Emission modification of CdSe quantum dots by titanium dioxide visible logpile photonic crystal

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Air band modes of three-dimensional photonic crystals (3DPCs) have a higher photonic density of states, potentially enabling greater emission enhancement. However, it is challenging to introduce emitters into the "air" region without significantly disturbing the photonic band structure of the PC. Here, we overcome this difficulty by introducing a low refractive index aerogel matrix containing CdSe quantum dots (625 nm peak emission) into a titanium dioxide logpile PC. We observe that the aerogel infiltration indeed preserves the bandstructure. We measure an emission suppression of ~0.25 times inside and an enhancement of approximately three times outside the bandgap with only one vertical unit cell. © *2009 American Institute of Physics*. [doi:10.1063/1.3245309]

Photonic crystals (PCs) provide an excellent platform for light emission control. The periodic arrangement of high and low refractive index in PCs modulates the electromagnetic vacuum[1] resulting in suppression or enhancement of light emission[2] across the frequency spectrum. Emission modification has been reported extensively in two-dimensional slab PC systems[3–5] demonstrating low threshold and ultrafast lasing,[6,7] strong coupling,[8] and single photon generation.[9] However, three-dimensional (3D) PCs, in particular complete 3D gap PCs, offer greater flexibility in directional control of emission as well as stronger emission suppression/enhancement. In 3D systems, emission control has been demonstrated in logpile PCs in the near-IR regime[10,11] and opal[12] and inverse opal PCs[13,14] in the visible. Emission modification of light emitters placed inside a PC depends on the photonic local density of states (PLDOS), which is a function both of the emitter wavelength as well as its position inside the unit cell of the PC.[13,15] Thus far, emission enhancement in PC has been studied by embedding[10,11] or by coating the surface[12,14,16,17] of the high index matrix of the PC with emitters such as quantum dots (QDs). In this case, the dielectric bands where the electric fields of the modes are concentrated in the high index region are responsible for emission modification. We believe this only partially demonstrates the PLDOS enhancement effect of the PC at the photonic band edge since an enhancement of $\sim n^3$ can be achieved even with an unstructured dielectric of refractive index n. On the other hand, if emitters can be localized in the "air" region of the PC, one can more explicitly observe the PLDOS enhancement of the 3DPC. Furthermore, we can also achieve greater enhancement at the higher frequency bandedge corresponding to air bands that has a higher density of states compared to the lower frequency band edge of the dielectric bands.[18,19] Unfortunately, the effects of these "air modes" have been more difficult to study because they involve introduction of liquid dyes[13] or other materials that reduce the refractive index contrast, significantly changing the underlying photonic band structure and potentially destroying the photonic bandgap. Here we demonstrate emission modification of visible emitting CdSe QD introduced into the air region of a four-layer (one vertical unit cell) titanium dioxide (TiO_2) logpile PC utilizing silica aerogel infiltration.

We fabricated the logpile PC in a layer-by-layer fashion using a multilevel electron-beam direct write approach[20] composed of sputter deposited TiO_2 rods.[21] We then infiltrated the air region of the PC and a 1×1 cm^2 piece of Si reference piece by spin coating an ethanolic organic modified silica sol. Upon the final stage of solvent evaporation, the silica gel network expands to form an aerogel without the requirement for supercritical processing as reported previously.[22] We measured the refractive index of the aerogel to be 1.1 ± 0.05 by ellipsometry of the reference sample. The PC/aerogel composite and the reference sample was then treated with 3-mercaptopropyltrimethoxysilane and a toluene suspension of CdSe/ZnS core/shell QDs (NN-Laboratories) with a nominal peak emission wavelength of 625 nm to form a covalently attached layer of QDs on the aerogel surface, following the procedure in our earlier report.[17] The scanning electron microscopy (SEM) image of $a=350$ nm logpile PC before [Fig. 1(a)] and after [Fig. 1(b)] the aerogel infiltration reveals uniform deposition of the aerogel across the sample [Fig. 1(b)], suggesting that the aerogel is mechanically robust despite the low refractive index. The magnified image in the inset further reveals that the aerogel completely fills the air region of the PC up to the third layer. Thus, the CdSe QDs are uniformly distributed within the air band of the PC.

