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# Enhancement of photoluminescence from defect states in ZnS random photonic crystal: An effect of electronic and photonic mode coupling

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This paper reports on the enhanced defect state emission from ZnS in the form of a random photonic crystal (RPC) medium. ZnS photonic crystals with varied randomness are fabricated by colloidal self assembly of ZnS nanospheres (215 ± 10 nm). Reflection and transmission studies reveal mid band gap wavelength at ∼435 nm. The band structure calculated for BCC lattice with reduced packing fraction (53%) is in good agreement with experimental results. The reflection due to the photonic band gap diminishes with increased randomness in the nanosphere arrangement. The features of fluorescence from ZnS are modified in the RPC medium, resulting in suppression at wavelengths in the photonic band gap region and an enhancement at band edge wavelengths of 415 and 468 nm. This enhancement becomes less prominent with increasing randomness in the structure. Interestingly these two modes correspond to the electronic defect states of ZnS. Emission enhancement is shown to be due to the strong coupling of electronic defect states and photonic band edge states which is facilitated by randomly scattering slow Bloch modes in the ZnS RPC. Fabrication of RPCs by colloidal self-assembly with specifically designed degrees of randomness (leading to controllable features of emission) provides scope for the design of low threshold random lasing systems. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4862927]

## I. INTRODUCTION

Spontaneous and stimulated emissions are the two significant emission processes that occur in material media. The emission rate is dependent on two major factors, namely, the strength of transition, given by transition dipole moment, and the electromagnetic (EM) modes available in the environment of the emitter. The nature of the emission can be modified by changing the EM modes available in the environment surrounding an emitter. Hence, control of emission and propagation can be achieved by modifying the structural environment of the medium in which the emitter is embedded. Based on this idea, artificial structures such as photonic crystals (PC) and photonic glass (PG) whose refractive index variation is periodic and random, respectively, are studied extensively in last decade.[1–8]

PC can provide the photonic stop band (forbidden band) for a certain frequency window due to its periodic variation of refractive index. Lasing or enhanced emission is achieved by two ways in PCs. One is by creating defects that induce a photonic defect mode emission where the PC works as the cavity and provides a high local density of states (LDOS). The other is the use of slow Bloch modes (SBM), which are the modes that travel with a relatively lower group velocity and has a high density of photonic states. These modes can enhance emission at wavelengths close to photonic band edges.[9,10] On the other hand, PG provides high light-matter interaction through multiple scattering due to the random arrangement of scattering centres. Several interesting phenomena such as weak localization and strong localization (Anderson localization) of light can be observed in PG with a high density of scatterers.[11]

From the lasing point of view, a lower threshold is possible in PC than PG medium. The idea of using PC and PG concepts together has recently been shown to be effective for the observation of random lasing at low thresholds. Such a structure which contains regular arrangements of particles with some degree of randomness is termed as random photonic crystal (RPC).[12] Modes with high quality factor are obtained by optimising the randomness in PC with sufficiently wide band gaps. Moreover, it is also shown that optimal randomness in RPC depends on size of RPC.[13] PCs of wide band gap with the appropriate amount of randomness have been shown to be good candidates for the realization of Anderson localization modes, which is possible due to scattering of slow Bloch modes (band edge modes).[14] In most of the reported works, RPC fabrication is done by lithographic techniques which have limitation in terms of wide area fabrication and cost.[13–15] Colloidal self-assembly is an easier and more economic technique for the fabrication of wide area PC. Using this technique, randomness in arrangement can be controlled by varying the colloidal pH and evaporation temperature. Theoretical studies have been carried out on colloidal self-assembly, formation of PC, introduction of randomness, and effect of disorder on the optical properties of RPC.[16] Fabrication of RPC with wide photonic band gap using a material that has broad absorption and emission is advantageous for study of localized states. In addition, the scattering of slow Bloch or band edge modes makes it a good medium for low threshold lasing applications.

Fabricating the RPC with fluorescent material provides scope for the study of the effect of environment on

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fluorescence emission from the dielectric backbone. ZnS is known to have a rather broad emission band in visible region upon UV excitation. ZnS being a direct and large band gap semiconductor with a high refractive index (2.3–2.4),[17] is a promising material for application in micro lasers and sensors. ZnS works as the dielectric backbone as well as the emitter in the RPC structure in the present work. A high refractive index contrast is possible because only the ZnS and the surrounding air medium contribute to the effective refractive index.

