Functionalisation of three-dimensional photonic crystals for emission control

A thesis submitted for the degree of
Doctor of Philosophy

by

Jiafang Li

Centre for Micro-Photonics
Faculty of Engineering and Industrial Sciences
Swinburne University of Technology
Melbourne, Australia

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for my beloved family.
Everything should be made as simple as possible, but no simpler.

— Albert Einstein
Manipulation of photons has become the core studies in area of photonics in the 21st century. Photons are fast and unlimited natural sources that could replace the roles of electronics. However, they are too fast and too delicate to be tamed by natural tools. In 1987, a novel class of artificial structures, named as ‘photonic crystal’ (PC), was invented by Yablonovitch and John for the inhibition of spontaneous emission and the localisation of photons, respectively. In such a PC, photons are scattered in a manner similar to the scattering of electrons by the crystalline array of atoms in semiconductor, resulting selective pathways or prohibition of photons.

When permittivity and/or permeability of a PC is periodically varied in a scale compared with optical wavelengths, photonic band gaps (PBGs) between energy bands are formed. Within these PBGs no electromagnetic wave of energy is allowed to propagate through the PCs. The unique PBGs and associated photonic effects of PCs have initiated vast applications, especially in one-dimensional (1D) and two-dimensional (2D) PCs for applications such as high quality-factor nanocavities and photonic crystal fibres.

However, to completely manipulate photons for desired applications, a strong confinement of light in three dimensions is necessary, which
can be realised in three-dimensional (3D) PCs. Through modulating the electromagnetic density of states (DOS), 3D PCs with/without defects have been proposed as an ideal cage for photons. For example, by engineering DOS, 3D PCs can enable highly frequency-selective changes in the rate of spontaneous emission (SE) from embedded emitters. For certain frequencies where DOS vanishes, SE can be completely inhibited.

To start 3D PC applications, one needs to build up high-quality 3D PC environments. Since the first attempt started with much large structures working in microwave wavelengths in 1989, state-of-the-art micro- and nano-fabrication technologies have been developed in the past decade, bringing up 3D PCs with useful PBGs in the near-infrared (NIR) and visible wavelength ranges. These sophisticated fabrication techniques have then pushed the functionalities of 3D PCs to the front as the main challenge for applications.

To functionalise 3D PCs, people have incorporated functional materials, such as fluorescent dyes and semiconductor nanocrystal quantum dots (QDs), into 3D PCs for studies on SE control. The studies in this aspect have been demonstrated by Lodahl et al. in 2004 with CdSe core/shell QDs in an inverted opal PC at visible wavelengths. However, most of the studies on SE control with 3D PCs and nanocrystals have been limited to opal/inverted opal PCs with fixed geometries and uncontrollable internal defects at visible wavelengths. On the other hand, scientists have coated metallic layers on the 3D dielectric PCs trying to explore their advanced functionalities. With such a scheme, 3D dielectric PCs can be directly transformed into 3D metallodielectric PCs (MDPCs). However, the metallic layers in those MDPCs have been employed with thickness far thicker than the skin depth of the metals which excluded the penetration of electromagnetic waves into the layers and limited their potential functionalities in plasmonics.
This thesis aims to develop a platform for studies on the functionalisation of 3D PCs with active QDs as well as with nano-scale metallic coating in the NIR wavelength range. The developed functionalities of 3D PCs can be applied on emission control such as SE control and thermal emission control. As a starting point, high-quality 3D woodpile PCs are fabricated with a convenient direct laser writing method called the two-photon polymerisation (2PP) technique. This technique is able to produce 1D, 2D and 3D arbitrary structures of sub-wavelength resolution with inexpensive polymer materials. More importantly, the fabricated 3D PCs can be easily functionalised by engineering chemical compositions, incorporating functional materials, or transforming structure conformations, which give rise to a great flexibility in subsequent studies on 3D PC applications.

For 3D PC applications, the matching of PBGs to the desired wavelengths is important since the PBGs are normally restricted in a specific spectral region. To this end, a structural engineering approach - a post-thermal treatment method - is proposed and demonstrated to improve the spatial resolution and engineer the stop gaps of 3D PCs, which can result in inorganic-organic 3D PCs operating from NIR to visible wavelength range.

To functionalise 3D PCs with active media, the woodpile PCs are directly fabricated in a NIR QDs doped composite with 2PP. With QDs homogeneously distributed inside the structure, 3D PCs with strong partial stop gaps are realised. In addition, an infiltration method is developed to flexibly embed home-made high-quality QDs into fabricated 3D PCs. With this method, the amount of incorporated QDs can be well controlled by simply changing QD concentration or adjusting infiltration times, which greatly facilitates future studies on QDs emission control.
Based on the functionalised 3D woodpile PCs incorporated with NIR QDs, control of SE with PBGs are studied. A spectral redistribution is observed from PbSe QDs infiltrated inside the PC with matched PBG. To find out the physical reason of such a spectral redistribution, a time-correlated single-photon counting system is built up to quantify the emission decay properties of QDs. Through careful analysis and comparisons, inhibition of the QDs radiation is verified in the stop gap region, indicating the feasibility for studying on emission control with polymeric 3D woodpile PCs. Moreover, the inhibition as well as the enhancement of SE from QDs inside a 3D PC are achieved in the mid-gap and at the centre of the band edge, respectively. These modifications of SE are further confirmed by consistent comparisons with the calculated decay time distributions. This study provides an effective way to tune the SE from QDs by engineering the PBG effects in a given 3D PC.

Along with the studies on emission control, advanced functionalities of 3D PCs are further explored with innovative 3D silver hybrid PCs. Here the 3D hybrid PCs refer to dielectric woodpile PCs coated with nano-scale (∼ 10 − 20 nm) metallic layers on the structure surfaces, which are conceptually different to conventional MDPCs. Besides the ultra-wide and complete photonic band gaps, the localised plasmon resonances (LPRs) are successfully introduced in 3D hybrid PCs. As a result, extraordinarily enhanced absorption channels are created and can be significantly tuned by structural parameters. Furthermore, 3D silver hybrid PCs with LPRs at NIR wavelengths are experimentally demonstrated with 2PP and a silver deposition method. More importantly, the scheme of creating LPRs in 3D hybrid PCs is confirmed to be applicable to a wide range of metals like gold and tungsten. The wide-range tunable LPR-enhanced absorption and the
LPR-induced localised electromagnetic field provide additional modulations for photon-matter interactions. These offer a new mechanism for application of 3D PCs on thermal emission control compared with the conventional approaches with the effects of PBGs and band edges.

The research conducted in this thesis is to build up solid and comprehensive studies on the functionalisation of 3D PCs in the technically important NIR wavelength range. Accompanying with the important demonstration that 3D woodpile PCs of low refractive-index are capable of modifying and engineering SE, this thesis proposes and proves a new concept to functionalise 3D PCs merged with LPRs, which can significantly enhance the structural absorption with a wide tunability. The research approaches as well as the conclusions reached in this thesis could lead to a profound understanding of the functionalisation of 3D PCs towards potential device applications in the NIR wavelength range.
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Jiafang Li
Melbourne, Australia
May 25, 2009
Declaration

I, Jiafang Li, declare that this thesis entitled:

“Functionalisation of three-dimensional photonic crystals for emission control”

is my own work and has not been submitted previously, in whole or in part, in respect of any other academic award.

Jiafang Li

Centre for Micro-Photonics
Faculty of Engineering and Industrial Science
Swinburne University of Technology
Australia

Dated this day, May 25, 2009
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Chapter 1

Introduction

Human beings have always desired to utilise nature resources to serve the society. From prehistoric Stone Age to modern Electronic Age, the unprecedented civilisation on Earth has witnessed the changes in human tools from a piece of stone to revolutionary electronics. Now it comes to the delicate photons. Photons are fast and unlimited natural sources that could replace the roles of electronics.

In 1987, two reports from Yablonovitch [1] and John [2] on the optical properties of three-dimensional (3D) photonic crystals (PCs) have triggered an enormous interest in scientific research on manipulation of photons or light. PCs are periodic structures that can affect the light propagation in a similar way that the periodicity of a semiconductor crystal affects the motion of electrons [3]. Because the variation of permittivity and/or permeability of a PC is in a scale compared to optical wavelengths, photonic band gaps (PBGs) between energy bands are formed and no electromagnetic wave of energy within these PBGs is allowed to propagate through the PCs [4–7], providing a promising tool for the control of light flow. The great
potentials of manipulation of light could lead to comprehensive applications from fundamental quantum optics to daily-used technologies such as low-threshold light sources, ultra-fast photonic devices, efficient solar energy harvesting systems, etc., which will revolutionise people’s life in the future.

This chapter serves as a basic introduction to PCs. Functionalisation of 3D PCs, one of the main challenges in 3D PC applications, is described. The objectives and the arrangement of this thesis are also presented in this chapter.

1.1 Introduction to photonic crystals

1.1.1 Basic of photonic crystals

PCs represent a novel class of optical materials that allow one to manipulate the flow of light and/or to modify the photon-matter interaction. Such functions are created in a way of on-resonance or off-resonance scattering of photons in PCs, which is determined by solving corresponding Maxwell equations [3]. The wave function for electromagnetic waves existing in PCs can be described as [3]

\[
\frac{1}{\varepsilon(r)} \nabla \times \left( \frac{1}{\mu(r)} \nabla \times E \right) - \frac{\omega^2}{c^2} E = 0. \tag{1.1}
\]

where \( E \) is the macroscopic electric field, \( \varepsilon(r) \) and \( \mu(r) \) are relative permittivity and permeability at spatial coordinate \( r \), \( \omega \) is the angular frequency of the light, and \( c \) is the speed of light in the vacuum.

It can be seen that the existence of electromagnetic fields is determined by
the periodic modulation in $\mu(\mathbf{r})$ and $\varepsilon(\mathbf{r})$. For example, in dielectric PCs [4], $\mu$ equals to 1 and only $\varepsilon(\mathbf{r})$ is periodically distributed. While for magnetic PCs [8], both spatial modulations in $\mu(\mathbf{r})$ and $\varepsilon(\mathbf{r})$ are of importance in manipulating electromagnetic waves.

The periodic dielectric function $\varepsilon(\mathbf{r})$ inside a PC can be defined as $\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r} + \mathbf{R})$, where $\mathbf{R}$ is the lattice vector characterising the periodic properties of PCs [Fig. 1.1a]. Dependent on the dimension of $\mathbf{R}$, PCs can be distinguished as one-dimensional (1D), two-dimensional (2D) and 3D PCs.
The initial concept of 1D PCs was firstly demonstrated by Lord Reyleigh in 1887 [9], who pointed out the prohibition of light propagation with 1D periodic lattices. Exactly one hundred years later in 1987, the 3D PC concept was invented by Yablonovitch [1] and John [2] for the inhibition of spontaneous emission and the localisation of photons, respectively. These findings explored a new frontier in photonics and have aroused enormous interest in both theoretical simulation and experimental realisation of such unique PCs.

Theoretically, geometries of PCs can be described by the first Brillouin zone in solid-state physics [10], which is the primitive lattice in reciprocal space (also called Fourier space or frequency space) that contain the full symmetry of the lattice [10], as shown in Fig. 1.1b. Through applying symmetry operations (mirror reflection, inversion and rotation), the first Brillouin zone can be further reduced to an irreducible Brillouin zone [10], where wave vectors (\( \mathbf{k} \)) are not related by symmetry [Fig. 1.1b]. Eventually, based on the Bloch wave description [3], solving the wave equation [Eq. 1.1] within the irreducible Brillouin zone will result in discrete solutions of eigenvalues \( \omega_n(\mathbf{k}) \) \((n = 1, 2, \ldots)\). These eigenvalues \( \omega_n(\mathbf{k}) \) form a serial of discrete bands which are the frequently used and most important photonic band structures, as shown in Fig. 1.1c. Due to the discretisation of the bands, a complete photonic band gap (CPBG), in which there are no propagating solutions to Maxwell’s equations for all \( \mathbf{k} \), can exist between the propagating bands. The PBG structures, together with resulted dispersion relations and associated mode distributions, build up the entire platform for theoretical studies.

To achieve such a 3D PC, Yablonovitch et al. fabricated the first 3D PC with band gaps in 1989 by using hand machining techniques [11]. Although
the band gap was in the microwave wavelength region, this first experimental attempt has convincingly demonstrated that artificial structures like 3D PCs have the functionality to manipulate light propagation. Since then, with joint efforts from various research communities, significant progresses have been made in developing state-of-the-art techniques to experimentally realise PCs. To date, PCs with periodicities from centimetres to nanometres have been successfully demonstrated with useful PBGs ranging from microwave to visible wavelengths. Those sophisticated fabrication techniques have enabled wide applications of PCs, such as photonic crystal fibres, high quality-factor nanocavities, emission control structures, thermophotovoltaic systems [12, 13], etc.

In this thesis, we focus the studies on 3D PCs, which hold the key for emission control due to their unique confinement of light in three dimensions.

1.1.2 Challenges in application of 3D photonic crystals

PCs of all dimensions (1D, 2D and 3D) have been successfully realised with the state-of-the-art micro- and nano-fabrication techniques. However, in the case of application, 3D PCs are less widely developed compared with 1D and 2D PCs such as photonic crystal fibres, mainly due to the complications in modeling, fabricating, and functionalising 3D PCs. The recent progresses in theoretical and experimental realisation of 3D PCs have greatly facilitated 3D PC applications, while the functionalisation of 3D PCs still remains as a main challenge. Functionalising 3D PCs is a critical step towards device applications and can be realised by exploring more attractive features of 3D PC templates through additional approaches. For example, incorporation of functional materials and metallisation of dielectric 3D PCs are two options
to increase the functionalities of 3D PCs, which will be discussed as follows.

Incorporation of functional materials in PCs is a convenient way to functionalise 3D PCs. In this case, functional elements, such as rare-earth ions [14], fluorescent dyes [15, 16], and semiconductor nanocrystal particles [14, 17, 18], have been embedded in 3D opal/inversed opal PCs for studies on emission control. In particular, radiation dynamics from nanocrystal quantum dots (QDs) inside inversed opal PCs, which was reported in 2004 [17], has clearly demonstrated the feasibility for applying 3D PCs into emission control. However, most of the studies in this aspect were limited to 3D opal/inversed opal PCs, in which case the uncontrollable internal defects and limited structure geometry made them less attractive in applications.

In addition, transforming dielectric PCs into metal-based 3D PCs is of great potential to significantly increase the functionalities. For example, by coating the dielectric PCs with metallic layers, 3D dielectric PCs can be transformed into 3D metallodielectric PCs (MDPCs) [19–21]. Due to the strong discontinuities of the dielectric function at the metal/air or metal/dielectric interfaces, metal-based 3D PCs can offer intriguing electromagnetic (EM) properties such as ultra-wide and complete photonic band gaps [7]. However, the metallic layers in most 3D MDPCs have been employed with thickness far thicker than the skin depth of the metals which excluded the penetration of EM waves into the rods or layers [20, 21]. This causes the major problem in all the current 3D MDPCs that they do not support localised plasmon resonances (LPRs) that are based on the metallic nanostructures [22]. The emerging studies on plasmonics [23, 24] and metamaterials [22] could enable metal-based 3D PCs with more promising functionalities, for example the enhanced absorption and negative refraction, which can lead to novel photonic applications but have yet been explored.
From these aspects, 3D polymeric PCs fabricated with the two-photon polymerisation (2PP) [25, 26] method provide an ideal host for the above-mentioned functionalisation approaches. With their functional chemical compositions and surfaces, 3D polymeric PCs have great advantages in incorporating functional materials such as fluorescent dyes [27] and semiconductor nanocrystals [28, 29], which can flexibly and significantly enhance the functionalities of 3D PCs. More importantly, the functional surfaces of 3D polymeric PCs make them ideal templates for flexible synthesis of 3D metal-based hybrid PCs, which could enable the introduction of plasmonics into 3D hybrid PCs. With the great flexibility of the 2PP technique, the plasmonic properties in 3D hybrid PCs can be widely and flexibly tuned by engineering the structural parameters or material properties (for example the electric-optical and magnetic-optical effects), which can lead to breakthroughs of the conventional concepts on functionalities of both 3D PCs and plasmonics.

1.2 Thesis objective

The objective of this thesis is to explore the functionalisation of 3D PCs fabricated by 2PP in the near-infrared (NIR) wavelength range. The innovation of this thesis is focused on the radiation dynamics of NIR QDs infiltrated into 3D polymeric PCs, as well as the absorption enhancement of 3D polymeric PCs coated with nano-scale metallic layers. Towards this motivation, the studies have been conducted in four major aspects.

Firstly, a 3D fabrication technique as well as its engineering method are developed in inorganic-organic hybrid polymeric materials to produce high-quality 3D PCs for potential applications at desired wavelength range, which is the technically important telecommunication wavelengths in this thesis.
Secondly, proper emitters such as semiconductor QDs is embedded inside 3D PCs to functionalise the structures for the next-step study on emission control. Therefore, synthesis of NIR QDs and corresponding techniques for introducing QDs into 3D PCs are developed.

Thirdly, a detailed investigation on controlling QDs emission with 3D PCs is performed. To this end, reliable experimental systems are built up to characterise QDs emission properties, including both emission spectra and radiation decays. Meanwhile, effective physical mechanisms, such as the effects of stop gaps and band edges, are employed to modify the emission properties of QDs with 3D PCs. Moreover, theoretical analysis and comparison are developed to identify the photonic effects of 3D PCs on QDs emission.

As a further functionalisation method of 3D PCs, a mechanism is developed to introduce the plasmonics into 3D hybrid PCs which consist of 3D polymeric PCs coated with nano-scale (∼10 – 20 nm) silver layers. The widely tunable localised plasmon resonances (LPRs), as well as the enhanced absorption channels, are theoretically demonstrated in 3D hybrid PCs. Finally, an experimental study is performed to realise such 3D silver hybrid PCs.

1.3 Preview of the thesis

Research conducted in this thesis involves with the fabrication and the functionalisation of 3D PCs in the NIR wavelength range. The functionalisation of 3D PCs, in particular, is focused on both scientifically and technically important studies on emission control, which includes the radiation dynamics
of NIR QDs in 3D polymeric PCs and the emission-associated absorption enhancement in 3D hybrid PCs.

As an introduction to the foundation of the work in this thesis, Chapter 2 presents a detailed review of the existing techniques involved in modeling, fabrication, characterisation and application of 3D PCs at optical wavelengths. Particularly, Sec. 2.5 reviews the significant achievements on emission control with 3D PCs and Sec. 2.6 outlines a novel extension of the functionalities of 3D dielectric PCs to 3D hybrid PCs towards studies on emission control.

Chapter 3 demonstrates the 2PP method as the basic fabrication technique for producing high-quality inorganic-organic 3D PCs with wide-range PBGs in the NIR wavelength range. In Sec. 3.3, a post-thermal treatment method is proposed to engineer the organic compositions of the inorganic-organic backbones of a 3D PC. This method is employed to efficiently improve the spatial resolution and engineer the stop gaps of the inorganic-organic 3D PCs. In particular, the stop gap of a 3D woodpile PC is tuned over a large wavelength range of \(\sim 318 \text{ nm} \) from the NIR to visible wavelength region.

As an important step towards emission control, Chapter 4 investigates the functionalisation of 3D PCs with two efficient methods, doping and infiltration techniques, by incorporating PbSe QDs into woodpile PCs. In Sec. 4.2, the doping method is implemented by direct fabrication of 3D PCs in PbSe QD-doped composite materials and 3D PCs with pronounced partial stop gaps are successfully realised. By comparison, Sec. 4.3 presents the infiltration method, in which QDs are directly infiltrated into pre-fabricated 3D PCs, as a flexible and controllable approach for studies on the radiation dynamics from QDs inside the 3D PCs.

