Pumping-power-dependent photoluminescence angular distribution from an opal photonic crystal composed of monodisperse Eu$^{3+}$/SiO$_2$ core/shell nanospheres

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Abstract: High quality opal photonic crystals (PhCs) were successfully fabricated by self-assembling of monodisperse Eu$^{3+}$/SiO$_2$ core/shell nanospheres. Angular resolved photoluminescence (PL) spectra of a PhC sample were measured with different pumping powers, and its PL emission strongly depended on spectroscopic position of the photonic stop band and the optical pumping power. Suppression of the PL occurred in the directions where the emission lines aligned with the center of the photonic stop band. Suppression and enhancement of the PL were observed at low- and high-pumping powers, respectively, in the directions where the emission lines were located at the edges of the photonic stop band. When pumping power exceeded 6 µJ/pulse, a super-linear dependence was found between the pumping power and PL intensity. The dramatic enhancement of PL was attributed to the amplification of spontaneous emission resulted from the creation of large population inversion and the slow group velocity of the emitted light inside the PhC. The opal PhC provided highly angular-selective quasi-monochromatic PL output, which can be useful for a variety of optical applications.

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1. Introduction
Highly ordered periodic nanostructures like photonic crystals (PhCs) show a variety of new and interesting properties for optoelectronic applications [1,2]. PhCs allow one to create
photonic band gaps (PBGs) to block photons with photon energy within the gaps to propagate through the structures, resulting in high reflectivity [2–4]. When the refractive index contrast is large enough, complete PBGs can be formed to inhibit photon propagation in all directions. For lower refractive index contrast, incomplete PBGs called photonic stop bands or pseudo-gaps occur in certain directions [1]. Among various applications of PhCs proposed so far, the utilization of the PBG or photonic stop band effect to manipulate light emission of a light-emitting PhC is especially getting much attention [3–17]. The spontaneous emission rate of a light emitter is determined by two factors: the “atomic part” which is related to the internal structure of the light emitter and the “field part” which is related to the local density of optical states (LDOS) of the environment [18]. The LDOS is reduced within a photonic stop band, while it is increased at the edges of a photonic stop band [19]. Suppression or enhancement of photoluminescence (PL) can be obtained from a light-emitting PhC, depending on the spectral position and width of the emission spectrum of light emitters embedded in the PhC relative to the photonic stop band: suppression of PL occurs as the emission wavelength of the light emitters overlaps with the photonic stop band, and the enhancement of PL takes place as the emission wavelength of the light emitters is at the edge of the photonic stop band [5,7,17].

The modification of PL of light emitters has been demonstrated in a variety of PhC structures, including 1D multilayer dielectrics [5,6], 1D cholesteric liquid crystals [7], 2D PhC slabs [8], 3D woodpile PhCs [9,10], 3D liquid crystal blue phase PhCs [11], and 3D opal and inverse opal PhCs [12–17]. Among them 3D opal and inverse opal PhCs are the most promising structures due to their cost-effective and the ease of fabrication via self-assembly techniques. Moreover, their photonic stop bands can be easily tuned by varying the diameter of spherical colloids [1,20].

Organic dyes, quantum dots, and rare-earth ions are commonly used as luminescent sources incorporated with a PhC. Among these luminescent sources, rare-earth ions are the most favorable because their emission bands derived from intrinsic 4f transitions are narrower than the bandwidth of a photonic stop band, whereas those of organic dyes and quantum dots are often much broader and results in a partial matching between the photonic stop band and emission band. Furthermore, rare-earth ions provide strong luminescence and do not exhibit photo-bleaching effect, which usually occurs to organic dyes [21,22].