## II. MATERIALS AND METHODS

The method used to synthesize the monodispersed nanospheres is similar to that reported by Kim *et al.*[18] In this method, 1.2 g of zinc nitrate hexa hydride and 3 g of TAA (thioacetamide) is dissolved in 100 ml of deionised water and stirred for 15 min by adding 150 $\mu$l of nitric acid, heated at 80 °C for 30 min. The solution is cooled rapidly in cold water and filtered to remove unreacted compounds. The filtered transparent solution is allowed to settle for 48 h at room temperature allowing the nanoparticles to agglomerate slowly and form monodispersed spheres. The solution slowly acquires milk white colour and is centrifuged for 10 min after which the light yellowish white coloured sediment is collected and dried. Material characterization is done by XRD, Field emission scanning electron microscope (FESEM), and energy dispersive spectra (EDS).

Colloidal solutions with different pH values are prepared by dispersing the ZnS nanosphere powder in ethylene glycol (6 mg/ml). All samples are fabricated in the form of films by horizontal substrate solvent evaporation technique. Samples are prepared at different pH values and different temperatures. First set of samples at pH 4, 7, and 11 are labelled as SP1, SP2, and SP3, respectively. The second set of samples fabricated at pH 7 but different evaporation temperatures 100 °C and 180 °C are labelled as ST1 and ST2, respectively.

The formation of photonic stop band and band edge effects on emission of the ZnS are analysed using reflection, transmission, and emission spectroscopy. Reflection studies are carried out using CARY 5E UV-VIS-NIR spectrometer by diffusive reflectance arrangement. Transmission studies are done using a JASCO V-570 UV–Vis-NIR spectrophotometer and emission studies are done using a JASCO FP-6600 spectrofluorometer. In emission studies, the sample is excited using 250 nm incoherent UV light. Simulation of the photonic band structure and band structure calculations is done using Lumerical Finite difference time domain (FDTD) solutions.[19]

## III. RESULTS AND DISCUSSION

Figure 1(a) shows the FESEM image of nanospheres synthesised by homogeneous precipitation method. Scattering in the samples is analysed using Mie plots software, with particle size 215 nm, refractive index of 2.35, zero absorption, and dispersity 5% as input parameters. There is a considerable match between theoretical and experimental extinction spectra at 390 nm and 350 nm (Figure 1(b)). From extinction spectra and the FESEM image, the mean size of the particle is determined to be ~215 nm with ±10 nm dispersion. The emission spectrum of the ZnS nanosphere powder dispersed in ethylene glycol is shown in Figure 2. The emission peak due to band to band transition occurs at 366 nm, with a considerable emission in the visible region which could be due to defect states.

A regular, almost periodic arrangement of the nanospheres is obtained when particles are self-assembled at pH 4. The FESEM image in Figure 3 shows such an arrangement of the nanospheres. It is also clear that the periodicity is not perfect and structural defects are present. The periodicity is of short range, with random or disordered arrangement of the nanospheres in some regions. This is due to the size dispersion of nanospheres.

The reflectance and transmission spectra of the self-assembled ZnS nanospheres illustrated in Figure 4 have reflection maxima (transmission minima) at ~435 nm. Considering the periodic arrangement of the ZnS nanospheres, the reflection peak at ~435 nm can be attributed to

