

Inhibition and enhancement of spontaneous emission using photonic band gap structures

Rajesh V. Nair^{1*}, Anjani K. Tiwari², Sushil Mujumdar², B.N. Jagatap¹

¹Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai, India 400 085

²Nano-Optics and Mesoscopic Optics Laboratory, Tata Institute of Fundamental Research, Mumbai, India 400 005

*Corresponding author. Tel: (+91) 22 25592306; Fax: (+91) 22 25505151; E-mail: rvnair@barc.gov.in

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ABSTRACT

We discuss experimental results demonstrating the inhibition and enhancement of spontaneous emission of dye molecules embedded in a nanophotonic structure. This is achieved in our all-solid self-assembled photonic crystals consisting of dyed-doped polystyrene spheres. Our samples exhibit well-resolved photonic stop gap with high reflectivity and photonic strength. Laser induced emission experiments reveal an inhibition of $\sim 70\%$ of emission intensity in the photonic stop gap wavelength range. Also, we discuss the enhancement of spontaneous emission intensity near the blue side of the stop gap. Our results have implications in photonic devices, such as, low-threshold lasers and efficient lighting devices. Copyright © 2013 VBRI press.

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micro cavities and Metamaterials. Currently, he is building an ambitious program on nanophotonics in BARC, Mumbai.

Rajesh V Nair obtained PhD in the area of light propagation in photonic crystals from Indian Institute of Technology, Mumbai. He was a postdoctoral research fellow at the complex photonic systems group at University of Twente, The Netherlands. He was the recipient of Dr K S Krishnan Fellowship from Department of Atomic Energy and young scientist award from Indian Science Congress Association. His research interests are light emission and propagation in random and non-random photonic structures, micro cavities and Metamaterials. Currently, he is building an ambitious program on nanophotonics in BARC, Mumbai.



Sushil Mujumdar completed his PhD in 2001 from the Raman Research Institute, Bangalore in the field of light propagation in passive and active random media. He followed up with postdoctoral research in coherent random lasing and near-field optics in LENS, Florence, University of Alberta, Canada, and ETH, Zurich. He has now set up a programme on Nano-optics and Mesoscopic Optics in the TIFR, Mumbai.

Introduction

Spontaneous emission is a process by which an excited atom de-excites to the ground state by emitting its excess energy in the form of photons [1]. Manipulating spontaneous emission of light source has paramount importance in understanding the light-matter interactions which in turn provides a platform for spectroscopic analysis and technological breakthroughs [2]. For example, in a laser system, spontaneous emission considered being the main component to the loss occur in laser cavity and therefore any attempt to suppress it will allow lasing threshold to reach at very low pump energies. On the other side, enhancement of spontaneous emission increases lighting capability in our house hold lighting devices, and in light emitting diodes (LED). Hence the suppression and enhancement of spontaneous emission is very important for future low-threshold lasers and lighting devices and a platform to perform such tailoring of spontaneous emission is high on demand. Photonic band gap structures are one such platform where the spontaneous emission can be enhanced or suppressed, at the desired frequencies, for different polarization states of light [3-7].

Photonic band gap structures (PBG) or photonic crystals is belonging to a class of nanophotonic structures in which dielectric constant or refractive index is periodically altered along three-orthogonal directions [4, 5]. The spatial periodicity is half the wavelength of light, for which the PBG structure is designed to function, in order to satisfy the Bragg's law $\lambda = 2d\cos\theta$ (where λ is the