Several works have employed the infiltration method to incorporate rare-earth ions into opal or inverse opal PhCs [13,23]. However, this method is not easy for precise control of the distribution of rare-earth ions. In addition, the infiltrated PhC structures are easily distorted after the thermal annealing process which is used for enhancing the PL output of rare-earth ions. These problems can be solved through synthesis and self-assembly of monodisperse rare-earth core/shell nanospheres. Core/shell nanospheres synthesized with silica cores covered with a layer of rare-earth doped material have been reported [24,25]. Although these nanospheres exhibited good PL properties, their rough surfaces, induced by the indispensable acid-based reaction for rare-earth shell coating, made them difficult to form opals by the self-assembly process. In contrast, monodisperse and smooth surface of Tb(OH)$_3$/SiO$_2$ core/shell nanospheres were successfully synthesized under basic conditions and opal PhCs were obtained based on self-assembly of those nanospheres [17,26]. It has been demonstrated that the Tb(OH)$_3$/SiO$_2$ opal PhC has the capability to generate laser emission by overlapping the emission wavelength of Tb$^{3+}$ ions to the band edge of the photonic stop band of the opal PhC [17]. Europium ion (Eu$^{3+}$) is a well-known red luminescent phosphor and is wildly used for display and lighting applications [24,27]. Eu$^{3+}$/SiO$_2$ core/shell nanospheres have great potential to serve as good building blocks for a high quality light-emitting PhC, whose PL properties can be manipulated via the photonic stop band effect.

Until now, most investigations are focused on PL properties of opal and inverse opal PhCs infiltrated with rare-earth ions, and only a few works have reported PL properties of opal PhCs composed of rare-earth ions/SiO$_2$ core/shell nanospheres [17,26]. Especially, no report has covered the fabrication and PL properties of opal PhCs composed of Eu$^{3+}$/SiO$_2$ core/shell
nanospheres. Furthermore, most researches only focused on angular dependence of PL for a fixed pumping power and still lacks of investigation about how the pumping power affects PL angular dependence of a light emitting opal PhC. In this work, we present the successful synthesis of monodisperse Eu³⁺/SiO₂ core/shell nanospheres and the fabrication of opal PhCs based on self-assembly of these monodisperse core/shell nanospheres. Angular resolved PL spectra of a suitable PhC were measured at different pumping powers to deduce the effects of photonic stop band and pumping power on PL properties. Suppression of PL was found as the emission wavelength of Eu³⁺ ions matched with the center of the photonic stop band independent of the pumping power. When the emission wavelength of Eu³⁺ ions was located at the edges of the photonic stop band, the PL output was suppressed during weak pumping excitation stage. As the pumping power was higher than a threshold value, the PL outputs were dramatically enhanced, i.e., much larger than those of a powder sample.

2. Experiments

Monodisperse Eu³⁺/SiO₂ core/shell nanospheres with the particle size in the range of 200-500 nm were synthesized following the modified Stöber method [20,28]. First, europium chloride hexahydrate (EuCl₃·6H₂O, 99.99%, Acrôs) and sodium citrate (C₆H₅Na₃O₇·2H₂O, 99.0%, Panreac) were mixed with the Eu/citrate molar ratio of 1:2, and aqueous ammonia (NH₄OH, 29%, Fisher Scientific) was added excess to make europium citrate complex as the seed solution. Citric acid is well-known as a protective agent to synthesize nanoparticles [29,30]. When the aqueous solution of europium chloride was mixed with citric acid, stable europium citrate acid complex was formed in the solution. Second, the seed solution, tetraethyl orthosilicate (TEOS, 98%, Acrôs), deionized water (18.2 MΩ.cm), and NH₄OH were added in sequence in ethanol (C₂H₅OH, 99.8%, Hy Biocare Chem) and stirred at temperature 30 ± 1 °C for 4 h to obtain a white turbid colloidal suspension. Using the seed of europium citrate complexes as the core, the SiO₂ shell was grown during the hydrolysis and condensation of TEOS in a mixture of NH₄OH, C₂H₅OH, and H₂O, forming the core/shell nanospheres. The diameter of the Eu³⁺ core can be controlled by varying the Eu/citrate molar ratio and the amount of seed solution. Similarly, the size of SiO₂ shell can be controlled by the amount of TEOS. To prepare nanospheres with a core diameter of 25 nm and particle diameter of 315 nm, the following parameters were used: 10 ml of H₂O; 160 µl of seed solution; 1.6 ml of TEOS; 6 ml of NH₄OH; and 80 ml C₂H₅OH.