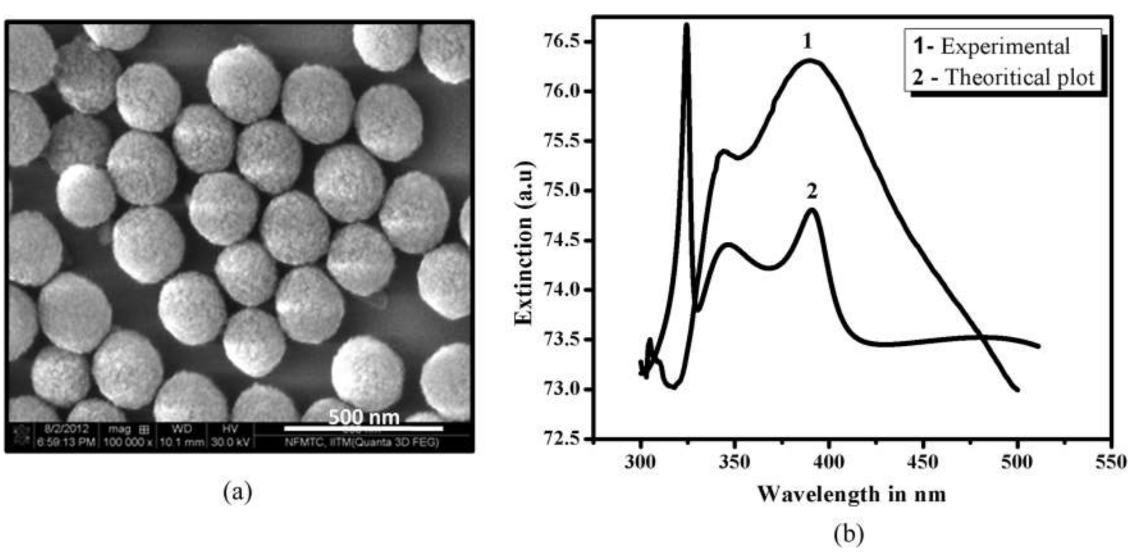


FIG. 1. (a) FESEM image of the ZnS nanospheres synthesized by homogeneous precipitation method; (b) Mie extinction plots (theoretical and experimental).

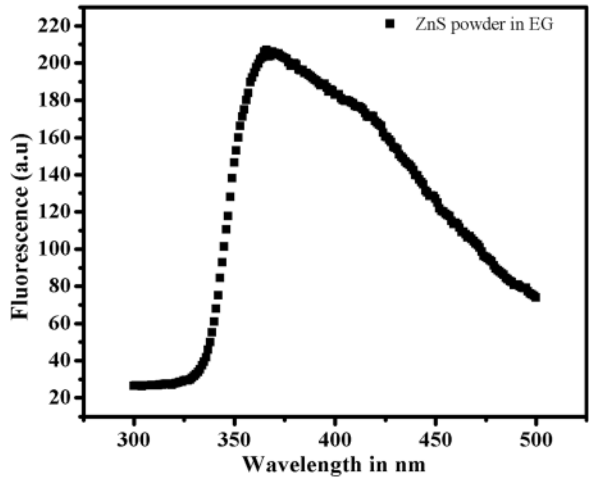


FIG. 2. Emission spectrum of ZnS nanospheres dispersed in ethylene glycol. Band to band emission is at 366 nm and the emission in 400 nm–500 nm region due to defect states.

Bragg's reflection. According to Bragg's law, the photonic mid band gap wavelength is

$$\lambda = 2dn_{eff}\sqrt{1-\sin^2 r}, \quad (1)$$

where $d$ is inter planar spacing, $r$ is the internal angle between the wave vector and the direction of plane, and $n_{eff}$ is the effective refractive index. $n_{eff}$ can be estimated using effective medium approximation.[20] According to most reports available, the probable arrangement arising from self assembly corresponds to FCC or HCP structure. However, for either of these structures corresponding to the present values of particle size and refractive index parameters, the mid band gap wavelength should occur at around 600 nm which is much different from the value of 435 nm, observed experimentally. On the other hand, it has been reported that the most probable structure is BCC when the self assembly process is done at low acidic and low weight percentage conditions.[21–23] This is the case in the present work, as the colloid pH value is ∼4 and weight percentage is less than 1,

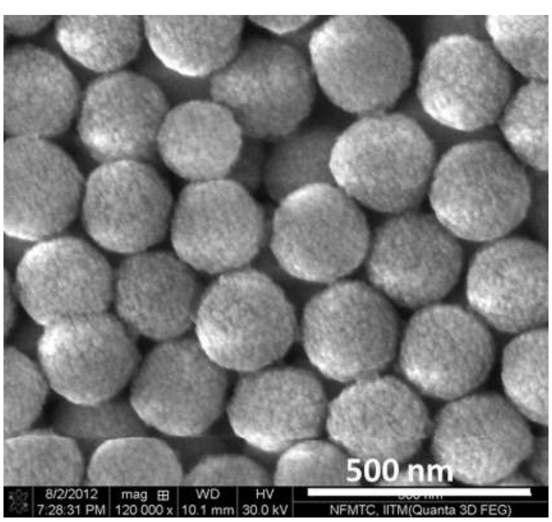


FIG. 3. FESEM image showing the arrangement of the nanospheres.

