

# Colour modification action of an upconversion photonic crystal†

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**Colour modification of the upconversion emission has been successfully achieved in a novel upconversion photonic crystal.**

According to Moore's Law, the number of components on an integrated circuit is being doubled approximately every eighteen months, with a subsequent impact on computing power.<sup>1</sup> As the electronic components continually get smaller in size, the mutual interference between components is becoming increasingly pronounced.<sup>2,3</sup> Therefore, the development of a new generation of information technology components is becoming urgent. Photons are ideal information carriers, instead of electrons in integrated circuits. Photons present several advantages over electrons: travelling faster, carrying a larger amount of information, and reducing the energy loss, because, as they are bosons, they are not as strongly interacting as electrons.<sup>4</sup> To completely realize the use of photons as information carriers, it is necessary to create integrated optical circuits to control photons analogous to electronic integrated circuits for the control of electrons. Photonic crystals provide an opportunity to solve this problem. Photonic crystals, first introduced by Yablonovitch<sup>5</sup> and John,<sup>6</sup> possess highly ordered structures with a periodically modulated refractive index (or dielectric constant), with periods typically on the length scale of optical wavelengths. This periodicity may lead to the formation of a photonic band gap (PBG), a band of frequencies for which light propagation in the photonic crystal is forbidden. Owing to the existence of the PBG, control over the propagation of photons can be achieved by designing and modulating the PBG structure. More importantly, photonic crystals can be functionalized by different photonic components. One such interesting possibility is the modification of the spontaneous emission of photoluminescent guests embedded in photonic crystals.<sup>7</sup> To date, there have been several experimental reports on the formation of macroporous photonic crystals and the modification of spontaneous emission of photoluminescent guests, including organic dyes, quantum dots and rare earth ions.<sup>8–10</sup> However, the emission bands of fluorescent dyes are often broader than the PBG, and thus only a part of the emission spectrum could be affected by photonic crystal structure.<sup>8</sup> In contrast, light emitters with

narrow emission bands would be ideal candidates to maximize the photonic crystal effect. Hence, rare earth ions involving *f*-orbital electrons would be a suitable tool to study the photonic crystal effect, as they have much narrower emission bands than the PBG of typical inverse opal structures (air voids in a silica-doped matrix).

Upconversion (UC) luminescence is an important feature of the optical properties of rare earth compounds, the study of which has grown rapidly owing to their extensive applications in solid-state lasers, three-dimensional (3D) flat-panel displays, optical fiber-based telecommunications and low-intensity IR imaging.<sup>11</sup> Among the various UC phosphors, hexagonal-phase NaYF<sub>4</sub>:Yb,Er is one of the most efficient; however, it is still a challenge to manipulate its UC emission behaviour. Herein, we present a novel UC photonic crystal fabricated by embedding NaYF<sub>4</sub>:Yb,Er nanoparticles in inverse opals, so as to manipulate the UC emission behaviour. The hexagonal-phase NaYF<sub>4</sub>:Yb,Er nanoparticles exhibit intense, and fairly narrow red and green emissions. Such a material was shaped into an inverse opal, in which the size of the holes was varied controllably in order to modulate the PBG in different positions and thus to tune the NaYF<sub>4</sub>:Yb,Er emission behaviour. Besides modification of the lifetime, which has been extensively observed by others,<sup>12</sup> we could suppress the spontaneous green emission that is located in the range of the PBG. Such tuning of spontaneous emission provides new possibilities for the design of more efficient devices for colour purification. The fabrication of SiO<sub>2</sub> inverse opals embedded with NaYF<sub>4</sub>:Yb,Er nanoparticles was achieved by simple infiltration of the silica sol doped with NaYF<sub>4</sub>:Yb,Er nanoparticles into polystyrene (PS) colloidal crystals. First, monodisperse PS colloidal spheres with a diameter of 528 nm (for sample PC1) were assembled into 3D colloidal crystals on a filter membrane. Then, the silica sol doped with NaYF<sub>4</sub>:Yb,Er nanoparticles was added dropwise to the colloidal crystal film in a Büchner funnel under vacuum, leading to deposition in the interstices of the colloidal crystals. Finally, the resultant samples were calcined at 500 °C for 3 h in air by slowly increasing the temperature from room temperature to 500 °C (1 °C min<sup>-1</sup> ramping rate). The fabricated inverse opals PC1 are thin films consisting of air spheres in silica.