wavelength of light, d is the spatial period of the structure and θ is the angle of incidence of light with normal to the surface). Light of wavelength satisfying the Bragg condition is reflected back that appear as a peak in reflectivity spectra and trough in transmittance spectra. This is called photonic stop gap wherein light is not allowed to propagate through the PBG structure, in that particular direction. Therefore the Bragg diffraction of light waves is the basis of photonic stop gap formation. This stop gap is also manifested in the dispersion relation for photons, similar to electrons propagating in a semiconductor, wherein stop gaps arises along particular symmetric point of primitive unit cell in reciprocal lattice space. When the stop gap is overlapped, at the same incident light wavelength, along different directions in reciprocal lattice for different polarization states of light, a photonic band gap is formed [8]. As a consequence of this, local density of states (LDOS) for photons is zero inside the band gap [4, 9]. Also the LDOS enhances near photonic band edges due to the presence of low group velocity modes as the LDOS is inversely proportional to the group velocity [10]. Away from the band gap the LDOS behaves similar to that in a homogenous medium [9]. At the stop gap wavelength light is not allowed to propagate in the PBG structure irrespective of the incident directions for different polarization states of the incident light. By the same reasoning that a light source which is being excited inside the photonic band gap and if the emitted frequency is same as the band gap frequency, the light source cannot emit as there is not states (LDOS ~ 0) available for the emitted photons to couple. This indicates that photons cannot decay through radiative process but can release its excess energy through non-radiative process which is independent of band gap frequency [11]. This can lead to atom-photon bound states, an active area of research in quantum optical regime. It is a challenging task to observe PBG due to constrains imposed by the crystal symmetry and the required refractive index contrast between the constituent building blocks [12]. For a crystal lattice in which unit cells having face centered cubic (*fcc*) symmetry, the required refractive index contrast for PBG is 2.8 whereas that for diamond-lattice unit cells is 2.0. Synthesis of PBG structures with diamond lattice symmetry is tedious and a difficult task whereas many easily achievable self-assembled nanophotonic structures with low refractive index contrast (< 2.8) exhibit *fcc* crystal symmetry [13]. Such self-assembled nanophotonic structures do not have PBG but they exhibit photonic stop gap and therefore serves the purpose to understand light propagation and emission in PBG structures [13].

In this communication, we present our results on all-solid self-assembled PBG structures consisting of dye-doped polystyrene spheres. Our photonic crystal sample avoids the post-infiltration of emitting materials. The emitting material is uniform everywhere inside the samples. Our PBG structures exhibit well-resolved photonic stop gap in the visible wavelength region with high photonic strength. Laser induced emission studies indicate the suppression of $\sim 70\%$ spontaneous emission intensity in the stop gap wavelength range and an enhancement near the blue side of the photonic stop gap.

Experimental

Sample synthesis method

We use inward growing self-assembling method for the synthesis of PBG structures in a time span of three hours [14]. We use colloidal suspensions of Rhodamine B dye-doped polystyrene (PS) spheres of diameter 295 nm (PS295). This diameter is specifically chosen so as to overlap the emission spectra of Rhodamine B dye with stop gap frequency [15]. We use a proper reference sample which is a PBG structure made of same dye-doped spheres of diameter 617 nm (PS617). The stop gap frequency for samples of this diameter does not overlap with Rhodamine B dye emission spectra and therefore can be taken as intrinsic dye emission. Samples are grown on a clean glass substrate of dimension $2\text{cm} \times 2\text{cm}$ which are cleaned in chromic acid overnight and washed well with de-ionized water and ethanol and dried in an oven. We use 200 μL of 2.5 wt% colloidal suspensions for the synthesis of samples. The colloids are dropped at the center of the substrate and it is spread over the entire substrate area using a laboratory syringe. The samples are kept in an isolated place so as to avoid any disturbance. Once the sample growth begins beautiful colors starts appearing on the boundary of the substrate and moves towards the center. The samples are grown in a time span of 3 hours and post-annealed at 75°C to increase the mechanical strength [14].

Characterization methods

Field emission scanning electron microscope (FE-SEM) is used to map the surface morphology of photonic crystal samples. Samples are silver coated prior to imaging to avoid charging effects during electron beam bombardment with samples. Reflectivity and transmittance spectra are measured to probe the photonic stop gap properties. This is done using a Perkin-Elmer spectrophotometer with Halogen lamp as light source with light beam being non-polarized. A silicon detector is used for collecting the reflected or transmitted photons. Laser induced emission experiments are performed using 532 nm light from a frequency doubled Nd: YAG laser as the excitation source with pulse duration of 6 ns. The laser beam is focused on the sample using a lens of focal length 300 mm which results in a spot size of the beam on the sample is $\sim 1\text{ mm}$. The emitted light is collected by another lens and sent to a monochromator and detected with a charge coupled device (CCD).