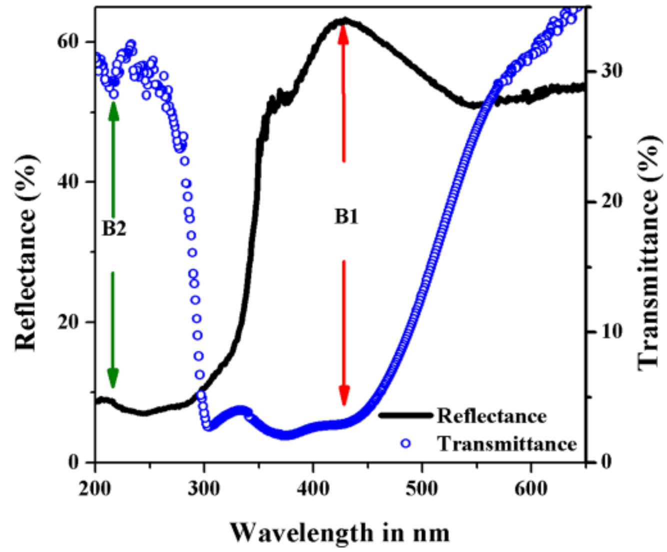


FIG. 4. Reflectance and transmission spectra of ZnS Random photonic crystal showing the mid band wavelength 435 nm.

corresponding to 6 mg/ml concentration. So in this calculation, the arrangement is taken to be a *BCC* lattice with orientation along the [111] plane. Further, self assembly is known to take place along the [111] plane, parallel to the substrate.[24] The variation observed in the theoretically estimated reflection peak (∼445 nm) and the experimentally obtained value (∼435 nm) can be attributed to presence of structural defects (random structures) which are formed during the process of self-assembly, arising from the nature of the fabrication process, which depends on factors such as temperature, colloid concentration, pH value, and the nature of the solvent.

Besides the first order Bragg's reflection at ∼435 nm, the second order Bragg's reflection at ∼210 nm can be observed in both reflection and transmission spectra. The two important features observed in the reflection spectrum are the large half width of the reflection band and the suppression of reflectance in the shorter wavelength side (from 200 to 340 nm). These can be understood by considering the scalar wave approximation for short and long range periodicities in the RPC.[16] The band in the reflection spectrum is wide and has an inverted "V" shape due to the existence of a regular arrangement domains or sites (short range and long

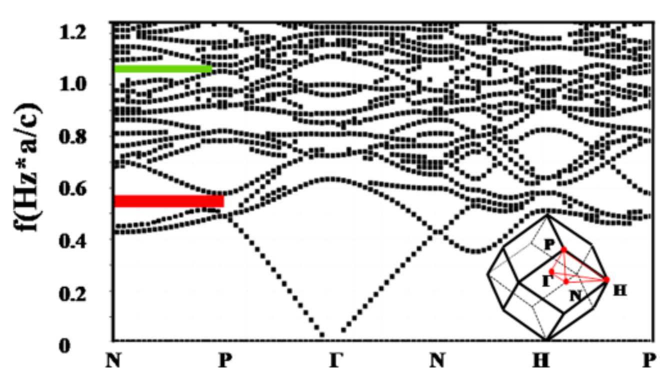


FIG. 5. The band structure calculated for the BCC lattice with reduced packing fraction 53%. Inset: the irreducible Brillouin zone of BCC structure.

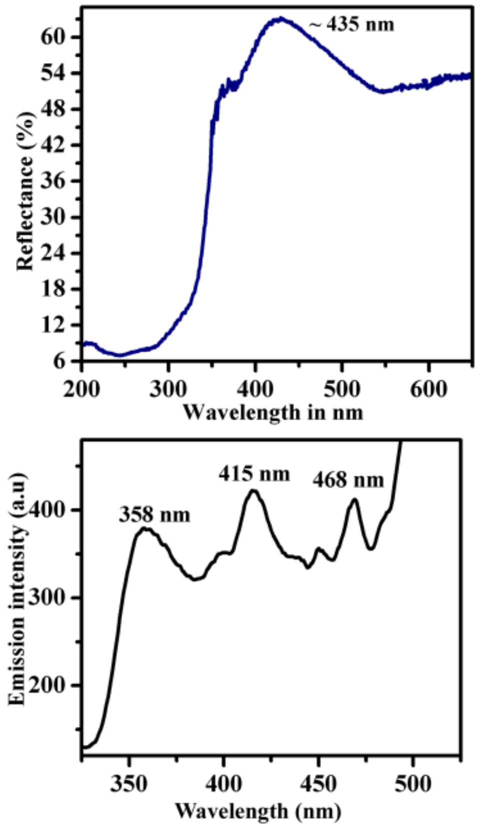


FIG. 6. Reflection (top) as well as the fluorescence emission (bottom) spectra (corresponding to excitation at 250 nm) of ZnS RPC.

range). Strong scattering of shorter wavelengths takes place due to the presence of short range regular domains which leads to suppression of reflection in that region.