Chapter 5 presents the important studies on manipulation of spontaneous
emission with 3D polymeric PCs. Sec. 5.1 demonstrates the experiments on the spectral redistribution and radiation decays from QDs inside a 3D PC, which confirms the modifications of spontaneous emission with 3D PCs. As a further study, Sec. 5.2 reports the direction-dependent radiation decays from NIR QDs at the angular band edges of a 3D PC. Both inhibition and enhancement effects of the stop gaps on the spontaneous emission have been observed in the mid-gap and at the centre of the band edge, respectively.

Chapter 6 introduces a novel functionalisation of 3D polymeric PCs through coating nano-scale silver layers on the polymerised rods. The functionalities of such 3D hybrid PCs are enriched by the introduced LPRs. The principle of this method is presented in Sec. 6.2. Sec. 6.3 theoretically shows that as a result of the existing LPRs, extraordinarily enhanced absorption channels are created in 3D PCs and can be significantly tuned by structural parameters. Further simulations on 3D hybrid PCs of other metals like gold and tungsten are described in Sec. 6.4, which verifys the generality of our scheme. Finally in Sec. 6.4, the experimental realisation of 3D silver hybrid PCs with band gaps and LPRs in the NIR wavelength range is demonstrated.

Chapter 7 summarises the work undertaken in this thesis and includes a discussion of future work in this field. For future studies, Sec. 7.2.1 proposes a method to experimentally resolve the 3D map of LDOS, while Sec. 7.2.2 suggests two schemes towards achieving significant control or manipulation of emission with the advanced functionalities of 3D hybrid PCs.
Chapter 2

Review

2.1 Introduction

Three-dimensional (3D) photonic crystals (PCs) are unique artificial structures that are able to confine light in three dimensions [1, 2]. By forming spatially periodic modulation of refractive-indices, 3D PCs can accurately control the diffraction of the incident light on a wavelength scale, resulting in scalable photonic band gaps (PBGs), in which the density of state (DOS) vanishes. The resultant PBG structures and associated optical properties have attracted intensive studies for more than twenty years, which stimulated much fundamental interest and promoted 3D PCs as a core element for novel photonic applications in quantum optics, optical communications, optical computing, solar cell and single photon sources. Generally, to study on 3D PCs and to achieve important photonic applications, an experimental platform is needed to be built up under the consideration of

- a theoretical calculation tool to predict and instruct the experiments;
• a feasible technique to realise a specific type of 3D PCs;
• a reliable method to characterise the 3D PCs;
• a promising functionality to develop the applications of 3D PCs.

This chapter describes a variety of methodologies and technologies regarding above-mentioned conditions. Sec. 2.2, Sec. 2.3 and Sec. 2.4 outline the realisation of 3D dielectric PCs, including theoretical calculation tools, experimental fabrication techniques and applicable characterisation methods. In particular, accurate spectral characterisation of micron-scale 3D PCs is emphasised, which is technically important but has always been overlooked. As one promising functionality for 3D PC applications, Sec. 2.5 reviews the important applications of 3D PCs on control of spontaneous emission (SE), which is firstly introduced in Sec. 2.5.1. Sec. 2.6 presents the advanced functionalisation of the 3D hybrid PCs transformed based on dielectric PCs.

2.2 Calculation tools for 3D photonic crystals

Theoretical calculations, which are able to explain and predict useful experimental results, are very helpful for performing experiments. Here we introduce several tools regarding 3D PC calculations which can be easily adopted by lab users.

The first one is the widely used MIT Photonic-Bands (MPB) software package [30]. This software is based on the plane wave method, which calculates definite-frequency eigenstates of Maxwell’s equations in periodic dielectric structures for arbitrary wavevectors, using fully-vectorial and 3D methods. Through translating the dielectric function periodicity into
reciprocal space, it can accurately and quickly calculate the photonic band structure and associated dispersion properties of 3D PCs. However, the software is limited to calculations of infinite and pure dielectric structures without losses.

BandSOLVE (Rsoft Design Group) [31] is a commercially available software which is capable of calculating band gaps of most 1D (one-dimensional), 2D (two-dimensional) and 3D PBG devices. This software is mainly based on the plane wave expansion (PME) algorithm with an additional finite-difference time-domain (FDTD) engine. It has well-arranged user interfaces and computer-aided design environments which give users more friendly design freedom. Furthermore, it is featured with the graphical display of electromagnetic (EM) fields and the ability to calculate metallic and anisotropic structures. One weakness of this software is that the calculation is still limited to infinite structures.

In the case of flexibility and applications, CST Microwave Studio® [32] is a good choice for lab users. This simulator is based on a finite integration technique (FIT), which can provide a universal spatial discretisation scheme applicable to various EM problems ranging from static field calculations to high frequency applications in time or frequency domains. With the advantages such as well-defined boundary approximation descriptions and adaptive meshing procedures, this software package can be applied on arbitrary devices to solve any high frequency field problem in both finite and infinite calculation domains.

Another important and popular electrodynamics modeling tools is FDTD [33]. This tool belongs in the general class of grid-based differential time-domain numerical modeling methods. The time-dependent Maxwell’s equa-
tions (in a partial differential form) are discretised using central-difference approximations to the space and time partial derivatives. FDTD can calculate arbitrary structures under the consideration of material parameters and aperture effects. However, FDTD normally requires an excessively large computational domain, resulting in very long solution times. When multiple dimensions are considered, for example calculations of 3D PCs, simulation becomes extremely heavy and is not applicable with normal computers.

Generally, every calculation technique has its strengths and weaknesses. The choice of calculation tools depends on specific conditions and requirements of lab users to effectively and conveniently serve the experimental studies. In this thesis, we use MPB software to predict the positions of the PBGs of our 3D PCs while employing CST Microwave Studio® to simulate the spectral properties of our PCs with actual sizes.

2.3 Realisation of 3D dielectric photonic crystals

2.3.1 General fabrication techniques

To experimentally achieve useful PBGs in visible or near-infrared (NIR) wavelength ranges, the periodic structures have to be arranged with a periodicity in wavelength scales, i.e. several hundreds of nanometers. To solve the challenges in fabrications, scientists and engineers from various communities have developed advanced techniques to realise 3D PCs with complete or partial PBGs ranging from the microwave to visible wavelength regions. The important milestones achieved in 3D PC fabrication have been
summarised in Table 2.1.

In the early stage, by using hand machining techniques [Table 2.1], Yablonovitch et al. fabricated the first 3D PC with band gaps in 1989 [11]. Although the band gap was in the microwave region, this first experimental attempt has convincingly demonstrated that artificial structures like 3D PCs have the power to manipulate light propagation. Thus their pioneering work established an important foundation for future PC researches and benefited the consequent developments of 3D PCs in the optical wavelength region.

Layer-by-layer lithography techniques are based on the approach followed in microelectronics to fabricate electronic chips [Table 2.1]. The procedure begins with the recording of a 2D layer pattern on a resist by means of photolithography or electron-beam lithography. With a repeating process or other manipulation process, the initial fabricated 2D layers are then replicated, transformed and stacked in a certain direction to form the layer-by-layer 3D PCs. With its high fabrication resolution (<50 nm) and high refractive-index contrast, 3D PCs with complete PBGs working in the NIR wavelength region have been realised [4, 5]. However, most layer-by-layer lithography techniques are very expensive and complicated to operate, and therefore are not affordable for most research laboratories.

By comparison, the fabrication of artificial opals by means of self-assembly techniques offers a cheap method accessible for most research laboratories [Table 2.1]. The first 3D PC in this type is demonstrated in 1996 by Tarhan et al. [37], who employed a colloidal suspension method to self-assemble polystyrene microspheres into an face-centred-cubic (fcc) geometry. By varying the size of the spheres this method allows for the ability to fabricate PCs with PBGs at desired wavelengths. Recently, novel methods such as cell-
<table>
<thead>
<tr>
<th>Techniques</th>
<th>Year</th>
<th>Materials</th>
<th>n</th>
<th>Lattice</th>
<th>λ&lt;sub&gt;gap&lt;/sub&gt; (µm)</th>
<th>Scale</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hand machining</td>
<td>1989</td>
<td>Dielectric</td>
<td>3.5</td>
<td>fcc</td>
<td>~20.000</td>
<td>&gt;cm</td>
<td>First PC [11]</td>
</tr>
<tr>
<td></td>
<td>1994</td>
<td>Al</td>
<td>3.1</td>
<td>Woodpile</td>
<td>~22.222</td>
<td>&gt;cm</td>
<td>First woodpile PC; Complete 3D PBG [34]</td>
</tr>
<tr>
<td>Layer-by-layer</td>
<td>1998</td>
<td>Si</td>
<td>3.6</td>
<td>Woodpile</td>
<td>11</td>
<td>cm</td>
<td>Large PBG at infrared wavelengths</td>
</tr>
<tr>
<td>lithography</td>
<td>2000</td>
<td>GaAs</td>
<td>3.2</td>
<td>Woodpile</td>
<td>1.3</td>
<td>µm</td>
<td>99.99% reflection in PBG; First 90° bend waveguide in 3D PCs [5]</td>
</tr>
<tr>
<td>(and related)</td>
<td>2003</td>
<td>InP</td>
<td>3.3</td>
<td>Woodpile</td>
<td>3</td>
<td>µm</td>
<td>First demonstration of the assembly of 3D woodpile PCs [35]</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>Si</td>
<td>3.6</td>
<td>fcc</td>
<td>1.3</td>
<td>µm</td>
<td>Point defects embedded within 3D PCs [36]</td>
</tr>
<tr>
<td>Self-assembly</td>
<td>1996</td>
<td>Polystyrene</td>
<td>1.59</td>
<td>Opal-like fcc</td>
<td>0.6</td>
<td>µm</td>
<td>First demonstration of self-assembly PC through precipitations [37]</td>
</tr>
<tr>
<td>method</td>
<td>1998</td>
<td>Polystyrene</td>
<td>1.59</td>
<td>Opal-like fcc</td>
<td>-</td>
<td>cm</td>
<td>Large area crystallisation with injection method [38]</td>
</tr>
<tr>
<td></td>
<td>1999</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.45</td>
<td>Opal-like fcc</td>
<td>~0.57</td>
<td>cm</td>
<td>Vertical deposition with controlled thickness [39]</td>
</tr>
<tr>
<td></td>
<td>2001</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.45</td>
<td>Opal-like fcc</td>
<td>-</td>
<td>mm</td>
<td>High-quality on-chip self-assembly PC for silicon inversion [40]</td>
</tr>
<tr>
<td>Holographic</td>
<td>2000</td>
<td>SU-8</td>
<td>1.6</td>
<td>fcc</td>
<td>-</td>
<td>µm</td>
<td>Proposal and demonstration of 3D PCs with holography [41]</td>
</tr>
<tr>
<td>technique</td>
<td>2000</td>
<td>KC1077</td>
<td>1.52</td>
<td>Flexible</td>
<td>-</td>
<td>µm</td>
<td>Proposal and demonstration of multiple exposure techniques [42]</td>
</tr>
<tr>
<td></td>
<td>2003</td>
<td>SU-8</td>
<td>1.6</td>
<td>fcc</td>
<td>0.7</td>
<td>mm</td>
<td>First holographic 3D PC with a visible PBG [43]</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>SU-8</td>
<td>1.6</td>
<td>Flexible</td>
<td>-</td>
<td>mm</td>
<td>Using conformable phase masks for 3D complex fabrication [44]</td>
</tr>
<tr>
<td>Direct laser</td>
<td>1999</td>
<td>NC800</td>
<td>1.6</td>
<td>Woodpile</td>
<td>3.92</td>
<td>µm</td>
<td>First polymer PC fabricated with 2PP [25]</td>
</tr>
<tr>
<td>writing</td>
<td>2003</td>
<td>NOA63</td>
<td>1.6</td>
<td>Woodpile</td>
<td>4.8</td>
<td>µm</td>
<td>First void-channel PC in a polymer material [45]</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.2</td>
<td>fcc</td>
<td>2.0</td>
<td>µm</td>
<td>First void-dot PC in an anisotropic and nonlinear crystal [46]</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.5</td>
<td>Woodpile</td>
<td>2.16</td>
<td>µm</td>
<td>High-quality woodpile PC in a high-nonlinear material [47]</td>
</tr>
<tr>
<td>Inversion</td>
<td>1998</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&gt;2.5</td>
<td>Inverted opal</td>
<td>~0.63</td>
<td>mm</td>
<td>First demonstration of inverted opal PC [48]</td>
</tr>
<tr>
<td>method</td>
<td>2000</td>
<td>Si</td>
<td>3.6</td>
<td>Inverted opal</td>
<td>1.46</td>
<td>µm</td>
<td>Large area synthesis of high-quality inverted opal PC [6]</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>Si</td>
<td>3.7</td>
<td>Woodpile</td>
<td>2.35</td>
<td>µm</td>
<td>First silicon double inversion of a SU-8 PC template [49]</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>Si</td>
<td>3.45</td>
<td>Hollow woodpile</td>
<td>~2.1</td>
<td>µm</td>
<td>First hollow woodpile PC [50]</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>Ge</td>
<td>4.1</td>
<td>Inverse woodpile</td>
<td>6</td>
<td>µm</td>
<td>Inverted woodpile PC with wide PBG (25%) [51]</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;&amp;SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.2</td>
<td>Inverse woodpile</td>
<td>2.04</td>
<td>µm</td>
<td>Inverted woodpile PC with a cheap sol-gel process [52]</td>
</tr>
<tr>
<td></td>
<td>2008</td>
<td>Si</td>
<td>3.6</td>
<td>fcc</td>
<td>1.32</td>
<td>mm</td>
<td>Large area inverted PC with SU-8 holographic template [53]</td>
</tr>
<tr>
<td>Other methods</td>
<td>2004</td>
<td>Ink</td>
<td>1.5</td>
<td>Woodpile</td>
<td>2</td>
<td>cm</td>
<td>3D arbitrary large-scale ink-deposition [54]</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>PDMS</td>
<td>1.47</td>
<td>Woodpile</td>
<td>-</td>
<td>mm</td>
<td>Large-scale two-polymer microtransfer molding [55]</td>
</tr>
</tbody>
</table>
injection [38], vertical deposition [39] and on-chip deposition [40], have been intensively investigated to rapidly synthesise large-scale PCs with minimised defects. However, the low refractive-index and the fixed fcc geometry of these opal PCs limit their functionalities.

The holographic technique is another type of the fabrication method which can realise rapid prototyping of large-scale 3D PCs with minimised defects [Table 2.1]. Through controlling the interference patterns of laser beams, the crystal periodicity and geometry can be accurately controlled. The application of holography to 3D PC fabrication was proposed by Berger et al. [56] in 1997 and firstly experimentally demonstrated by Campbell et al. [41] in 2000 through interfering four non-coplanar laser beams within a photo-resistive resin to form 3D fcc PCs. In 2003, high-quality 3D PCs with PBGs at visible wavelengths were achieved [43]. Current holographic techniques are still being developed and improved to reduce their complexities and increase their flexibilities.

In terms of the flexibility, the direct laser writing (DLW) technique is the first choice for 3D PC fabrications [Table 2.1]. Two-photon polymerisation (2PP) is a DLW process, in which case resolution can reach less than 100 nm [25,26]. By focusing femtosecond pulsed laser light into a photo-sensitive material and by scanning the sample three-dimensionally, arbitrary 3D PCs with sub-wavelength spatial resolution can be generated using inexpensive polymer materials. Another type of the DLW technique is the micro-explosion method, which has been demonstrated in fabrication of 3D PCs with both low and high refractive-index materials [45,46]. Although it is a cheap, fast, high-quality and flexible fabrication method, DLW also has its weaknesses, such as the difficulties in fabricating 3D PCs of high refractive-index materials.
As mentioned earlier, fabrication of 3D PCs in high refractive-index materials has remained as a challenge for most fabrication methods including self-assembly, holographic, and DLW. To solve the challenges, people in materials community created versatile inversion techniques [Table 2.1]. The inversion technique was first applied on self-assembly opal templates in 1998 by Wijnhoven et al. with TiO$_2$ [48]. This technology was then widely applied on opal-like structures to build up 3D PCs of high refractive-index materials like silicon. By comparison, the inversion method was not applied to holographic templates until 2008 by Ramanan et al. [53], who realised inversed 3D PCs with silicon backbones and designed defects. For the DLW method, it is also until recently that the inversion technique was adopted for preparing double inversion woodpile [49], hollow woodpile [50] and pure inversed woodpile PCs [51,52]. It can be expected that the inversion methods will play more important roles with DLW templates in the near future since the DLW techniques provide more flexibilities in designing arbitrary lattice structures.

In addition to the above-mentioned fabrication techniques, some other types of techniques, for example the ink-deposition [54] and microtransfer molding [55] methods, also played an important role in fabrications of 3D PCs to meet particular demands such as large-scale fabrication with convenient designs.

In this thesis, we employ the convenient DLW method, particularly the 2PP technique [25], to fabricate our 3D PCs, which will be introduced in next section.
2.3.2 Two-photon polymerisation method in this thesis

The fabrication technique we use in this thesis is the 2PP method [Figs. 2.1a,b] [25, 57]. Generally, photosensitive liquid materials can be converted into solid phase upon light exposure by photopolymerisation. Specifically in 2PP, a photon initiator absorbs two photons simultaneously through a nonlinear absorption process called two-photon absorption (2PA). The initiator is then dissociated into free radicals, which are active and react

![Figure 2.1](image)

(a) Schematic for 2PP fabrication. (b) Chemical reactions in the process of 2PP. (c) Normalised intensity ($I$) in the focal volume of an objective ($NA=1.4$, $\lambda = 800$ nm). (d) Contour of $I^2$ (in log scale) in the focal volume. (e) SEM images of fabricated voxels under different laser power. The shape and size of the voxels change with fabrication power ($P$), as indicated in the contour of (d).
with monomer molecules to form monomer radicals. The monomer radicals react with other monomer molecules to form even larger active groups, which finally results in cross-linked polymer macromolecules of a solid form through such a chain reaction [Fig. 2.1b].

Since two photons have to be absorbed simultaneously, a tightly focused laser beam with a high peak intensity, such as a femtosecond pulse laser, is required. The optimum wavelength of the fabrication laser is two times as that of the maximum absorption wavelength of the initiator. For example, if an initiator has an absorption band ranged from $\lambda_1$ to $\lambda_2$, the 2PP fabrication wavelength ($\lambda_L$) should satisfy $\lambda_L/2 < \lambda_2 < \lambda_L$. When $\lambda_L$ is larger than $\lambda_2$, the laser beam can be focused into the volume of the resin without having any single-photon-induced polymerisation (1PP) reaction. Only in the tightly focused region where 2PA happens, the solid phase can be formed and final structures can be obtained by washing out unpolymerised parts through post process. Thus, 2PP happens inside the resin and is a real 3D fabrication technique, whereas conventional 1PP is a planar process restricted to the surface of the resin. By scanning the laser focus three-dimensionally within the resin, any arbitrary 3D microstructure can be generated with pre-programmed patterns.

The resolution of 2PP fabrication is determined by a combination of the optical resolution and the propagation effects during fabrication. In the optical part, the resolution is defined by the spatial distribution of absorbed photons, which is mainly governed by the numerical aperture (NA) of the focal lens or objective [58]. Figure 2.1c show the normalised intensity distribution of the focal volume of an objective with NA=1.4. In 2PP, because of the existing threshold, only the focal region with photon energy above the threshold energy can be polymerised. Therefore, resolution beyond the
diffraction limit can be realised by controlling the laser-pulse energy and the number of applied pulses [26]. However, the resolution cannot be infinitely small because of the diffusion of the radicals in the resin [59]. This influence from material aspect makes the fabrication not strictly duplicating the focal volume of an objective. Therefore, to achieve high resolution fabrication, the concentration of initiators and quenchers in the resin need to be considered [60]. Moreover, the mechanical strength, i.e. the polymer rigidity, also limit the fabrication resolution because any useful polymerised structure has to be strong enough to withstand the post-washing process or/and subsequently added dimensions. For example, although the resolution of 2D features of 2PP has reached approximately 15 $\text{nm}$ [61], the resolution of distortion-free 3D PCs is still around 100 $\text{nm}$ [62, 63].