The nanospheres were separated from mother liquid and purified by using centrifugation (3000 rpm) with deionized water or ethanol for three times. Then, the colloidal solution was used to fabricate opal PhC by dispersing of Eu³⁺/SiO₂ core/shell nanospheres in deionized water with a weight ratio of 2%. Opal PhCs were fabricated by self-assembly process via thermal-assisted gravity sedimentation method. A glass slide (1 x 1 cm²) was kept nearly horizontal into the bottom of a small vase filled with the core/shell colloidal solution. The small vase was put on the top of a heat plate at 50 °C for 2 days and the environmental humidity was kept at 55%. When water was slowly evaporated, the nanospheres self-assembled into opal structure on the substrate. The mechanical stability of the opal films was improved by heating at 100 °C for 30 min. Then, they were carefully removed from the substrate and the free-standing Eu³⁺/SiO₂ core/shell nanosphere opal was further annealed for 2 h in air at 900 °C, which was achieved with a temperature raising rate of 2 °C/min from room temperature.

Transmission electron microscopy (TEM) (JEOL 2100), and field emission scanning electron microscopy (FESEM) (Hitachi S4800) were used to characterize and inspect core/shell nanospheres and the structure of the opal films, respectively. The reflection spectra of the opal films were measured using a fiber optics spectrometer (Ocean S2000) and a halogen tungsten light source. Figure 1 shows the setup for measuring angle-resolved PL spectra of the opal films. The excitation light source used in the measurement was the fourth-harmonic of the single output
of an optical parametric amplifier (TOPAS-C), which was pumped by the output of a Ti:sapphire femtosecond laser amplifier (Spitfire Pro amplifier). The excitation laser was with pulse duration 100 fs, repetition rate 1 kHz, and its wavelength was chosen at 395 nm to match the absorption of Eu$^{3+}$ ions. The average excitation power was varied from 0.5 to 12 mW. A lens with a focal length of 10 cm was employed to focus the excitation laser on the sample with a spot size about 100 µm. The sample was mounted on a rotating stage, which allows PL signal to be measured at different angles. The angle between the excitation beam and the normal direction of the detector was fixed at 20° to avoid the input of the detector being flooded by the excitation light during the experiment. A small lens was used to collect and focus the PL signal onto a fiber bundle connected to a MicroHR spectrometer (Jobin Yvon) equipped with a low temperature CCD detector. An aperture with 5 mm of opening diameter was put in front of the lens with a distance about 8 cm to the sample to limit the PL signal collection solid angle about 0.003 str (~1.8°). Both reflection and PL experiments were measured in air atmosphere and at room temperature.

3. Results and discussions

Figure 2(a) shows a TEM image of Eu$^{3+}$/SiO$_2$ core-shell nanospheres. As shown in the TEM image, small dark cores (~25 nm diameter) contain Eu$^{3+}$ ions appearing at the center of each nanosphere and each core is coated with silica shell with a smooth surface. Figure 2(b) shows a SEM top-view image of an opal PhC formed by self-assembly of Eu$^{3+}$/SiO$_2$ core/shell nanospheres after thermal annealing treatment at 900 °C for 2 h. As illustrated in the SEM image, the opal film exhibited highly ordered close-packed face-centered-cubic (fcc) structure. The thickness of the opal film was about 500 µm and its (111) plane was parallel to the substrate.

Fig. 2. (a) Transmission electron microscopy (TEM) image of Eu$^{3+}$/SiO$_2$ core/shell nanospheres. (b) Top view scanning electron microscopy (SEM) image of an Eu$^{3+}$/SiO$_2$ core/shell opal film after thermal annealing at 900 °C for 2 h.
Both SEM and TEM images show that Eu³⁺/SiO₂ core/shell nanospheres were highly monodispersed, and their narrow size distribution paved the way for fabricating high quality opal PhCs. Although the diameter of the core/shell nanospheres shrank about 8% from the original (the diameter of spheres decreased from original 315 to 290 nm) after the thermal annealing treatment process, the opal PhC structures still remained good periodicity. The thermal annealing treatment not only improved the mechanical stability of the opal thin films but also increased their PL intensity due to reduction of quenching effect caused by OH vibration [13,24]. All the opal PhCs presented in this work have gone through the thermal annealing treatment.

Several opal PhCs with different diameters of core/shell nanospheres were fabricated. Figure 3 shows the reflection spectra of these opal PhCs at normal incidence. The reflection peak shifted from 468 to 850 nm as the diameters of nanospheres increased from 215 to 390 nm. It represents the photonic stop band of the PhC can be tuned by varying the diameter of core/shell nanospheres. The quality of the opal PhCs can be judged by the band-width to peak wavelength ratio (Δλ/λ₀) of the reflection peak, where λ₀ is the wavelength of the reflection peak, and Δλ is the full width at half maximum (FWHM) of the reflection peak. The band-width to peak wavelength ratio of the opal PhCs fabricated in this work ranges from 5.5 to 6.3%, close to the theoretical value of 5% in the Γ-L direction [20,31].