For a better understanding of the experimentally observed features of the ZnS RPC, we have theoretically calculated the photonic band structure for BCC lattice with a reduced packing fraction 53% and refractive index 2.35 (Figure 5). The reduced packing fraction is considered because the dispersity of particle size distribution can create voids in the lattice during the process of self assembly. The features of the reflection and the transmission match well with the calculated band structure in Γ-P direction, representing the [111] plane of BCC. The reflection peaks observed experimentally (Figure 4) at 435 nm (B1) and 210 nm (B2) are due to the pseudo photonic band gaps shown in the band diagram (Figure 5) with differently shaded regions.

Figure 6 shows the reflection and emission spectra (excitation at 250 nm) of the ZnS RPC. The emission peak observed at ∼358 nm is due to band to band emission of the material. The two new peaks found at 415 nm and 468 nm with considerably high intensity are due to electronic defect state transitions in ZnS, which are generally weak compared to band to band transitions (358 nm). On comparing the emission and reflection spectra, it is clear that emission corresponding to the reflection band is suppressed, whereas emissions corresponding to reflection band edges (at 415 nm, 468 nm) are enhanced. This indicates that photonic band of RPC structure has a role in controlling the emission of ZnS.

To bring more clarity to the analysis, the emission and corresponding reflection spectra of the two sets of samples prepared at different colloidal pH values (SP1, SP2, and SP3) and evaporation temperatures (ST1 and ST2) are shown in Figures 7 and 8. In both cases, the reduction in the intensity of the reflection peak indicates the increased randomness in nanosphere arrangement. We observe that emission increases from SP3 to SP1 and ST2 to ST1, which is in accordance with the increase in the reflection peak intensity. Thus, it is evident that the defect state emission (415 nm, 468 nm) is enhanced when photonic stop band is strong. As these electronic defect states are close to the photonic band edges, there exists a strong coupling between photonic band edge modes and electronic defect modes.

The coupling of the photonic band edge with the defect states can be explained on the basis of the increased local density of states at photonic band edges due to the existence of slow Bloch modes. In RPC systems, the slow Bloch modes travel from one regular domain to another through random domains by changing their wave vectors, thus undergoing multiple random scattering. Slow Bloch modes are modes