A number of resins, as summarised in Table 2.2, have been employed for 2PP fabrication, some of which have been commercialised. Regarding the chemical process, only the resin SU-8 [62] has a two-step crosslink-

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
<th>Refractive-index studied</th>
<th>Resolution (nm)</th>
<th>Band gap ($\mu$m)</th>
<th>Suppression rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>Nopcocure800 [25]</td>
<td>1.6</td>
<td>600</td>
<td>3.9</td>
<td>~20%</td>
</tr>
<tr>
<td>2002</td>
<td>SCR500 [64]</td>
<td>1.6</td>
<td>200</td>
<td>1.5</td>
<td>50%</td>
</tr>
<tr>
<td>2004</td>
<td>SU-8 [62]</td>
<td>1.6</td>
<td>180</td>
<td>1.3</td>
<td>72%</td>
</tr>
<tr>
<td>2004</td>
<td>IPG [65]</td>
<td>1.5</td>
<td>350</td>
<td>1.6</td>
<td>20%</td>
</tr>
<tr>
<td>2005</td>
<td>LN1 [66]</td>
<td>1.5</td>
<td>200</td>
<td>2.3</td>
<td>40%</td>
</tr>
<tr>
<td>2005</td>
<td>SR348 [67]</td>
<td>1.5</td>
<td>300</td>
<td>1.9</td>
<td>39%</td>
</tr>
<tr>
<td>2006</td>
<td>Ormocer [68]</td>
<td>1.5</td>
<td>120</td>
<td>1.2</td>
<td>70%</td>
</tr>
<tr>
<td>2006</td>
<td>EviComposites [28]</td>
<td>1.5</td>
<td>250</td>
<td>1.6</td>
<td>50%</td>
</tr>
<tr>
<td>2007</td>
<td>Sol-gel TiO$_2$ [69]</td>
<td>2.2</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2006</td>
<td>As$_2$S$_3$ [47]</td>
<td>2.5</td>
<td>150</td>
<td>2.2</td>
<td>74%</td>
</tr>
</tbody>
</table>
ing procedure. Other popular commercialised resins, including SCR500 (Japan Synthetic Rubber Company (limited customer)) [64], Ormocer (the Fraunhofer Institute for Silicate research) [70], Nopcocure 800 (San Nopco, Japan) [25] and NOA63 (Norland Products, Inc) [71], are polymerised through a single-step radical initiated process. Light induced polymerisation occurs immediately upon exposure; therefore the fabrication process can be monitored and optimised in real time by adjusting the fabrication parameters, i.e. exposure time and intensity. The first 3D PC realised with 2PP was demonstrated by Sun et al. in 1999 in the infrared wavelength region [25]. Subsequent achievements were made by Straub et al. [64] in realisation of 3D PCs with higher order stop gaps working in important telecommunication wavelengths (\(\sim 1.5 \mu m\)). Later in 2004, Deubel et al. [62] used the popular SU-8 resin to push the main stop gap of a PC to 1.3 \(\mu m\). Recent research was focused on modifying the material properties to push the wavelength of the stop gap to below 1 \(\mu m\) [72]. One of the innovations in this thesis is to enhance the spatial resolution of 3D PCs and realise 3D woodpile PCs with stop gaps in the visible wavelength region.

2.4 Characterisation methods for 3D photonic crystals

Precise characterisations of 3D PCs cannot only provide feedbacks to fabrications and avoid misleading conclusions, but also hold the keys to explore potential functionalities of 3D PCs beyond existing knowledge. In such a case, people have developed versatile methods to characterise 3D PCs, which can be sorted into three types: structure imaging, spectral
characterisation and near-field optical detection.

Figure 2.2 Images of woodpile PCs took from (a) scanning microscopy, (b) SEM and (c) AFM, respectively. It can be seen that the visibility of the structure features is increased from (a) to (c).

For structure imaging, far-field optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) can provide specific information about the structure quality of 3D PCs [see Fig. 2.2]. Among them, far-field optical microscopy provides a convenient and cheap tool for quick characterisations. However, due to the existing optical diffraction limit and optical scatterings, it is hard to characterise structures with a feature size of tens of nanometres [Fig. 2.2a]. By comparison, SEM is more frequently used for its high resolution, fast 3D imaging ability, and possible combinations with focused ion beam or/and X-ray analysis facilities. However, the structures normally need metal coating before high-resolution imaging and the surface roughness cannot be quantified. In this aspect, AFM provide a good supplement because it does not need pre-coating and is capable to provide sufficient topographical information like surface roughness [Fig. 2.2c].

Spectral characterisation is the most important process to characterise the PBGs of 3D PCs. The challenge in spectral characterisation is to focus light into PCs and collect output signals correctly, especially for PCs in
micrometre scales. Due to the broad band optical properties of 3D PCs, optical aberrations need to be considered in all measurement systems. For large-scale PCs in the visible wavelength region, for example opal PCs, these issues can be solved by using apochromatic lens to focus and collect light signals. However, in the NIR or infrared wavelength region, for example from 1 to 10 \( \mu m \), apochromatic lens and spectrometers are not compatible for measuring such a wide range of spectra. In such a case, Fourier transform infrared spectroscopy (FTIR) and an infrared microscope with reflective objectives have been widely used. However, the reflective objective of a standard FTIR microscope provides a hollow light cone in a certain range [see Fig. 2.3a], of which the measuring angles are averaged and fixed [25, 73]. To make it more flexible, people started to tilt the sample normal to the axis of one part of the light cone, as shown in Fig. 2.3b [36]. However, this arrangement actually make the measurements more complicated other than simpler because incident light from the other parts of the light cone still pass through the sample with more complicated incident angles. To accurately measure the transmission and reflection spectra from 3D PCs with
flexible angles, researchers modified the reflective objective setup with a beam blocker, as shown in Fig. 2.3c [28, 74]. By tilting the sample with an angle and by putting a small pinhole in front of the objective, the measurements can be accurately confined in certain direction with a small angle range. This method is adopted in this thesis.

Figure 2.4  Topography signals (a, c, e) and corresponding optical signals (b, d, f) recorded simultaneously with a SNOM from 3D woodpile structures fabricated with different conditions. (a, b) The voids between the rods were fully filled with unwanted resin. (c, d) The voids between the rods were partially filled with unwanted resin. (e, f) A well-developed woodpile PC with a high-quality PBG. Units of x and y axes: µm. Units of vertical z axes: nm (for a, c, e) or a.u. (for b, d, f).

Near-field optical detection of 3D PCs can be realised with a scanning near-field optical microscope (SNOM). By scanning a subwavelength-sized fibre tip (typically 50-100 nm) over the surface of the source with a distance of ~10 nm, the light confined in the sample can be collected into the fibre tip of SNOM. Thus SNOM has the unique ability to reveal direct information of the evanescent field near the sample surface, which is not detectable in far field. At the same time, topography information of the sample can also be obtained by the shear-force system of the SNOM, which allows the measurement of point-to-point loss of PCs. Figure 2.4 shows the topography and optical signals recorded simultaneously with a SNOM head (NT-MDT)
with a 633 nm illumination source from a He-Ne laser coupled by an NA=0.6, 40× objective (Olympus). The structures look very similar under far-field optical microscope but show significant difference in the near-field regarding the topography and optical signals [28], which provide direct feedbacks for optimising the fabrications. Moreover, SNOM has great potentials to characterise 3D PCs involving local mode characterisation, phase sensitive measurements and combinations of spectroscopy and microscopy [75].

### 2.5 Spontaneous emission control in 3D photonic crystals

#### 2.5.1 Introduction

SE is a fundamental process that exits in many phenomena in nature and builds up the basis of many applications, such as fluorescence tube and light emitting diodes (LEDs). Physically, SE happens when a light source, such as atom and molecule, undergoes a transition from an excited state \( E_2 \) to a ground state \( E_1 \) and emits a photon. The energy of the emitted photon is defined by \( \hbar \omega = E_2 - E_1 \), where \( \hbar \) is Dirac’s constant and \( \omega \) is the angular frequency of the photon. The phase of the photon in SE is random, which made people think SE is not controllable until Purcell discovered the enhancement of SE with a resonant cavity (the Purcell effect) in 1946 [76].

Now it is well known that the decay rate \( \gamma \) of SE with frequency \( \omega \) at position \( r \) is determined by the local DOS (LDOS, \( N(r, \omega) \)) as [77]

\[
\gamma(r) = \frac{1}{\tau} \propto N(r, \omega), \tag{2.1}
\]
where $\tau$ is the lifetime of the particle on the excited energy state. LDOS represents the number of photonic states (with energy $\hbar \omega$) that are available at position $\mathbf{r}$. When the emitter is put into an ideal environment with $N(\mathbf{r}, \omega) = 0$, the emission rate equals to zero which means the emitter cannot transit from the excited state to the ground state and SE is completely inhibited.

The control of SE is very important for applications such as quantum optics, low-threshold lasers, high efficient LEDs, solar cells, et al. To build up the environment for SE control, scientists have adopted PCs [1, 2] to manipulate SE of embedded emitters.

In PCs, LDOS [78] is defined as an integral of the electric field of EM mode(s), $\mathbf{E}_{nk}$, overlapped with a Dirac ($\delta$) function over the the first Brillouin zone (BZ) with a summation over all transmission bands

$$N(\mathbf{r}, \omega) = \sum_n \int_{BZ} d^3k |\mathbf{E}_{nk}(\mathbf{r})|^2 \delta(\omega - \omega_n(\mathbf{k})),$$  \hspace{1cm} (2.2)

where $\omega_n(\mathbf{k})$ is the eigen-angular frequency of the $n^{th}$ band with a wave vector of $\mathbf{k}$. Since LDOS is much complicated to calculate, DOS, which counts all allowed photonic states in BZ with a given frequency $\omega$, is more often used

$$N(\omega) = \sum_n \int_{BZ} d^3k \delta(\omega - \omega_n(\mathbf{k})).$$  \hspace{1cm} (2.3)

With PBGs in all directions, 3D PCs provide an ideal platform for control of SE. Although fabrication of 3D PCs with complete PBGs is still challenging, the modifications of radiation rate of SE have been realised in recent years [17, 29, 79–81], which will be introduced in next section.
2.5.2 Application of 3D photonic crystals for emission control

Application on emission control represents one of the most unique functionalities of 3D PCs. Although the concept inhibited spontaneous emission was the first motivation of 3D PCs [1], the experiments on “real” modifications of SE with 3D PCs were limited to a few examples, mainly due to the lack of high-quality 3D PCs and proper emitters for investigations.

The first experiment regarding SE control was reported in 1990 by Martorell and Lawandy [82], who observed 1.7-time inhibition of fluorescence decays from dye molecules in an ordered aqueous suspension of polystyrene spheres. Although the origin of this inhibition was later identified as the interactions between molecules and medium [83], this work has triggered intensive studies on SE in opal-like 3D PCs with fluorescence dyes [15, 16], rare-earth ions [14], and semiconductor nanocrystals [14, 17, 18]. However, most of the researches were focused on the changes in SE spectra [15, 16, 84], which, strictly speaking, are not “real” modifications of SE because the detected signals were just from one part of the full solid emitting angle and cannot represent the fundamental properties of SE. The “real” modifications of SE have to be manifested on the changes in the decay rates of the emitters, i.e., the lifetime of the emitters [17, 85]. A longer lifetime is associated with decreased decay rate (SE inhibition) and a shorter lifetime means increased decay rate (SE enhancement). However, opal-like 3D PCs are less efficient to modify the SE because of its low refractive-index contrast [18, 86]. To solve this challenge, inverse opal PCs with high refractive-index materials were applied with the developed inversion technique [16, 17]. Meanwhile, the emerging nanotechnology provides more efficient emitters
such as semiconductor quantum dots (QDs) that surpass conventional dye molecules.

Semiconductor QDs are unique class of semiconductor with diameter ranging from 2-10 nanometres. At these small sizes, electrons are confined in all three dimensions and materials behave differently compared to bulk, giving QDs unprecedented tunability and enabling never before seen applications to science and technology. The confinement leads to a discrete energy spectrum and results in size-dependent properties of QDs, such as tunable absorption and emission, which are among the most important optical features of QDs. Compared with dye molecules, QDs are highly efficient with a narrow bandwidth which effectively resemble the two-level systems preferred by theoretical calculations. Therefore, the nanometer size, high efficiency, narrow line width, and readily tunable emission properties have made nanocrystal QDs the most appealing candidate for internal point light sources for radiation control with 3D PCs.

With the advantages of inversed opal PCs and semiconductor QDs, Lodahl et al. in 2004 demonstrated the changes in emission spectra as well as both inhibition and enhancement of decay rates from QDs embedded within 3D Titania inversed opal PCs [17]. With a goal towards a platform that could provide all-solid-state dynamic control for optical quantum systems, inverse opal lattices were embedded with ZnSe-coated CdSe QDs with emission at wavelength 625 nm. An inhibition by 30% and an enhancement by 40% have been observed in radiative lifetime from QDs inside PCs with variable lattice parameters. Furthermore, their calculations of DOS well explained the experimental results, which provided a direct evidence that 3D PCs could be used towards tailoring SE through modifying the vacuum fluctuations.
Another type of 3D PCs applied to SE control is semiconductor 3D PCs fabricated with nanofabrication methods. In 2004 Ogawa et al. reported the control of light emission from InGaAsP multiple quantum well with such kind of PCs [79]. By employing pure woodpile PCs and woodpile PCs with artificial point-defects of different sizes, suppressed light emission and size-dependent enhancement of cavity modes have been achieved. However, measurements in decay rates or lifetimes were not presented for comparisons.

Although the experimental progresses made in SE control with opal/inversed opal is encouraging, limitations arising from the fixed geometry, uncontrolled internal defects and unknown emitter position make it very challenging to fully understand the effect of 3D PCs. For example, the filling ratios of packed opal and inversed opal are 74% and 26%, respectively, with the same \( fcc \) geometry. Therefore, the current studies on SE control are desired for more functionalities with defect-free PCs riched in geometries and materials. To this end, the experiments on SE control with 3D polymeric PCs in the telecommunication wavelength range will be presented in Chap. 5.

### 2.6 3D metallic photonic crystals

Accompanying with emission control demonstrated in dielectric PCs, there is also emerging interest on developing metal-based 3D PCs for thermal emission control [87], mainly attributed to their intriguing EM properties, such as ultra-wide and complete band gaps [7, 88], the intrinsic ability to modify structure absorption [89] and the promising capability to tailor thermal emission [12, 55, 90].

In the band gap region of 3D metallic PCs (MPCs), no electromagnetic
Bloch mode exists. At the band edge region where the Bloch wave starts to propagate, the group velocity is very low (light propagates very slowly) and photonic density of states are greatly enhanced. The result of these effects is the enhanced absorption at the band edge of 3D MPC, which was firstly demonstrated by Fleming et al. [7] in experiments. More importantly, according to Kirchhoff’s law of thermal radiation [91], an absorption in a specified region equals an emission in that region. Therefore, the enhanced absorption at the band edge region can act as a selective thermal emission channel. Similar to that of dielectric PCs, the concept of emission control with a 3D MPC is to suppress the thermal emission in the band gap region and to redistribute the energy or enhance the thermal emission at the desired band edge region. Such a concept has been recently demonstrated by Lin et al. [87, 90] to modify the thermal emission spectra of tungsten woodpile PCs. This could be very useful for energy harvesting, for example the thermophotovoltaic (TPV) system. In a TPV system, the emitting MPC would convert all absorbed energy into a narrow band of thermal emission that matches an available narrow-bandgap photocell, and therefore increase the efficiency of the TPV process. By using a 3D MPC, Lin et al. have demonstrated a PBG emitter yielding an optical-to-electric conversion efficiency of $\sim 34\%$ and electrical power density of $\sim 14 \text{ W/cm}^2$ at $T=1535 \text{ K}$ [12].

However, the fabrications of 3D MPC are much more challenging than that of 3D dielectric PCs [Table 2.3]. The expensive and complicated chemical evaporation deposition (CVD) [7, 22] techniques limit the researches on this topic. To solve the challenges, people developed techniques to combine the 3D dielectric PC templates with metallisation process to create the 3D metallodielectric PCs (MDPCs) [19–22].
Table 2.3  Fabrication techniques for metal-based 3D PCs

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Year</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical vapour</td>
<td>2002</td>
<td>Tungsten MPC</td>
<td>First MPC with ultra-wide PBGs [7]</td>
</tr>
<tr>
<td>deposition</td>
<td>2006</td>
<td>Copper MDPC</td>
<td>PBGs close to visible wavelengths [19]</td>
</tr>
<tr>
<td>Photo-reduction</td>
<td>2002</td>
<td>Silver woodpile</td>
<td>One-step photoreductive writing [92]</td>
</tr>
<tr>
<td>Infiltration</td>
<td>2005</td>
<td>Gold MDPC</td>
<td>Core/shell gold-silica inverted opal [93]</td>
</tr>
<tr>
<td>Electron-beam</td>
<td>2007</td>
<td>Gold MDPC</td>
<td>3D MDPC with PBGs at visible wavelengths [94]</td>
</tr>
<tr>
<td>lithography</td>
<td>2007</td>
<td>Nickel MPC</td>
<td>Low-cost large-scale fabrication [55]</td>
</tr>
<tr>
<td></td>
<td>2008</td>
<td>Gold opal MPC</td>
<td>Complete PBGs [95]</td>
</tr>
<tr>
<td>Electroless deposition</td>
<td>2006</td>
<td>Silver MDPC</td>
<td>High-quality structures [96]</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>Nickel MDPC</td>
<td>Demonstration of metallic PBGs [20]</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>Copper MDPC</td>
<td>Pronounced metallic band edges [21]</td>
</tr>
<tr>
<td></td>
<td>2008</td>
<td>Molybdenum and tungsten MDPC</td>
<td>High efficiency low-temperature thermophotovoltaic emitters [13]</td>
</tr>
</tbody>
</table>

Three major steps are involved in preparations of 3D MDPCs [96]: fabrication of 3D dielectric PC templates, surface modification of the structures and selective metallisation of the PCs. In the case of PC fabrication, the state-of-the-art 2PP has been widely used because it has a great flexibility to create complex 3D structures and the surfaces of polymerised structures can be easily functionalised for selective metallisation. The metallisation process was generally realised with an electroless deposition method or the conventional CVD process. Compared with CVD and other metallisation methods, electroless deposition is a low-cost and fast process which allows coating of complex surfaces by smooth metallic films with controllable thickness.

So far, 3D MDPCs have been realised operating in the visible or infrared wavelength range with various metals, such as silver, nickel, copper,
molybdenum and tungsten [Table 2.3]. Both the metallic band gap and the band edge have been observed in calculations and experiments. More excitingly, Nagpal et al. recently demonstrated the applications of 3D MDPCs on increasing the efficiency of low-temperature TPV emitters [13]. By using tungsten or molybdenum coated woodpile PCs, their structures achieved an optical-to-electrical conversion efficiency above 32% near 650°C when matched to InGaAsSb photocells. The emitters were over ten times powerful than solid emitters and are very promising in harvesting solar energy, as well as geothermal and industrial waste heat. It can be expected that with the flexibility in sample preparations and with the feasibility of low-temperature TPV operation, more interesting studies will come out towards the applications of 3D MDPCs for emission control.

For most of the reported 3D MPCs and MDPCs, the metallic rods or layers have been employed with thickness far thicker than the skin depth of the metals which excluded the penetration of EM waves into the rods or layers [20, 21]. This causes the major problem in all the current 3D MPCs and MDPCs that they do not support localised plasmon resonances (LPRs) that are based on the metallic nanostructures [22]. The emerging studies on plasmonics [23, 24] and metamaterials [22] could enable metal-based 3D PCs with more promising functionalities, for example the enhanced absorption and negative refraction, which can lead to novel photonic applications but have yet been explored.