![Fig. 3. Normal incident reflection spectra of opal PhCs composed of different diameters of Eu³⁺/SiO₂ core/shell nanospheres.](image)

To investigate the photonic stop band effect on PL, the opal PhC formed by 290 nm diameter of core/shell nanospheres was chosen, because its photonic stop band was close to the emission wavelengths of Eu³⁺ ions. Figure 4(a) shows the PL spectrum of Eu³⁺/SiO₂ core/shell nanosphere powders pumped by the excitation laser source at 395 nm. The PL spectrum mainly consist of narrow emission lines corresponding to the well-known Eu³⁺ emission from intra 4f transition ⁵D₀ - ⁷F₉ (j = 0, 1, 2, 3) [13,24]. The inset shows the PL photograph of the Eu³⁺/SiO₂ core/shell nanosphere powders exhibiting strong red luminescence of Eu³⁺ ions. The strongest emission peak was the hypersensitive transition ⁵D₀ - ⁷F₂ at 612 nm, and other peaks were at 579 nm (⁵D₀ - ⁷F₀), 592 nm (⁵D₀ - ⁷F₁), and 655 nm (⁵D₀ - ⁷F₃). The FWHM of the emission peak at 612 nm is 9.5 nm. Figure 4(b) shows the specular reflection spectra of the opal PhC obtained with various incident angles, ranging from 0° to 40° with respect to the surface normal direction. The photonic stop band blue-shifts with the increase of incident angle.

The angular-dependence of the reflection spectra in Fig. 4(b) indicates that in the setup shown in Fig. 1 by rotating the sample from θ = 0° to 40°, the photonic stop band sweeps through the spectral range of peaks in Fig. 4(a) for the PL signal collected by the detector. The
Figures 4(a) and 4(b) show the PL spectra of Eu$^{3+}/$SiO$_2$ core/shell nanosphere powders after the thermal annealing treatment. The inset photograph of the PL emission of the sample pumped by the excitation laser at 395 nm. (a) Angular dependent specular reflection spectra of an opal PhC composed of Eu$^{3+}/$SiO$_2$ core/shell nanospheres with the diameter of 290 nm. Interaction between the photonic stop band and the Eu$^{3+}$ emission leads to strong angular-dependence of PL spectra. Figure 5(a) shows the PL spectra 1, 2, and 3 obtained by rotating the sample to three different angles $\theta = 0^\circ$, $20^\circ$, and $40^\circ$, respectively. The sample was excited with a low pulse pumping power of 1 $\mu$J/pulse. As illustrated, the over-all PL intensities vary strongly with $\theta$, i.e., the PL emission from the opal is anisotropic. Furthermore, the $\theta$ dependence varies with peak wavelength: for peak intensity at 612 nm ($^5D_0 - ^7F_2$), the $\theta$ dependence gives $I_1 > I_2 > I_3$. However, for peak intensity at 592 nm ($^5D_0 - ^7F_1$) (inset of Fig. 5(a)), the trend becomes $I_1 > I_3 > I_2$. Figure 5(b) shows the PL spectra obtained with a higher pulse pumping power of 12 $\mu$J/pulse. The trend of the peak intensity at 612 nm becomes $I_1 >> I_3 > I_2$, and that for the peak intensity at 592 nm (see inset of Fig. 5(b)) is $I_2 > I_1 >> I_3$. It is clear that angular-dependence of the PL emission also depends on the pumping power.