Results and discussion

The structural morphology of the synthesized photonic crystals as seen in FE-SEM is given in **Fig.1**. **Fig. 1(a)** shows top surfaces of photonic crystals where some point defects are clearly observed. These kinds of point defects are inevitable in self-assembled photonic crystals but it does not affect the optical properties in the low-frequency region. **Fig. 1(b)** shows the representative of (111) plane of the *fcc* lattice [15]. The FE-SEM images confirms the well-ordering of spheres with (111) plane parallel to substrate. All the optical characterization results discussed in the present work are measured from the (111) plane.

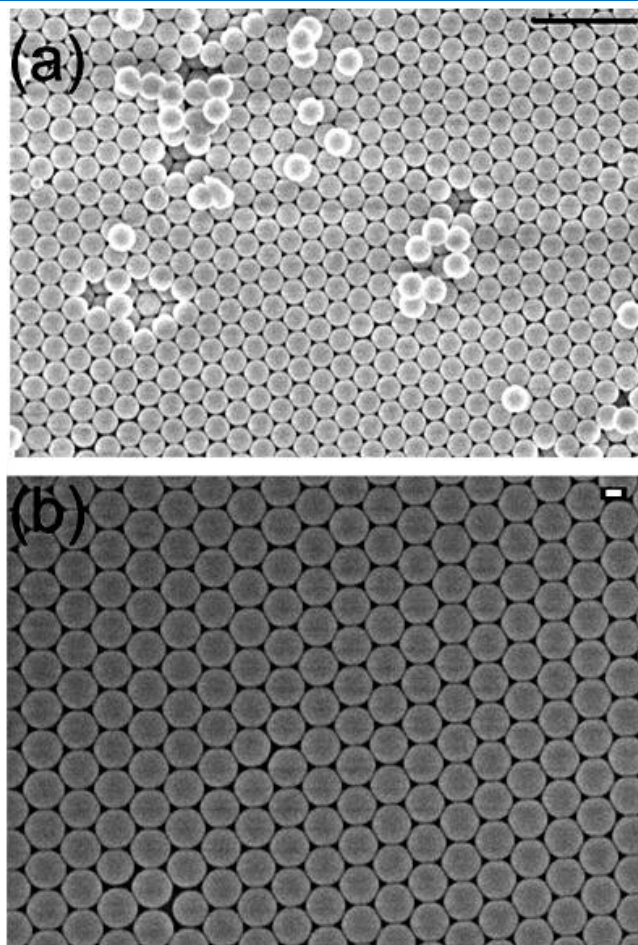


Fig. 1. (a) The FE-SEM image of photonic crystals shows point defects on the surface. (b) Image represents the (111) plane of *fcc* lattice which is parallel to the substrate. The image confirms good ordering of spheres on the surface. The scale bar is 1 μm in Fig. 1(a) and 100 nm Fig. 1(b).

Fig. 2 shows reflectivity and transmittance spectra measured from the (111) plane of PS295 (a) and PS617 (b) photonic crystals, respectively. A peak in reflectivity spectra (solid line) is accompanied by a trough in transmittance spectra (open symbols) represents the signature of photonic stop gap [13]. At the stop gap frequency the structure becomes photonic insulator. The stop gap wavelength is at ~ 603 nm in **Fig. 2(a)** and that at 1350 nm in **Fig. 2(b)** due to difference in lattice constant (sphere diameter) even though the photonic crystals are fabricated using the same material. In **Fig. 2(a)** transmittance spectra shows abrupt decrease in transmittance value (marked with a box) near the blue side of the stop gap which is due to the Rhodamine B dye absorption. This is absent in **Fig. 2(b)** near the blue side of the stop gap and hence it is not related to the photonic structure.