To explore the advanced functionalities of 3D PCs, the direction towards development of 3D hybrid PCs is of great potentials. The 3D hybrid PCs in this thesis refer to dielectric woodpile PCs coated with nano-scale (~10 – 20 nm) metallic layers on the structure surfaces, which are conceptually different to conventional metal-based 3D PCs. In such a case, the metallic
layer thickness is comparable with the skin depth of corresponding metals and the EM waves can penetrate through the metallic layers. As a result, plasmon interactions on both surfaces of the metallic layers can be formed, which could result in localised plasmon resonances (LPRs). Chapter 6 is the focus on LPRs in 3D hybrid PCs.

2.7 Chapter summary

This chapter has reviewed important methodologies and technologies regarding theoretical calculation tools, experimental fabrication and reliable characterisation of 3D PCs. The introduced achievements on emission control with 3D PCs at visible wavelengths, as well as the progresses in synthesising 3D metal-based PCs, build up an important platform for functionalisation of 3D PCs for potential applications.
Chapter 3

Fabrication and engineering of passive 3D photonic crystals

3.1 Introduction

Fabrication of high-quality three-dimensional (3D) photonic crystals (PCs) is the first and most important step for exploring the functionalities and applications. The fabrication technique employed in this thesis is the two-photon polymerisation (2PP) method, which is a direct laser writing method. As introduced in Sec. 2.3.2, the 2PP technique allows the robust and flexible fabrication of arbitrary 3D structures with sub-diffraction limited resolution. The schematic of the fabrication system is shown in Fig. 3.1 [64].

In the system, femtosecond ($fs$) pulses with wavelength 580 $nm$ from an optical parametric oscillator (Coherent Mira OPO) are used for fabrication. The OPO is pumped by a Ti:sapphire laser (Mira 900-F, Coherent) operating with a wavelength of 810 $nm$, a repetition rate of 76 MHz and a pulse width of
200 $f$s. A telescopic setup is used to expand, collimate and confine the laser beam for uniform illumination. The pulses were then focused into the sample resin with an oil immersion objective [Olympus, numerical aperture (NA) =1.4, 100×]. The sample, with photosensitive resin sandwiched by two cover glasses, is affixed to a $200\times200\times200\ \mu m$ x-y-z piezoelectric translation stage (P562, Physik Instrumente) for fabrication. A mechanical shutter together with the scanning stage are synchronised and controlled by a computer which is operated according to the programmed patterns of desired structures. The entire fabrication process is monitored in situ with a charge-coupled device (CCD) camera, which provides real-time inspection of the fabrication progress.

Based on this fabrication system, Sec. 3.2 presents the studies on basic fabrications of inorganic-organic woodpile 3D PCs, where structure designs for wide-range stop gaps of 3D PCs are discussed. To explore the functionalities of such inorganic-organic 3D PCs, Sec. 3.3 demonstrates post-thermal treatment as a useful method to improve the spatial resolution and
engineer the stop gaps of inorganic-organic 3D PCs. As a result, the stop
gap of a 3D woodpile PC is tuned over a large wavelength range of 318 nm
from the NIR to visible wavelength region.

### 3.2 Fabrication of 3D woodpile photonic crystals

#### 3.2.1 Structure geometry

One of the advantages of 2PP technique is the flexible fabrication of arbitrary
one-dimensional (1D), two-dimensional (2D) and 3D structures [26,57,65,97].
In the realistic fabrication of 3D PCs, not only flexibility is preferred, but also
the robustness and repeatability of the fabrication are required [98]. For this
reason, woodpile geometry [Fig. 3.2] was proposed by Ozbay et al. in 1994
[99] and has been successfully implemented in robust fabrication of 3D PCs
[4,5,7,64]. As shown in Fig. 3.2, the woodpile structure consists of layers of

![Figure 3.2](image)

**Figure 3.2**  (a) Schematic view of a woodpile PC. (b) The woodpile structure consists of
layers of parallel rods with parameters: \( w \), rod width; \( h \), rod height; \( a \), in-plane rod spacing
(lattice constant); \( c \), height of one unit cell (four times of the vertical layer spacing).
1D rods. Within each layer, the serial of the rods are separated with a lattice constant $a$. The adjacent layers are rotated by $90^\circ$ and between every other layer, the rods are shifted relative to each other by half of the period. Every four layers form one unit with a height $c$. The final woodpile is formed through repeating the unit consequently. In general cases the woodpile structure has a face-centred-tetragonal ($fct$) lattice symmetry and in a particular condition ($c/a = \sqrt{2}$) it belongs to a face-centred-cubic ($fcc$) lattice, both of which have been widely adopted in experimental researches [28, 64, 100].

As mentioned in Sec. 2.3.2, there are numbers of photosensitive resins available for 2PP fabrication. In this thesis, we mainly use Ormocer® resin [70], which is a kind of the silicate-based inorganic-organic hybrid material synthesised with sol-gel techniques. This resin has been successfully used to demonstrate functional photonic structures with enhanced thermal stability and mechanical strength [63, 68, 70, 101]. Moreover, this hybrid resin provide the possibility to explore the functionalities of 3D PCs through engineering their chemical compositions, which will be described in Sec. 3.3. In our experiments, the fabrication speed is empirically controlled around 60 $\mu m/s$ and the fabrication power is varied according to different lattice parameters. After 2PP fabrication with the system in Fig. 3.1, the polymerised resin is washed with a mixture of 4-methyl-2-pentanone and isopropanol (1:2 in volume) for $\sim$30 seconds and rinsed with isopropanol for $\sim$1 minute. The desired structure is finally obtained after a post-exposure of the washed sample under a UV lamp for $\sim$1 minute. Figure 3.3 shows the SEM images of a woodpile PC fabricated in Ormocer® resin with 2PP, which shows high-quality structures with clear view of top three layers. It should be mentioned that four solid frames are fabricated surrounding the woodpile to minimise the shrinkage effects induced during polymerisation.
3.2.2 Stop gaps of 3D woodpile photonic crystals

Due to the low refractive-index of polymer (∼1.5), such 3D PCs fabricated with 2PP do not possess a complete PBG. Nevertheless, a stop gap can exist in certain direction and has been demonstrated in experiments for significant photonic applications [29, 63, 68]. Figure 3.4a shows the numerical calculation of the band gap structure of a woodpile PC, which indicates a stop gap in the Γ-X direction, i.e. in the stacking direction along the z axis. The experimental transmission spectrum of a woodpile PC with the same parameters in calculations is given in Fig. 3.4b (thick solid line), which shows a transmission dip with suppression rate of ∼90% at wavelength 1575 nm as predicted in Fig. 3.4a. One may notice that the transmission in the longer wavelength is ∼100% while the transmission drops at shorter wavelengths outside the dip. This is caused by the light scatterings intrinsically happening in the structures during measurements (as indicated by the dashed line in Fig. 3.4b), which has a complex relation proportional to $1/\lambda$ and can be corrected with the baseline process [73].
Figure 3.4  (a) Calculated band gap structure of a woodpile PC with refractive-index of 1.5375. Partial stop gap in the Γ-X direction is marked by the grey box. (b) Measured transmission spectra of 3D woodpile PCs with a=1.1 µm under different fabrication power (P). Spectra are measured with a pinhole-assisted FTIR (Fourier transform infrared spectroscopy) [Fig. 2.3]. Dashed line guides the light scattering induced drops in transmission.

The stop gap position of 3D PCs is dependent on the rod sizes (w and h in Fig. 3.2b) and lattice parameters (a and c in Fig. 3.2b). Generally, a higher fabrication power generates rods with a larger width and height [58], increases the filling ratio of the PCs and finally pushes the stop gap towards a longer wavelength, as shown in Fig. 3.4b. It should be mentioned that the rod aspect ratio, h/w, is mainly defined by the intensity profile of the objective and is around 2.4:1 for an objective with NA=1.4 [58]. It is also found that the diffusion of the resin in the focal volume can influence the rod aspect ratio [59]. For example, for fabrications with the same total pulse energy, a higher power with less time illumination creates a higher aspect ratio than that of lower power combined with longer time exposure. That is why low repetition rate lasers with highly intensified pulses can create rods with higher aspect ratios, which can reach 5:1 for a Ti:Sapphire regenerative amplifier (Spitfire, Spectra-Physics) [72].

Figure 3.5a shows the transmission spectra of PCs with different lattice constants from 1.5 to 0.8 µm (fcc geometry is conserved). As expected, the
Figure 3.5 (a) Measured transmission spectra of 3D woodpile PCs with a lattice constant from 0.8 to 1.5 $\mu$m. Spectra are shown as measured. Shorter wavelength parts of the spectra are chopped for clarity. (b) Stop gap position as a function of the lattice constant. Experimental data are well fit with a linear curve. A special point (486, 750) is noted as the condition to realise visible woodpile PCs.

Stop gaps of the woodpile PCs are very sensitive to the lattice parameters. One can see that the position of the stop gap is monotonically shifted from 2105 to 1142 nm with decreased lattice, which can be further pushed to 1057 nm with a lattice constant of 700 nm. The measured gap position ($\lambda_c$) of 3D PCs shows a good linear relationship with the lattice constant ($a$) under $\lambda_c = 100 + 1.3375a$, as shown in Fig. 3.5b. This relation is very useful for choosing matched structural parameters to fabricate 3D PCs with stop gaps at desired wavelengths. For example, to achieve a stop gap at visible
wavelengths, the lattice constant needs to be reduced below 486 \(\text{nm}\) and the corresponding layer spacing is less than 172 \(\text{nm}\). However, realisation of 3D PCs with such parameters is very challenging because the resolution limit for 3D PC fabrication is \(\sim 150 \text{ nm}\) in inorganic-organic polymers [63] and \(\sim 120 \text{ nm}\) in pure organic polymers [62], respectively. Although 2D features with \(\sim 30 \text{ nm}\) can be achieved [61, 102], the fragile structures are not applicable for robust 3D PC fabrications. In such a case, we develop a post-thermal treatment method to improve the spatial resolution and engineer the stop gaps of inorganic-organic 3D PCs, which will be presented in the next section.

### 3.3 Engineering 3D photonic crystals with post-thermal treatment

#### 3.3.1 Introduction

Direct laser writing (DLW) is an effective and flexible approach to inducing 2PP in various photoresists and has been intensively studied for the fabrication of 3D arbitrary micro-structures such as 3D PCs [97]. The use of all-organic materials such as SCR and SU-8 [57, 62] cannot only produce 3D PCs with stop gaps in the NIR wavelength range, but also provide useful templates for further preparations of “inverted” PCs with high refractive-index [49, 52]. Though the feature size of 2D polymerised rods can be reduced down to less than 30 \(\text{nm}\) by employing pre-treatment methods [61, 102], their poor thermal and mechanical stability [60, 72, 98] makes them less applicable for fabricating 3D PCs and 3D templates of high quality [103].
These problems do not exist in all-inorganic photoresists, such as chalcogenide glasses [47]. However, the feature size of the fabricated 3D PCs is much poorer than the diffraction limit of the laser writing beam because of the high refractive-index of those materials, which restricts the writing depth and increases the structure distortion due to optical aberrations [47, 104]. The inorganic-organic hybrid materials [28, 70, 103] combine the advantages of both organic and inorganic materials. With the reliable thermal and mechanical stability, such hybrid materials have been successfully applied in the fabrication of functional 3D PCs [29, 68]. However the incorporation of the inorganic part into the polymerised structures has limited the fabrication resolution to approximately 150 nm [63].

Here we use a post-thermal treatment (PTT) method to engineer 3D inorganic-organic PCs through removing the organic compositions of the inorganic-organic backbones [101]. This method is employed to efficiently improve the spatial resolution and engineer the stop gaps of the inorganic-organic 3D PCs. Ultimately, the feature size of the suspended rods is reduced to $\sim 33\text{ nm}$ and the spatial resolution of 3D woodpile PCs is improved to $\sim 86\text{ nm}$. A combination of PTT and the threshold fabrication technique leads to the stop gap of a 3D woodpile PC that can be tuned over a large wavelength range of 318 nm from the NIR to visible wavelength region.

### 3.3.2 Experimental details

Film samples for material characterisations were prepared by illuminating spin-coated photosensitive resins on cover glass with a UV lamp, followed by washing with 4-methyl-2-pentanone and rinsing with isopropanol [29, 70]. The photosensitive resin we used is Ormocer® which is a kind of the silicate-
based inorganic-organic hybrid material. The polymerised structures are stable upon heating at temperature (T) up to 270°C [105]. Before the PTT process, the polymerised films (and all the following samples fabricated by 2PP) were hard-baked at 150°C for 3 h. Then the samples were put onto a hot plate under certain temperature for the PTT process. After each heating process, the samples were naturally cooled down to room temperature for measurements. The absorption spectra of the polymerised films were characterised with a Fourier-transform IR spectrometer (FTIR, Thermo Nicolet) in conjunction with an infrared microscope (Continuum).

The choosing of temperature for PTT is critical. Here the temperature we used for PTT is 300°C, where the thermal gravimetric analysis curve of Ormocer® shows a slow weight loss of less than 1% and the overall structures are stable under heating for 10 hours (h) [106, 107]. In fact, our PTT experiments at 300°C showed the best performance on PC engineering among the tests with temperatures ranging from 150°C to 450°C. The reason is that at this temperature, some organic parts of the polymerised structures starts to be slowly decomposed while the inorganic part is well preserved, behaved as backbones to support the whole structure. As shown in Fig. 3.6, at 300°C, C-H groups belonging to alkyl terminations of Ormocer® molecules are decomposed and Si-OH group are formed [107]. Meanwhile, the methacrylic phase is further polymerised as depicted by the decrease in absorbance of C=O and C=C groups. As a consequence, the structures result more condensed with improved mechanical stability. Meanwhile, the refractive-index of the polymerised films, measured with Becke line method [28], was 1.554±0.002 before PTT and increased to 1.566±0.002 at the PTT time of 3 h and then remained nearly unchanged from 3 to 48 h.

The micron-scale samples in this section were fabricated with the 2PP
method [Fig. 3.1, Sec. 3.2]. A serial of 1D and 2D structures were fabricated with variable exposure power and fabrication speed for comparison purposes. 3D woodpile PCs of different rod spacing were fabricated with various exposure power under a constant fabrication speed of 60 µm/s. The transmission spectra (>900 nm) of the woodpile PCs in the stacking direction were characterised with a pinhole-assisted FTIR [Fig. 2.3, Sec. 2.4]. The transmission spectra of PCs which had a stop gap below wavelength 900 nm were measured with a CCD (Pixis 100, Princeton Instruments): a broadband light source (Oriel Apex QTH Source) was focused into the PCs by an apochromatic objective and the transmitted signals were then collected by another apochromatic objective, dispersed by a spectrograph (Acton Spectropro 300i), and finally detected by the CCD. A small aperture was inserted before the back aperture of each objective to confine the divergence angle to 10° with respect to the stacking direction of the PCs.
3.3.3 Post-thermal treatment effects on 1D and 2D structures

![AFM images of the top surface of a laser-generated thin film (a) before and (b) after 3-h heating at 300°C.](image)

To study the effects of PTT on polymerised structures, firstly, we heated a laser-generated thin film for 3 h at temperature 300°C. As shown in Fig. 3.7, after 3-h PTT the surface roughness of the polymerised film is improved significantly by 45% from 10 to 5.5 nm, which is similar to the thermal annealing effects on other polymers [108]. Meanwhile, the maximum height of the features is reduced.

The effect of PTT on the height of the polymerised structures was then tested on an array of the fabricated parallel rods with ascending heights [Fig. 3.8a]. The truncated rods were heated with several steps and the sample was characterised by an atomic force microscope (AFM) after each process. As shown in Figs. 3.8b-d, both the height ($H$) and width ($W$) of the rods are significantly reduced after PTT, different for rods with different initial heights [Fig. 3.8d]. In particular, the amount of reduction reaches 79% for a 69.6-nm-high rod, of which the height is reduced to 14.4 nm after 36-h PTT (see another sample in the inset of Fig. 3.8e). The plots of the height ratio ($H/H_0$), where $H_0$ is the height of the rod before PTT, as a function of
The data beyond 3 h are fitted with the exponential decay curve. The fitted decay speeds are 0.162, 0.199 and 0.223 h⁻¹ for rods with \( H_0 \) of 193, 287 and 361 nm. Inset: Cross-sections of rods before and after 36-h PTT.

the heating time reveal that the lower the rod, the larger the reduction (see Fig. 3.8e). However, the exponential decay behaviour of the plots shows that the lower rod has a decay speed slower than that of the higher one after 3 h. This is because the lower rods have larger surface-to-volume ratios, which leads to faster heat dissipation and slower PTT effects in the case of thermal conduction.

We further studied the effect of PTT on the suspended rods fabricated between two solid supporters. Figures 3.9a-b show the SEM images of the rods with a length of \( \sim 1.5 \, \mu m \) before and after 3-h PTT, respectively. One
can see that the width of the rods is significantly reduced without cracks (the nonuniform sizes of the rods were induced by the stretches from the solid supporters [109]). For comparison, we plot the rod width before and after 3-h PTT as a function of the fabrication speed $V$ and power $P$ in Figs. 3.9c-d, respectively. It can be seen that the rod width is monotonically reduced but thicker rods are reduced by a larger percentage than the thinner ones. This is because the thicker rods have a smaller surface-to-volume ratio that results in slow heat dissipation, which makes the PTT effect more efficient. One important feature of the rods after 3-h PTT is that the suspended thin rods can preserve a good mechanical property such as rods with a long length of $\sim 5.5 \mu m$ shown in Fig. 3.9e, while the reported all-organic polymer structures are less robust under such high temperature ($300^\circ$C). Furthermore, it is found that the minimum rod width of $\sim 50 \ nm$ fabricated with 2PP can be efficiently reduced to $\sim 33 \ nm$ with PTT for only 3 h, as shown in Figs. 3.9f-g.
3.3.4 Tuning stop gaps of 3D photonic crystals with post-thermal treatment

![Figure 3.10](baseline_corrected_transmission_spectra.png)

**Figure 3.10** Baseline corrected transmission spectra of a 3D woodpile PC in the stacking direction upon heating for 30 minutes under different temperatures. Spectra are translated for better view. The schematic on the right side shows the indicated side view of the PC after corresponding heating process.

The reliable mechanical properties of the structures after PTT lead to a new way to engineer 3D inorganic-organic PCs. However, to maintain the geometry of 3D PCs, one needs to carefully choose the temperature for PTT (as mentioned earlier). Figure 3.10(left) shows the transmission spectra of a woodpile PC under heating at different temperature for 30 minutes. We can see that the spectrum keeps unchanged for temperature up to 250°C because polymerised Ormocer® are stable up to 270°C [105]. When the heating temperature is higher than 350°C, dramatic changes happen in both gap positions and gap shapes, which are caused by the fast thermal effects and indicate the symmetry of the PC is destroyed (asymmetric reduction, noted as the right side of Fig. 3.10). It is very interesting that at a balanced
temperature of 300°C, the gap position shifts but the gap shape preserves, which reflects the maintained geometry of the woodpile structure (symmetric reduction).