According to electromagnetic field theory, the solutions of Maxwell equations in a periodic dielectric medium are used to describe the behaviour of light in photonic crystals. Through mathematical analysis, they can be rewritten in the form:<sup>13</sup>

$$\left[ \nabla^2 \times \left[ \frac{1}{\epsilon(r)} \nabla \times H(r) \right] \right] = \frac{\omega^2}{c^2} H(r) \quad (1)$$

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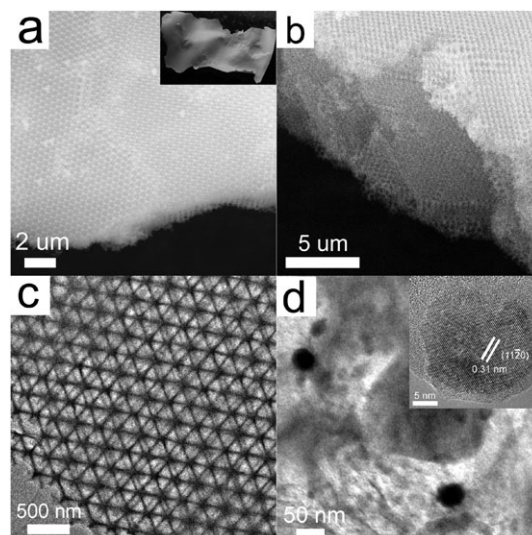
where  $\epsilon(r)$  is the dielectric function,  $H(r)$  is the magnetic field of the photon,  $\omega$  is the frequency and  $c$  is the speed of light. The equation has solutions only in certain frequencies, while it has no solution in other frequency ranges. That is to say, certain frequencies are prohibited in the periodic dielectric medium, and those prohibited frequencies are the PBG. An approximate estimation of the position of the PBG can be obtained by a modified version of Bragg's law, combined with Snell's law to account for the reduced angle with respect to the normal that light travels upon entering the inverse opal:<sup>14,15</sup>

$$\lambda = \frac{2d_{hkl}}{m} \sqrt{(\varphi n_1 + (1 - \varphi)n_2)^2 - \sin^2 \theta} \quad (2)$$

where  $\lambda$  is the wavelength of the stop band,  $d_{hkl}$  is the spacing between  $(hkl)$  planes,  $m$  is the order of Bragg diffraction,  $\theta$  is the angle measured from the normal to the planes,  $n_1$  and  $n_2$  are the refractive indices of the materials constituting the structure, and  $\varphi$  is the volume fraction of one of the refractive indices, the other being the complementary  $(1 - \varphi)$ . For inverse opals, where the periodicity of the system is distorted by defects, the PBGs are relatively broader and eqn (2) is a good prediction of the photonic stop band position.

The scanning electron microscopy (SEM) images of PC1 are presented (Fig. 1a and b), which indicate that the obtained sample exhibits a long-range 3D ordered structure comprised of interconnected macropores that form an ordered hexagonal arrangement of air spheres. The inset of Fig. 1a displays a typical photograph of PC1 film taken with a digital camera, and its length is over 2 cm. Fig. 1c shows the transmission electron microscopy (TEM) image of PC1 with macropore arrays viewed from  $(111)$  planes. The high-magnification TEM image shows that the NaYF<sub>4</sub>:Yb,Er nanoparticles are dispersed in the macroporous wall (Fig. 1d). The high-resolution TEM image (the inset in Fig. 1d) also demonstrates that the embedded NaYF<sub>4</sub>:Yb,Er nanoparticles are of single-crystalline nature enclosed by the  $(11\bar{2}0)$  plane, and the polyhedron shape is affected by the calcination.

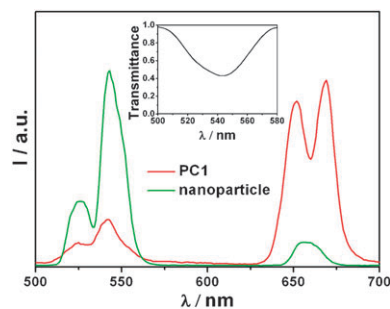
The UC luminescence spectrum of NaYF<sub>4</sub>:Yb,Er nanoparticles displays two typical emission bands upon excitation with a 980 nm laser diode: at 520–570 nm, attributable to the radiative transitions from (<sup>4</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>) to <sup>4</sup>I<sub>15/2</sub> (green, relatively intensive), and at 630–680 nm from <sup>4</sup>F<sub>9/2</sub> to <sup>4</sup>I<sub>15/2</sub> (red, relatively weak) of Er<sup>3+</sup> (Fig. 2).<sup>16</sup> The UC luminescence spectrum of PC1 is also presented in Fig. 2. Interestingly, a relatively intense red emission at about 655 nm was observed, while the intensity of green emission at 520–570 nm decreased sharply. The inset of Fig. 2 clearly shows the presence of a stop band at about 545 nm for the PC1 sample, which compared well with the expected value calculated from eqn (2). More importantly, this PBG matches well with the green emission of NaYF<sub>4</sub>:Yb,Er. Hence, the luminescence spectrum is affected by the 3D ordered structure and the green emission from (<sup>4</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>) to <sup>4</sup>I<sub>15/2</sub> is suppressed significantly. That is, the emission of an emitter could be tuned by employing photonic crystals with a PBG in a desired range of wavelengths. Meanwhile the emission spectra of the PC1 sample were measured at different angles with respect to the surface normal (ESI,† Fig. S2). The green emission gradually recovered with