The photonic strength (S) or the full width at half maximum of the reflectivity peak is estimated to be 6.1% which is in good agreement with theoretical calculation on similar PBG structures [16]. The Bragg length (L_B), i.e., the distance through which light propagates inside the structure at the stop gap wavelength in the [111] direction is estimated using the relation [16]; $L_B = 2\pi/d_{111}S$, where $d_{111} = 0.816D$ is the distance between the lattice planes, D being

the sphere diameter. The L_B is estimated to be 2 μm . In the long wavelength side of the stop gap, in **Fig. 2(a)** and 2(b), the observed oscillations of interference fringes is due to uniform thickness of sample and are called Fabry-Perot (F-P) fringes. The thickness of the samples can be estimated from these F-P fringes using the relation [17], $t = 1239/2n_{\text{eff}}\Delta E$, where n_{eff} is the effective refractive index of the photonic crystal structure, ΔE is the difference in energy values in eV of the F-P fringes. The estimated value of t is ~ 7 μm and $t \sim 2.8L_B$. This indicates that finite size effects are avoided in our photonic crystals and therefore exhibit rich optical response [18]. In **Fig. 2(b)**, in the wavelength range of 400 to 800 nm, many reflectivity peaks appear with low value of reflectance $\sim 10\%$. These are second- and third- order photonic stop gaps. Their observation indicates superior optical quality of our photonic crystals [19].

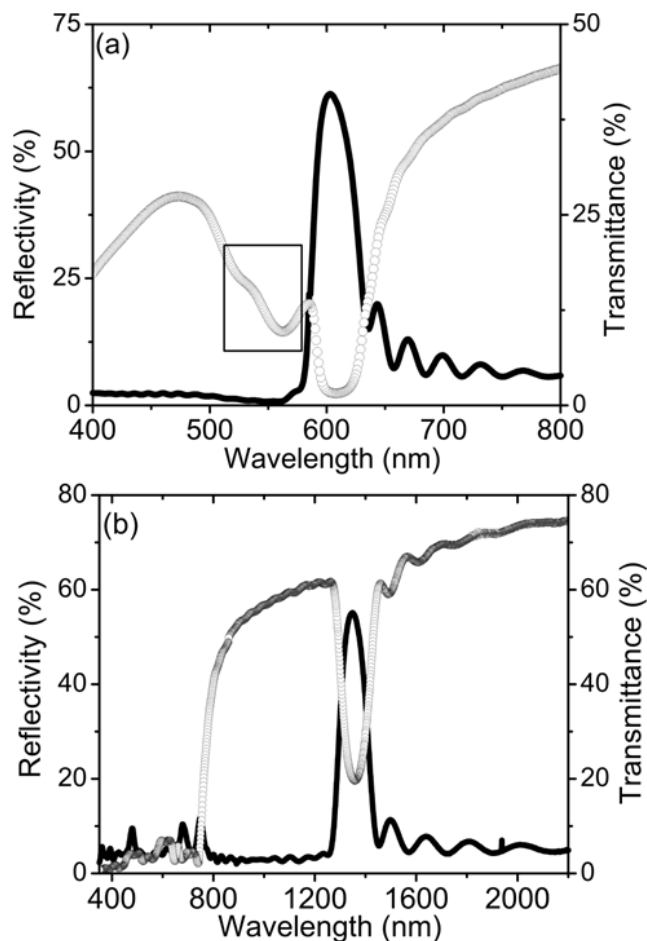


Fig. 2. (a) Reflectivity (solid line) and transmittance (symbols) spectra for photonic crystals of sphere diameter 295 nm indicates stop gap at 603 nm. The decrease in transmittance around 550 nm (marked with square box) is due to absorption of Rhodamine B dye. (b) Reflectivity (solid line) and transmittance (symbols) for photonic crystals of sphere diameter 617 nm indicates stop gap at 1350 nm. The peak in reflectivity spectra and trough in transmittance spectra are in good agreement indicate the signature of stop gap in both (a) and (b).

