Incorporation of Quantum Dots into 3D Photonic Crystals for Emission Control

Jiafang Li, Jesper Serbin, Craig Bullen, Min Gu
CUDOS and Centre for Micro-Photonics
Faculty of Engineering and Industrial Sciences
Swinburne University of Technology
PO Box 218, Hawthorn, 3122 Victoria, Australia
Email: jli@swin.edu.au, mgu@swin.edu.au

***Abstract*—In this article we demonstrate infiltration and doping as two efficient and flexible methods for incorporation of PbSe quantum dots (QDs) into three-dimensional (3D) photonic crystals. QDs induced photonic band gap shift was observed by the infiltration method. By employing the two-photon polymerisation technique, 3D photonic crystals were fabricated with QDs doped resin. Investigation will be focused on radiation dynamics and emission control of QDs in 3D photonic crystals.**

Keywords-quantum dots; photonic crystal; infiltration; doping

I. INTRODUCTION

The strong three-dimensional (3D) confinement of light in 3D photonic crystals (PhCs) provides a powerful tool for research on nanocrystals and quantum electrodynamics. Recently, the control of radiation dynamics of quantum dots (QDs) inside PhCs has received a great attention for its scientific significance in quantum optics, as well as its potentials for diverse applications like miniature lasers and solar energy harvesting [1-3]. Here we demonstrate two simple but efficient methods, infiltration and doping techniques, to incorporate PbSe QDs into 3D woodpile PhCs fabricated by the two-photon polymerisation method. Compared with the strict requirements either on operation conditions or on fabrication techniques [1-3], our incorporation methods can be realised in normal environment and has the flexibility for future investigation on emission control at communication wavelength of 1.5 μm.

II. EXPERIMENTS

A. Fabrication of PbSe QDs and 3D PhCs

Based on our technique of fabricating 3D woodpile PhCs [4], we infiltrated the QDs directly into the fabricated PhC structures. By controlling the size distribution of QDs and the fabrication parameters of PhCs, we can achieve the emission wavelength of QDs within, outside, or at the edge of the band gaps of PhCs.

The PbSe QDs in our experiments were prepared by using the method described in [5]. To realise the emission peak around 1.5 μm, we used 0.8 g lead oxide instead of 0.892 g in [5]. Finally, PbSe QDs with absorption spectrum centred at 1400 nm were produced. The diameters of our QDs had a distribution centred at 4.5 nm according to the relationship between absorption peaks and diameters [5]. The QDs in tetrachloroethylene solution and dried QDs on a cover slip were excited by the continuous wave beam generated by a Ti:sapphire laser (Coherent) ranging from 700 to 1000 nm, respectively. Excitation spectra were collected by a single mode optical fibre and measured by an optical spectrum analyzer (AQ-6315E). As shown in Fig 1, the PbSe QDs have an emission spectrum centred at 1473 nm.

Our 3D photonic crystal was a woodpile structure fabricated with ORMOCERs (inorganic–organic hybrid polymer) [6] by employing the two-photon polymerisation technique, which has the flexibility to fabricate arbitrary 3D structures with spatial resolution of 200 nm. By optimising fabrication parameters, a PhC with a partial band gap at stacking direction at 1470 nm was fabricated (see Fig. 1). The transmission spectrum was measured with a Nicolet Nexus fourier transform infrared (FTIR) spectrometer with continuum infrared microscope (Thermo Nicolet). The position of band gap fits well the emission spectrum of QDs, showing the flexibility of investigating the influence of 3D PhCs on QDs radiation.

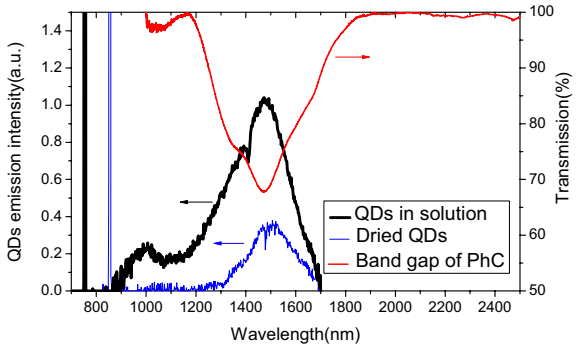

Figure 1. (left) Excitation spectrum of self-made PbSe QDs in solution (black line) and dried QDs on cover slip (blue line). (right) Band gap of 3D woodpile PhC (red line, after baseline).