Figures 5(c) and 5(d) display the $\theta$ dependence of the PL emission peak intensities at 612 and 592 nm, respectively, obtained with two different pumping powers. In Fig. 5(c), a minimum occurs at $20^\circ$ in spite of the pumping power due to the fact that of the photonic stop band (see Figs. 4(a) and 4(b)) centers at 612 nm for $\theta = 20^\circ$, which leads to maximum suppression of PL by the photonic stop band. For the 1 $\mu$J/pulse low pumping power, the PL intensity increases as $\theta$ moves away from $20^\circ$ and reaches normal level at $40^\circ$, where the photonic stop band center is out of the emission peak wavelength at 612 nm (see Fig. 4) and thus no suppression of the PL signal by the photonic stop band. This is consistent with the fact that the PL intensity detected at $40^\circ$ was equal to that of a powder sample composed of the same density of core/shell nanospheres. At low pumping power, the PL signals were mainly from spontaneous emission. The PL signals, detected in $0^\circ \leq \theta < 40^\circ$, were suppressed due to the reduction of LDOS caused by the photonic stop band effect, even including the edges ($0^\circ$ and $30^\circ$ directions) of the photonic stop band. Considering angles like $0^\circ$ and $30^\circ$, in which the emission wavelength was located at the edges of their photonic stop bands, the PL intensities detected from these angles were smaller than that of $40^\circ$ for low pumping power. However, as the pumping power increased to 12 $\mu$J/pulse, the $\theta$ dependence changed most dramatically.
where the 612 nm peak aligned with the edge of the stop band, i.e. θ = 0° and θ = 30°. The PL intensities were much larger than that of 40° at the same pumping power. This large amplification of spontaneous emission resulted from the creation of large population inversion and small group velocity of spontaneous emission light inside the PhC [5,32–35]. Since the line-width of the 612 nm peak did not sharpen as it should have for the case of lasing (see Fig. 5(b)). Therefore the laser action (coherent stimulated emission) had not occur yet, The PL emission was probably still in the mode of amplified spontaneous emission stage (incoherent stimulated emission).

Similar pumping power dependence was also observed for the PL intensities at 592 nm peak wavelength. At θ = 20°, where the photonic stop band edge aligned with PL emission peak, the PL intensity was significantly enhanced at high pumping power, and suppressed at low pumping power. At θ = 30° a minimum occur for both high and low pumping powers due to the fact that the emission wavelength overlapped with the center of the photonic stop band (see Figs. 4(a) and 4(b)). Maximum suppression of PL occurred in this direction for the 592 nm emission. For θ = 0° and θ = 40°, the 592 nm emission line was outside of the stop band (see Figs. 4(a) and 4(b)), and the PL intensities detected in these directions reached normal level.

Figure 6 shows how the relation between the pumping power and PL intensity at 612 nm varies with θ. For comparison, the result of a powder sample is also included. As illustrated, the PL intensity with θ = 40° coincides with that of the powder sample, which confirms the photonic stop band was insignificant to the PL output in this direction. The PL intensities detected at θ = 20° were always smaller than those with θ = 40°. This is consistent with the picture of strong suppression of PL resulted from the photonic stop band. For θ = 0° and θ = 30°, the PL intensities were lower than those of θ = 40° with pumping powers below 6 µJ/pulse. During this stage, the same suppression of PL occurred caused by the reduction of LDOS from the photonic stop band effect. For pumping power higher than 6 µJ/pulse, their PL intensity followed a super-linear dependence and significantly exceeded those of θ = 40°.
This kind of dramatic growth of PL output only occurred when the emission wavelength matched with the edges of photonic stop band. Small group velocity and large population inversion brought a strong interaction between radiation field and light emitters and produced high efficient PL output. This kind of highly angular-selective quasi-mono-chromatic PL output can be useful for a variety of applications such as light projection, display, and optical excitation and illumination, etc.

4. Conclusions

Monodisperse Eu³⁺/SiO₂ core/shell nanospheres were successfully synthesized following the modified Stöber method. High quality opal PhCs were fabricated by self-assembling those monodisperse core/shell nanospheres, and their photonic stop bands can be tuned by varying the diameter of nanospheres. By overlapping of the photonic stop band and the emission peaks of Eu³⁺ ions, the PL emission from the opal PhC was strongly modified. As the emission line overlapped with the center of the photonic stop band, PL was suppressed independent of the pumping power. As the emission line was at the edges of the photonic stop band, two-step dependence was found between the pumping power and the PL intensity. At low pumping power, suppression of PL was observed. As the pumping power was over a threshold value 6 µJ/pulse, PL was dramatically increased due to large amplification of spontaneous emission contributed from the formation of large population inversion and slow group velocity of spontaneous emission light inside the PhC. The opal PhC provided highly angular-selective quasi-mono-chromatic PL output, which can be useful for a variety of optical applications.

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