Further heating PCs at the temperature of 300°C shows that the periodical structures of the PCs are well preserved after heating for 3 and 20 h [Figs. 3.11a-b], respectively, showing a good mechanical strength under PTT. The rod spacing of the woodpile, initially designed and fabricated at 1.1 µm, was reduced to 1.0 µm after the PTT [Fig. 3.11b]. Meanwhile, the

Figure 3.11  (a) and (b) SEM images of 3D woodpile PCs after PTT for 3 and 20 h, respectively. (c) Measured transmission spectra of a 32-layer woodpile PC in the stacking direction before and after 3-h PTT. The four areas noted by dashed circles indicate the increased transmission at shorter wavelengths. The two vertical arrows point out the “defect” within the stop gap, which disappears after PTT. (d) Baseline corrected transmission spectra of a 32-layer woodpile PC at different heating time (from right to left): 0, 3, 6, 9, 15, 38 h. (e) Relationship between \( \Delta \lambda / \lambda_c \) and the heating time. Experimental data beyond 3 h are fitted well with the exponential decay model with a decay speed of 0.117 h\(^{-1}\). Inset: Microscope image of the PC after PTT. The outer dashed square and the inner solid square mark the woodpile before and after heating for 38 h, respectively.
measured transmission spectra of a woodpile PC, as shown in Fig. 3.11c, reveal that the centre of the stop gap is shifted from 1621 to 1458 nm after 3-h PTT, indicating that the periodicity in the stacking direction is significantly reduced. Moreover, one can notice that the transmission at shorter wavelengths increases, which means less scattering losses of the heated structures due to the improved surface roughness. Another improvement is that unwanted “defects” within the stop gap, induced by the residual stresses inherent in the fabrication process, can be cured by the PTT process that release these residual stresses, as noted in Fig. 3.11c.

The blue-shift effect of stop gaps induced by PTT can be applied to tune the stop gaps of PCs. As shown in Fig. 3.11d, the stop gap of a PC can be continuously tuned from 1596 to 1345 nm with increasing the PTT time, which covers the important telecommunication wavelengths. During this process, the suppression rate of the stop gap reaches a maximum at the heating time of 3 h. On the other hand, the gap/midgap ratio of the stop gap, which is related with the symmetry of the PC, keeps constant around 7.63% with a small fluctuation of less than 0.37% for heating up to 9 h, indicating the internal symmetry of the PC was perfectly preserved within 9 h. After 9 h, small modifications have been observed [Fig. 3.11d] in the shapes of stop gaps, which indicates the original geometry of part of the woodpile was slightly changed. Nevertheless, the position of stop gaps was consistently shifted towards shorter wavelengths. Figure 3.11e shows the relative blue-shift of the stop gap (Δλc/λc0, λc0 is the centre wavelength of the stop gap before PTT) as a function of the heating time. One can see that the experimental data beyond 3 h fit well an exponential decay curve, which is similar to the change in heights of 2D rods on the cover glass [see Fig. 3.8e]. Since the refractive-index of the polymerised structures has no noticeable
change when the PTT time is longer than 3 h, the value of $\lambda_c$ is proportional to the lattice period in the stacking direction. Thus, the change in $\Delta \lambda_c / \lambda_{c0}$ reasonably reflects the change in the period in the stacking direction and the corresponding fitting relation consistently indicates a smooth reduction in size without much distortions and cracks inside the structure. Meanwhile, in the in-layer plane, a microscope image of the PC after 38-h heating [inset of Fig. 3.11e] shows the lateral size of the woodpile is reduced by $\sim 16.3\%$, similar to the corresponding value of $\Delta \lambda_c / \lambda_{c0}$ (15.7%), which indicates that the overall 3D structure is symmetrically reduced during PTT.

It should be emphasised that the measured transmission spectra of the PCs were very sensitive to the structure geometry. Any effect of PTT, including the influence of the substrate, can be reflected in the changes of stop gaps of PCs. Deviation of PTT temperature from $300^\circ C$ would result in no engineering effects ($T<300^\circ C$) or distortions of the stop gaps ($T>300^\circ C$). That is why it is very important to perform the PTT process at $300^\circ C$ to realise symmetric engineering of PCs.

3.3.5 Realisation of visible 3D woodpile photonic crystals

The combination of PTT and the threshold laser writing method [26,68,110] can improve the resolution in fabricating inorganic-organic 3D PCs and thus realise the operation in the visible wavelength range. As shown in Fig. 3.12a, the stop gap of a 700-nm-lattice woodpile PC, fabricated by the threshold method at a power of 1.3 $mW$, can be tuned from wavelength 1007 to 746 $nm$ after 21-h PTT. For comparison, a PC with a rod spacing of 800 $nm$ was
Figure 3.12  (a) Measured transmission spectra of a 20-layer woodpile PC with a rod spacing of 700 nm. The centres of the stop gaps before and after 21-h heating are located at wavelengths 1007 and 746 nm, respectively. (b) and (c) Measured transmission spectra of 20-layer PCs with rod spacings of 800 and 700 nm after PTT for 21 and 6 h, respectively. The centres of the stop gaps are located at wavelengths 831 and 723 nm, respectively. Inset of (c): SEM image of the PC in (c). The width of the rod is reduced to ~86 nm.

fabricated along with the 700-nm PC and experienced the same process. As shown in Fig. 3.12b, its stop gap was finally tuned to wavelength 831 nm but shows a smoother and deeper gap than that in Fig. 3.12a, which reveals that the PC with a larger lattice constant can maintain better performance for long-time PTT. Moreover, the appearance of a higher order gap [64] at wavelength 531 nm [in Fig. 3.12b] indicates that the symmetry of the woodpile is well preserved. The SEM image depicted in the inset of Fig. 3.12c
shows that the width of the rods of the 3D PC can be reduced to \(\sim 86\) \(nm\), which is reduced by a factor of two compared with the previously reported value of \(\sim 150\) \(nm\) in the inorganic-organic hybrid polymer [63].

Since the PTT speed is related to the surface-to-volume ratio of the initial rods [see Figs. 3.9], we fabricated another 700-nm-lattice PC with a slightly higher power of 1.35 \(mW\), which results in thicker rods than those of the PC in Fig. 3.12a. It is noted that the stop gap of this PC, initially at wavelength 1041 \(nm\), is tuned to 723 \(nm\) after PTT only for 6 \(h\) [Fig. 3.12c]. The fast tuning in the stop gap is caused by the more efficient PTT of the thick rods due to their slow heat dissipation, which results in the large speed in the overall size reduction. It should be mentioned that the \(\Delta\lambda_c/\lambda_{c0}\) of this PC reaches \(\sim 30\%\), which is the largest ratio in gap tuning of the 3D PC to our knowledge.

### 3.4 Chapter conclusion

This chapter has demonstrated high-quality fabrication and wide-range engineering of 3D woodpile PCs, which provide a reliable platform for subsequent studies such as active 3D PCs, spontaneous emission control and 3D hybrid PCs.

It has been shown that in 2PP fabrications, high-quality 3D PCs with stop gaps from wavelength 1.05 to 2.10 \(\mu m\) can be realised when the lattice varies from 0.7 to 1.5 \(\mu m\). This wide range of stop gaps offers a great flexibility in subsequent studies where the wavelength matching is needed. Furthermore, a linear relationship between the stop gap and the lattice constant is verified and will act as a direct guide for 3D PC fabrications. The linear relationship
also predicts the condition for realising visible 3D PCs, of which the lattice needs to be shortened to 0.49 \( \mu m \).

In the aspect of stop gap engineering, we have proposed and demonstrated a PTT method as an engineering approach to improve the fabrication resolution of the structures fabricated with 2PP in inorganic-organic hybrid materials. In the cases of the 2D truncated rods on cover glass, the 2D suspended rods and the 3D woodpile PCs, the limits of the feature size reach \( \sim 14.4 \), \( \sim 33 \) and \( \sim 86 \) \( nm \), respectively. This PTT method results in structures with high mechanical stability and has been successfully applied to substantially tune the stop gaps of the woodpile PCs. In particular, a continuous 251-nm-tuning range of the stop gap of a 3D PC has been achieved. The integration of this PTT method with the threshold fabrication method has resulted in a 3D woodpile PC operating at visible wavelengths. This work provides a useful option for producing smaller templates for the fabrication of NIR or visible high refractive-index inverse woodpile PCs [49, 52] as well as a constructive platform for promising applications of 3D visible woodpile PCs. Varying the ratio between organic and inorganic parts in the hybrid polymers provides another dimension to functionalise the structures to meet various demands through a temperature-dependent PTT process.
Chapter 4

Quantum-dot-based active 3D photonic crystals

4.1 Introduction

Incorporating functional materials is a convenient approach to functionalise three-dimensional (3D) photonic crystals (PCs). The strong 3D confinement of light in 3D PCs provides a powerful tool to study the emitting properties of incorporated materials. Recently, the control of radiation dynamics of quantum dots (QDs) inside PCs 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 [17, 79, 80, 111]. To explore the important potentials of 3D PCs on emission control, active 3D PCs other than passive PCs are required, in which case the critical step is to incorporate active media into 3D PCs.

In this chapter, we will demonstrate the functionalisation of 3D PCs by
using two simple but efficient methods, doping and infiltration techniques [Fig. 4.1], to incorporate PbSe QDs into 3D woodpile PCs fabricated by the two-photon polymerisation (2PP) method. Sec. 4.2 presents the approach to firstly dope QDs into the resin and fabricate the 3D PCs subsequently, which is outlined as scheme 1 in Fig. 4.1. With this scheme, 3D PCs with pronounced partial stop gaps are successfully realised in a PbSe QD-doped composite material. As another convenient way of incorporating QDs, scheme 2 in section 4.3 directly employs the 3D PC templates fabricated with 2PP (see Chapter 3) and introduces QDs into 3D PCs with a flexible infiltration method. It shows that both QDs incorporation schemes can be realised in normal environment and have the flexibility for investigations on emission control at telecommunication wavelengths.
4.2 Direct fabrication of 3D photonic crystals in QD-doped nanocomposites

In this section, we demonstrate, for the first time, the feasibility to functionalise 3D PCs by incorporating PbSe QDs into 3D PCs through directly fabricating the PCs in a commercial QD composite. By using the 2PP technique, 3D QD-doped PCs have been successfully fabricated with pronounced PBGs (suppression rate $\sim 50\%$) in the near-infrared (NIR) wavelength region [28].

4.2.1 Fabrication process

To test the feasibility of polymerisation of QD composite, we used a commercial PbSe QD composite bought from Evident Technologies (1550 nm Java PbSe Core Shell Evidots in UV Curable Sol-Gel with a concentration of $5 \text{ mg ml}^{-1}$). The PbSe QDs had a peak absorption at wavelength 1537 nm and a peak emission at wavelength 1600 nm. Before fabrication, the PbSe QD composite was dropped onto a coverslip and heated in an oven for 10 minutes at a temperature of 70°C. The pre-baked resin was then sandwiched by another coverslip and fixed to a computer controlled piezoelectric-driven nano-scanner (PI, 200×200×200 $\mu\text{m}$) for fabrication.

With the fabrication system in Sec. 3.1, laser pulses were focused into the resin with an oil immersion objective [Olympus, numerical aperture (NA) =1.4, 100×]. The threshold for 2PP with this QD composite was $\sim 3.25 \text{ mW}$ before the aperture of the objective and 3D structures can be well-developed with irradiation power above 4.5 mW with a scanning speed of 50 $\mu\text{m/s}$. Under such a low power level, no degradation of QDs was observed. After
the polymerisation process, the sample was washed in methanol for \( \sim 1 \) minute and rinsed with isopropanol for \( \sim 1.5 \) minutes to remove the unpolymerised resin. The developed sample was then illuminated by a UV lamp for 30 seconds to strengthen the structure. Due to the low volume fraction ratio of QDs (\( \sim 0.06\% \) calculated from the concentration), no noticeable influence of QDs on the 2PP process has been observed during the experiments. The refractive-index of the polymerised QD composite was measured to be 1.494\( \pm 0.002 \) by using the traditional Becke line method with a serial of refractive-index liquids (Cargille Laboratories).

### 4.2.2 Stop gap properties of QD-doped 3D photonic crystals

Figure 4.2a outlines the sketch of a 3D woodpile PC with a rod spacing of \( a \) and a four-layer height of \( c \). As shown in the unit cell of the reciprocal

![Figure 4.2](image)

**Figure 4.2** (a) Sketch of a woodpile structure fabricated with 2PP. (b) The first Brillouin zone of the woodpile structure. (c) SEM image of a 50\( \times \)50\( \times \)13.5 \( \mu m^3 \) 3D woodpile PC with a solid frame to support the structure. (d) SEM image of polymerised rods with rough surfaces after improper post processing. (e) SEM image of smooth rods after proper post processing.
lattice (the first Brillouin zone) in Fig. 4.2b, the Γ-X direction represents the stacking direction of the woodpile structure. Figure 4.2c shows the SEM image of a 3D woodpile QD-doped PC with a face-centred-tetragonal (fct) lattice fabricated by means of 2PP. To prevent the structure from collapsing and to minimise the polymer shrinkage during the post development, a solid frame was fabricated around the woodpile structure.

The post treatment after the polymerisation process is critical for fabrication of high-quality woodpile structures in the QD composite with good PBGs. In some circumstance, due to improper post processing, the embedded QDs may cause rough surfaces of the structure [Fig. 4.2d], leading to the disappearance of the PBG which may exist for structures with smooth surfaces for the same lattice parameters. The problem can be improved by carefully optimising the post processing, such as controlling the time for washing and rinsing. As shown in Fig. 4.2e, the structure with smooth rods can be realised by increasing the washout time to ~1.5 minutes compared to ~1 minute used for the structure shown in Fig. 4.2d.

Due to the low refractive-index of the polymerised QD composite, the fabricated crystals did not possess a complete PBG. Nevertheless, 3D PCs with partial PBGs can also find applications in photonics [63,68]. In this section, we mainly investigate the partial PBGs around the stacking direction. The transmission spectra of the fabricated 3D QD-doped PCs were measured by using a Fourier-transform infrared (FTIR) spectrometer (Thermo Nicolet) in conjunction with an infrared microscope (Continuum). The reflective objective of the microscope (Reflechromat, 32×, NA=0.65) provides a hollow light cone varying from 18° to 41° [see Fig. 4.3a]. To measure the PBG in the Γ-X direction accurately, a wedge with an angle of 31° was used to tilt the sample and a small pinhole was placed in front of the objective to confine
(a) Sketch of the reflective objective of FTIR with a pinhole setup for the measurement of PBGs. The pinhole provides a confined light cone with a half angle of $\theta$. (b) Transmission spectra of a 3D QD-doped PC measured in the stacking direction with different confined angles. [N means no pinhole being used. R, suppression rate after baseline correction. Spectra were translated along y-axis to 100% at 2200 nm. The shadow area corresponds to the calculated PBG as (c).] (c) Calculated band structure of the woodpile PC with an fct lattice ($n=1.494$) by using the free MPB software package [30]. The shadow area indicates the PBG in the stacking direction, i.e., the $\Gamma$-X direction. (d) Transmission spectra of 3D QD-doped PCs with different lattice constants measured in the stacking direction with $\theta = 5^\circ$.

Because the partial PBGs are directional, the size of the pinhole, i.e., the size of the confined angle, influences the transmission spectra significantly. The minimum angle of confinement determines the maximum transmission suppression rate [shown in Fig. 4.3b]. When the measurements were performed with a half angle of $5^\circ$, $10^\circ$ and without the pinhole, the suppression rate of the PBG decreased from $\sim50\%$ to $\sim28\%$ and $\sim13\%$, respectively.
while the gap/midgap ($\Delta \omega/\omega$) ratio of PBG increased from $\sim 11\%$ to $\sim 15\%$ and $\sim 23\%$, accompanying with a blue shift of the midgap wavelength from 1636.8 $nm$ to 1636.3 and 1621.4 $nm$. This phenomenon can be explained by the calculated PBG structure in Fig. 4.3c. Because we measured the PBGs around the stacking direction (noted by the shadow area in Fig. 4.3b-c), the position of the PBG could be slightly shifted towards the shorter wavelength when the measured direction deviated from the $\Gamma$-$X$ direction towards, for example, the $\Gamma$-$W$ direction. If the range of the detection angle increased, the measured transmission spectra could include PBG information from multiple directions rather than in a single direction. The effects of overlapped PBGs finally resulted in the broadening of the PBG and the decreasing of the suppression rate in the transmission spectra. Therefore, a small confined angle needs to be employed for measuring the partial PBG accurately.

Another thing needs to be pointed is that the size of confined angle should be chosen under the precondition that the Airy disk diameter of the pinhole setup is less than the lateral size of the sample. Figure 4.3d shows the transmission spectra of three different 3D QD-doped PCs measured with the confined angle of $5^\circ$. With lattice constants of 1.2, 1.3 and 1.4 $\mu m$, the three woodpile PCs show partial band gaps at wavelengths 1637, 1728, and 1818 $nm$, respectively. The band gaps of the former two PCs have suppression rates of $\sim 50\%$. 
4.3 Infiltration of QDs into 3D photonic crystals

4.3.1 Sample preparations

Infiltrating QDs into fabricated PC templates is another method to functionalise 3D PCs [scheme 2 in Fig. 4.1]. In this scheme, the 3D PCs were firstly fabricated by using the 2PP method [Sec. 3.1]. The fabricated 3D woodpile PCs possess high-quality stop gaps with a wide range from wavelength 1.05 to 2.10 $\mu$m [Sec. 3.2], which cover the important telecommunication wavelength region.

On the other hand, synthesising PbSe QDs with emission close to wavelength 1550 nm was based on a modified wet chemical method reported by Yu et al. [112]. The lead pre-cursor, a mixture of 0.8 g PbO, 2.86 g oleic acid, and technological grade 1-octadecene (ODE) (to a total mass of 16 g), was gradually heated to 150$^\circ$C after de-gassed at a temperature of 80$^\circ$C for one hour. When the solution turned clear, an injection solution containing 0.64 g selenium, 6.0 g trioctylphosphine and technological grade ODE (to a total mass of 10.1 g) was swiftly injected. The mixed solution was cooked at a constant reaction temperature of 150$^\circ$C for short-term growth (normally 0.5 to 5 minutes dependent on requirements) and then cooled to room temperature. The synthesised QDs were purified by 1:1 chloroform/methanol solution repeatedly and finally dissolved in toluene after filtered by a 0.2 $\mu$m filter. The mean diameter of the resulted QDs is mainly dependent on the growing time. For example, a long-time growth results in QDs of large sizes. In this section, the PbSe QDs has grown for 1 minute and resulted with size distribution centred at $\sim$4.8 nm. The PbSe QDs solution prepared by such
method can have a quantum efficiency of more than 85% [112]. In solid thin film, the quantum efficiency was estimated to be \( \sim 4\% \).

### 4.3.2 QDs infiltration process

The process for infiltrating PbSe QDs into 3D woodpile PC is illustrated in Fig. 4.4. Here the 3D woodpile PC fabricated by using the 2PP method was formed layer-by-layer, directly on a cover glass, as drawn in Fig. 4.4a. Figure 4.4b shows the SEM image of a fabricated 3D woodpile PC with a

![Figure 4.4](image)

(a) Schematic of a 3D woodpile PC fabricated on a cover glass. For the face-centred-cubic (fcc) symmetry, the lattice period \( a \), and the height of every four layers \( c \), satisfy \( c/a = \sqrt{2} \). (b) SEM image of a 3D woodpile PC with a 10-\( \mu \)m-wide frame. An enlarged view is superposed at the centre of the image. A square through-hole was fabricated within each side of the frame (noted by arrows). (c) Schematic of the infiltration process.
lattice constant of 1 \( \mu m \) and an overall size of 50\times50\times13.5 \( \mu m^3 \). A massive frame with a height of 14.5 \( \mu m \) and a width of 10 \( \mu m \) was built around the woodpile PC to prevent the structure from collapsing and to minimise the polymer shrinkage during the post-development. The frame also acted as a wall to protect the woodpile structure from the disturbance during the QD infiltration process [see Fig. 4.4c]. In addition, a 3\times3 \( \mu m^2 \) square through-hole was fabricated at the bottom of each side of the frame (as shown in Fig. 4.4b), which facilitated the flow of air and solvent through the PC during the infiltration process.