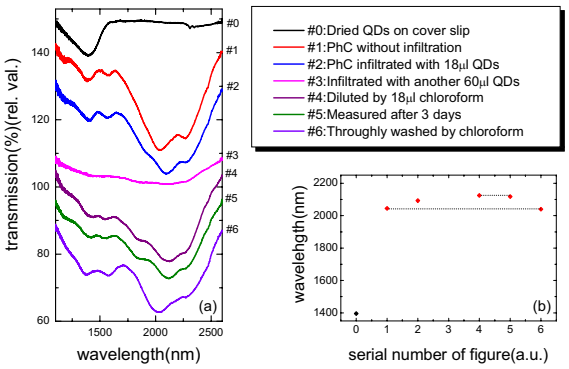

Figure 2. (a) Baselined transmission spectra of QDs and PhC under different processes; (b) Centre wavelength of the photonic band gap in (a). From #0 to #6, the wavelength is 1396, 2045, 2093, none, 2125, 2118, 2040 nm, respectively. From #4 to #5, the spectrum remained unchanged for three days, which showed the repeatable measurements and the stability of infiltrated structures.

B. Infiltration induced shift of band gap of PhC

Fig. 2 shows the experimental results obtained by infiltrating QDs dissolved in chloroform solution directly into a 3D PhC. To avoid the influence of absorption of QDs, the PhC was fabricated with a lattice constant of 1.45 μm and showed a band gap centred at 2.04 μm. The fabricated structure was firstly put into chloroform solution for 30 minutes to verify its stability. Secondly, the PhC was infiltrated with QDs having a concentration of 10^{-5} mol litre^{-1}. The whole experiment was applied by seven measurements and spaned three days. Each transmission spectrum was measured by FTIR ten minutes after the corresponding process. As seen from Fig. 2, the band gap of the PhC shifts to longer wavelengths when the amount of the infiltrated QDs increases and returns to shorter wavelength with the decrease of the amount of the infiltrated QDs. It should be mentioned that the infiltration experiments were performed under the normal experimental environment and the band gap of PhC remained unchanged three days after the infiltration. Due to the unique quality of the polymerised materials, QDs can attach to the surface of the PhC structure and can be washed away by chloroform solution even after three days.

C. Fabrication of 3D PhCs with QDs composite

Doping QDs into photoresists before polymerisation is another technique for incorporation. Here we demonstrate a successful fabrication of 3D PhCs using a commercial PbSe QDs doped resin (1550 nm PbSe Evicomposite, EVIDENT TECHNOLOGIES). Before fabrication, the composite was baked at 75 ^{0}C for five minutes. Then the structures were fabricated on a PMMA cover slide using the two-photon polymerisation technique and rinsed by methanol for one minute. Finally, the structure was cured by UV light for 30 seconds. As shown in Fig. 3, a 3D woodpile PhC with a lattice spacing of 1 μm can be fabricated. The whole process for fabricating such a structure lasted less than 150 minutes with

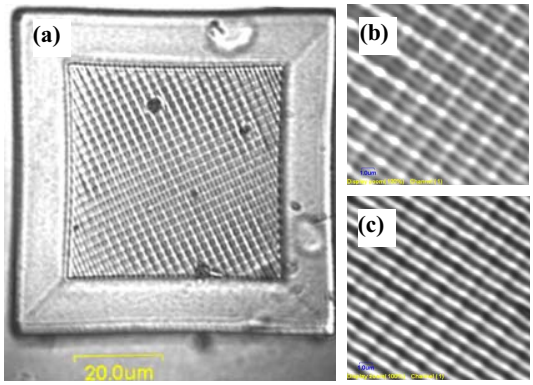

Figure 4. Microscopy images of 3D woodpile PhC fabricated with QDs doped composite. (a) Overall image; (b) Image of cross layers; (b) Image of single layer. Lattice constant: 1 μm; Size: 50×50×14 μm.

frame and 100 minutes without frame. Due to some aggregations of QDs during the fabrication process, the surfaces of the polymerised structure caught defects, which can be improved by optimising structure parameters and improving fabrication techniques. The measurement of the band gaps is under investigation.

III. DISCUSSION AND CONCLUSION

Since the size of QDs (~ 4.5 nm) is far less than the lattice constant of PhCs (~ 1000 nm), the infiltration induced band gap shift was mainly caused by the change of refractive index contrast induced by QDs infiltration.

Although the infiltration experiments revealed the flexible manipulation with QDs and 3D PhCs, it is still a challenge to produce the homogeneous distribution of QDs within the structures. In that sense, the doping method may have advantages. In addition, the doping method allows one to introduce arbitrary localized QDs to a desired position within the 3D PhCs by employing the two-photon polymerisation technique.

In conclusion, both infiltration and doping methods have been demonstrated to be efficient and flexible approaches to incorporate PbSe QDs into 3D woodpile PhCs. Two-photon excitation is a useful way for fabricating the 3D PCs as well as exploring their advanced functionalities for emission control.

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