We characterized near normal incidence reflectance spectra of logpile PCs with two different lattice constants ($a=350$ nm and $a=400$ nm) and a rod width of $0.4a$ and rod height of 100 nm before and after CdSe QD infiltration with microspot spectroscopy (Fig. 2), using a silver mirror (>95% reflectivity) as a reference. The reflected light was collected by a $20\times$ objective and coupled to a spectrometer by a 600 μm diameter multimode optical fiber. An iris was inserted behind the objective to limit the range of incidence angle to ~5° while maintaining a sampling spot diameter of ~20 μm. This arrangement enables us to probe interaction of the QD PL with the stacking direction bandgap (ΓX). We characterized the emission modification of CdSe QDs by the

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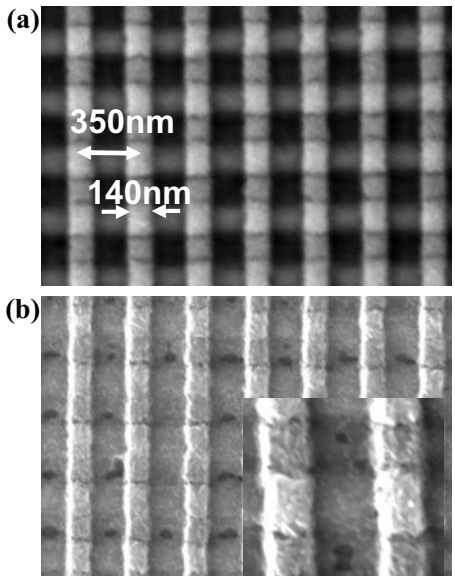

FIG. 1. (a) Top view SEM image of $a=350$ nm lattice constant four-layer logpile PC before the infiltration of aerogel. The rod width is 140 nm. (b) SEM image showing uniform infiltration of the aerogel. Inset shows the aerogel filling up approximately to three layers.

PCs by pumping the sample with a 532 nm solid state laser with 5 mW power and a spot size of ~30 μm incident at 45° to the sample normal (Fig. 2). We introduced a low pass filter with a cutoff wavelength of 550 nm in the collection path to block the scattered pump beam, and collected the emitted light with the same microspot spectrometer setup.

The stacking direction (ΓX) lower order (second to third) bandgap for this structure[21] is seen as a reflectance feature with ~60% maximum at 620 nm and a short wavelength edge at ~600 nm [Fig. 3(a) black solid] for the $a=350$ nm PC. The corresponding values for $a=400$ nm PC [Fig. 3(b) black solid] is at 670 and 640 nm. Upon infiltration with aerogel and CdSe QDs, the reflectance spectra of both lattice constant PCs [Figs. 3(a) and 3(b) gray dashed] shows that the spectral profiles remain essentially unaffected except for a minor shift of <10 nm. This result confirms that the infiltration with aerogel does not adversely affect the band structure of the logpile PC and hence allows us to study its effect on the emission behavior of the light sources. Flouresence microscopy reveals a uniform far-field emission pattern from the PC when excited with the pump laser. We therefore quantitatively measured the PL intensity from $a=350$ nm and $a=400$ nm PCs as well as the reference. Figure 4(a) shows a typical near-normal PL response corresponding to the ΓX direction collected by the apertured microscope objective (collection angle of ~5°). For a meaningful comparison, the PL intensity of the reference sample is normalized to an equivalent volume of CdSe coated aerogel as that of the two PCs. The reference PL shows a Gaussian spectrum centered at 625 nm with a full width at half maximum of 30 nm. The PL response from the $a=350$ nm PC appears strongly modified both in magnitude and spectral shape with a peak at 608 nm; a similar but less pronounced effect is observed for $a=400$ nm PC with a peak at 620 nm. This difference in the PL response between the

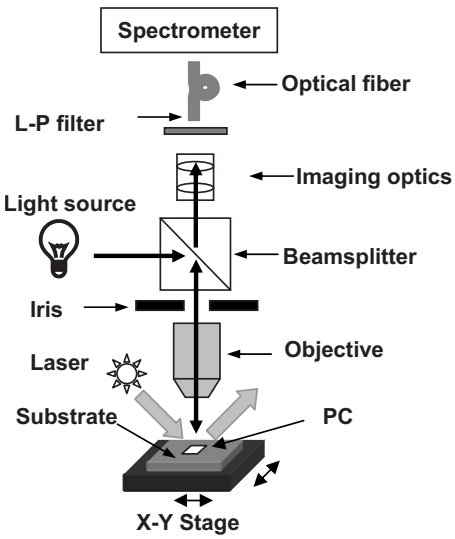

FIG. 2. Optical setup for microreflectance and photoluminescence measurements. Substrate is mounted on a *X-Y* stage to enable the alignment of the laser pump spot with the focus of the objective.