Here, we utilised PbSe QDs with emission properties matching the band gaps of the 3D woodpile PCs. PbSe QDs stabilised with oleic acid were prepared using the method described in Sec. 4.3.1. To achieve a high QD packing density on the surface of the PC structure (ca. 20%), the QDs were deposited directly from their toluene solution (\( \sim 10^{-6} \text{ mol/l} \)). The infiltration process was performed through drop casting of 50 \( \mu L \) QD solution onto the PC sample. To obtain homogeneous infiltration, the QD solution was added in four 12.5 \( \mu L \) steps while the sample was kept on a hot plate set at a temperature of 75\(^\circ\)C (Fig. 4.4c). The toluene evaporated rapidly before the concentration of QD solution inside the PC was significantly influenced by the surface tension of liquid. In this way, the QDs were deposited uniformly on the surface of polymerised rods of the PC through physical adsorption after the independent evaporation of the solvent. A QD film with a thickness of \( \sim 0.5-1 \mu m \) was formed outside the PC during the infiltration, thus providing a direct and convenient reference for our studies of QD emission inside the PC. Unlike incorporation techniques performed with composites [28], this method allows the infiltration and washing processes to be repeated by many times for a given sample, giving a reliable comparison between different QD
loading levels in the PC.

4.3.3 QDs infiltration induced red-shift in stop gaps of a 3D photonic crystal

By varying the infiltration condition, a concentration-dependent red-shift of the stop gap of the infiltrated 3D PC was observed, as shown in Fig. 4.5. The red-shift of the mid-gap increases with the concentration of the QD solution, reaching a maximum of 68 nm at $3C_0$ ($C_0$ corresponds to $\sim 7.7 \times 10^{-7} \text{ mol/l}$ in Fig. 4.5) and then decreases slightly at $4C_0$ when the scattering of the infiltrated QDs becomes so strong that the band gap shape is significantly affected (see the inset of Fig. 4.5). The physical reason for the red-shift is that the filling ratio and therefore the average refractive-index of the structure increase as the QD concentration increases. Based on an iterative eigensolver program [30] we can estimate that a red-shift of 68 nm corresponds to a

![Figure 4.5](image)

**Figure 4.5** Baseline corrected transmission spectra of a PC in the stacking direction after the infiltration of PbSe QDs with different concentrations. (Inset) Experimental (Exp, square points) band gap shift ($\Delta\lambda_c$) for different concentrations of the PbSe QD solution and calculated (Cal, dashed curve) $\Delta\lambda_c$ for uniform QD layers with different average thickness.
QD layer (with a volume fraction of 20%) with a thickness of $\sim 10-20$ nm, corresponding to 2-3 monolayers of QDs. This is in reasonable agreement with an estimate of 2 monolayers based on the known quantity of QDs loaded into the PC.

4.4 Chapter conclusion

This chapter has demonstrated doping and infiltration as two efficient and flexible approaches to functionalise 3D PCs, which provide a critical step to effectively engineering spontaneous emission for the next-generation NIR photonic applications.

It has been shown that fabrication of 3D PCs in PbSe QD-doped composite materials is a delicate approach to achieve homogeneous distribution of QDs inside the PCs. 3D PCs with pronounced partial stop gaps (with suppression rate $>50\%$) have been successfully realised in the NIR wavelength region. Based on this technique, two issues need to be considered in future applications. The first one is the concentration of QDs in the doped composite. When using QDs of high concentrations, laser scattering from high refractive-index QDs and the corresponding decrease in photoinitiator concentration may cause the challenges in realisation of 2PP. Another issue is that the functionalities of QDs might be influenced by the resin. For example, the emission from QDs can be quenched due to the energy transfer process between QDs and the doped resin. The second issue actually hindered our further studies on emission control with QDs inside the 3D PCs. Nevertheless, this scheme is able to induce homogeneous distribution of QDs inside the PCs and the challenges can be solved according to recent progresses in material science [27].
By comparison, the infiltration method provides a more controllable approach to study on the radiation dynamics from QDs inside the 3D PCs. The PC templates are pre-formed and the amount of QDs inside PCs can be flexibly varied by simply changing QD concentration or adjusting infiltration times, which can greatly facilitate future studies. Therefore in this thesis, the infiltration method is mainly chosen for the study on radiation dynamics of QDs embedded in 3D PCs, which will be described in Chapter 5.
Chapter 5

Manipulation of near-infrared QDs radiation with 3D photonic crystals

5.1 Introduction

Radiation dynamics and spectral modification of spontaneous emission (SE) [17] with three-dimensional (3D) photonic crystals (PCs) have been investigated with QDs emitting visible light. However, experimental study on emission control of QDs with 3D PCs in the near-infrared (NIR) wavelength region, which holds a key to next generation photonic devices for telecommunications [112–115], has not yet been demonstrated. By using the two-photon polymerisation (2PP) method, high-quality 3D woodpile structures with photonic band gaps (PBGs) in the telecommunication wavelength range can be fabricated [62,64,73], providing an excellent platform to study the radiation dynamics of QDs emitting in the telecommunication
wavelength range inside 3D PCs.

Based on the QD-based active 3D PCs in previous chapter [Sec. 4.3], in this chapter we demonstrate the functionalities of 3D polymeric PCs on manipulation of SE from embedded QDs in the NIR wavelength region [29, 116]. Section 5.2 is built on the experimental studies on the spectral redistribution of QDs emission inside a 3D PC. As an observation, Section 5.2.2 describes the redistributed QDs emission spectra within a 3D PC. Section 5.2.3 presents the studies on the radiation decay properties from QDs inside the PCs by utilising a time-correlated single photon counting system. With careful comparisons of the measured average lifetimes, the stop gap effects of 3D PCs on SE are resolved, which approves the modifications of SE with 3D polymeric PCs [29]. As a further study, Section 5.3 reports the direction-dependent radiation decays from near-infrared QDs at the angular band edges of a 3D PC [116]. The inhibition of SE, as well as the enhancement effects, have been observed in the mid-gap and at the centre of the band edge, respectively.

5.2 Spectral redistribution in spontaneous emission from QDs inside 3D photonic crystals

5.2.1 QDs emission in free space

The PbSe QDs studied in this chapter was synthesised by using the method in Sec. 4.3.1. One of the most remarkable properties of QDs is their size-dependent emission spectra. As shown in Fig. 5.1, the emission peaks of
the QDs can be shifted from 1453 to 1589 nm when the mean size of QDs increases from $\sim$4.2 to $\sim$4.9 nm. It is found that QDs exhibit isotropic emission properties in homogeneous free space, i.e. the emission properties of QDs are independent on spatial position and emission angles, which provide ideal references for subsequent studies on QDs emission inside 3D PCs.

### 5.2.2 Redistributed QDs emission spectra inside a 3D photonic crystal

To study the photonic effects of 3D PCs on QDs radiation, 3D PCs embedded with PbSe QDs were firstly prepared with the infiltration method described in Sec. 4.3.2. The absorption spectra of the QDs film on the cover glass were measured with a Fourier-transform infrared spectrometer (FTIR, Thermo Nicolet) while the emission properties of QDs before and after infiltration were characterised using the setup depicted in Fig. 5.2. As the setup of Detection Path #1 in Fig. 5.2, a high numerical-aperture (NA) objective
(NA=1.45) was used to focus a femtosecond (fs) pulsed beam of wavelength 800 \textit{nm}, generated from a Ti:Sapphire laser (linearly polarised, Spectra Physics Mai Tai), on a sample and to collect the emission signals. The size of the focal spot was approximately 2.5 \textit{µm}$^2$, allowing for specific excitation of QDs inside the small PC. The position of the excitation spot was monitored by a CCD camera to ensure that the focus spot was located in the central part of the PC. The emission spectra were measured by a spectrograph (Acton Spectropro 300i) with an InGaAs detector (Hamamatsu G6122). A lock-in amplifier (Stanford Research Systems SR850) connected with a mechanical chopper was employed in the system to enhance the signal-to-noise ratio of weak signal detection.

As shown in Fig. 5.3a, the dried PbSe QDs had absorption and photoluminescence (PL) emission peaks centred at wavelengths of 1500 and 1580 \textit{nm}, respectively. The broad PL emission results from the size distribution of the QDs but can match well the stop gap of a PC (shown in Fig. 5.3b),
Chapter 5

Figure 5.3  (a) Normalised absorption and PL spectra from PbSe QDs on a cover glass. (b) (solid curve) Baseline corrected transmission spectra of a PC in the stacking direction after QDs infiltration. (dashed curve) PL spectrum of QDs outside the PC.

Figure 5.4  PL spectra from QDs outside (a) and inside (b) the PC under different power (P) levels. Inset: normalised PL spectra from the QDs outside (a) and inside (b) the PC. The spectra in the inset of (b) show the relative increase in intensity at shorter wavelengths.
which was infiltrated with a QDs solution with a concentration of \(\sim 2C_0\) (\(C_0\) corresponds to \(\sim 7.7 \times 10^{-7}\) mol/l in Fig. 4.5).

To study the influence of the PC on the QDs emission spectra, we excited the PbSe QDs inside and outside the PC, respectively. As shown in Fig. 5.4a, the PL spectra from the QDs outside the PC increase uniformly with the excitation power and the normalised spectra show an almost identical shape (see the inset of Fig. 5.4a). By comparison, the normalised PL spectra from QDs inside the PC show a wavelength-dependent change, as seen in the inset of Fig. 5.4b. The intensity in the shorter wavelength range increases more quickly with the excitation power than that in the longer wavelength range.

Figure 5.5 shows the intensity ratio between wavelengths 1350 and 1580 nm for QDs inside and outside the PC, respectively. While the intensity ratio for QDs outside the PC remains constant at approximately 0.24, the ratio for QDs inside the PC increases with the excitation power and is nearly twice as large as that of QDs outside PC, indicating a spectral redistribution.

![Figure 5.5](image)

**Figure 5.5** Ratio of the PL intensity between wavelengths 1350 nm (I\(_{1350}\)) and 1580 nm (I\(_{1580}\)) versus the excitation power for QDs inside and outside the PC, respectively.
in SE from QDs inside the PC. It should be pointed out that 3D woodpile structures with band gaps mismatching the QDs emission wavelength range did not exhibit such a spectral redistribution. A possible physical explanation on this phenomenon is that the emission of the QDs in the longer wavelength range is inside the stop gap of the PC where the emission is inhibited while the emission of the QDs in the shorter wavelength range is close to the edge of the stop gap where the emission is permitted.

5.2.3 Modified QDs radiation decays inside a 3D photonic crystal

To confirm the PBG effects on the QDs radiation, time-resolved experiments were performed to investigate radiative decays of QDs under different environments.

5.2.3.1 Time-resolved measurement system

The time-resolved experiments in this thesis were conducted by employing a time-correlated single photon counting technique (TCSPC) [117]. As shown in the setup of Detection Path #2 in Fig. 5.2, linearly polarised laser excitation at wavelength 800 nm was provided by a Ti:Sapphire femtosecond pulse laser (Spitfire, Spectra Physics), operating with a pulse of 100 fs and a repetition rate of 1 kHz. The signals were collected by an objective (NA=0.8, 100×, IR enhanced), focused on the entrance slit of the spectrograph, dispersed by the spectrograph gratings (600 lines/mm, blazed at 1600 nm), and finally detected by a fast NIR photomultiplier (PMT, Hamamatsu, H10330-75). The focal length of the lens before the
spectrograph and entrance slit width of the spectrograph were well matched confocal conditions. Therefore, only QDs emission from the focal volume of the objective can be detected, which makes it suitable to resolve the density of states (DOS) or local DOS (LDOS) related radiation properties.

To conduct the TCSPC measurement, the arrival time of photons at the PMT was correlated to the pump reference as measured by a trigger diode (PicoQuant TDA 200). Both the trigger diode and PMT were interfaced to

![Diagram](image)

**Figure 5.6** Principle of the time-correlated single photon counting technique. (a) Primitive decay curve $\rho(t)$. (b) Schematic of photon recordings at time channel $t_1$ and $t_2$ relative to the exciting laser pulse. The number of counts at each time channel $t$ is used to form a histogram. (c) Reconstruction of the decay curve based on the histogram obtained with TCSPC.
a TCSPC module (PicoHarp 300, PicoQuant GmbH), which carried on the single photon counting and reconstructed the PL decay curve based on the counted histogram [Fig. 5.6]. In the case of direct detection of the PL decay in Fig. 5.6a, the number of photons received by the detector in period $\Delta t$ can be simplified as 
$$n_p(t) = \int_{t}^{t+\Delta t} \rho(t')dt',$$
where $\Delta t$ is normally confined by $t_{\text{response}} < \Delta t \ll \tau$ ($t_{\text{response}}$ is the system response time resolution and $\tau$ is the lifetime of the decay). It can be seen that when the decay is extremely fast ($\tau$ is very small like in magnitude of picoseconds or nanoseconds) or when the signal level is ultra-weak ($\rho(t)$ is ultra-small), the detector is not able to respond due to the negligible $n_p$. The TCSPC, remarkably, is able to solve such kind of problems by histogramming of photon arrival times over many cycles [Fig. 5.6b-c]. This process, on the other hand, can be understood as that for each monitored time channel $[t, t + \Delta t]$, the number of detected photons is counted after every exciting pulse. With a certain number of cycles (pulses) $N_c$, the detected intensity is defined by 
$$N(t) = N_c \times n'_p(t),$$
where $n'_p(t)$ is the probability of seeing an emitted photon at time period $[t, t + \Delta t]$ after each excitation and is linearly proportional to $\rho(t)$. Therefore, the enhancement in detection with TCSPC is determined by $N_c$, which can be efficiently increased by using high repetition rate pulse lasers or long time detection with repeated cycles. To achieve the best performance of TCSPC experiments, the repetition rate ($t_r$) of the excitation is about $t_r = 1/(100\tau)$ and the maximum counting rate (number of photon counted per second) is $0.05t_r$, under the consideration of preventing the system from photon piling.
5.2.3.2 Observation of modifications in QDs radiation decays

To reduce the influence of energy transfer on QDs PL decays, a dilute QDs solution with a concentration of $\sim 10^{-6}$ mol/l was used. The PL from QDs in toluene solution shows a good single-exponential decay with a lifetime of $\sim 480$ ns (nanoseconds) at wavelength 1580 nm (see the inset of Fig. 5.7), which is comparable with that reported previously [118]. For dried QDs in the air, the PL decays were much faster with a magnitude of only tens of ns. As shown in Fig. 5.7, the time-resolved PL decays from QDs inside and outside the PC show different nonexponential characteristics, which result from both the inherent radiative properties of QDs and the influence of surrounding dielectric environments, such as defect states, energy transfer, and electronic coupling [119,120]. Nevertheless, careful measurements and comparisons with QDs in identical environments can reduce the influence of these effects and

Figure 5.7  Normalised PL decays of dried QDs inside and outside the PC at wavelength 1580 nm. (Inset) Normalised PL decays of QDs in air and in toluene solution at wavelength 1580 nm. White solid line: fitted line with a single exponential decay function. Background noise has been subtracted.
thus resolve the changes in radiative decays caused by the PBG of the PC [17]. Another thing needs to be pointed out is that the PL decays from QDs are intrinsically dependent on the detection wavelength. Figure 5.8 shows the PL decays from QDs outside PC at wavelength 1350 and 1580 nm, respectively, where the decay at wavelength 1350 nm is much faster than that at wavelength 1580 nm. Therefore, direct comparison of changes in PL decays between wavelengths 1350 and 1580 nm is not justified and a proper way needs to be explored to resolve the PBG effects.

In this study, to resolve the PBG effects and eliminate other influences, we compared the PL decays detected from QDs at three different depths (I, II, and III) inside the same PC (see the inset of Fig. 5.9). In such a way, the QDs at three positions had an almost identical material environment, which resulted in an almost identical non-radiative contribution to the PL decays of QDs while the influence from PBG on QDs radiative decays were different at each position. The deeper the QDs locate, the stronger the influence of
PBG. Therefore, the changes in measured time-resolved PL decays mainly reflect the influence of PBG on the radiation properties of QDs.

For comparison purposes, the measured PL decay curves from QDs at different depths inside the PC were fitted by using the stretched exponential model \[ I(t) = I_0 \exp\left[\frac{-t}{\tau_{1/e}}\right]^{\beta} \], where \( \tau_{1/e} \) is the time constant when the intensity decreases to \( I_0/e \) and \( \beta \) (\( 0 < \beta \leq 1 \)) is the stretching parameter. An average lifetime \( \langle \tau \rangle \) can be calculated by \[ \langle \tau \rangle = \left(\frac{\tau_{1/e}}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right) \], where \( \Gamma \) represents the gamma function [119, 121].

A serial of average lifetimes \( \langle \tau \rangle \) at different wavelengths have been extracted and plotted in Fig. 5.9. One can see that the average lifetimes \( \langle \tau \rangle \) are wavelength-dependent for all cases. The values of \( \langle \tau \rangle \) increase gradually with wavelength, similar to the trend of the wavelength-dependent decays of CdSe and CdTe nanocrystals [121]. A comparison of Fig. 5.9b shows
an obvious difference in values of \(< \tau >\), at different depths in the longer wavelength range where the stop gap of the PC exists (see Fig. 3a). The values of \(< \tau >\) in the longer wavelength range increase more quickly with increasing the detection depths than those in the shorter wavelength range. Specifically, the value of \(< \tau >_{1580}\) (\(< \tau >\) at wavelength 1580 nm) from detection positions I to III increases from 34.9, 37.6 to 41.7 ns, respectively, showing the inhibition of the SE by up to \(\sim 20\%\), while the values of \(< \tau >_{1350}\) are 15.1, 15.3, and 15.5 ns, showing a weak inhibition by up to \(\sim 2.6\%).

These wavelength-dependent lifetime changes clearly reflect the PBG effects on QDs radiation, which can be physically understood as follows. The longer wavelength part of QDs radiation is inhibited by the stop gap of the PC [17] where the wavelengths of the QDs emission match the PBG and the effect of PBG became stronger at a deeper depth. In the shorter wavelength range, the influence of PBG is less as a result of the mismatch between QDs radiation and the stop gap of the PC. This inhibition of the QDs emission in the longer wavelength range finally contributes to the redistribution of QDs emission spectra observed in Fig. 5.4b.

5.3 Direction-dependent radiation decays from QDs inside a 3D photonic crystal

One of the important properties of the PBG is its band edge effects. At the band edges of the stop gaps, the LDOS are significantly accumulated [17,122]. Moreover, pronounced superprism and negative refraction effects, which are highly sensitive to the angle and the frequency of the incident light in the propagation direction inside the crystal, have been observed at the band edges
in the telecommunication wavelength range \([63, 68]\). These PBG and band edge effects provide an interesting physical environment for the investigation of controlling the emission from NIR QDs embedded in a polymer woodpile 3D PC.

In this section, we present the direction-dependent PL dynamics from PbSe QDs infiltrated in a 3D woodpile polymeric PC at the angular band edges of the PC \([116]\). Instead of using different PCs or QDs samples, we have directly achieved different modification effects by altering the detection angles of light propagation. Particularly, the inhibition and enhancement effects of the stop gaps on the SE have been observed in the mid-gap and at the centre of the band edge, respectively.