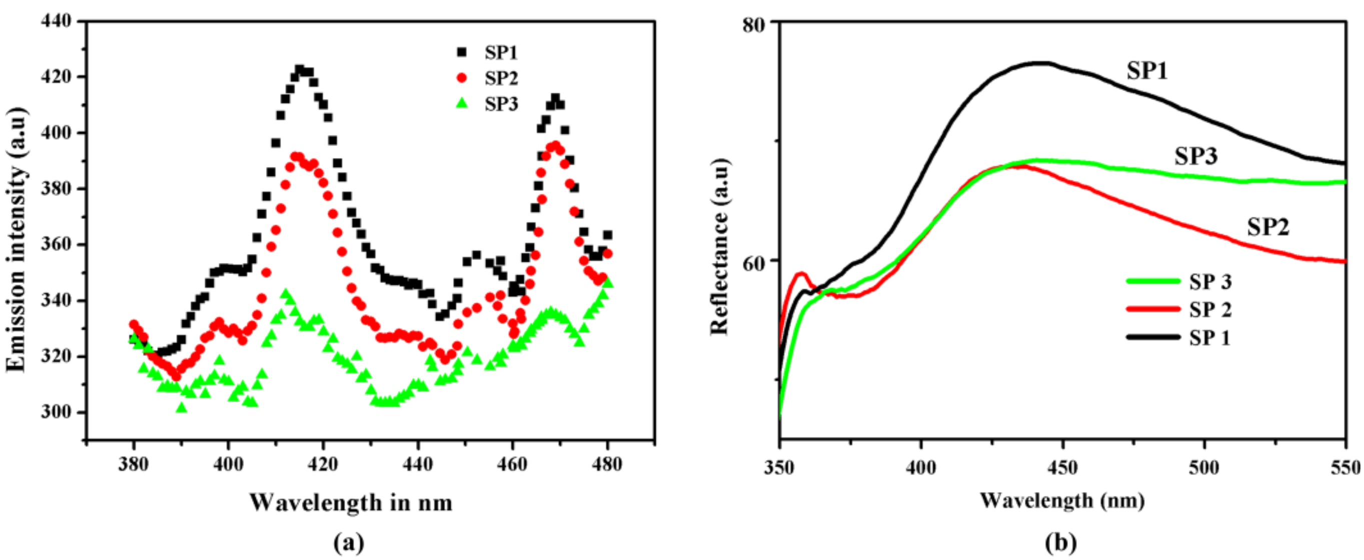


FIG. 7. (a) Emission spectra and (b) reflection spectra of SP1, SP2, and SP3 upon excitation at 250 nm.

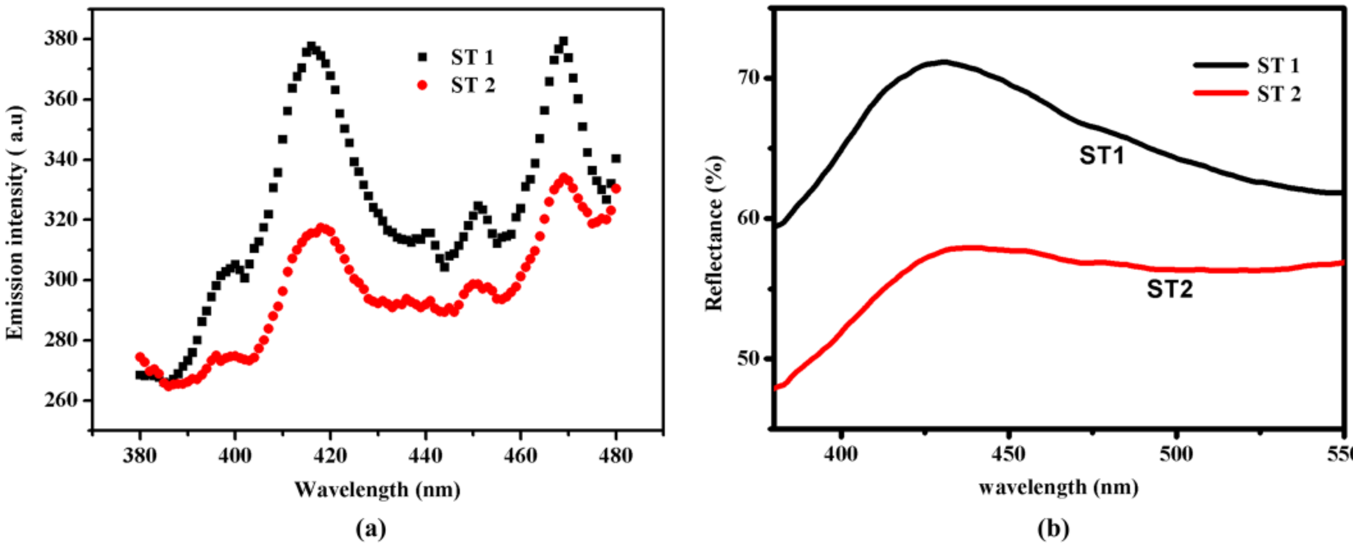


FIG. 8. (a) Emission spectra and (b) reflection spectra of ST1 and ST2.

with high density of states and can provide high probability for electronic transitions at these corresponding wavelengths. In the present case of ZnS RPC, with a dominant periodicity in arrangement, strong Bloch modes can exist and undergo multiple scattering inside the system. The ZnS electronic defect state modes (415 nm and 468 nm) are near the band edge and happen to coincide with the slow Bloch modes. Due to the high interaction between randomly scattering slow Bloch modes and ZnS defect modes, the electronic transitions which are responsible for defect mode emission become more probable thus leading to the defect mode enhanced emission.

## IV. CONCLUSIONS

We have fabricated ZnS random photonic crystals that exhibit the properties of both regular (photonic stop band) and random (Mie scattering) structures. The reflection (Transmission) spectra agree well with the theoretically calculated photonic band structure for BCC lattice (with reduced packing fraction) and show stop bands at around 435 nm and 210 nm. The electronic defect states of ZnS are shown to be coupled strongly with slow Bloch modes (band edge modes) of the RPC, leading to enhancement of emission intensities at 415 and 468 nm. Band edge coupled defect state emission indicates the possibility of using ZnS RPC as an ideal system for low threshold random lasing applications.

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