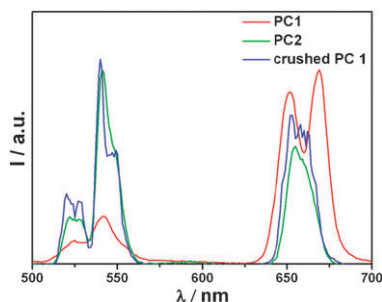
**Fig. 1** (a) SEM image of SiO<sub>2</sub> inverse opals embedded with NaYF<sub>4</sub>:Yb,Er nanoparticles (inset: photographic image of the inverse opals). (b) SEM image under a 45° angle showing the thickness of the inverse opals. (c) TEM image of the inverse opals. (d) High-magnification TEM image showing the NaYF<sub>4</sub>:Yb,Er nanoparticles in the inverse opal wall (inset: HRTEM image of the NaYF<sub>4</sub>:Yb,Er nanoparticles).

increasing angle, and this indicates that the stop band of PC1 changes with angle, in agreement with eqn (2).

We are motivated to disclose the effects of the stop band on the optical properties of the guest NaYF<sub>4</sub>:Yb,Er nanoparticles. For this purpose, the choice of reference is of fundamental importance. The best way to study the effect of the PBG is to mismatch the PBG and the NaYF<sub>4</sub>:Yb,Er nanoparticles, by growing the inverse opal from PS colloidal spheres of a different size. Therefore, the reference sample PC2 was grown from 807 nm PS colloidal spheres (ESI,† Fig. S3) and the PBG position was around 836 nm (ESI,† Fig. S4). Since the PBG of PC2 resides out of the range of both the red and green emission bands of the NaYF<sub>4</sub>:Yb,Er nanoparticles, the UC luminescence spectra of PC2 is unaffected by the 3D ordered structure, and it shows a more intense green emission compared to the red one (Fig. 3). Thus, it is reasonable to deduce that the photonic crystal effects are responsible for the difference in the optical properties of the PC1 and PC2 samples, since the two samples were fabricated under the same conditions and with similar 3D ordered structures. To further confirm the influence of the PBG of the materials on the UC



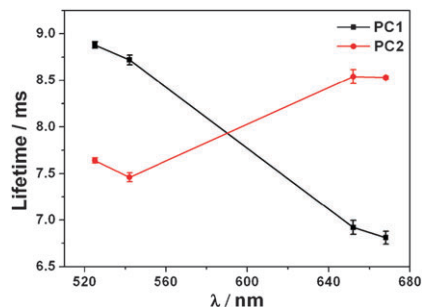
**Fig. 2** The emission spectra of the PC1 sample and NaYF<sub>4</sub>:Yb,Er nanoparticles (inset: transmission spectrum).



**Fig. 3** The emission spectra of the PC1 sample, reference PC2, and crushed PC1 sample.

photoluminescence properties, the as-prepared PC1 sample was directly ground to destroy the regular 3D ordered structure, and this was confirmed by the SEM image (ESI,† Fig. S5). The emission spectra of the original and crushed PC1 samples are shown in Fig. 3. The green emission intensity is recovered when the framework was crumbled, which further confirms that the suppression of the green emission of the guest NaYF<sub>4</sub>:Yb,Er nanoparticles was attributable to the influence of Bragg diffraction in the PC1 sample. The behaviour of the lifetimes of the PC1 and PC2 samples at different wavelengths is presented in Fig. 4, which unambiguously shows lengthening within the range of the PBG. Owing to the complex behavior of the lifetimes, which can be explained by the different quenching constants of Er<sup>3+</sup> depending on their locations, the PC1 and PC2 samples were fabricated under the same conditions. Therefore, the non-radiative contributions were the same for all samples, and the lifetime changes were a result of the changes in the radiative lifetime. According to theoretical calculations that have been done for perfect photonic crystals with high dielectric contrast,<sup>17</sup> the formation of a PBG changes the density of states, and as the density of states increases, the lifetime becomes shorter. Since the green emission of the guest NaYF<sub>4</sub>:Yb,Er nanoparticles is in the PBG range for PC1, this spontaneous decay is inhibited, which leads to the increase of the corresponding luminescence lifetime. In contrast, the photonic stop band of the reference sample PC2 is out of the green emission wavelength, so the lifetime decreased. Photonic crystals have been demonstrated as an effective way of controlling the radiative lifetime.

In this work, a novel UC photonic crystal was fabricated as an air sphere SiO<sub>2</sub> inverse opal embedded with NaYF<sub>4</sub>:Yb,Er nanoparticles. Furthermore, we successfully achieved the



**Fig. 4** Lifetimes of the PC1 and the reference sample PC2 at different wavelengths.

tuning of the UC optical properties of the NaYF<sub>4</sub>:Yb,Er nanoparticles by controlling the structure of the photonic crystal and the direction of measurement. It has been shown that the luminescence lifetime of the NaYF<sub>4</sub>:Yb,Er nanoparticles within this photonic crystal structure is altered. This increase of luminescence lifetime can be explained by the suppression effect of the PBG on the spontaneous emission of NaYF<sub>4</sub>:Yb,Er. This research not only realizes the colour modification of UC emission, but also opens the opportunity to control the propagation of photons.

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