### 5.3.1 Experimental realisation of angular measurements

The 3D woodpile PC in this work was fabricated on a cover glass with Ormocers® (Micro Resist Technology) by using the 2PP method. To match the stop gaps of the PCs, we synthesised PbSe QDs with tunable emission in the NIR wavelength range by using the method described in Sec. 4.3.1. The QDs were then infiltrated into the PC with the method described in Sec. 4.3.2 and a QDs layer with a thickness of \(\sim 10-20 \, \text{nm} \) was deposited onto the surfaces of the PC rods during the infiltration. In the meantime, a QDs film with a thickness of \(\sim 0.5-1 \, \mu\text{m} \) was formed outside the PC on the cover glass, providing a direct and convenient reference for our studies of QDs emission inside the PC. The dried PbSe QDs on the cover glass were measured to have absorption and emission peaks centred at wavelengths of 1500 and 1580 \(\text{nm} \), respectively, with broad PL spectra ranging from 1250 to
The stop gaps of the PC before and after infiltration were measured with an FTIR in conjunction with an infrared microscope (Continuum). To reduce the averaging effect from the angular distribution of the incident beam in the FTIR on the stop gap measurement, a wedge with a certain angle was used to tilt the sample and a small pinhole was placed in front of the objective to confine the angular distribution to ∼5° (see the inset of Fig. 5.10). The PC without infiltration was measured to have a stop gap centred at wavelength 1383 nm. After QDs infiltration, the mid-gap of the PC was shifted to a longer wavelength at 1400 nm due to the increase in filling ratio and the average refractive-index of the structure [29]. Angle-dependent stop gaps of the infiltrated sample were measured by varying the tilting angle \( \theta \), while the position of the pinhole was kept unchanged (see the inset of Fig. 5.10).

**Figure 5.10** Sketch for angle-resolved PL decay experiments. Inset: sketch of the reflective objective of FTIR with a pinhole for the angle-confined measurements of stop gaps of the PCs. Angular measurements are realised by changing the tilting angle \( \theta \) with respect to the axis of the incident beam.
To study the PL decays from QDs inside the PC at different angles, angle-resolved experiments of the PL decay were conducted by employing the TCSPC technique. As shown in Fig. 5.10, a high NA (1.45) objective with a back aperture diameter of 12 mm was used to focus the beam on the sample and to collect the PL from QDs. To obtain angle-resolved signals, a small aperture (with a diameter of ~2 mm) was placed at the back aperture of the objective [18]. By tuning the lateral position of the small aperture, signals from certain solid angles can be resolved correspondingly. The angle-resolved PL signals were dispersed by a spectrograph (Acton Spectropro 300i) and detected by a fast NIR photomultiplier (Hamamatsu). Single photon counting was carried out using a TCSPC module (PicoHarp 300) connected to a computer. This system avoided the rotation of the sample and the change of the focus positions, making it suitable for the angle-resolved measurements performed under a constant condition [18].

5.3.2 Observation of direction-dependent radiation decays

As shown in Figs. 5.11a-e, the position of the stop gaps of the 3D PC changes with the angle of incidence $\theta$, especially at larger angles, which is consistent with the prediction of the band gap calculation. Since the PL decays from ensemble QDs are wavelength-dependent [29], we focus on the study of the SE from QDs at a fixed wavelength of 1400 nm, which is the mid-gap position at $\theta=0^\circ$. As shown in Figs. 5.11a-e, the relative position of the detection wavelength (1400 nm) with respect to the stop gap is tuned from the mid-gap through the band edge when $\theta$ increases from $0^\circ$ to $40^\circ$. 
Figure 5.11 (a-e) Baseline corrected transmission spectra of the PC at different angles $\theta$. The vertical solid line indicates the position at wavelength 1400 nm. (f-j) Normalised PL decay curves (and $<\tau>$) from PbSe QDs inside the PC at wavelength 1400 nm at the detection angles corresponding to (a-e). Background noise has been subtracted.

The corresponding PL decays from QDs inside the PC at wavelength 1400 nm are measured with the system in Fig. 5.10 and plotted in Figs. 5.11f-j. To get a quantitative evaluate of the radiation properties from the non-exponential PL decays, we fit the decay curves with the stretched exponential model $I(t) = I_0 \exp[-(t/\tau_1)^{\beta}]$ and the average lifetime $<\tau>$ is used to characterise the decay properties (similar as in Sec. 5.2.3). It shows clearly that the average lifetime $<\tau>$ from QDs inside the PC changes significantly with $\theta$, while for QDs outside the PC, little change in $<\tau>$ has been
observed under the same conditions (not shown), which indicates that the angle-dependent change in $<\tau>$ in Figs. 5.11f-j is induced by the stop gaps.

The dependence of $<\tau>$ on $\theta$ is depicted in Fig. 5.12 while the dependence of the stop gap and the transmittance at wavelength 1400 nm on $\theta$ is illustrated in the inset of Fig. 5.12, which shows the blue-shift of the mid-gaps ($\Delta\lambda_c$) and the decrease in suppression as $\theta$ increases. Since the detection wavelength is far outside the corresponding stop gap at angle 40° [Figs. 5.11e], it is reasonable to use the measured $<\tau>$ at this angle ($<\tau>_{40}$) as a reference parameter without the influence of the PBG effects. As shown in Fig. 5.12, $<\tau>$ is increased by 35% at $\theta=0^\circ$, indicating that the QDs emission is significantly inhibited at the mid-gap of the PC. However, at $\theta=20^\circ$, $<\tau>$ is decreased by 8.5%, which is a clear reflection of the QDs emission enhancement at the centre of the band edge of the PC. It should be mentioned that SE from infiltrated QDs at wavelength 1625 nm, which is outside the stop gaps of the PC, does not show such significant angle-

![Figure 5.12](image_url)

**Figure 5.12** Relationship between the average lifetime $<\tau>$ and detection angle $\theta$, for PbSe QDs inside the PC at wavelength 1400 nm. Inset: the shift of the mid-gap ($\Delta\lambda_c$, left) and the change in transmission suppression at wavelength 1400 nm ($\Delta T_s$, right) as a function of $\theta$. 
dependent decay properties as those at 1400 \( \text{nm} \).

### 5.3.3 Angle-dependent decay time distributions

The angle-dependent PL decay properties at wavelength 1400 \( \text{nm} \) can result in the changes in the decay time distributions [119, 123], which indicate the relative strength of transitions with specific lifetimes. The decay time distribution function is given by

\[
G(\tau) = \tau \rho(\tau),
\]

where \( \rho(\tau) \) is defined by

\[
e^{-\left(\frac{t}{\tau_1}\right)^a} = \int_0^\infty e^{-t/\tau} \rho(\tau) d\tau \tag{5.1}
\]

with

\[
\rho(\tau) = -\frac{\tau_1}{\pi \tau^2} \sum_0^k \frac{(-1)^k}{k!} \sin(\pi \beta k) \Gamma(\beta k + 1) \left(\frac{\tau}{\tau_1}\right)^{\beta k + 1}, \tag{5.2}
\]

which can be calculated with the corresponding parameters \( \tau_1/\epsilon \) and \( \beta \). The inset of Fig. 5.13 shows the normalised decay time distribution at different angles.

**Figure 5.13**  Calculated \( R_{<\tau>} \) and \( R_{\tau_{\text{max}}} \) as a function of \( \theta \) at wavelength 1400 \( \text{nm} \). Inset: normalised calculated decay time distribution at wavelength 1400 \( \text{nm} \) as a function of decay time constant (\( \tau \)) at different angles (\( \theta \)).
angles $\theta$. It can be seen that the maximum of the decay time distribution, $\tau_{\text{max}}$, is shifted to shorter times when $\theta$ increases from $0^\circ$ to $20^\circ$ and that a further increase in $\theta$, however, results in the increase in $\tau_{\text{max}}$, which is similar to the angular dependence of $<\tau>$. For comparison, the variations of $<\tau>$ and $\tau_{\text{max}}$ at different angles at wavelength 1400 nm are evaluated by the ratios

$$R_{<\tau>} = \frac{<\tau> - <\tau>_{40}}{<\tau>_{40}} \quad \& \quad R_{\tau_{\text{max}}} = \frac{\tau_{\text{max}} - \tau_{\text{max}40}}{\tau_{\text{max}40}}, \quad (5.3)$$

where $<\tau>_{40}$ is the reference average lifetime and $\tau_{\text{max}40}$ is the maximum decay time distribution, respectively, at $\theta=40^\circ$. As shown in Fig. 5.13, $R_{<\tau>}$ and $R_{\tau_{\text{max}}}$ agree well at all angles, which further confirms the angle-dependent PBG effect on the radiation decays of QDs inside the PC.

### 5.4 Chapter conclusion

This chapter has experimentally demonstrated the functionalities of 3D PCs for manipulation of SE from incorporated QDs. For the first time, 3D woodpile PCs were utilised to control the emission from PbSe QDs in the NIR wavelength range. Although the 3D PCs were fabricated in low refractive-index materials, it has been shown that both emission spectra and radiation decays from QDs radiation have been modified by the 3D PCs, which provides important information for studies on radiation dynamics in the NIR wavelength range.

In particular, redistributed SE spectra have been observed from QDs infiltrated inside a PC with matched PBG. Time-resolved experiments
reveal that a 20% inhibition of the QDs emission in the longer wavelength region, caused by the stop gap effect, physically contributes to the spectral redistribution of the QDs emission. Furthermore, controlling the dynamics of the SE from NIR QDs has been explored by adjusting the angle-dependent stop gaps of a 3D PC. An inhibition by up to 35% and an enhancement by up to 8.5% of the emission have been observed in the mid-gap and at the centre of the band edge, respectively, which demonstrates an effective way to tune the SE from QDs by engineering the PBG effects in a given 3D PC. The work in both aspects provides an important step towards controlling NIR QDs emission with 3D PCs, which could facilitate the exploration of advanced functionalities of the 3D PCs for active devices, especially in the important telecommunication wavelength range.
Chapter 6

Plasmon merged 3D hybrid photonic crystals

6.1 Introduction

Along with the encouraging studies on emission control with dielectric three-dimensional (3D) photonic crystals (PCs), there are emerging interests on developing 3D metallic PCs (MPCs) for thermal emission control purposes [87]. 3D MPCs, either all-metallic [7, 95, 124, 125] or partial-metallic (sometimes called “metallodielectric”) [19–22] MPCs, are artificial structures formed by arranging metallic elements in three dimensions. Due to the strong discontinuities of the dielectric function at the metal/air or metal/dielectric interfaces, 3D MPCs offer intriguing electromagnetic (EM) properties and important applications such as enhanced metal absorption [89], modified blackbody radiation [12, 87, 90], ultra-wide complete photonic band gaps [7, 88], negative refraction [126, 127], sub-wavelength imaging [126], and microwave antenna and circuits [128]. The metallic rods or metallic layers
in those MPCs have been employed with thickness far thicker than the skin depth of the metals which excluded the penetration of EM waves into the rods or layers [7, 21, 88]. The major problem in all the current 3D MPCs is that they do not support localised plasmon resonances (LPRs) that are based on the metallic nanostructures [22]. Plasmonics [23, 24], one of the most important characters in metallic systems, provides a promising new way to control the photon-matter interaction at a nanometer scale and has found wide applications in optical switching, near-field optics and surface-enhanced Raman spectroscopy [23]. Therefore, creating LPRs in 3D PCs is of great potential to significantly increase the functionalities of 3D PCs but has not yet been demonstrated.

In this chapter, we explore the advanced functionalities of 3D PCs through proposing a new concept of 3D PCs stacked by hybrid rods (HRods) made of dielectric-cores and metallic-nanoshells. This kind of 3D hybrid photonic crystals (HPCs) facilitates multiple LPRs due to the existence of metallic nanoshells. The resultant LPRs significantly enhance the absorption of 3D HPCs by more than two orders of magnitude and can be finely controlled with a broad spectral tunability by mediating the dielectrics part. Thus the thermal radiation of 3D HPCs can be modified not only at the band edge region but also in a wide spectral range with desired absorption band width. This feature can be immediately applied to the next-generation nanostructured plasmonics-based light harvesting devices [129].

In details, Section 6.2 presents the principle to introduce and tune localised plasmon resonances in 2D silver HRods. Section 6.3.1 demonstrates the theoretical observations of LPRs in 3D silver HPCs while the flexible tunability of these LPRs is described in Sec. 6.3.2. Furthermore, Section 6.4 demonstrates the generality of our scheme on creating LPRs in 3D
HPCs with various metals, such as gold and tungsten. As an experimental demonstration, Section 6.5 presents the realisation of 3D HPCs based on the 2PP technique and an electroless silver deposition method.

### 6.2 Localised plasmon resonances in hybrid nanoshelled rods

#### 6.2.1 Scheme for introducing localised plasmon resonances

The principle of HRods that are used to form the 3D HPCs are shown in Fig. 6.1. Figures 6.1a, b show parallel elliptical metallic rods (MRods) and HRods, respectively. HRods, whose width ($w$), height ($h$) and thickness ($D_s$) are illustrated by Fig. 6.1b, can be formed by coating ultra-thin silver nanoshells ($D_s \sim 10-20 \text{ nm}$) on elliptical dielectric rods and are the basic elements to form 3D HPCs. It is well known that when p-polarised light interacts with a metal/dielectric interface, charge density oscillations are introduced as plasmons [23, 24]. In the case of MRods (Fig. 6.1a), the resultant plasmons are difficult to form resonances due to the lack of confinement (Fig. 6.1c). However, for the HRods, plasmons can be coupled from the outer surfaces to the inner surfaces of the nanoshells due to the small thickness which is comparable with the skin depth ($\sim 22 \text{ nm at wavelength } 1.5 \mu m$ by calculation [130]). Due to the close loop of the rod cross section, the surface charges which are localised on the inner and outer surfaces of the nanoshells form ring-cavity-like plasmon resonances (Fig. 6.1d). As a result, the localised electric-field (E-field) can be formed inside the HRods.
Figure 6.1  (a, b) Schematic of parallel MRods (a) and HRods (b) in simulations. The HRod consists of a dielectric rod (with width $w$, height $h$, rod spacing $a$, refractive-index $n$) and a silver nanoshell (with thickness $D_s$). (c, d, e) Schematic of the charge density distributions (top panels) and snapshots of the calculated E-field (linear scale, bottom panels) in the cross section plane for an MRod (c) and an HRod (d, e) at noted frequency. The distributions of E-field correspond well with the charge distributions. HRod parameters: $w=240$ nm, $h=2.5w$ (for all calculations in this chapter if not noticed), $a=1 \mu$m, $D_s=10$ nm and $n=1.56$. MRods are calculated based on HRod parameters by replacing dielectrics with silver.

To confirm the assumptions, we simulate a 2D HRod array as well as an MRod array with the software package CST Microwave Studio. For simplicity, here we use silver with permittivity described by the Drude model with plasma frequency $\omega_{pl} = 1.37 \times 10^{16}$ s$^{-1}$ and collision frequency $\omega_{col} = 8.5 \times 10^{13}$ s$^{-1}$ [22]. Figures 6.1c,d (bottom panels) show the simulated E-field distributions around an MRod and an HRod under the same light excitation, respectively. The calculated E-field maps (bottom panels) confirm that the E-field cannot exist within an MRod as expected but can exist inside an
HRod at certain resonant frequency. It is this internal E-field that facilitates the charge distribution on the inner and outer surfaces of the nanoshells as illustrated in Figs. 6.1c, d (top panels), which verify the excitation of LPRs in HRods. It should be mentioned that higher-order LPRs at higher frequencies also exist, as pictured in Fig. 6.1e. At the LPR frequencies/wavelengths, due to the back and forth coupling between electromagnetic waves and plasmons as well as the coupling between plasmons on the inner and outer surfaces of the nanoshells, the photon-matter interaction in HRods is significantly enhanced. As a result, the absorption of HRods can be greatly enhanced at LPRs.

The corresponding absorption spectra of the HRods in Fig. 6.1 are displayed in Fig. 6.2a. It indeed shows that two LPR enhanced absorption channels emerging at the corresponding LPR wavelengths, where the enhancement factors are \( \sim 82 \) and \( \sim 83 \) at 1\(^{st}\) and 2\(^{nd}\) LPR wavelengths, respectively, compared with the absorption of MRods. The higher-frequency or higher-order LPRs are very useful to create multiple absorption channels and

![Figure 6.2](image)

**Figure 6.2** (a) Calculated absorption spectra of the HRods (solid line) and MRods (dashed line) with the same parameters in Figs. 6.1c-e. Inset: centre wavelength (\( \lambda_c \)) of the 1\(^{st}\) LPR versus dielectric rod width (w) for \( a=1 \, \mu m \), \( D_s=10 \, nm \), \( n=1.56 \). (b) Calculated LPR absorption spectra of HRods with different w as noted. Variations in peak values <1.2%. Other calculation parameters are the same as those in (a).
advantageous to extend the working wavelengths to the visible wavelength range. However, to simplify the analysis, we consider only the 1st order LPR in the following discussion.

### 6.2.2 Structural sensitivity of localised plasmon resonances

It is important to point out that the position of the LPR is extremely sensitive to the rod parameters except the rod spacing $a$ (see the inset of Fig. 6.2a, Fig. 6.2b and Figs. 6.3a-c). First, the position of the LPR shifts to a shorter wavelength and its strength is reduced dramatically when $D_s$ becomes larger (Fig. 6.3b). As expected, the LPR is negligible for $D_s > 60 \, \text{nm}$, mainly caused by the weak plasmon coupling between the inner and outer surfaces as $D_s$ is 2-3 times of corresponding skin depth. This is the main reason why the LPRs have never been discovered in all the current 3D MPCs [7, 21, 88, 124].

Second, it is interesting to note that the strength of the LPR absorption remains constant when varying the rod width $w$ (Fig. 6.2b), while its position can be linearly tuned from 1.1 to 6.0 $\mu\text{m}$ by increasing the rod width $w$ from 80 to 800 $\text{nm}$, as shown in the inset of Fig. 6.2b.

Third, increasing the refractive-index of the dielectric rods within HRods results in a linearly increased dependence of the LPR wavelength with a reduced strength (Fig. 6.3c), which physically originates from the reduced surface charge strength for high refractive-index dielectrics. This dependence of the LPR position on the refractive-index of the HRods may prove to be advantageous for developing broadband tunable HPC-based devices.
Figure 6.3  (a, b, c) Absorption spectra of HRods with variable parameters of $a$ (a), $D_s$ (b) and $n$ (c). Inset: Peak position ($\lambda_c$) and peak absorption ($A_{\text{max}}$) as a function of corresponding variable parameters. Calculation parameters are noted at the right side of each figure.
6.3 3D hybrid photonic crystals with localised plasmon resonances

6.3.1 Enhanced absorption in 3D hybrid photonic crystals

Figures 6.4a, b illustrate the schematic of 3D woodpile MPC and HPC structures of a face-centred-cubic geometry with the same parameters. Due to the existence of LPRs in HRods, the 3D HPC shows significant spectral differences compared with those of the 3D MPC when the E-field is linearly polarised perpendicular to the first-layer rods. (c,d) Calculated reflection and absorption spectra of a 3D MPC (c) and a 3D HPC (d). Simulation parameters of the HPC: $a=1\ \mu m$, $w=200\ \text{nm}$, $D_{s}=20\ \text{nm}$, $n=1.56$; the MPC is based on the corresponding HPC by replacing dielectrics with silver (this condition holds for all MPCs under comparisons).
is perpendicular to the first-layer rods. As shown in Fig. 6.4c, the 3D MPC has a high reflection region above wavelength $1.6 \ \mu m$ and a band edge region centred at wavelength $1.45 \ \mu m$, where the enhanced absorption is about 0.10. Impressively, in addition to this enhanced absorption peak caused by the slow light effect of the photonic band edge [89], there exists an LPR enhanced absorption peak in the 3D HPC, reaching 0.59 at wavelength $1.73 \ \mu m$ (Fig. 6.4d), which is approximately 5.9 times of that in the band edge region of the 3D MPC and about 12 times of that of the MPC at wavelength $1.73 \ \mu m$. Meanwhile, the density of this absorption channel, defined as $A_{max}/W_{FWHM}$ ($W_{FWHM}$ is the full width at half maximum of the absorption channel), is enhanced by $\sim 29$ times compared with the band-edge absorption channel of the MPC. Moreover, as a result of the LPR, the E-field inside the 3D HPC is strongly localised, as shown in Fig. 6.5.

