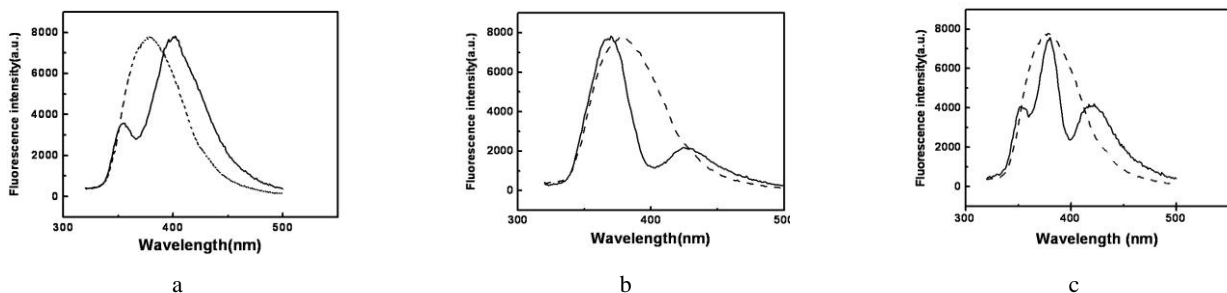


Fig. 4. Modification of the fluorescence of dye by: a–sample 1; b–sample 2; c–sample 3; modified spontaneous emission spectrum of dye in photonic crystal (solid line), reference emission spectrum of dye in solution without stop band effect (dash line)

3.2. Spectral narrowing of emission

To clearly observe the modification effect of photonic crystal on spontaneous emission, light sources must be placed in which strongly interacts with light. However, in most of the previous references, light sources such as dyes and lanthanide ions were introduced into photonic crystals just by simple infiltration or homogeneous embedding. In a previous report, it was found that when fluorophore was embedded inside photonic crystal, the stop band in the transmission spectrum was much deeper than the stop band in the emission spectrum, because of the omnidirectional nature of the emission and the incomplete band gap of silica photonic crystal [29]. To study spectral features of passband and stop band in emission spectrum, in our case, we put fluorophore outside the photonic crystal, which can show strongest effect on the light emission in perpendicular direction.

To analyze the modification effect of photonic crystal on spontaneous emission spectra, the stop band and the passband were tuned by proper choice of sphere sizes and superlattices of colloidal crystals. β -Naphthalene methylformate was chosen as the fluorophore. In proper solvent, it gave spontaneous emission which overlapped the stop band region of our fabricated colloidal crystals.

We obtained fluorescence spectra of dye in different photonic crystal samples to analyze the relative influence of stop band and passband on emission. Comparisons of these modified spontaneous emission spectra are shown in Fig. 3 and Fig. 4 for sample 1–3.

Fig. 4 a and b show the fluorescence spectra of β -naphthalene methylformate dye in sample 1 and 2. For comparison, the corresponding transmission spectra are shown in Fig. 3 a and b. The dips in emission spectra due to suppressing effect can be clearly observed, and they are in positions corresponding to the stop bands in transmission spectra. For each single-slab photonic crystal with the stop band locating at the edge of emission (sample 1 and sample 2), with the suppressing effect on emission, the spectral narrowing effects are also observed. However, simultaneously, suppression also results in a shift of emission peak.

In order to get stronger narrowing effect, we studied the modification effect of sample 3 (with multilayer structure) on emission spectrum. Between the linearly combined two stop bands, there is a dip, which is also called passband. Comparing with the passband caused by defect in photonic crystals reported previously [14–19], the dip in Fig. 4 c is much deeper. Also, the combined stop band allows the complete overlapping of emission spectrum. In Fig. 3 c, we can see that two single stop bands are located at the shortwave edge and the longwave edge of the emission spectrum. Simultaneously, the passband of superlattice allows a better narrowing effect on the central wavelength region of emission.

For comparison, the FWHM values of each stop band modified emission spectrum were given in Table 1. The data also support that engineered multilayer colloidal crystal can give a strong spectral narrowing effect on emission.

We also prepared another sample, which is a physical combination of two single slabs of colloidal crystals, by

spectral feature of sample 3. That means that the second deposition of the slab of bigger silica spheres on the surface of the slab of smaller ones don't change much of the superlattice structure.

Table 1. Comparison of spectral features of modified emission spectra from different photonic crystal structures

Crystal samples	Stop band, nm	Emission maximum, nm	FWHM total stop band, nm
–	–	378	59
A	366	402	49
B	400	370	32
AB superlattice	366,400	380	22

4. CONCLUSIONS

Multilayer colloidal crystal has been fabricated by the layer-by-layer deposition of single slabs of silica microspheres. By changing the size of silica microspheres, the stop band of each slab of photonic crystal can be tuned. The spectral feature of the whole multilayer superlattice is a linear combination of stop bands of each single slab. In properly engineered multilayer superlattice, deep passband locates between two stop bands.

For emission outside photonic crystal, in this report, all the detected emitted light has strong interaction with (111) crystalline planes of colloidal crystal. We engineered AB photonic crystal superlattice by silica colloidal particles of different sizes A (168 nm) and B (184 nm). With the stop bands (A:366 nm and B:400 nm) at the shortwave and longwave edges of emission spectrum (378 nm). In this way, we observed a very strong and clear passband in emission spectrum, which is corresponding to the dip between two stop bands in the transmission spectrum. This reduction of suppression results in a spectral narrowing in emission spectrum. The FWHM values of stop band modified emission spectrum were narrowed from 59 nm to 22 nm. In another word, it is a kind of enhancement of emission in a certain narrow wavelength region. It is believed that this experiment can be appreciated by considering engineered colloidal crystal with superlattices and heterostructures as a powerful tool for optical filter and lasing.

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