Angle-resolved reflectivity measurements reveal stop gap at different angles of incidence. With increase in angle of incidence, the stop gap shifts towards shorter wavelength region in accordance with Bragg's law [14]. The peak reflectance and the width of the stop gap are nearly constant

for an angle of incidence of 8° to 40° . Beyond this angle of incidence, multiple crystal planes contribute to the Bragg diffraction and are called Bragg wave coupling regime [20]. **Fig. 3** represents the low (open circle) and high (closed circle) band edge wavelength, at the half maximum of reflectivity peak, in the angular range of 8° to 30° . The closed and open squares represent the edge wavelength at the half maximum of emission spectra measured from the Rhodamine B dye-doped polystyrene colloidal suspensions. The strong overlap between the stop gap and the emission spectra occur in the angular range of 20° to 30° is clearly evident in **Fig. 3** (see the dashed rectangle). Therefore we expect a strong modification of dye emission in this angular range due to the presence of stop gap.

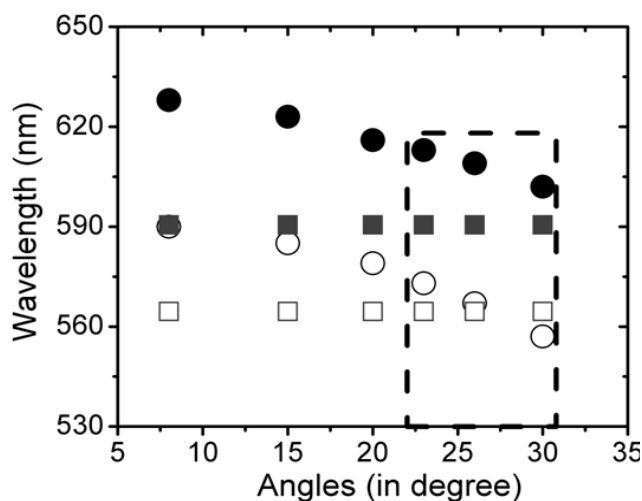


Fig. 3. The stop gap edge wavelength and the dye emission spectra in the angular range of 8° to 30° . The open and closed circles represent the low and high band edge wavelength of the photonic stop gap. The open and closed squares represent the edge wavelength at the half-maximum of emission spectra from Rhodamine dye-doped colloidal suspensions.

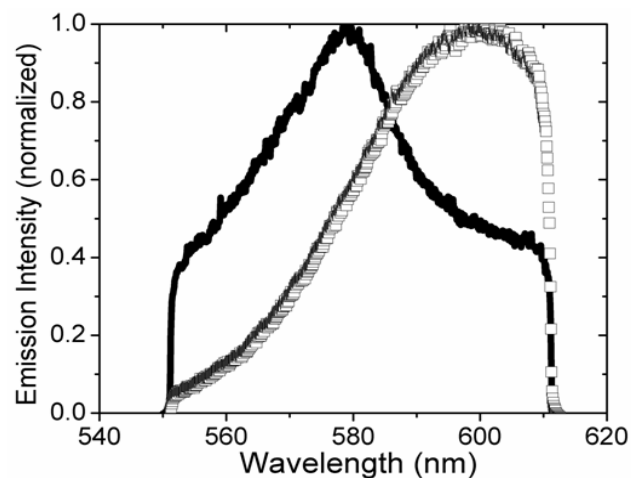


Fig. 4. The emission spectra measured at an angle of 23° to the [111] direction from PS295 (solid line) and PS617 (symbols). Emission spectra measured from PS295 photonic crystal shows abrupt decrease in emission intensity around 595 nm due to the presence of stop gap. The emission spectra measured from PS617 do not show any changes in emission intensity as it do not have stop gap in the spectral range of emission measurements.

The laser induced emission spectra measured at very low pump energy (~ 0.73 mJ) from PS295 and PS617 photonic crystals is given in **Fig. 4** as solid line and symbols, respectively. The measurements are done at an angle of 23° with normal to the [111] direction. The pump energy is kept low in order to avoid any gain effects to participate in the emission process. The emission intensity measured from PS617 shows emission spectra centered at 600 nm. This represents intrinsic emission spectra of Rhodamine B dye as the stop gap is not overlapped with emission wavelength range. Therefore we use PS617 as a proper reference sample as it has the same crystal symmetry, filling fraction, and the same dye is doped within the sphere. The only difference is in the stop gap wavelength range. The emission spectra measured from PS295 shows inhibition of emission intensity in the wavelength range of 585 to 610 nm and also the emission maximum is blue shifted.