### 6.3.2 Tuning localised plasmon resonances in 3D hybrid photonic crystals

The dielectrics mediated LPR offers a great flexibility in designing desired absorption channels of 3D HPCs. As shown in Fig. 6.6a, by increasing the dielectric refractive-index from 1.0 to 1.56, the position of the LPR-enhanced absorption is red-shifted by $\sim 730 \ nm$. It is noticed that the absorption peak at the metallic band edge does not change with the dielectric refractive-index because it is only dependent on the periodic metal structure. Therefore, one can tune the LPR-enhanced absorption by simply choosing dielectrics of different refractive-indices without altering the overall metallic band gaps. As illustrated in Fig. 6.6b, the wavelength of the LPR-enhanced absorption,
Calculated spatial distribution of the amplitude of the E-field inside a pure dielectric PC (DPC, left column), HPC (central column) and MPC (right column) at wavelength 1.51 $\mu$m (a,d,g), 1.73 $\mu$m (b,e,h) and 2.31 $\mu$m (c,f,i), respectively. Field distributions are normalised to the maximum electric field at each wavelength. Structural parameters are the same as those in Fig. 6.4. One can see that the E-field is strongly localised in the HPC at wavelength 1.73 $\mu$m, where the LPR only exists in HPC (Figs. 6.4c,d). At other wavelengths, the HPC shows similar properties as those of the MPC.

\[ \lambda_c \], is linearly tuned from outside the metallic band gap, at the band edge, and inside the bang gap, respectively.

Apart from the refractive-index of the dielectric rods, the thickness of the silver nanoshells and the filling ratio ($w/a$) of the dielectric rods also play very important roles in engineering the LPR-enhanced absorption of HPCs, as
Figure 6.6  (a) Calculated absorption spectra of 3D HPCs for different refractive-indices \( n \) at 1.0, 1.2 and 1.56. The metallic band edge enhanced absorption does not change with \( n \). (b) (bottom, left) Linear dependence of \( \lambda_c \) on \( n \) in the 3D HPC. (top, right) Reflection spectrum of a HPC with \( n=1.0 \), showing the photonic band contributed by the metallic part only. The LPR can be relatively tuned outside the band gap, at the band edge, and inside the band gap, respectively, depending on \( n \). Calculation parameters: \( a=1.25 \, \mu m \), \( w=250 \, nm \), \( D_s=20 \, nm \).

Figure 6.7  (a) Calculated absorption spectra of 3D HPCs with different shell thickness \( (D_s) \) at 15, 10, 7.5 nm. Inset: \( \lambda_c \) of 3D HPCs as a function of \( D_s \) (calculated with \( a=1.25 \, \mu m \), \( w=250 \, nm \), \( n=1.56 \)). (b) Calculated absorption spectra of HPCs with different filling ratios: 0.15 (thin solid line), 0.16 (thick solid line), 0.20 (dashed line) and 0.21 (dotted line). Inset: \( \lambda_c \) as a function of \( w/a \) (calculated with \( a=1.25 \, \mu m \), \( D_s=20 \, nm \), \( n=1.56 \)).

shown in Fig. 6.7. For example, the LPR-enhanced absorption peak can be blue-shifted by \(~540 \, nm\) when \( D_s \) increases from 7.5 to 50 nm and diminishes when \( D_s > 60 \, nm \). On the other hand, the LPR wavelength can be easily tuned by \(~889 \, nm\) when the filling ratio of HPCs varies from 0.15 to 0.25.
6.4 Gold- and tungsten-based 3D hybrid photonic crystals

It is remarkable that the LPRs exist not only in a silver-based 3D HPC but also in gold- and tungsten-based 3D HPCs (see Figs. 6.8a,b). Particularly, the absorption density of the LPR-enhanced absorption channel is enhanced by \( \sim 199 \) times compared with the band-edge absorption channel of the gold-based 3D MPC (Fig. 6.8a). Moreover, the geometry of the HRods in 3D HPCs is not limited to the elliptical shape. In fact, any closed-loop rod shape capable of forming a cavity can generate the LPR (see Fig. 6.8b). It should be mentioned that 3D HPCs of different types of metals have different strengths at the LPR absorption peak, mainly because of the different intrinsic absorption properties of bulk metals [89]. Nevertheless, the creation of the pronounced LPR-enhanced absorption channels in silver-, gold- and tungsten-based HPCs indicates the generality of the proposed scheme.

Figure 6.8  (a) Calculated reflection and absorption spectra a gold-based 3D HPC. \((a=1 \mu m, \ w=200 \ nm, \ D_s=20 \ nm, \ n=1.56, \) gold permittivity is described by Drude model with plasma frequency \( \omega_p=2172 \ THz \) and relaxation time \( \tau=27.4 \ fs \) [131].) (b) Calculated reflection and absorption spectra of a tungsten-based MPC and HPC with similar parameters in Ref. [89]. Inset: the schematic of the rectangular rod in the HPC. The refractive-index of the inner part is 2.7 and the outer layer is tungsten. For the MPC, both the inner and the outer parts are composed of tungsten. Tungsten permittivity is described by the Drude model with plasma frequency \( \omega_{pl}=9.118 \times 10^{15} \ s^{-1} \) and collision frequency \( \omega_{col}=8.158 \times 10^{13} \ s^{-1} \) [89].
6.5 Realisation of silver-based 3D hybrid photonic crystals

The proposed LPR-merged 3D HPCs can be fabricated by applying the versatile metallisation methods [19–22, 96] on 3D PC templates generated with the sophisticated direct laser writing techniques [22, 47, 62, 64]. Here, we demonstrate this feasibility by employing the well-established 2PP technique [64] and a simple electroless silver deposition method [132].

The recipe includes four steps:

1. Fabricate 3D PCs by 2PP with an inorganic-organic photosensitive resin named Ormocer [see Sec. 3.2];

2. Functionalise the surfaces of the fabricated 3D PCs by immersing the structure into a toluene solution with 1.0% 3-aminopropytriethoxysilane (APTES) for 2 minutes, rinsing with toluene and drying in air [133];

3. Attach gold nanoparticles to the aminated structures: immersing the sample into $5.0 \times 10^{-4} \, M \, HAuCl_4(aq)$ for 2 hours, washing with water, reducing gold with a $0.1 \, M \, NaBH_4(aq)$ for 2 minutes, then rinsing with water and drying in air [132];

4. Deposit silver layers on the structures: immersing the samples into a silver bath solution for desired time, rinsing with water and drying in air [132]. Our silver bath solution contains: 12 ml filtered 33 wt-% aqueous gum Arabic, 2 ml of aqueous citrate buffer (1.5 M citric acid and 0.5 M Sodium Citrate), 3 ml aqueous 0.52 M hydroquinone and 3 ml of aqueous silver lactate. The concentration of aqueous silver lactate is determined by the silver concentration of the mixed silver
bath, which is 4.5 mM for the first hour deposition and 3.75 mM for the rest of the time in our recipe, intending to achieve small granular particles on the surfaces of the structures [132].

As shown in Fig. 6.9a, a silver layer (with averaged effective thickness of \( \sim 15 \) nm) has been clearly deposited on the surfaces of a fabricated 3D

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**Figure 6.9** (a) SEM image of a 3D polymeric woodpile PC after the electroless silver deposition process. Silver particles were nucleated on the surfaces of the polymeric PC to form a 3D silver HPC. Inset: close view of a polymeric DPC and the silver HPC. (b, c) Measured and calculated reflection and absorption spectra of the 3D silver HPC in (a). Simulation parameters are \( a=0.9 \) \( \mu \)m, \( w=360 \) nm, \( h=510 \) nm, \( D_s=15 \) nm, \( n=1.47 \), \( \omega_{pl}=1.37 \times 10^{16} \) s\(^{-1}\), and \( \omega_{col}=1.7 \times 10^{14} \) s\(^{-1}\), which fit best with our experimental conditions. (d) Measured (Exp) and calculated (Cal) \( \lambda_c \) as a function of the dielectric rod width of the HPC.
polymeric woodpile PC. As a result, the reflection spectrum of the 3D HPC in Fig. 6.9b shows a high reflection region at longer wavelengths which represents the band gap characteristic of 3D MPCs and a “dip” within the high reflection region which indicates the existence of the LPR at wavelength \( \sim 1.7 \, \mu m \). Moreover, the absorption peak at this wavelength is enhanced by approximately 7.3 times compared with that of silver layers. This feature is consistent with the theoretical simulations (Fig. 6.9c) in terms of the position and depth of the “dip”. The deviation of the measured reflection and absorption spectra (Fig. 6.9b) from the calculation in Fig. 6.9c was caused by the averaging effect in measurements [28], the roughness of the silver layers, and the scattering losses. To demonstrate the tunability of the LPR, HPCs with increased rod width were realised through fabricating HPCs with increased laser power while the other lattice parameters were kept unchanged. As illustrated in Fig. 6.9d, the LPR wavelength is monotonically tuned by \( \sim 240 \) nm when simply increasing the dielectric rod width by \( \sim 80 \) nm for HPCs with the same lattice constant. Further experiments should be performed to improve the structure surface roughness with an optimised silver deposition recipe and thus decrease the structure scatterings in potential applications.

6.6 Chapter conclusion

This chapter has demonstrated the functionalisation of 3D PCs by employing the dielectrics mediated LPR in 3D HPCs in the NIR wavelength region. Unlike the band edge enhanced absorption, the much more enhanced absorption channel in this chapter results from the LPR. Through adjusting the structural parameters of HPCs, such as silver layer thickness, rod width,
structural filling ratio and dielectric refractive-index, the LPR absorption channel can be flexibly and widely tuned to meet possible applications related with wavelength matching purposes.

More importantly, it has been shown that our scheme of creating LPRs in 3D HPCs can be generally applied to a wide range of metals like gold and tungsten. Therefore the work opens a new frontier where localised plasmonic effects and photonic band effects are merged to lead more interesting studies on photonic applications of both 3D PCs and plasmonics like energy harvesting systems. A straightforward study will be on the efficient low-temperature thermophotovoltaic applications with 3D HPCs [13]. In addition, the strongly localised E-field inside the rods of HPCs provides a promising environment for researches on nonlinearities and emission control if the embedded dielectric rods are of functionalities, for example containing gain media like semiconductor quantum dots [28, 81]. Therefore, studies with such 3D HPCs could lead significant contributions to emission control.
Chapter 7

Conclusion

7.1 Thesis conclusions

Functionalisation of three-dimensional (3D) photonic crystals (PCs) is the key challenge confronted by the application of 3D PCs. This thesis has built up detailed and comprehensive studies on the functionalisation of 3D polymeric woodpile PCs fabricated with the two-photon polymerisation (2PP) method in the near-infrared (NIR) wavelength range, which can be summarised in four key areas.

1. Wide-range fabrication and engineering of high-quality polymeric 3D woodpile PCs. It was the first time to explore the post-thermal treatment method to improve the spatial resolution and engineer the stop gaps of 3D PCs, which resulted in inorganic-organic 3D PCs working from the NIR to visible wavelength range.

2. Functionalisation of 3D woodpile PCs by incorporation of NIR PbSe quantum dots (QDs). Through employing two independent schemes,
doping and infiltration methods, QD-based active NIR 3D PCs were successfully realised. It was the first experiment that demonstrated the feasibility of direct fabrication of 3D PCs in a NIR QD-doped composite material.

3. Experimental verification of modifications in spontaneous emission from NIR QDs with 3D woodpile PCs. Spectral redistributions, as well as the underlying inhibited emission decays, were for the first time observed in the NIR wavelength region with a 3D woodpile PC. Both inhibition and enhancement in spontaneous emission were demonstrated at the angle-dependent stop gap of a 3D PC.

4. Demonstration of the functionalised 3D silver hybrid PCs (HPCs) with extraordinarily enhanced absorption channels. For the first time, localised plasmon resonances (LPRs) were proposed in 3D HPCs, which were demonstrated in both calculations and experiments. Importantly, it was verified that the scheme of creating LPRs in this thesis can be widely applied with various metals like gold and tungsten.

To explore the functionalities and to serve the purpose for emission control, proper 3D PCs with high quality are required. One important criterion in this aspect is wavelength matching. This is because the photonic band gaps (PBGs) of 3D PCs are generally characterised as three regions: inside the PBG, outside the PBG and at the band edge regions. To meet various requirements, one needs to match different regions of the PBGs to the desired wavelengths. Therefore, a flexible way of tuning the PBGs is very advantageous. It was shown that by varying the crystal lattice from 0.7 to 1.5 \( \mu m \), 3D PCs with stop gaps from 1.05 to 2.10 \( \mu m \) can be realised with the 2PP method, which covered the important NIR wavelength range and
fully matched the desired QDs emission spectra.

In addition to the basic fabrication technique, a post-thermal treatment (PTT) method, for the first time, was proposed and demonstrated to engineer the 3D inorganic-organic PCs fabricated by the 2PP method. Through removing the organic functional groups inside the fabricated woodpile PCs, the spatial resolution of 2D and 3D structure was improved to $\sim 33$ and $\sim 86$ nm, respectively. More importantly, smooth and wide-range tunings of the stop gaps of the 3D PCs were achieved with this PTT method. With the help of PTT, a 3D woodpile PC operating at visible wavelengths was realised after a stop gap shift of 318 nm towards the shorter wavelength range. Therefore, the challenges in wavelength matching can be fully addressed with the 2PP technique and the PTT method.

To study on radiation dynamics with 3D PCs, functionalisation of 3D PCs by incorporating proper emitters is necessary. Based on the advantages of 2PP techniques, two schemes, doping and infiltration methods, were proposed and demonstrated to synthesize NIR active 3D PCs. It was the first time that 3D woodpile PCs were directly fabricated in a NIR QD-doped composite material. With PbSe QDs homogeneously distributed inside the structure, 3D PCs with strong partial stop gaps (with suppression rate $>50\%$) were realised with this doping scheme. In addition, the infiltration scheme provides a controllable approach to study on the radiation dynamics from QDs inside the 3D PCs. Based on the fabricated PC templates, the amount of introduced QDs can be flexibly varied by simply changing QD concentration or adjusting infiltration times, which greatly facilitates further studies on QDs emission control.
Based on the functionalised 3D PCs prepared with the QDs infiltration scheme, emission control from NIR QDs was firstly studied on 3D woodpile PCs. This study is important to solve the question marks in the area of radiation dynamics such as whether or not 3D PC of low refractive-index materials can modify the spontaneous emission. The experiments with polymeric 3D woodpile PCs, indeed, confirmed the SE modifications. A spectral redistribution was observed from QDs inside the PC with matched PBG and a 20% inhibition of the QD emission decays was observed in the stop gap region. This is a clear verification of the feasibility for studies on emission control with polymeric 3D woodpile PCs.

The modifications of spontaneous emission are of great interest in the band edge region of 3D PCs. It showed that through adjusting the angle-dependent stop gaps of a 3D PC, an inhibition by up to 35% and an enhancement by up to 8.5% of the emission were achieved in the mid-gap and at the centre of the band edge, respectively, which demonstrated an effective way to tune the SE from QDs by engineering the PBG effects in a given 3D PC. These modifications in spontaneous emission were further confirmed by consistent comparisons with the calculated decay time distributions.

Along with the studies on emission control, 3D PCs were further functionalised by creating 3D silver HPCs, which possess extraordinarily enhanced absorption channels that can be used for enhanced thermal emission. Besides the ultra-wide and complete photonic band gaps of 3D metallic PCs, for the first time, the localised plasmon resonances were introduced to enrich the functionalities of 3D HPCs. It showed that as a result of the existing LPRs, extraordinarily enhanced absorption channels were created in 3D HPCs and can be significantly tuned by structural parameters. Meanwhile, the experiments with 2PP and a silver deposition method verified
3D silver HPCs with both band gaps and LPRs in the NIR wavelength range. More importantly, it was shown that the scheme of creating LPRs in 3D HPCs can be generally applied to a wide range of metals like gold and tungsten. The work in this aspect opens a new frontier where plasmonic effects and photonic band effects are merged to initiate more interesting functionalities of both 3D PCs and plasmonics, as well as promising photonic applications including emission control.

In conclusion, the research work conducted in this thesis has built up solid and comprehensive studies on the functionalisation of 3D PCs in the technically important NIR wavelength range. High-quality 3D woodpile PCs with wide-range stop gaps from the NIR to visible wavelength region have been realised with the convenient 2PP fabrication technique and the PTT engineering method. Based on the 2PP, 3D PCs have been functionalised by incorporating NIR QDs with a doping method and an infiltration scheme, respectively. Taking advantages of the QD-based 3D PCs, functionalities of 3D PCs have been further demonstrated in the modifications of spontaneous emission from NIR QDs in 3D woodpile PCs. Both inhibition and enhancement in spontaneous emission have been demonstrated at the angle-dependent stop gap of a 3D PC. This thesis has further proposed and proved a new concept to functionalise 3D PCs merged with LPRs, which can significantly enhance the structural absorption with a wide tunability. The research approaches as well as the conclusions reached in this thesis could lead to a profound understanding of the functionalisation of 3D PCs towards potential device applications in the NIR wavelength range.
7.2 Future work

In case of emission control with 3D PCs, two directions of work can be extended based on the functionalities of 3D PCs explored in this thesis.

7.2.1 3D mapping of decay distributions from QDs inside 3D photonic crystals

To gain a better understanding of SE in 3D PCs, it is necessary to obtain the complete information of the LDOS (local density of states) in 3D PCs. So far, most of the LDOS related researches have been conducted on 1D or 2D structures. Regarding LDOS in 3D PCs, very rare experiments, even calculations, have been performed, mainly because of the large amount of calculations and challenges in resolving LDOS from complex 3D PCs.

Since LDOS is related with the decay properties of emitters, 3D LDOS distributions can be indirectly deduced if 3D decay distributions from emitters inside 3D PCs can be mapped. Based on the work in Chapter 5, 3D mapping of decay distributions from NIR QDs inside 3D woodpile PCs can be realised with a scheme named NIR fluorescence lifetime imaging (FLIM).

In FLIM, lifetimes of the decays, other than the emission intensity, are used for imaging. Thus, each point in the image represents the lifetime of the emitter at that position and the whole image corresponds to the spatial distributions of the related LDOS. Therefore, carefully performing FLIM in 3D could reveal detailed 3D distributions of the LDOS in 3D PCs, giving constructive feedbacks for designing 3D PC structures as well as for effective emission control.
7.2.2 Radiation dynamics of QDs inside 3D hybrid photonic crystals

As mentioned in Section 2.6 and Chapter 6, the introduced LPRs in 3D silver HPCs, along with their ultra-wide and complete band gaps, provide an ideal platform for studies on emission control. Based on the researches in this thesis [Chapter 5 and Chapter 6], there are very natural extensions towards the direction on control of QDs emission with 3D HPCs. This work can be sorted into two parts.

The first part is to utilise the metallic band edge effects of 3D HPCs by attaching QDs on the metallic surfaces of the structures (similarly as demonstrated in Sec. 4.2). In the band edge region of the 3D HPCs the DOS is significantly enhanced, which will result in dramatically enhanced emission in this region. Meanwhile, in the ultra-wide and complete band gap region the emission can be fully suppressed due to the complete PBGs of 3D HPCs. Therefore, the manipulation of photons in such kind of 3D HPCs can be very efficient.

The second direction is to dope QDs into the dielectric rods (demonstrated in Sec. 4.1) and utilise the localised electric field (E-field) within the dielectric rods of 3D HPCs (shown in Sec. 6.3). As described in Chapter 6, the strongly localised E-field provides ideal environments for enhancing photon-matter interactions and thus modifying the emission properties of the emitters inside the rods. When QDs emission is matched with the LPRs, the emission will be strongly enhanced. Otherwise, the emission will be fully suppressed by the complete PBGs.

It is very important to note that due to the broad and complete PBGs,
the enhancement or suppression of QDs emission in both cases will be more significant than that in 3D dielectric PCs. Therefore, it can be predicted that the modifications of SE are more efficient with 3D HPCs, which can be a very important step or a shortcut towards the complete control of SE.
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