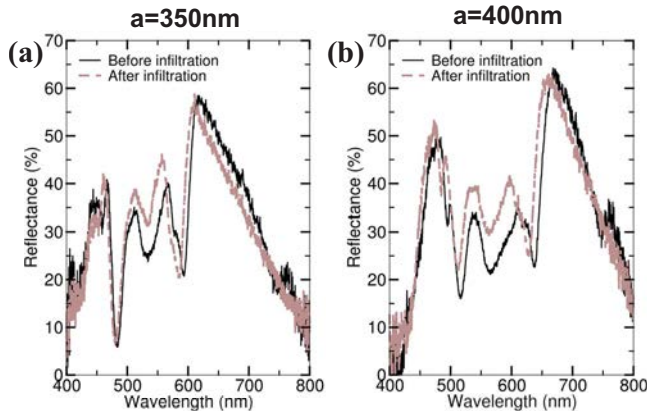

FIG. 3. (Color online) (a) Near-normal optical microreflectance response before (black solid) and after (gray dotted) the infiltration of aerogel and CdSe QDs in $a=350$ nm PC. (b) Near-normal optical microreflectance response before (black solid) and after (gray dotted) the infiltration of aerogel and CdSe QDs in $a=400$ nm PC. In both cases, a negligible change in the spectra is revealed as a result of aerogel infiltration.

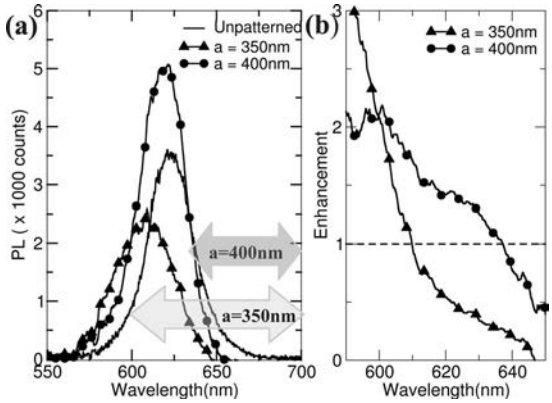

FIG. 4. (a) Photoluminescence response from aerogel+CdSe QD infiltrated $a=350$ nm PC (triangle), $a=400$ nm PC (circle), and reference unpatterned aerogel coated sample (black solid). The bandgap in the normal direction indicated by the light shaded double arrow for $a=350$ nm starts from ~600 nm and for $a=400$ nm from ~640 nm indicated by darker shaded region. PL spectrum from the unpatterned region falls mostly inside the bandgap of $a=350$ nm and outside $a=400$ nm. (b) Ratio of the PL of the devices with respect to the unpatterned reference showing enhancement and suppression of emission by both the devices.

two lattice constants clearly indicates the role of the PC bands on the QD emission. For the $a=350$ nm PC, the QD PL falls predominantly inside the ΓX bandgap [Fig. 4(a) light shaded double arrow], which is suppressed except for a short wavelength tail below 610 nm, which is enhanced. In the case of $a=400$ nm PC, the PL response is blue shifted with respect to the ΓX bandgap [Fig. 4(a) dark shaded double arrow], and thus suppression of the PL response was observed only at the long wavelength tail. We quantified the emission enhancement of the QD by the two PCs by calculating the ratio of emission intensity from the device to that from the reference, between the wavelengths of 590–650 nm [Fig. 4(b)] where the PL response of the QDs is appreciable. This emission enhancement factor for the $a=350$ nm PC drops sharply from ~3.0 down to about 0.25 in this window crossing unity at ~610 nm with a modulation ratio defined as the ratio of enhancement to suppression of ~12.0, while for the $a=400$ nm PC it drops more slowly from ~2.0 down to ~0.6 crossing unity at ~640 nm with a modulation ratio of 3.3. The unity crossing points match closely with the band edges of both the PCs. Edge effects during spin coating resulted in approximately 25% variation in aerogel thickness across the PC sample, which in turn introduced variation in PL intensity from nominally identical devices due to the different quantity of CdSe attached. However, we found that the PL modulation ratio is unaffected as the change in the PL intensity is uniform across all wavelengths. PL modulation ratio for the $a=350$ nm device is approximately twice the value previously reported for a near-IR band gap four-layer GaAs logpile[10] at the short wavelength bandedge. This further evidences stronger interaction of the air band modes when the emitters are in the air region as opposed to the dielectric region.

In summary, we have demonstrated the emission enhancement of CdSe QDs by the air band modes of a visible bandgap TiO_2 logpile PC. We achieved this by spin-coating a low refractive index aerogel nanoparticle suspension followed by covalent attachment of the QDs into the aerogel without perturbing the photonic bandstructure.

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