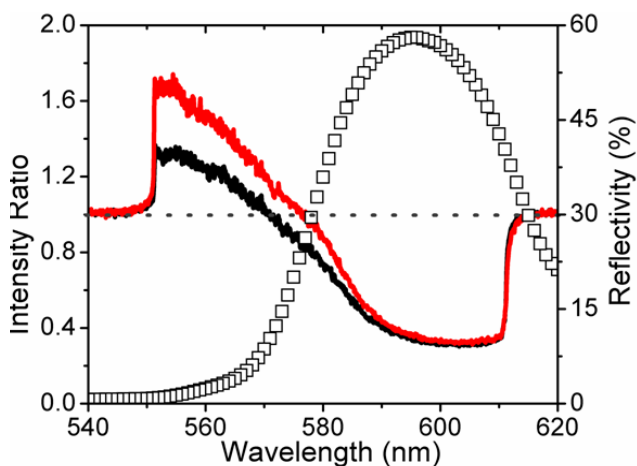


Fig. 5. The emission intensity ratio between PS295 and PS617 photonic crystal samples at two different incident pump energies of 0.72 mJ (red line) and 0.12 mJ (black line) together with the photonic stop gap (open symbols). The intensity ratio shows clear inhibition of emission intensity which is in agreement with stop gap. Note that the intensity ratio is above unity in the blue side of stop gap.

The emission intensity ratio between PS295 and PS617 photonic crystals is given in **Fig. 5** for two incident pump energies of 0.72 mJ (red line) and 0.12 mJ (black line). Normally one expects the intensity ratio to be unity. But in **Fig. 5** we observe strong suppression of emission intensity in the wavelength region of photonic stop gap (open symbols). The suppression in emission intensity is quantified as $\Delta I/I_0$ and is estimated to be 70% at 600 nm. This suppression in emission intensity is higher than that reported for photonic crystals infiltrated with dye suspensions [16]. It is also interesting to see the peak reflectivity at the stop gap wavelength is $\sim 60\%$ and the suppression in emission intensity is observed to be 70%. Therefore we quantitatively showed the photonic stop gap using an externally incident waves (symbols) and an internally excited light source (solid line) in **Fig. 5**. The suppression of spontaneous emission which in turn provides the platform to design the low-threshold lasing action from nanophotonic structures [21-23]. Also we observe an enhancement of spontaneous emission intensity near the blue side of the stop gap. This can be qualitatively visualized as follows. When a source is excited inside the

photonic crystal, the emitted photons are diffuse and propagate in all-possible directions. If the emission wavelength matches with stop gap wavelength, then the emitted photons cannot escape in the stop gap direction where it is back reflected due to Bragg diffraction. But the diffused photons are found to have a higher probability to escape near the blue side of the stop gap. This can be explained using the so-called escape function which essentially quantifies the probability of photons to escape from photonic crystals [24, 25]. Therefore, we have conclusively demonstrated that well-resolved inhibition and enhancement of spontaneous emission can be achieved using self-assembled PBG structures. Such inhibition and enhancement of spontaneous emission is helpful to design better lighting source, for example, low-threshold lasers and LED. Our results also have implications in quantum information processing and quantum electrodynamics.

Conclusion

We have discussed the synthesis and characterization of all-solid dye-doped polystyrene colloidal photonic crystals. Our photonic crystals exhibit well-resolved photonic stop gap in the visible and near-infrared wavelength region. Through laser induced emission measurements we observed an inhibition of 70% in emission intensity inside the stop gap and an enhancement of emission intensity near the blue side of the stop gap. The experimental results are compared with a proper reference sample. Our results open new avenues for designing low-threshold lasers and high efficient lighting devices.

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